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I am submitting herewith a dissertation written by Debra L. Joslin entitled "Ion Mixing in Oxide-Sapphire Systems." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Metallurgical Engineering.



Carl J. McHargue, Major Professor

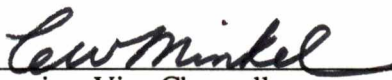
We have read this dissertation
and recommend its acceptance:







Accepted for the Council:



Associate Vice Chancellor
And Dean of the Graduate School

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A Dissertation

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Doctor of Philosophy Degree

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Debra L. Joslin

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ABSTRACT

Ion beam mixing of thin oxide films, Cr_2O_3 and ZrO_2 , on sapphire substrates has been studied. The systems were chosen according to their solubilities in $\alpha\text{-Al}_2\text{O}_3$: Cr_2O_3 is completely soluble, while ZrO_2 is insoluble. Mixing experiments were performed on 50-80 nm-thick Cr_2O_3 and ZrO_2 films deposited on $\alpha\text{-Al}_2\text{O}_3$ by rf sputter deposition. Experiments were also performed on 50 nm thick Zr and Cr films deposited on $\alpha\text{-Al}_2\text{O}_3$ by electron beam evaporation. The oxide-sapphire specimens were bombarded with Cr ions at an energies between 160 and 340 keV to fluences near 5×10^{16} ions- cm^{-2} . Irradiations were also performed with 475 keV Kr ions, to similar fluences. These irradiations were performed at temperatures between 20°C and 900°C. The metal-sapphire samples were irradiated at 20 °C with 320 keV Kr, to similar fluences. Rutherford backscattering spectrometry, x-ray photoelectron spectroscopy, and transmission electron microscopy were used to analyze samples before and after irradiation to analyze the interface modifications. No long-range mixing was found to occur in any of the systems studied.

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CHAPTER 1

LITERATURE REVIEW

1. Introduction

While ion mixing is similar to ion implantation in many ways, the two processes differ in emphasis. The goal of ion implantation is to modify a solid via addition of the ion. Examples of this include doping of silicon to form semiconductor devices, and the formation of buried SiO_2 layers in silicon by implantation of oxygen [1]. In contrast, the goal of ion mixing is to produce atomic mixing at an interface between two solid phases so that a new alloy or compound is formed at the interface as a result of ion bombardment. The phenomenon of ion-induced mixing was first observed in 1972 by Lee et al. [2], who observed that intermixing of Pd and Si occurred at the interface between a Pd/Si film/substrate combination which had been bombarded with phosphorus ions. Ion mixing has been studied for several years as a method for enhancing the adhesion of thin films on their substrates, and as a way to synthesize metastable materials with desirable chemical, electrical, mechanical or tribological properties [3].

To date, most studies of ion beam mixing of materials have involved metal-metal or metal-silicon systems. The interest in these materials combinations arose primarily from the observation that ion bombardment often enhances film/substrate adhesion. Comparatively few studies of metal-insulator and insulator-insulator systems have been made, thus ion beam mixing in systems containing insulators either as a substrate or as a deposited film is in an early stage of understanding and development. Relatively few materials systems have been studied, and the range of experimental conditions has been limited. This work is directed toward obtaining a better understanding of the relative roles of thermodynamics and kinetics in mixing of oxide-oxide bilayers. Toward this goal, the systems $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{ZrO}_2/\text{Al}_2\text{O}_3$ were chosen for study. The former system has complete solubility with Al_2O_3 , while the latter is completely insoluble in Al_2O_3 below 1710°C [4].

2. Ion-solid interactions: a review of concepts

Upon entering a solid, an ion loses energy through collisions with both the nuclei and the electrons surrounding the nuclei of the atoms making up the solid. When the energy of the ion falls below some threshold level, the ion comes to rest in the solid.

Implantation of many mono-energetic ions results in an approximate Gaussian distribution of the ions, due to the statistical nature of nuclear and electronic energy-loss collisions [5]. Such irradiation produces damage in the irradiated target: atoms are displaced from their usual lattice sites. These concepts are illustrated in Figs. 1 and 2 [5]. At the boundary between layers of different composition, ion-induced atomic mixing may occur. Intermixing may result from simple collisional (ballistic) mixing, or it may involve complicated radiation-induced diffusional processes [5].

The phenomena associated with ion bombardment can be divided into three stages [1, 6-8], which are described below.

Stage 1 (prompt stage): As the ion enters the solid, it transfers part of its kinetic energy to the solid via collisions with target atoms (primary collisions). These atoms recoil, colliding with other atoms (secondary collisions), thus evolving higher generations of collisions. The later generation collisions produce many recoils of low energy, which produce small displacements in nearly random directions. This process is known as a collision cascade; the cascade lasts approximately 10^{-13} to 10^{-11} s.

Stage 2 (thermal spike stage): Near the end of a collision cascade, the velocity of the moving atoms assumes a Boltzmann distribution, and the idea of temperature is re-established. During this stage, the kinetic energy of the atoms involved in a collision cascade is dissipated through both lattice and electron conduction. This stage lasts an additional 10^{-11} to 10^{-10} s.

Stage 3 (relaxation stage): A uniform temperature is achieved in the solid. Processes occurring at this ambient temperature, such as thermally activated motion of previously generated defects can continue for periods of time exceeding 10^{-9} s.

The existence of stages 1 and 2 has been supported by computer simulations [6, 9, 10]. However, these simulations are limited by problems associated with following the processes from the time of ion impact through the establishment of a uniform temperature in the solid. This requires keeping track of processes with both long and short time scales, and is therefore time consuming and expensive with existing computer technology. The question of which of the three stages dominates in a given set of experimental conditions cannot be answered by computer simulations alone.

Stages 1 and 3 have been studied extensively, while stage 2 has not. Stages 1 and 3 must be present, but the existence and consequences of stage 2 have been the subject of much controversy [1, 11]. It is hard to observe the effects of stages 1 and 2 in real time because they occur in an extremely short time period. Instead, their aftereffects can be experimentally examined and compared to results from theoretical models. Ion mixing is

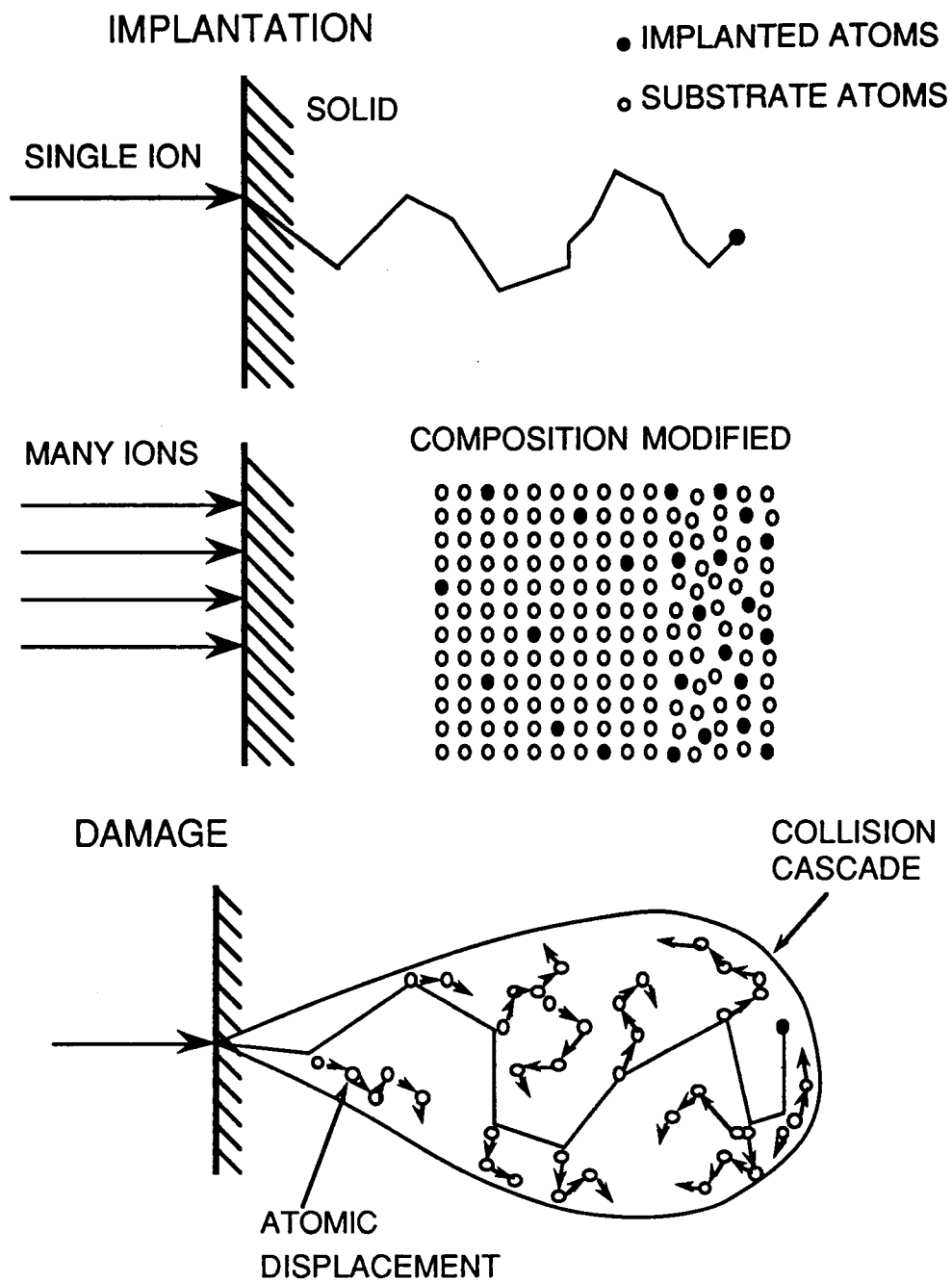


Fig. 1. Schematic of ion implantation processes [1].

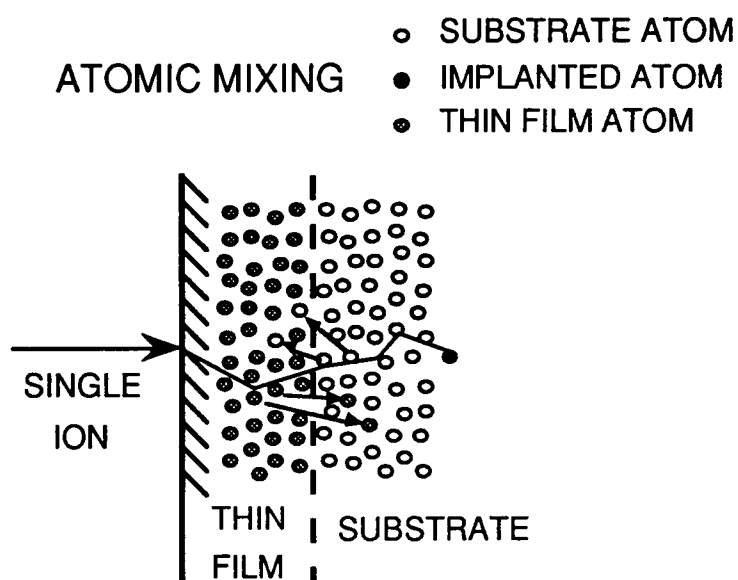


Fig. 2. Schematic of the ion mixing process [1].

one of the aftereffects which can be studied to reveal the effects of stages 1 and 2. In contrast, stage 3 can be observed *in situ* since it occurs more slowly in comparison to stages 1 and 2.

2.1. Ballistic mixing

The basic ballistic mixing processes are recoil mixing and cascade mixing. In recoil mixing, collisions between the projectile and target atoms result in relocation of the target atoms. Cascade mixing refers to the displacement of atoms in a collision cascade.

Several models of ion mixing due to ballistic processes have been based on the transport theory of atomic collisions in solids developed by Lindhard, Scharff, and Schiøtt (LSS theory) [12-14] and further developed by Winterbon, Sigmund, and Sanders (WSS theory) [15, 16]. These models assume that only binary collisions occur, that the materials involved are amorphous, and that the interatomic potentials are described by an inverse power potential. Generally, these models consider a target in a "marker" configuration where an impurity layer tens of angstroms thick is embedded in single component matrix. Other models have been developed to describe mixing due to collision cascades [17, 18]; these models describe the random walk process which approximates the displacement of atoms in a cascade.

2.1.1. Recoil mixing

The probability that a target atom will be displaced from its lattice site by a projectile ion is obtained from the relocation cross section $d\sigma_{ij}(E(x), T)$, where $E(x)$ is the energy of the incoming ion, i , at depth x in the target, and T is the energy transferred to the target atom, j . The energy transferred, T , depends on the masses of the two particles i and j . From LSS theory, the relocation cross section is

$$d\sigma_{ij}(E, T) = C_{ij} E^{-m} T^{-1-m} dT$$

where C_{ij} is a constant for a given i and j combination, and m depends on the kinetic energy of the incoming ion ($m = 1/3$ for incident energies of a few keV; $m = 1/2$ for energies of hundreds of keV) [19].

The cross section $d\sigma_{ij}$ can be expressed as a function of the depth of the target atom of interest, x , and the relocation depth, z , which is the projection of the path of the recoiling atom in the direction of incidence of the incoming ion [12-14]: $d\sigma_{ij}(E, T) = d\sigma(x, z)$.

In a typical ion mixing experiment, the impurity atoms undergo several collisions with impurity atoms implanted to a fluence ϕ . Taking the direction of incidence as the x -direction, the total relocation depth is $\Delta x = \sum z$. The probability density for impurity relocation is

$$P(\Delta x) d(\sigma) = \phi d\sigma(x, \Delta x)$$

for large Δx and small ϕ [20].

Long-range recoil implantation is mainly due to single ion-impurity knock-on events. For this process, the cross section $d\sigma$ is on the order of the square of the atomic radius (i.e. $\sim 10^{-16} \text{ cm}^2$). From this, long-range recoil implantation is rare at typical fluences ($\sim 10^{16} \text{ ions-cm}^{-2}$). Calculations based on the above expression for the probability density for impurity relocation predict that the concentration of impurity atoms knocked into the matrix by this process is proportional to $1/\Delta x$. Such recoil tails on concentration profiles have been observed experimentally by Banwell and Nicolet in Ni/SiO₂ couples irradiated with Xe [21].

2.1.2. Cascade mixing

In a collision cascade, primary collisions between the incident ions and the target atoms knock the target atoms into other target atoms (secondary collisions), and so on, until many atoms are in motion. Higher generation collisions produce many recoils of low energy, which produce small displacements in nearly random directions. Because more atoms are involved in the process, multiple relocations of atoms at low energies dominates cascade mixing [1].

Because the orientation of the incoming ion produces a preferred mixing direction, the mixing process is basically anisotropic. However, for relocation distances (Δx) which are small enough so that the variation of $d\sigma(x, z)$ on the interval between x and $x + \Delta x$ is inappreciable, the average mixing can be considered isotropic, since most of the atomic relocations are unrelated. The displacements of the atoms can be approximated by a random walk process [1, 20].

The mean relocation distance, $\langle \Delta x \rangle$, and the spread, Ω^2 , are the first and second moment of the probability distribution, $d\sigma(x, z)$:

$$\langle \Delta x \rangle = \int z d\sigma(x, z)$$

and

$$\Omega^2 = \left\langle \left(\Delta x - \langle \Delta x \rangle \right)^2 \right\rangle = \phi \int z^2 d\sigma(x, z)$$

In the range where the recoiling atoms have an energy of a few eV, the impurity profile for an initially sharp impurity distribution becomes a Gaussian spread.

The isotropic part of $d\sigma(x, z)$ can be calculated from LSS and WSS theories. For a threshold recoil energy E_c corresponding to a minimal displacement distance $R_c = AE_c^\alpha$, (where A is a constant and $\alpha \approx 1/2$), the spread is

$$\Omega^2 = (1/3) \Gamma_0 (F_d / \rho) \xi_{21} (R_c^2 / E_c) \phi$$

where Γ_0 is a dimensionless parameter with a value near 0.6; F_d is the energy deposited by the incoming ion per unit length; ρ is the atomic density; and $\xi_{21} = [4M_1M_2/(M_1+M_2)^2]^{1/2}$, where M_1 and M_2 are the masses of the atoms involved in collisions. The threshold recoil energy E_c is often identified with E_d , the threshold energy for Frenkel pair (vacancy-interstitial pair) formation. R_c^2 is the mean-square range associated with E_d . This suggests that atomic relocation due to cascade mixing is equivalent to stable Frenkel pair formation. The threshold recoil energy E_c is related to the atomic jumping mechanisms in the random walk process. If other relocation mechanisms such as linear or circular replacement sequences are involved, then E_c must be replaced accordingly. The value of α must approach zero, because in low-energy cascades the displacement range of individual atoms should only weakly depend on the transferred energy; it will be determined by the vacancy-interstitial recombination distance [20].

The physical parameters in the above expression for Ω^2 depend only on the atomic number, masses, and density of the components; this is a ballistic model. However, from this equation, Ω is proportional to $\sqrt{\phi}$, which is comparable to a thermal random walk process where Ω is proportional to $\sqrt{\phi}$. By setting $\Omega^2 = 4Dt$, an expression is obtained for an effective diffusion coefficient for low-energy cascade mixing:

$$D_{\text{eff}} = (1/4) \left(d\Omega^2 / d\phi \right) \phi$$

for experiments with a constant rate of fluence, $\dot{\phi}$ [23].

Both high- and low-energy ion mixing have been analyzed using the equation for Ω^2 . The linear dependence of Ω^2 on ϕ has been observed experimentally [1, 23, 24]; however, other experiments have shown that the predicted behavior may deviate by an order of magnitude [25-27].

2.2. Radiation-enhanced diffusion (RED)

The ballistic processes described in section 2.1.1 are essentially independent of the temperature of the target. This can be understood by considering the times and energies involved in the processes. The ion initiating the cascade comes to rest in the target within $\approx 10^{-12}$ s. A single lattice vibration lasts between 10^{-13} and 10^{-12} s. The kinetic energy of atoms displaced by ballistic processes is well above the typical thermal vibration energies of a few eV [20].

However, a non-equilibrium number of vacancy and interstitial defects can exist in the volume of material affected by the cascade. Recombination times for these defects may exceed the duration of the cascade ($\approx 10^{-11}$ s), so that many defects remain after the initial energy deposited in the cascade volume has been dissipated. As these defects become mobile at a high enough ambient temperature, thermally activated defect migration can occur, contributing to atomic mixing during the relaxation stage (stage 3).

Experimental evidence indicates that radiation-enhanced diffusion becomes the dominant mixing mechanism when the matrix temperature exceeds some critical temperature, T_c [28]. The theory of RED is based on a set of coupled chemical rate equations, along with an equation for the radiation-enhanced diffusion coefficient, D_{red} . Lam and Rothman [29] give an equation for D_{red} :

$$D_{red} = C_v D_v + C_i D_i$$

where D_v and D_i are the diffusivities of vacancies and interstitials, respectively, and C_v and C_i are the concentrations of vacancies and interstitials produced by ion irradiation. D_v and D_i exhibit Arrhenius-type behavior, e.g., for vacancies:

$$D_v = D_{0v} \exp\left(-\Delta H_v^m / kT\right)$$

where ΔH_V^m is the migration enthalpy of vacancy atoms, and k is Boltzmann's constant. The concentrations C_v and C_i are calculated from the coupled chemical rate equations:

$$dC_i/dt = \sigma \dot{\phi} K_{iv} C_i (C_v + C_{v0}) - K_{is} C_i C_s$$

$$dC_v/dt = \sigma \dot{\phi} K_{iv} C_v (C_i + C_{i0}) - K_{vs} C_v C_s$$

where C_{v0} and C_{i0} are the equilibrium concentrations of vacancies and interstitials, σ is the cross section for Frenkel pair production, and $\dot{\phi}$ is the ion flux. The constants K_{iv} , K_{is} , and K_{vs} , are rate constants for interstitial-vacancy recombination, interstitial-sink annihilation (e.g., at fixed sinks such as grain boundaries and dislocation loops), and vacancy-sink annihilation, respectively. Using values for C_i and C_v calculated from the rate equations, D_{red} may be determined.

The theory of RED employs the following assumptions [30]: (a) there exists a steady state for the concentrations of vacancies and interstitials under ion bombardment, (b) RED is due to recombination and/or annihilation processes only (neglecting mechanisms such as divacancy migration, and clustering of vacancies or interstitials), and (c) ion bombardment affects the concentration, but not the migration of point defects. At sufficiently high temperatures, when recombination occurs, D_{red} may be approximated by

$$D_{red} = \left(\dot{\phi} D_v / \pi \rho r_{iv} \right)^{1/2}$$

where ρ is the atomic density and r_{iv} is the maximal separation distance for spontaneous recombination of a vacancy-interstitial pair. From this equation and the equation for D_v , the activation energy for RED is half the vacancy migration energy. The lower activation energy for RED is related to the non-equilibrium density of vacancies. At higher temperatures, D_{red} becomes independent of temperature, since the average diffusion distance is increased and annihilation of vacancies at fixed sinks becomes important. At even higher temperatures, thermal generation of vacancies dominates, and $D_{red} = D_v C_v^{th}$, where C_v^{th} is the vacancy concentration in thermal equilibrium.

The theory of radiation-enhanced diffusion has successfully described the results of some ion mixing experiments. Matteson et al. [28] showed that radiation-enhanced

diffusion becomes the dominant mixing mechanism in ion mixing of Si and Nb. They found that, above a critical temperature, the mixing rate depends exponentially on the inverse temperature. They showed that, for this system, the activation energy for RED is 0.9 eV; this is about one half the vacancy migration energy in Nb.

2.3. Thermal spikes

Seitz and Koehler [31] defined a thermal spike to be a limited volume inside a solid within which the majority of atoms are simultaneously in motion. In order for the thermal spike concept to be quantitatively meaningful, several conditions must be met [32]. First, the mean deposited energy density, θ , in the cascade must exceed a critical energy density, θ_c , for a phase change to occur (~ 1 eV/atom for melting; 3-4 eV/atom for evaporation). Then the cascade dimensions must be large enough for statistical dynamics to be valid; for example, for 10 keV Au⁺ in Au, the cascade diameter is approximately 20 Å, and would therefore contain only about 500 atoms. Also, the thermal gradient across the spike must be reasonably small. For the previous example, 10 keV Au⁺ in Au, the initial θ is approximately 25 eV/atom. This is about 10^3 greater than the energy of the surrounding material; the initial thermal gradient would be about a factor of 10 per lattice spacing. Finally, the quenching time constant ($t_q = R/4k$; R is the range, and k is the target material's thermal diffusivity) must be longer than the time necessary for electron-phonon coupling (10^{-11} s); else, two different "temperatures" are needed to describe the atomic motion and the electron system.

Assuming the above criteria are met within the spike, atomic motion has reached a state of quasi-equilibrium (the law of equipartition of energy holds in the spike volume and the velocity distribution follows Maxwell-Boltzmann statistics). Molecular dynamics simulations have indicated that this state could be reached after a relatively small number of collisions [9].

Under these conditions, a local temperature within the spike can be defined. The temperature evolution within the spike can be described by the classical heat diffusion equation with appropriate boundary conditions. The estimated temperature within the spike is obviously very high. Although the state of the matter in the spike volume is uncertain, values for the thermal conductivity, κ , and the heat capacity, C , may be taken as those of the bulk gas or liquid [33, 34].

Vinyard [35] modeled the temperature evolution in a thermal spike starting from the Fourier equation for heat conduction in a uniform, isotropic material. From Vinyard's

calculations for a cylindrical thermal spike, it may be found that the total number of atomic jumps per unit length of a thermal spike is

$$\eta = n^3 \Gamma(2n) A F_d^2 k^{2n} / 8\pi \kappa_0 C_0 Q^{2n}$$

where k is Boltzmann's constant, A is a constant, Q is the activation energy for the atomic jump, and $\Gamma(2n)$ is the gamma function of $2n$. At very high temperatures such as those associated with a thermal spike, κ and C are approximately temperature independent. The equation for η becomes

$$\eta = A F_d^2 k^{2n} / 8\pi \kappa_0 C_0 Q^2$$

From Einstein's relation, the effective diffusion coefficient in the thermal spike is proportional to η , and is thus proportional to $(F_d/Q)^2$.

3. Thermodynamics and ion mixing

Several studies on metal-metal and metal-silicon systems have suggested that the thermochemical properties of the film and the substrate are important in mixing phenomena. For metal films and substrates, the compositions of layers formed at the film/substrate interface are often those that form during thermal annealing [23, 36-38]. In transition metal-silicon systems, the metal silicides formed during ion irradiation have been correlated with the stable phases that lie near eutectic compositions in the respective equilibrium phase diagrams [37].

In order to explain the occurrence of metastable phase formation during ion mixing, Lilienfield et al. [39] qualitatively introduced kinetic factors in their guidelines for prediction of mixing phenomena. Crystalline phases form during ion mixing of constituents that normally form: (a) solid solutions with extended solubilities, (b) intermetallic compounds having simple crystal structures and wide phase fields, or (c) complex crystal structures with high atomic mobility. Amorphous alloys result during mixing if the constituents normally form compounds having either (i) simple crystal structures and narrow phase fields or (ii) complex crystal structures.

Studies of collisionally similar but thermochemically dissimilar systems have revealed large variations in the amount of mixing observed in such systems. The observation of differences in the amounts of mixing in collisionally similar but chemically different

systems implies that cascade mixing is strongly influenced by local chemical processes. For example, Saris et al. [40] performed mixing experiments on the systems Au-Cu and Cu-W in the "marker" configuration (i.e., Cu-Au-Cu and Cu-W-Cu). These systems are collisionally similar (i.e., the relative masses of Cu-Au and Cu-W are similar) but are thermodynamically very different. The equilibrium phase diagrams show that Cu and Au have extensive solid solubility, with the formation of ordered intermediate phases. In contrast, Cu and W are virtually immiscible. In the Cu-W samples, the amount of mixing was near that predicted from calculations of recoil mixing alone, while the amount of mixing in the Cu-Au-Cu samples was an order of magnitude greater. In another experiment, van Rossum and co-workers [41] found that the amount of mixing in Hf-Ni bilayers is much greater than for Hf-Ti bilayers. They proposed that the difference in heat of mixing, ΔH_m , could be responsible. For the Hf-Ni system, $\Delta H_m = -62$ kJ/g, while for the Hf-Ti system, $\Delta H_m = 0$ kJ/g.

The enthalpy of formation between the metal and substrate has been considered an important parameter in determining the nature of the interfacial reactions occurring during ion irradiation. Mixing rates have been linked with the solubility of metals in metal-metal couples; solubility is determined in part by the enthalpy of chemical mixing [42, 43]. For metal bilayers, the extent of mixing has been correlated with the square of the difference between the electronegativities of the different metals. The enthalpy of mixing is proportional to the difference in the electronegativities of the different metals [44]. From these various studies, an "enthalpy rule" has been suggested: mixing is expected only if the heat of reaction between the components is negative. Farlow et al. [45] applied this enthalpy rule in a study of mixing of 33 materials combinations involving ceramic substrates. Mixing always occurred when predicted; however, mixing sometimes occurred when not predicted by the rule.

To explain the variations in collisionally similar but chemically dissimilar systems, Johnson and co-workers [46-49] proposed a model in which the final distribution of chemical species is determined by chemically biased diffusion within a thermal spike. This model uses the differences in enthalpies of mixing (ΔH_m) and cohesive energies (ΔH_c) to analyze the variations in the amount of mixing between systems with similar collisional properties. Their experiments involved both heavy ions and heavy metal matrices ($Z > 20$) where dense collision cascades are likely to occur, and low temperature irradiation where radiation-enhanced diffusion is suppressed. Data obtained for bilayers of 4d-5d metals irradiated with 600 keV Xe⁺⁺ at 77K correlated well with this model when

the materials were assumed to behave as regular solutions and the values for $\Delta H_m/\Delta H_c$ used were those for a 50-50 mixture of the metals [45].

CHAPTER 2

THERMOCHEMISTRY OF Al, Cr, Zr, AND THEIR OXIDES

1. Sapphire: characteristics determining post implantation structure

Ceramics in general are made up of two or more chemical species distributed in an ordered manner over at least two sublattices. Atoms displaced during elastic collisions (e.g. during ion bombardment) are unlikely to come to rest at the lattice sites of the other type. Different amounts of energy are required to displace the different atom species from their lattice sites. Ceramics exhibit several chemical bonding types ranging from ionic to covalent to metal-like.

The ceramic of interest in this study, sapphire (α -Al₂O₃), is rhombohedral, and belongs to the space group R3C. The O²⁻ anions are approximately hexagonal close-packed. The Al³⁺ cations are ordered, occupying 2/3 of the available octahedral sites. It is convenient to describe the structure on the basis of the close packing; however, there are significant deviations from the ideal close-packed structure due to the electrostatic interactions between the ions. The Al³⁺ ions and the vacant octahedral sites are arranged to achieve maximum separation of like charges and minimum separation of unlike charges, consistent with the necessary bonding between aluminum and oxygen and with maintaining overall electrical neutrality. The bonding is mainly ionic, but exhibits some covalent character [50].

While many oxides may exhibit large deviations from stoichiometry (as much as several percent), any deviation from stoichiometry in α -Al₂O₃ is too small to be detected [50]. Therefore, while it is possible to substitute 3+ impurities for Al³⁺, impurities cannot be added without creating charge-compensating defects. The vacant octahedral sites are structural vacancies and are ordered to maintain the electrostatic forces within the crystal.

The principal point defects observed in α -Al₂O₃ are oxygen vacancies containing trapped electrons: the F⁺-center (an oxygen vacancy containing one electron) and the F-center (an oxygen vacancy containing two electrons). Oxygen divacancy centers are also observed, and there is evidence for Al³⁺ interstitial-type defects in the form of Al pairs. No evidence for aluminum vacancies exists [50]. Dislocations are also observed, as are impurity-defect complexes.

2. Chromium oxide and zirconium oxide: solubility in sapphire

This work is directed toward obtaining a better understanding of the relative roles of thermodynamics and kinetics in mixing of oxide-oxide bilayers. With this goal in mind, the systems $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{ZrO}_2/\text{Al}_2\text{O}_3$ were chosen for study.

The equilibrium phase diagrams (Figs. 3 and 4) show that Cr_2O_3 has complete solubility with Al_2O_3 , while ZrO_2 is completely insoluble in Al_2O_3 below 1710°C [4]. Solid solutions of Cr_2O_3 and Al_2O_3 have been formed by sintering the oxides as powders at temperatures between 1400 and 1500°C [51-53].

A miscibility gap has been reported in the system $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ at high pressure (1×10^8 Pa; 10^5 Pa = 1 atm) in the temperature range $440\text{-}1200^\circ\text{C}$ [54]. According to experiments by Jacob [55], a miscibility gap exists in this system below 900°C at atmospheric pressure, as well. Jacob determined the activities of Cr_2O_3 in $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solutions from electromotive force measurements on galvanic cells containing $\text{Cr}_x\text{Al}_{2-x}\text{O}_3$. From these data, the heat of mixing (ΔH_m , J-mole $^{-1}$) and entropy of mixing (ΔS_m , J-mole $^{-1}\text{-K}^{-1}$) of the solid solution were determined:

$$\Delta H_m = X_{\text{Cr}_2\text{O}_3} X_{\text{Al}_2\text{O}_3} [31,700 X_{\text{Cr}_2\text{O}_3} + 37,470 X_{\text{Al}_2\text{O}_3}]$$

$$\Delta S_m = -1.8R [X_{\text{Cr}_2\text{O}_3} \ln X_{\text{Cr}_2\text{O}_3} + X_{\text{Al}_2\text{O}_3} \ln X_{\text{Al}_2\text{O}_3}]$$

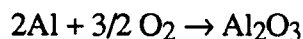
where the X_i are the mole fractions of the particular oxides.

For a 50-50 mixture of Cr_2O_3 and Al_2O_3 (taking both X_i to be 0.5), $\Delta H_m = 8271$ J-mole $^{-1}$, and $\Delta S_m = 10.37$ J-mole $^{-1}\text{-K}^{-1}$. From this, the Gibbs free energy of mixing (ΔG_m) at 300 K is 5,159 J-mole $^{-1}$. At 1200 K, $\Delta G_m = -3,136$ J-mole $^{-1}$. These values indicate that mixing of these oxides should not occur at 300 K, but that mixing is favored at 900 K.

No heat of mixing data is available for the system $\text{ZrO}_2\text{-Al}_2\text{O}_3$.

3. Possible reactions between the components

Data on the heats of formation (at 298 K) for Al_2O_3 , Cr_2O_3 , and ZrO_2 are available in the literature [56]:



$$\Delta H_f = -1,677 \text{ kJ-mole}^{-1}$$

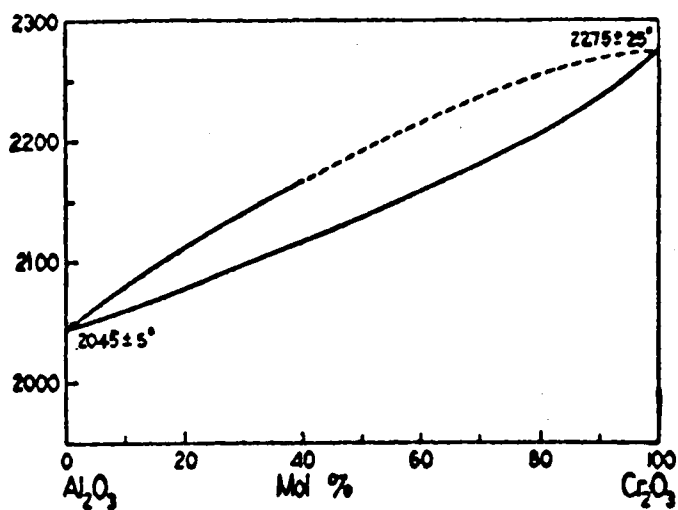


Figure 3. Cr_2O_3 - Al_2O_3 phase diagram [4]. Temperatures are in degrees Centigrade.

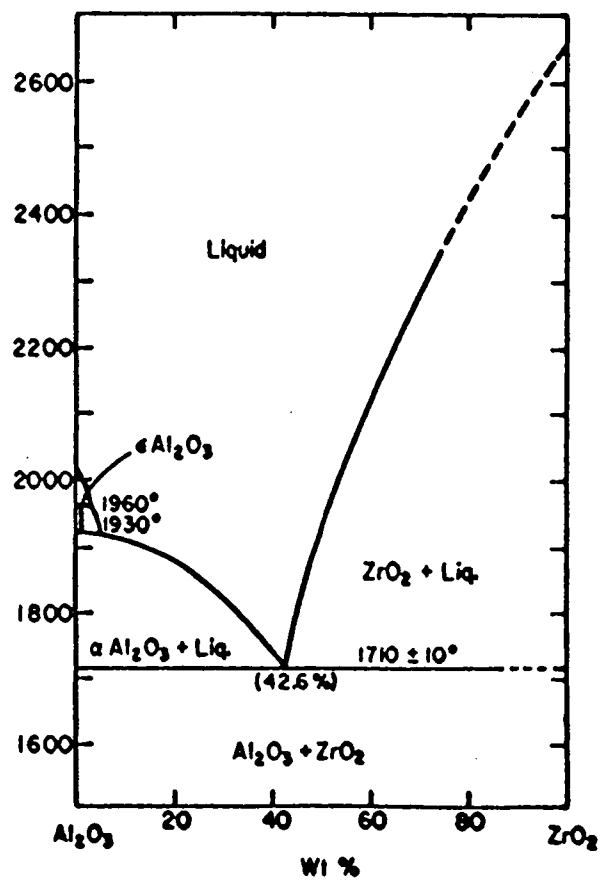
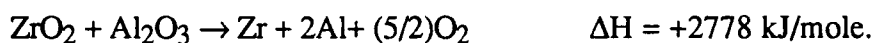


Figure 4. ZrO_2 - Al_2O_3 phase diagram [4]. Temperatures are in degrees Centigrade.



From these values for ΔH_f , the heats of reaction can be calculated for the following possible reactions in the systems under study in this work:



The "enthalpy rule," i.e., that mixing should occur only if the enthalpy for the reaction is favorable, was discussed in Chapter 1. Applying this rule to the reactions above, and to the enthalpy of mixing for the formation of $\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3$ solid solutions discussed in Section 3 above, it appears as though mixing will occur in the $\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3$ system only at elevated temperatures, near 900°C . The calculated values for ΔH are positive for the chemical reactions listed above, therefore no mixing should occur in these systems.

CHAPTER 3

EXPERIMENTAL

1. Film deposition

Single crystal sapphire (Al_2O_3) disks (c- axis oriented) were used as substrates for film deposition. These substrates were supplied with an optical-grade polish by the manufacturer (Crystal Systems, Inc., Bedford, MA). Prior to film deposition, the substrates were ultrasonically cleaned, first in Micro[®] cleaning solution, followed by acetone and then ethanol and finally rinsed in distilled water. Then, they were annealed in flowing air at 1350°C for 120 h to remove residual polishing damage and organic contamination on the surface.

Mixing experiments were performed on metal-sapphire (Cr, Zr) and oxide-sapphire (Cr_2O_3 , ZrO_2) combinations. The films were prepared as follows.

Thin films (50 ± 5 nm thick) of either Cr or Zr were evaporated onto the Al_2O_3 substrates at a rate of 1 nm/s using an electron beam evaporation system. The base pressure was around 5×10^{-7} torr. These films are known to be polycrystalline when deposited under these conditions [57]; therefore, no characterization of the crystalline state of these films was performed.

Thin films (80 ± 5 or 50 ± 5 nm) of Cr_2O_3 or ZrO_2 were deposited from sintered oxide targets onto the substrates via an rf sputter unit equipped with a magnetron sputter gun. The oxide targets were sputtered by ionized Ar. For both oxide targets, the energy density applied was 5 watts-cm^{-2} . The base pressure was about 4×10^{-6} torr; the Ar pressure in the chamber was 2×10^{-3} torr. The sputter rate from each target was approximately 3 nm/min. The as-deposited films were oxygen-rich, as evidenced by RBS analysis of both kinds of oxide films deposited on diamond film substrates. In order to obtain proper stoichiometry, the samples were annealed for 2 h at 500°C in an atmosphere of 96% Ar-4% H. The RBS spectra of oxide/diamond samples annealed in this manner show that this treatment produces stoichiometric oxides.

Oxide films deposited via rf sputter deposition are generally found to be amorphous [57], however, after the anneal in 96% Ar-4% H, the films are microcrystalline as determined by electron diffraction (transmission electron microscopy--see Section 7).

2. Implantations

In order to determine the importance of ballistic effects in mixing, samples of each metal/sapphire system were bombarded with Kr ions, with the energy chosen so that the ions come to rest far from the interface. The computer code TRIM [58] was used to calculate the range parameters. The model is based on Monte Carlo simulation of binary collisions between a moving ion and stationary target atoms. TRIM calculations show that R_p of Kr ions in 50 nm of Zr on Al_2O_3 is 109 nm; ΔR_p is 42 nm. For 50 nm of Cr on Al_2O_3 , R_p is approximately 96 nm, and ΔR_p is around 41 nm. The fluences were 1×10^{16} and 1×10^{17} ions-cm⁻².

Implantations on the oxide/sapphire systems were carried out somewhat differently. Samples of each system were implanted at room temperature and at elevated temperature (near 900 °C) with Cr ions. The 80 nm-thick films were implanted at an energy of 340 keV; the 50 nm-thick films were implanted at an energy of 160 keV. This energy was chosen so that the majority of the Cr ions would come to rest relatively far from the film/substrate interface. The projected range of the Cr ions in the 80 nm Cr_2O_3 on Al_2O_3 samples is about 119 nm, with ΔR_p of 39 nm. For 80 nm of ZrO_2 on Al_2O_3 , R_p is approximately 166 nm, and ΔR_p is around 49 nm. The projected range of the Cr ions in the 50 nm Cr_2O_3 on Al_2O_3 samples is about 76 nm, with ΔR_p of 28 nm. For 50 nm of ZrO_2 on Al_2O_3 , R_p is approximately 78 nm, and ΔR_p is around 30 nm. Two fluences (4×10^{16} and 1×10^{17} ions-cm⁻²) were investigated to provide a basis for determining any fluence dependence of any possible mixing. In addition, one set of 50 nm-thick ZrO_2/Al_2O_3 and Cr_2O_3/Al_2O_3 samples was implanted at liquid nitrogen temperature with 160 keV Cr to a fluence of 4×10^{16} ions-cm⁻² to determine whether the mixing process is thermally activated even at room temperature.

Mixing experiments with Kr were performed on the oxide/sapphire systems. The fluences were 4 and 8×10^{16} ions-cm⁻² (room temperature), and 5×10^{16} and 1×10^{17} ions-cm⁻² (825°C). The energy was 475 keV. This energy was chosen to provide the same energy deposition at the film/substrate interface as that achieved during the Kr implantations in the metal-oxide systems. This energy was determined via the computer simulation EDEP-1 (Version 5.0) [59], which calculates the energy deposited by the incoming ions as a function of depth for a given initial ion energy. This code is also based on a binary collision model; it employs the stopping cross sections of Wilson et al. [60] in analyzing the damage energy deposited in discrete depth intervals. According to TRIM calculations, R_p of the Kr ions in the 80 nm Cr_2O_3 on Al_2O_3 samples is about 155 nm, with ΔR_p of 51 nm. For 80 nm of ZrO_2 on Al_2O_3 , R_p is approximately 155 nm, and ΔR_p

is around 52 nm. These experiments with Kr were performed to allow comparison of ballistic effects due to ion size, as well as comparison of the behavior of the metal-oxide and oxide-oxide systems. The elevated temperature Kr implantations were performed at lower temperature than the elevated temperature Cr implantations (825°C vs. 860 or 900°C) to guard against failure of the heaters in the heating stage on which the samples are mounted during implantation. Such failures did occur during some implantation attempts.

An area on each of the specimens remained masked to provide an unimplanted region for comparison. Stage temperatures were monitored with an optical pyrometer during the elevated temperature implantations. Table 1 summarizes the implantation conditions used in this work. Table 2 summarizes the ranges of the implanted ions in each material combination.

3. Thermal annealing experiments

To confirm the solubility of these as-deposited oxide films in single crystal Al_2O_3 , samples of both Cr_2O_3 and ZrO_2 films on sapphire were annealed in flowing air for 1 h at 1450°C. This temperature was chosen because it is within the range of sintering temperatures for $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ reported in the literature [51-53]. Rutherford backscattering spectrometry (RBS) (see Section 5) was used to determine whether diffusion occurred after this treatment. Based on the results, other as-deposited $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ specimens were annealed for 1 h at either 1450, 1150, or 1050°C, and then examined using RBS analysis.

4. Scanning electron microscopy

Selected as-deposited and as-irradiated samples were examined via scanning electron microscopy to determine the change in surface appearance after irradiation. Thermally annealed samples were also inspected. Microscopy was performed on either a Hitachi S-800 or an S-900 field emission gun (FEG) scanning electron microscope. Samples examined on the S-900 were coated with 1.5 nm Cr to minimize charging, while the samples examined on the S-800 were left bare (a charging problem did exist; however some useful information was obtained). Operating voltages ranged between 1 and 6 kV.

5. Rutherford backscattering spectrometry

Both the masked and implanted areas of each specimen were analyzed using Rutherford backscattering spectrometry. This technique involves the scattering of light particles (e.g. He ions) by atoms in the material of interest (target). The target material is bombarded with

Table 1. Implantation conditions

Set: Film/Substrate Film/Substrate	Films' Thick- nesses (nm)	Ion, Energy (keV)	Fluence (one set each) (ions-cm ⁻²)	Temp. (°C)
Cr/Al ₂ O ₃	50	Kr, 320	5 x 10 ¹⁶	70
Zr/Al ₂ O ₃			1 x 10 ¹⁷	70
Cr ₂ O ₃ /Al ₂ O ₃	50	Cr, 160	4 x 10 ¹⁶	70, 860
ZrO ₂ /Al ₂ O ₃			5 x 10 ¹⁶	-196
Cr ₂ O ₃ /Al ₂ O ₃	80	Cr, 340	4 x 10 ¹⁶	70, 900
ZrO ₂ /Al ₂ O ₃			8 x 10 ¹⁶	70, 900
Cr ₂ O ₃ /Al ₂ O ₃	80	Kr, 475	4 x 10 ¹⁶	70, 825
ZrO ₂ /Al ₂ O ₃			8 x 10 ¹⁶	70, 825

Table 2. Ion ranges

Film/Substrate	Film thickness (nm)	Ion, Energy (keV)	Range, R _p (nm)	Straggle, ΔR _p (nm)
Cr/Al ₂ O ₃	50	Kr, 320	96	41
Zr/Al ₂ O ₃	50	Kr, 320	109	42
Cr ₂ O ₃ /Al ₂ O ₃	50	Cr, 160	76	28
ZrO ₂ /Al ₂ O ₃	50	Cr, 160	78	30
Cr ₂ O ₃ /Al ₂ O ₃	80	Cr, 340	119	39
ZrO ₂ /Al ₂ O ₃	80	Cr, 340	166	49
Cr ₂ O ₃ /Al ₂ O ₃	80	Kr, 475	155	51
ZrO ₂ /Al ₂ O ₃	80	Kr, 475	155	52

MeV energy range particles, and the number and energy of the particles scattered back toward a solid state detector is recorded. The technique is sensitive to mass and depth differences within the target material; however, the measurements are insensitive to chemical bonding within the material.

The depth resolution in RBS is dependent on the energy resolution of the detector, the energy of the incoming particles, the energy of the backscattered particles, and the angle between the target's surface and the detector. Depth resolution may be improved by performing the analysis with the target material in glancing exit angle geometry (with the target's surface at a steep angle to the detector, as opposed to nearly normal to it), which maximizes the energy loss of particles backscattered from a given depth in the target, because the particles have farther to travel to reach the detector. With the scattering angle near 90° , the depth resolution can be as small as 2 nm. In addition, the detector acceptance angle, surface roughness of the target material, and energy straggling affect the depth resolution. Energy straggling is a function of the depth of penetration; for layers ≤ 100 nm, energy straggling is small compared to the resolution of the detector, and thus does not affect the obtainable depth resolution at these depths. The detector acceptance angle is finite, and therefore broadens the scattering angle from that dictated by the geometry between the beam, sample, and detector. The surface roughness of the sample broadens the scattering angle as well, and sets the ultimate limit of the depth resolution [61].

This technique is more sensitive to heavy elements because the Rutherford scattering cross section depends on the square of the atomic number of the element in question. For a heavy element such as Au on the surface of an elemental bulk target, the detectable minimum is around 10^{13} atoms-cm $^{-2}$. A trace amount of an impurity on a substrate of mass number greater than the mass number of the impurity cannot be detected because the impurity signal will be buried under the substrate signal [62]. Further information on RBS analysis may be obtained in references 61 and 62.

A few of the bare Al $_2$ O $_3$ substrates (i. e., with no metal or ceramic film) implanted at the same time as the oxide films were examined using RBS in the channeling mode (RBS-C). Single-crystal target materials can be oriented with a major symmetry axis along the incoming beam direction such that the He particles are steered between rows of atoms in the material. The backscattering yield from a well-annealed crystal is thus greatly reduced. The yield increases as the damage (disorder) in the crystal increases. As an example, by comparing the spectra from an ion implanted specimen with the spectra from an unimplanted part of the specimen aligned with the analysis beam, and with a spectrum from an unimplanted part purposely not aligned with the beam (a *random* spectra), it is possible

to determine the amount of damage in the implanted specimen. The random spectra is obtained by rotating the target with respect to the analysis beam.

In this work, RBS analysis was performed with 2.3 MeV He^{2+} and a scattering angle of 160° . The spectra were taken in glancing exit angle geometry ($\theta = 40^\circ$) to enhance depth resolution when examining the specimens for evidence of mixing. The analysis was performed after implantation, on implanted and unimplanted (masked) sections of the samples.

6. X-ray photoelectron spectroscopy

The chemical states of the components of selected samples were determined via X-ray photoelectron spectroscopy (XPS). This technique provides information on the binding energies of electrons emitted from the atoms in a material after excitation by x-rays of a set wavelength. Electrons emitted from a given element in a given chemical state have a characteristic binding energy. Electrons emitted from the same element in a different chemical state have binding energies shifted by some characteristic amount. Data on different chemical species (common chemical species) are available in the literature for comparison. This technique is extremely surface sensitive.

The mean free path of electrons ejected from a specimen depends on the energy of the electrons. It is relatively insensitive to the elemental components of the specimen. The average escape depth for electrons from most materials is about 3 nm for electron energies between 0 and 1000 eV, which is the kinetic energy range generally analyzed in XPS [61] Further information on XPS can be found in references 61 and 63.

Due to equipment problems, the spectra were taken on two different XPS units from different manufacturers (thus the data are in slightly different formats). Generally, XPS was performed in an ultra-high vacuum chamber operating with a base pressure of approximately 1×10^{-9} Torr. Survey scans were obtained on the "as-introduced" samples. Spectral features of these scans were located and elements of both surface residue and the thin films were identified.

For the first apparatus, the survey scans were obtained with Mg K_α x-rays (1253.6 eV) as the analyzing radiation. The scan parameters were as follows: the analyzer pass energy was 100 eV for all analyses; the analysis area on the sample was 300 μm in diameter.

For the second machine, the survey scans were obtained with Al K_α x-rays (1486.6 eV). The parameters used were as follows: the analyzer pass energy was 93.9 eV over a binding energy range from 0 to 1000 eV; the analysis area on the sample was 800 μm in diameter.

Sputter depth profiling was used to track the components from the film through the film/substrate interface and into the substrate. In both XPS units, an Ar ion sputter gun was used to sputter away a portion of the sample, then XPS data were acquired. Data from successive depths in the sample were obtained by alternately sputtering for a given amount of time at a set ion energy, and then analyzing a region from the center of the sputtered area. This was done in an effort to minimize crater edge effects. For these studies, the oxide sputter rates varied from approximately 3 nm/min on both XPS units. The metal sputter rates were approximately 6 nm/min. The sputter rates were estimated through knowledge of the film thicknesses in the unimplanted portions of the samples.

7. Transmission electron microscopy

The crystalline state of the as-deposited oxide films at room temperature and at elevated temperature was characterized via transmission electron microscopy (TEM). Thin films of both oxides were deposited on NaCl using the same parameters as for the depositions on sapphire. The NaCl was dissolved away in distilled water, and the films were caught on platinum TEM grids and allowed to dry.

Characterization of these films at elevated temperature was performed *in situ* in a heating stage inside a Philips CM12 transmission electron microscope operating at 120 keV. Energy dispersive analysis (EDS) was performed on each specimen to verify the films' elemental composition. Diffraction patterns were taken at room temperature, then the stage was heated to 900°C in 100°C increments. The specimen was held at constant temperature for about ten minutes at each intermediate temperature. Changes in the diffraction pattern were recorded at the end of each "hold" period.

Cross-section specimens for transmission electron microscopy were prepared according to the method of Horton, et al. [64]. Cross-section specimens from selected samples (both an irradiated and unirradiated portion from selected implantation conditions) were glued together (oxide film-to-oxide film) with M-BOND TYPE 610 ADHESIVE epoxy. The freshly glued cross sections were placed in a vise so that the glue line thickness was minimized, and the epoxy was allowed to cure overnight at room temperature. The composite specimens were cut perpendicular to the glue line using a low speed diamond saw. Typically, the resulting specimens were around 600 μm thick. The sections were ground to approximately 180 μm with 6 μm diamond paste, and then one side was polished with 3 μm diamond paste. The samples were then dimpled on the unpolished side with 6 μm diamond paste followed by 3 μm diamond paste. The final thickness in the dimpled area was approximately 30 μm . After dimpling, the specimens were glued to

carbon rings, and then ion milled to electron transparency in a Gatan ion mill. The specimens were milled at liquid nitrogen temperature with 6 kV Ar. The beam current on each gun was 0.5 mA. Following ion milling, the sample was coated with about 10 nm of carbon to reduce charging during TEM examination.

Analytical electron microscopy was performed on cross-section specimens in a Philips EM 400T/FEG analytical electron microscope equipped with an EDAX 9100 energy dispersive x-ray spectrometer for EDS analysis. Typically, the microscope as operated at 100 kV. The EDS probe is 15 nm in diameter in TEM mode; it is 2 nm in diameter in scanning (STEM) mode.

CHAPTER 4

RESULTS AND DISCUSSION

1. Calculations: on the amount of mixing expected

In order to make an estimate of the amount of mixing which might be expected from a purely collisional point of view (recoil, cascade mixing), two sets of TRIM simulations were made. First, simulations were run with each of the ion/target combinations investigated in this work. TRIM output includes several calculations in addition to the ion range and the deposited energy. One of these is the range and concentration of the recoils (target atoms knocked off their lattice sites by the incoming ions). Recoils of each atomic species in the target are tracked. For each ion/target combination, plots of recoil density of the metallic species of the film and the substrate were plotted versus depth. Appropriate depths were chosen for the interface (50 or 80 nm); only the metallic species recoiling across the interface were considered (i.e. aluminum recoils into the film, and chromium or zirconium recoils into the sapphire). Representative plots are shown in Figs. 5a and 5b. These plots are normalized to a fluence of 4×10^{16} ions-cm⁻²; this is the fluence examined in the AEM work. Note the high concentration of recoils from the film near the substrate in these figures. These values for recoil density are near the atomic concentration of the host material, i.e., sapphire. The point of these calculations is to determine the extent of the predicted ballistically mixed region, which should be limited to the recoil range. The results are summarized in Table 3.

In the second set of TRIM simulations, the energy of the incoming ion at the film/substrate interface was determined (the energy loss per Å was multiplied by the appropriate film thickness and then subtracted from the initial ion energy). It was assumed that this energy was transferred to the film components at the interface. A kinematic factor

$$K = \frac{E_1}{E_0} = \left[\frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_2 + M_1} \right]^2$$

for each ion/film component pair was determined, where E_0 and E_1 are the energies of the incident particle before and after scattering; M_1 is the mass of the incident particle; M_2 is the mass of the target atom which is initially at rest; and θ is angle at which the incident particle

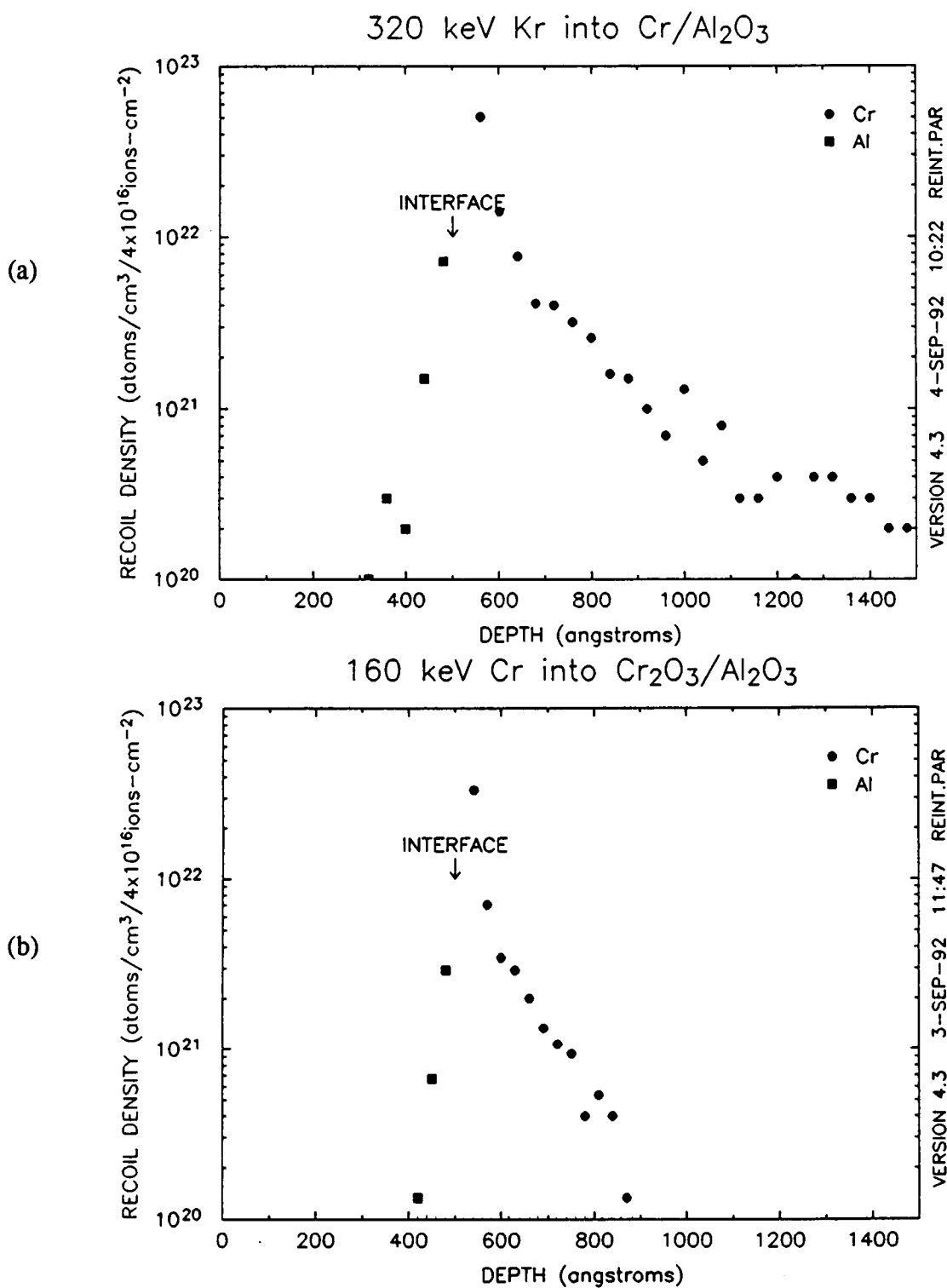


Fig. 5. Representative plots of recoil density of the metallic species of the film and the substrate vs. depth, normalized to a fluence of 4×10^{16} ions-cm⁻²: (a) is a plot for implantation of 160 keV Cr into Cr₂O₃/Al₂O₃; (b) is a plot for implantation of 320 keV Kr into Cr/Al₂O₃.

Table 3. Estimate of the extent of the mixed region from TRIM calculations (distances computed for recoil density of 10^{21} atoms-cm⁻³/(4x10¹⁶ ions-cm⁻²)).

Ion-Target Combination	Energy (keV)	Interface Position (nm)	Al: distance recoiled into film (nm)	Film's metal species: distance recoiled into substrate (nm)
Kr - Cr/Al ₂ O ₃	320	50	10	42
Kr - Zr/Al ₂ O ₃	320	50	8	30
Cr - Cr ₂ O ₃ /Al ₂ O ₃	160	50	4	24
Cr - ZrO ₂ /Al ₂ O ₃	160	50	6	18
Cr - Cr ₂ O ₃ /Al ₂ O ₃	340	80	2	20
Cr - ZrO ₂ /Al ₂ O ₃	340	80	6	17
Kr - Cr ₂ O ₃ /Al ₂ O ₃	475	80	3	26
Kr - ZrO ₂ /Al ₂ O ₃	475	80	8	30

is scattered. For these calculations, e.g. for a Kr ion bombarding $\text{ZrO}_2/\text{Al}_2\text{O}_3$, kinematic factors were determined for a Kr ion hitting a Zr atom, and for a Kr ion hitting an O atom. This kinematic factor was applied to the energy of the Kr atom at the film/substrate interface, and the resulting energy was taken as the energy transferred to each film component at the interface. TRIM calculations were run as though the film components were actually ions with this calculated energy, being implanted into Al_2O_3 . This calculation gives a maximum (worst case) distance for an atom near the interface to be knocked into the Al_2O_3 by the original incoming ion. The results are shown in Table 4.

Calculations by Lewis [65] indicate that, in ceramic targets under bombardment by energetic heavy ions, the light atom in the target recoils with a range significantly beyond that of the implanted ion. In those calculations, the range of the recoils was estimated by a relocation cross section formula. Calculations were made for several cases, including TiB_2 irradiated with 1 MeV Ni ions. Experimentally, a deep-lying defect structure was found at twice the range of the Ni ions [66]. Lewis's calculations showed that the range of recoiling B atoms corresponded to the depth of this defect structure. The results presented in Table 4 are an approximation of Lewis's calculations; the two sets of calculations are in general agreement concerning the behavior of the light ion in a ceramic target.

According to the calculations presented in Tables 3 and 4, the film component atoms will travel significant distances (in comparison to the film thickness) before coming to rest in the material. However, the results in Table 4 imply a more diffuse mixed region than predicted by the numbers in Table 3 because of the longer recoil range.

Collisional mixing is only one possible mixing mechanism. The possibility of enhanced mixing due to the occurrence of a thermal spike must also be evaluated. As discussed in Chapter 1, a thermal spike is a limited volume with the majority of atoms temporarily in motion [31]. This corresponds to a "hot zone" which occurs when the deposited energy density within the collision cascade becomes large enough so that the assumption of isolated binary collisions (linear cascade theory) is no longer valid [67].

As stated in Chapter 1, when the deposited energy density per atom, θ_0 , exceeds a few eV per atom, the possibility for spike behavior (melting, surface evaporation, etc.) exists [32, 67]. In the ion implantation regime, $\theta_0 = v(E)/V_{\text{cas}}$, where $v(E)$ is the energy deposited in atomic motion (nuclear energy deposition) and V_{cas} is the volume of the cascade. Since the individual cascade volume is a function of the ion range, spike effects are favored for high Z, low E ions in high density substrates [67].

Table 4. Estimate of the depth into the sapphire substrate attained by the film's component atoms, taking the film components to be implanted atoms.

Original Ion-Target (thickness, nm)	Original Ion Energy (keV)	Energy of Orig. Ion at Interface (keV)	Effective Energy Transferred at Interface (keV)	New "Ion" at Effective Energy	"Range" in Al ₂ O ₃ Substrate (nm)
Kr - Cr/Al ₂ O ₃ (50)	320	175	165	Cr	82.5 ± 26.4
Kr - Zr/Al ₂ O ₃ (50)	320	175	175	Zr	56.3 ± 16.6
Cr - Cr ₂ O ₃ /Al ₂ O ₃ (50)	160	110	110	Cr	55.2 ± 17.8
			79	O	105.8 ± 32.4
Cr - ZrO ₂ /Al ₂ O ₃ (50)	160	110	102	Zr	35.1 ± 10.1
			79	O	105.8 ± 32.4
Cr - Cr ₂ O ₃ /Al ₂ O ₃ (80)	340	270	270	Cr	134.6 ± 34.2
			194	O	238.8 ± 49.6
Cr - ZrO ₂ /Al ₂ O ₃ (80)	340	270	250	Zr	78.3 ± 22.7
			194	O	238.8 ± 49.6
Kr - Cr ₂ O ₃ /Al ₂ O ₃ (80)	475	335	316	Cr	155.0 ± 42.8
			180	O	224.7 ± 44.7
Kr - ZrO ₂ /Al ₂ O ₃ (80)	475	335	334	Zr	103.8 ± 28.9
			180	O	224.7 ± 44.7

Sigmund [33, 34] reported energy densities and time constants for elastic collision spikes which he estimated from established energy deposition profiles. He presented plots of constants (G_2 and H_2) for both the effective maximum energy density expression

$$\theta_0 = G_2 N^2 / E^2$$

and for the time constant, τ , of a spike

$$\tau = H_2 E^3 / N^2.$$

where N is the number of target atoms per unit volume, and E is the ion energy in keV [33]. Both constants, G_2 and H_2 are valid only for the value $m = 1/2$ in the inverse power potential equation $V \propto r^{-1/m}$, where r is the internuclear distance and $0 \leq m \leq 1$. These constants also depend on the mass and atomic number of the projectile and the target atoms.

The equations for θ_0 and τ depend on the value of m , which is generally taken to be $1/3$ or $1/2$ ($m = 1/3$ for incident energies of a few keV; $m = 1/2$ for energies of hundreds of keV) [18].

The slowing down time of the projectile (cascade lifetime) is given by

$$\tau_0 \equiv \frac{2mR(E)}{\left(2m - \frac{1}{2}\right)v}$$

where $R(E)$ is the total path length of the ion, and v is the velocity of the projectile [33].

At characteristic particle energies near the mean deposited energy, θ , most atoms within a certain volume are in motion, and there is a tendency toward a local equilibrium. The occurrence of this equilibrium depends on the time constant of the spike and the cascade lifetime: equilibrium is achieved only if $\tau > \tau_0$. Also, the energy density must also be above the energy required for sublimation.

The values of G_2 and H_2 given in reference 33 are strictly valid only for single component targets. In order to determine whether the materials examined in this work should at all be expected to sustain a thermal spike under the implantation conditions used, calculations were made with simplifications. Values for energy deposition were taken from TRIM calculations; the values used were those at the appropriate film/substrate interface depth in each material (50 or 80 nm, depending on the material). For the

oxides, weighted average masses and atomic numbers were used. For the ion/ion energy/target combinations in this study, the equations for $m = 1/2$ were used ($m=1/2$ for ion energies in the keV range [19])

Table 5 is a compilation of the data used and the outcome of the calculations for θ_0 , τ , and τ_0 . These data indicate that, from a time point of view, thermal spikes might be possible only for the implantations into the oxides, i.e., for $\tau > \tau_0$. Data on heats of sublimation for the oxides is scarce, so this aspect is not discussed. It should be noted that in all cases, the values of θ_0 are much less than those required for thermally activated processes, i.e., phase changes such as melting or evaporation (a few eV/atom). Caution must be used in interpreting and applying the data in Table 5, because of the inaccuracies introduced by simplifying these oxide compounds into "weighted average" elements.

Chen et al. [68] present another approach to determining the possibility of spike behavior. This approach does not require the simplifying assumption used above. Instead, they define a parameter χ :

$$\chi \equiv \frac{-F_d}{\Delta H_{\text{coh}}}$$

where F_d is the energy density and ΔH_{coh} is the cohesive energy of the matrix. The mixing parameter Dt/ϕ is dependent on this parameter. Chen and coworkers relate values of χ to the behavior of the mixing parameter, and thus to the mixing regime. For $\chi < 22 \text{ \AA}^{-1}$, Dt/ϕ depends linearly on χ . This is the collision cascade (ballistic) mixing region. For values of χ between $22 \text{ \AA}^{-1}$ and $75 \text{ \AA}^{-1}$, defect generation follows linear collision cascade behavior, but nonlinear effects on atomic migration start to appear. In this region, $Dt/\phi \propto \chi^2$. For $\chi > 75 \text{ \AA}^{-1}$, nonlinear effects of spike-induced mixing are significant. The creation of defects also follows nonlinear behavior. Here, $Dt/\phi \propto \chi^3$. Chen et al. compare these results to experimental data available in the literature [47, 48], and find that the data compare well, although the mixing parameter seems to show a slightly higher order dependence on χ .

Calculations based on the analysis of Chen and coworkers were performed for the systems under investigation in this work. Cohesive energies for metals and common ceramics are available in the literature [69-72]. Here, they are presented in units of eV/unit, where the unit is either an atom (for the metals), or a molecule (for the oxides). The densities are from Ref. [73]. The data are presented in Table 6.

These calculations indicate that, for all but two of the ion/target combinations, no thermal spike should occur. For implantations of Kr into both $\text{Zr/Al}_2\text{O}_3$ and $\text{Cr/Al}_2\text{O}_3$,

Table 5. Calculation of parameters for Sigmund's treatment of thermal spikes

Ion/Material (Energy, keV)	G_2 (eV Å ⁶ keV)	H_2 (sec Å ⁻⁶ keV)	θ_0 (eV/atom)	τ (sec)	τ_0 (sec)
Kr/Cr (320)	2.3×10^5	5×10^{-19}	2×10^{-1}	2×10^{-9}	1.25×10^{-8}
Kr/Zr (320)	1.5×10^5	1×10^{-19}	6×10^{-2}	2×10^{-9}	1.25×10^{-8}
Cr/Cr ₂ O ₃ (160)	6.0×10^4	2.8×10^{-18}	5×10^{-3}	7×10^{-7}	1.02×10^{-8}
Cr/ZrO ₂ (160)	1.8×10^5	8×10^{-19}	2×10^{-2}	1×10^{-7}	1.02×10^{-8}
Cr/Cr ₂ O ₃ (340)	2×10^4	8×10^{-18}	4×10^{-3}	7×10^{-7}	9.52×10^{-9}
Cr/ZrO ₂ (340)	5×10^4	3×10^{-18}	1×10^{-2}	2×10^{-7}	9.52×10^{-9}
Kr//Cr ₂ O ₃ (475)	2×10^4	8×10^{-18}	2×10^{-2}	8×10^{-8}	1.39×10^{-8}
Kr/ZrO ₂ (475)	5×10^4	3×10^{-18}	5×10^{-2}	1×10^{-8}	1.39×10^{-8}

Table 6. Calculation of the parameter χ , for evaluating the possibility of thermal spike behavior

Material	Mol. Wt. (g/mole)	Density (g/cm ³)	ΔH_{coh} (eV/unit)	Ion and Energy, (keV)	Fd (eV/Å)	$\chi =$ $F_d/\Delta H_{\text{coh}}$ (1/Å)
Cr	51.996	7.20	4.1	Kr (320)	300	73.17
Zr	91.22	6.49	6.3	Kr (320)	200	31.75
Cr ₂ O ₃	151.99	5.21	157.394	Cr (160)	200	1.27
				Cr (340)	127	0.81
				Kr (475)	220	1.40
ZrO ₂	123.21	5.89	116.035	Cr (160)	122	1.05
				Cr (340)	124	1.07
				Kr (475)	220	1.90
Al ₂ O ₃	101.961	3.96	160			

however, the calculations indicate that thermal spikes may exist ($\chi = 73.17$ and 31.75 , respectively).

2. Scanning electron microscopy

In this section, scanning electron micrographs of representative samples are presented to indicate the surface roughness of the as-deposited films, and to show the effects of the ion implantations performed in this study on the surface roughness.

A micrograph of an unimplanted Cr/Al₂O₃ sample taken at 5 kV is shown in Fig. 6. The micrograph was taken at 0° tilt. This sample had been exposed to air for several weeks, and the portion of the sample in the micrograph is unusually dirty. The point of interest on this micrograph is the roughness of the film, as evidenced by the "waves" running down the sample. The roughness is on a fine scale; the distance between the "waves" is about 375 nm. Figures 7a and 7b are micrographs (taken at 2.5 kV) of Zr/Al₂O₃ (a) before and (b) after room temperature implantation with 320 keV Kr to a fluence of 1×10^{17} ions-cm⁻². Both micrographs were taken at a 45° tilt, which enhances sensitivity to surface roughness. The surface roughness shown here is on an extremely fine scale. It appears to be worsened after implantation; the bumps appearing on the micrograph of the implanted specimen are probably bubbles formed by the implanted Kr [74].

Figure 8 is a low magnification micrograph of a ZrO₂ film on Al₂O₃, taken at 1 kV and 0° tilt. This picture shows the contrast between the bare sapphire and the film (not coated with 1.5 nm Cr to alleviate charging problems). Charging became a problem even on the Cr-coated specimens and prevented the acquisition of good micrographs, thus micrographs of both Cr₂O₃ and ZrO₂ films in each condition are not presented here.

Figures 9a and 9b are micrographs of a Cr₂O₃/Al₂O₃ sample (a) before and (b) after bombardment with 160 keV Cr to a fluence of 5×10^{16} ions-cm⁻² at liquid nitrogen temperature. The micrographs were taken at 6 kV and 45° tilt; the sample was coated with Cr. In Fig. 9a, the main features are pieces of dirt on the film, and wavy lines running diagonally across the picture. These lines are probably steps on the surface of the sapphire substrate, caused by thermal etching during the initial annealing process (before film deposition). Such features have been reported in the literature [75]. The sample is roughened somewhat by the ion bombardment, as shown in Fig. 9b. However, the scale of the roughening is extremely fine (virtually atomic scale), as evidenced by the micron marker. The appearance of both the implanted and unimplanted portions of the ZrO₂/Al₂O₃ specimen subjected to the same conditions as this sample was similar; the sample was

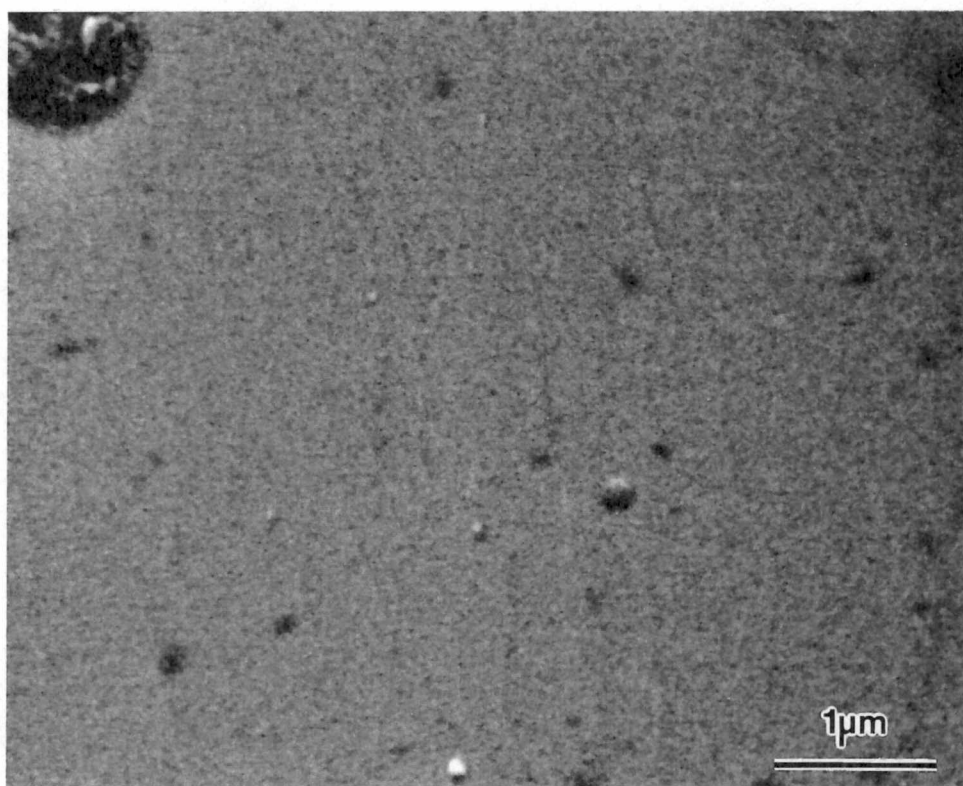
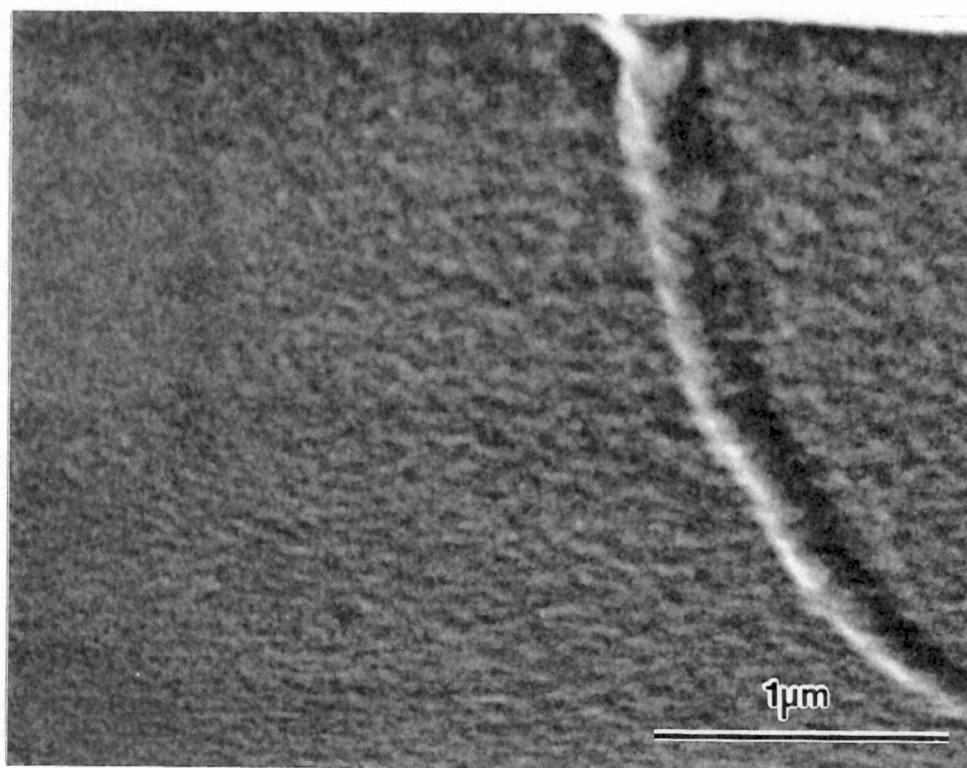


Fig. 6. A micrograph of an unimplanted Cr/Al₂O₃ sample taken at 5 kV and 0° tilt.

(a)



(b)

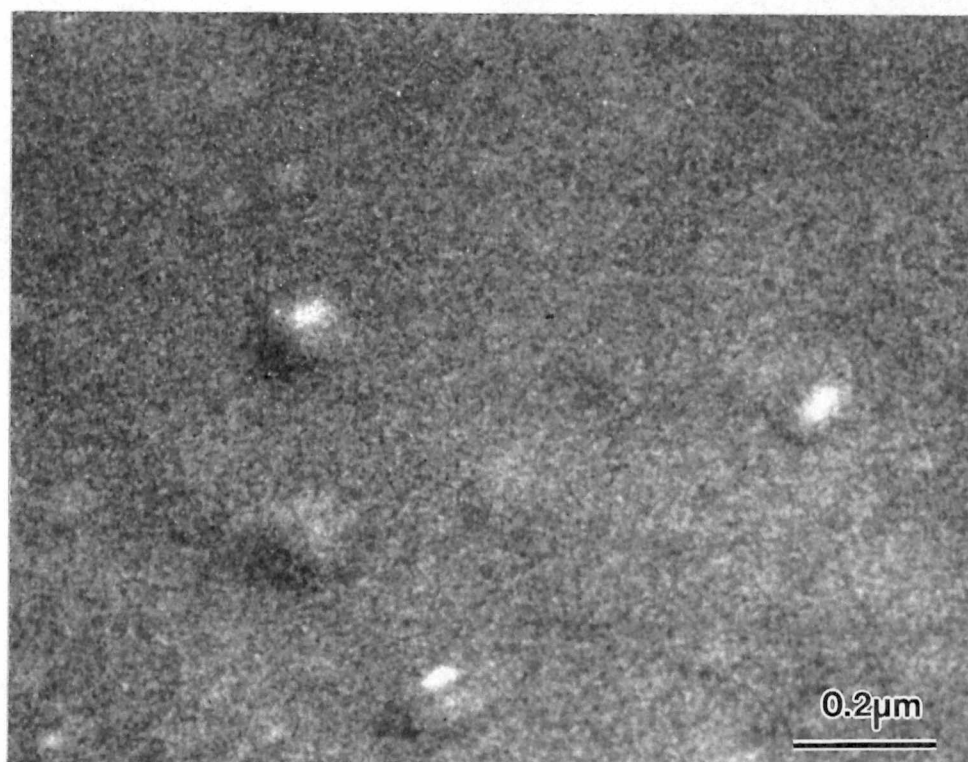


Fig. 7. Micrographs (taken at 2.5 kV) of Zr/Al₂O₃ (a) before and (b) after implantation with 320 keV Kr to a fluence of 1×10^{17} ions-cm⁻². Both micrographs were taken at a 45° tilt, which enhances sensitivity to surface roughness.

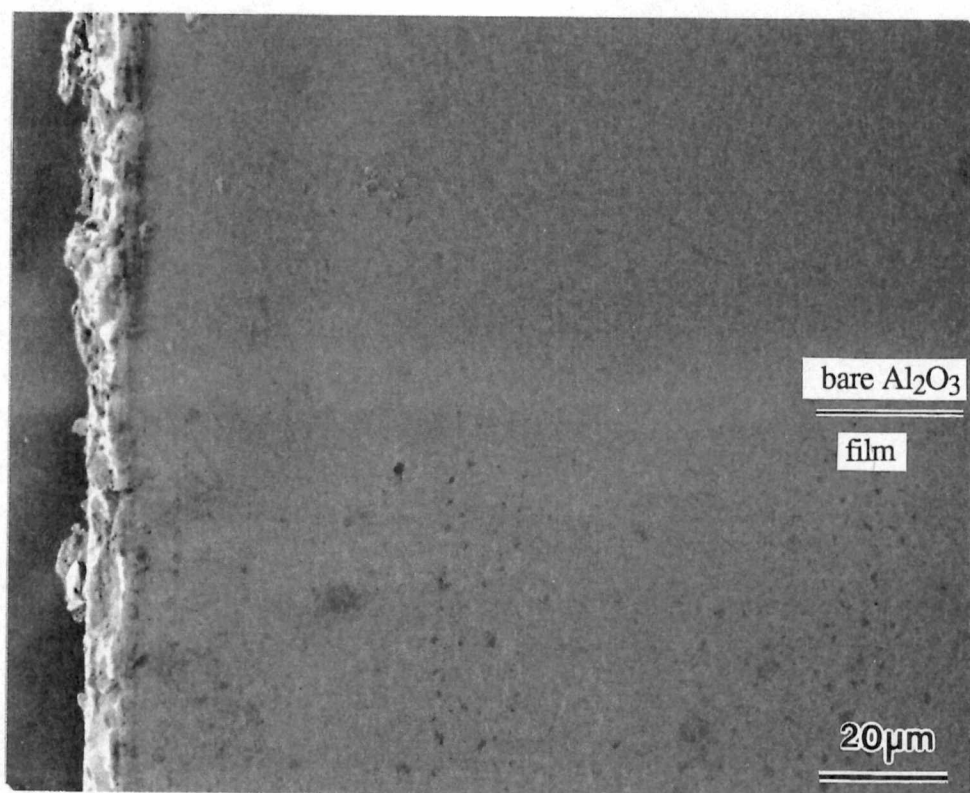
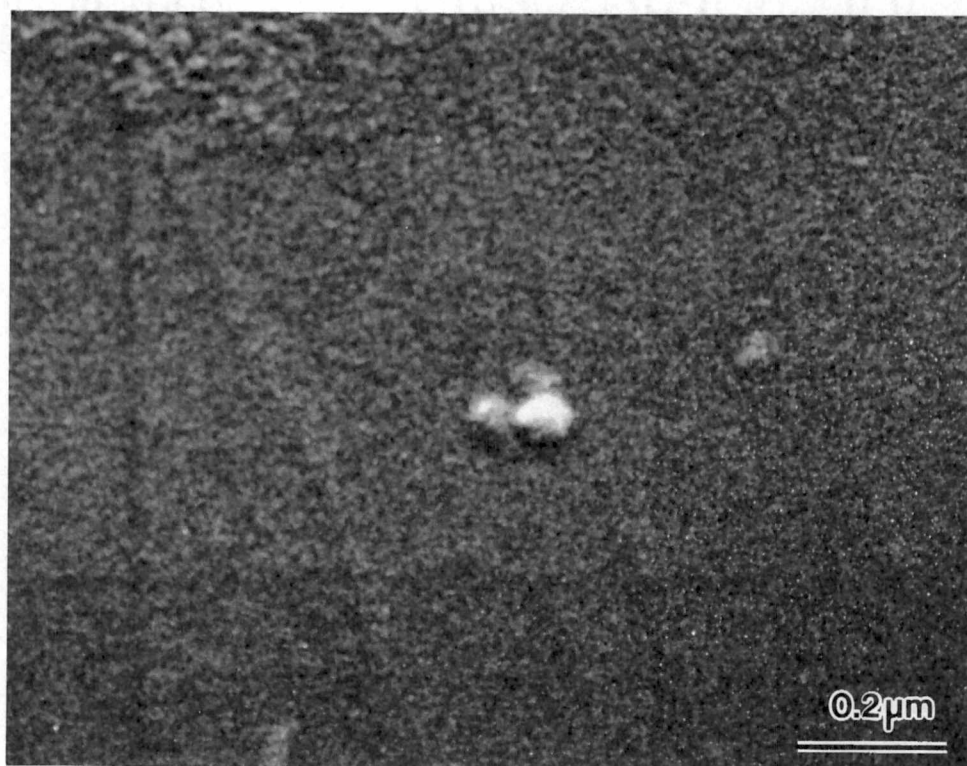


Fig. 8 . A low magnification micrograph of a ZrO₂ film on Al₂O₃, taken at 1 kV and O° tilt. This picture shows the contrast between the bare sapphire and the film .

(a)



(b)

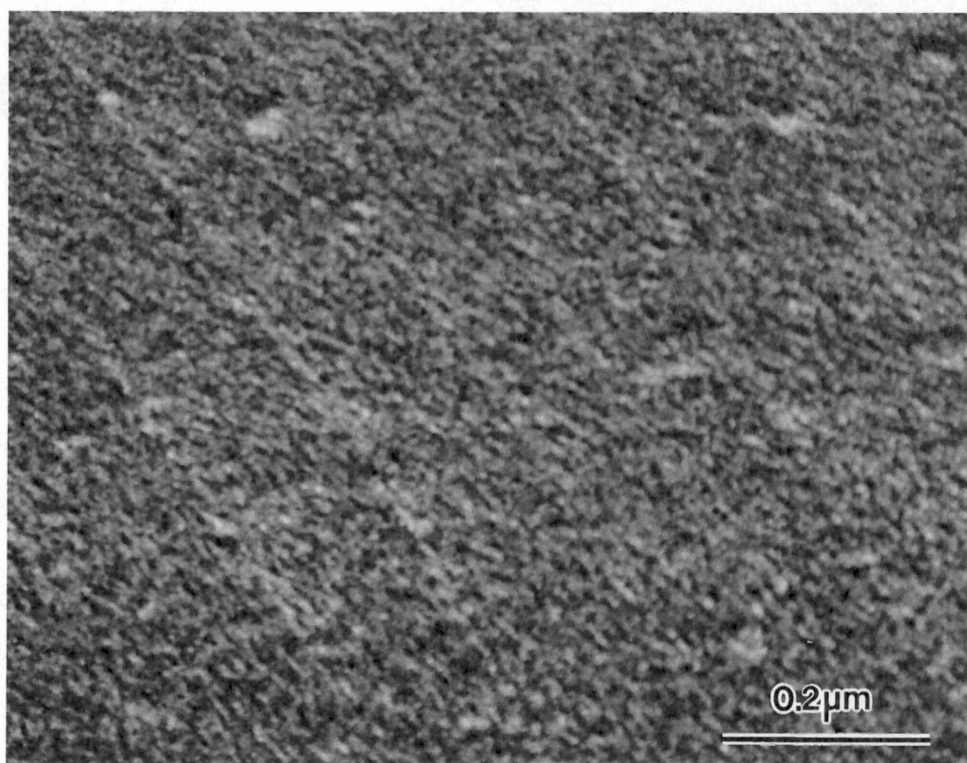


Fig. 9. A micrograph of a Cr₂O₃/Al₂O₃ sample (a) before and (b) after bombardment with 160 keV Cr to a fluence of 5×10^{16} ions-cm⁻² at liquid nitrogen temperature. The micrographs were taken at 6 kV and 45° tilt; the sample was coated with Cr.

roughened on a fine scale by the bombardment. Both $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{ZrO}_2/\text{Al}_2\text{O}_3$ specimens implanted with Cr at room temperature and 860°C looked much like Figs. 9a and 9b.

Figures 10a-c are micrographs of a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ specimen; the micrographs were taken at 6 kV and 45° tilt, and the sample was coated with Cr. Figure 10a is the unimplanted portion of the specimen. Figures 10b and 10c are photographs of the section bombarded with 475 keV Kr to a fluence of 8×10^{16} ions- cm^{-2} at 825°C . The bumps shown in Fig. 10b are bubbles formed by the implanted Kr, as in Fig 7. The implanted portion shows considerable surface damage; cracks in the film are evident in Fig. 10c. Figures 11a and 11b are micrographs of the implanted portion of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ specimen bombarded under the same conditions as the sample shown in Figs. 10b-c. The photographs were taken under the same conditions as Figs. 8a-c. No cracking is evident between the Kr bubbles, but a few of them have burst as in Fig. 11b, which shows the top of a burst bubble. The $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{ZrO}_2/\text{Al}_2\text{O}_3$ specimens implanted with Kr at room temperature were similar in appearance to Figs. 10 and 11.

Micrographs from a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ specimen annealed at 1450°C for 1 h are presented in Figs. 12a and 12b. This specimen was not coated with Cr prior to examination. The micrographs were taken at 3 kV and at 45° tilt. Figure 12a is a micrograph of a representative area on the surface of this sample. A surface texture, which is not present on the unimplanted samples, is apparent. Figure 12b is a higher magnification micrograph of the surface; hills and valleys are evident.

The SEM observations are summarized in Table 7.

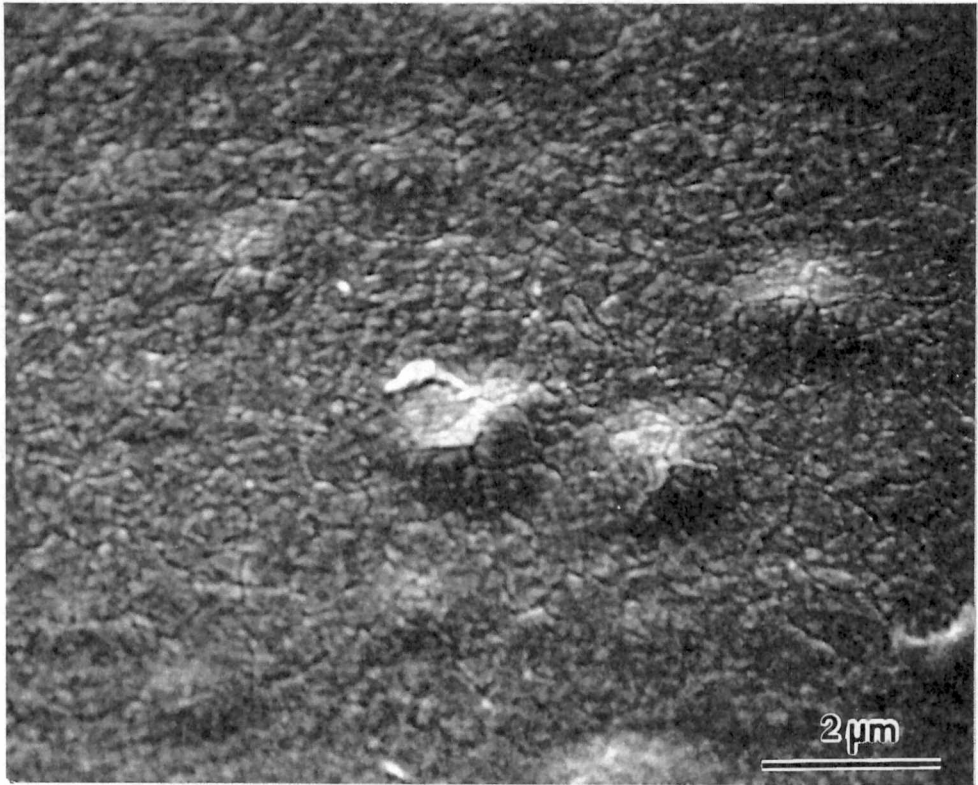
3. Rutherford backscattering spectrometry

All of the data presented here are plotted in terms of backscattering yield (of He), vs. energy (of the backscattered particle reaching the detector). On the plots of these spectra, the surface edges of the metallic components and the implanted ions are indicated. In the cases where the oxygen edge is included in the plot, its position is not marked. It appears as the "bump" in the spectra at lower energy than the Al edge. Generally, mixing between the film and the substrate is indicated by either a noticeable change in slope of the substrate edge (mixing on a small scale--distance as well as concentration), or by a step in the substrate edge (toward higher energy) along with a corresponding change in the signal from the film (indicative of chemical mixing). However, changes in slope of the substrate edge may also be caused by surface roughening, and sputtering will cause the substrate edge to move to higher energies.



Fig. 10. Micrographs of a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ specimen; the micrographs were taken at 6 kV and 45° tilt, and the sample was coated with Cr: (a) is the unimplanted portion of the specimen; (b) and (c) are photographs of the section bombarded with 475 keV Kr. The bumps shown in (b) are bubbles formed by the implanted Kr. Cracks in the film are evident in (c).

(b)



(c)

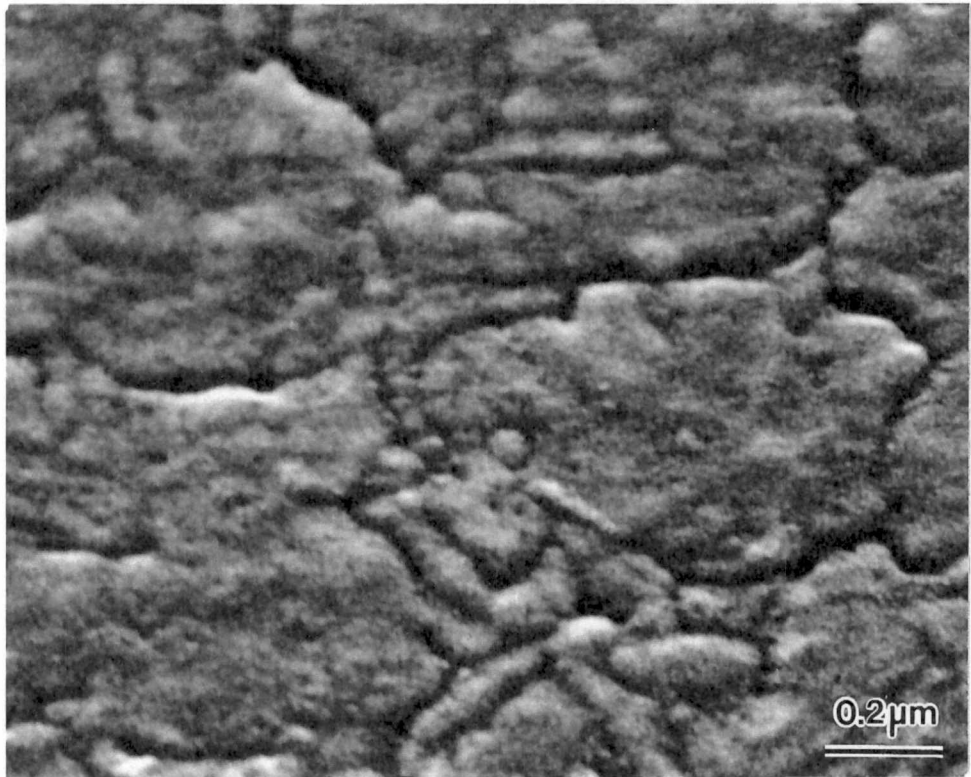
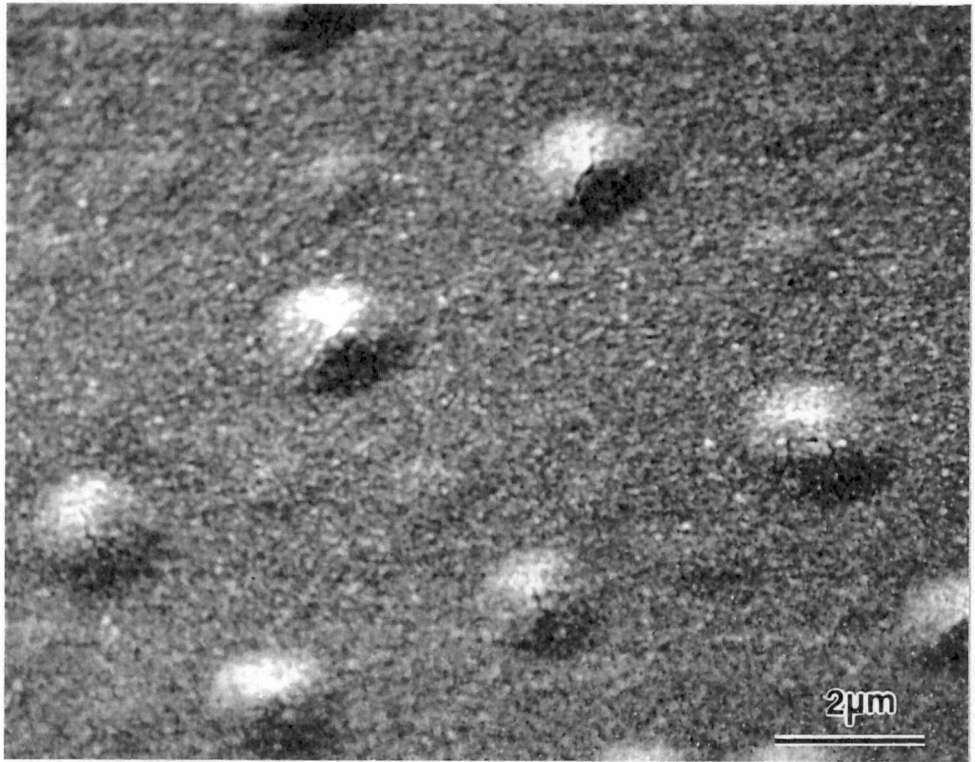


Fig. 10. Continued.

(a)



(b)

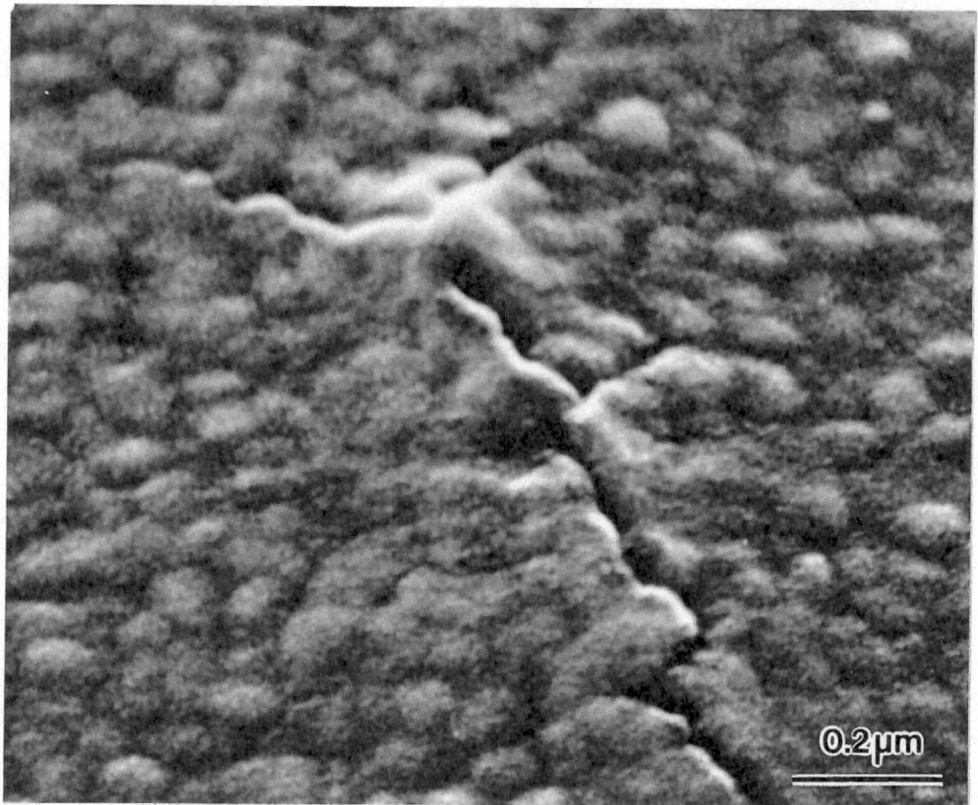
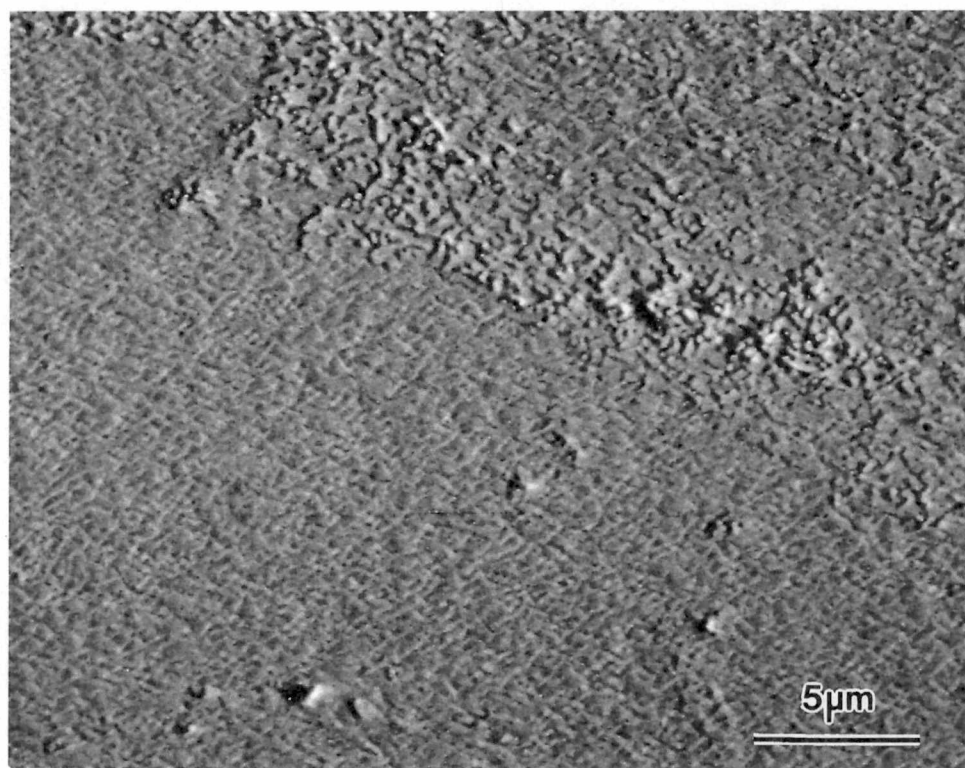


Fig. 11. Micrographs of the implanted portion of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ specimen bombarded under the same conditions as the sample shown in Figs. 10b-c.

(a)



(b)

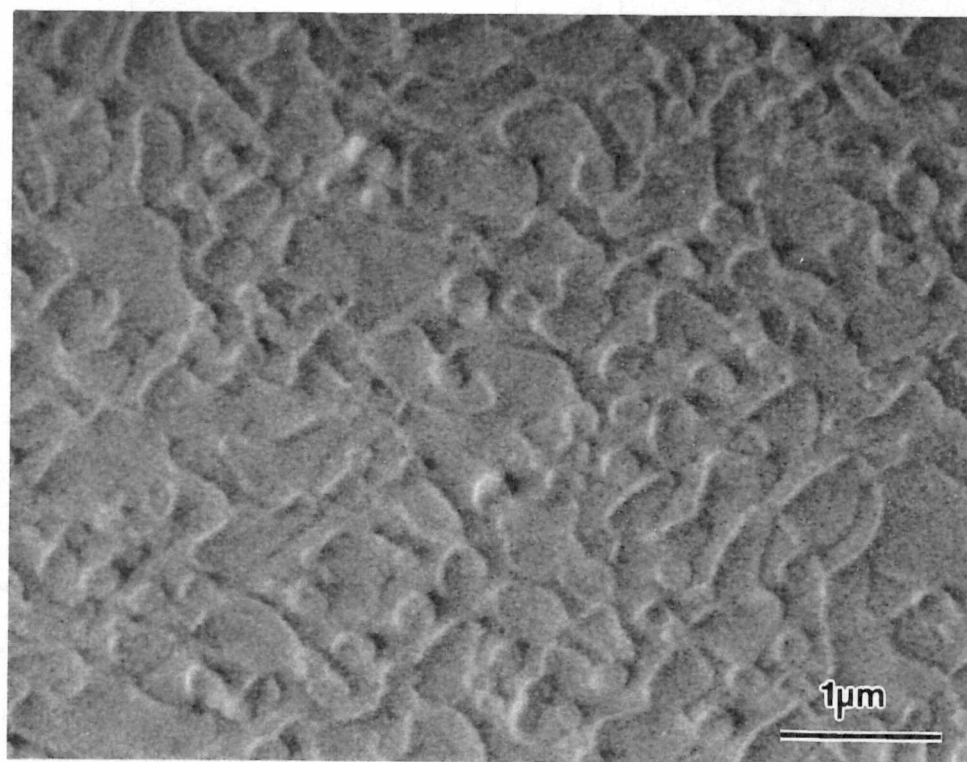


Fig. 12. Micrographs from a ZrO₂/Al₂O₃ specimen annealed at 1450°C for 1 h: (a) a representative area on the surface of this sample; (b) higher magnification micrograph of the surface.

Table 7. Scanning electron microscopy results

Film/substrate combination	Treatment	SEM observations
Cr/Al ₂ O ₃	Kr, 320 keV 1 x 10 ¹⁷ ions- cm ⁻² 20°C	<u>Unimplanted sample</u> : rough on a fine scale; waves spaced about 375 nm apart
Zr/Al ₂ O ₃	Kr, 320 keV 1 x 10 ¹⁷ ions- cm ⁻² 20°C	<u>Unimplanted sample</u> : rough on a fine scale. <u>Implanted sample</u> : Kr bubbles evident; approximately 100 nm in diameter..
Cr ₂ O ₃ /Al ₂ O ₃ ZrO ₂ /Al ₂ O ₃	Cr, 160 keV 5 x 10 ¹⁶ ions- cm ⁻² -196°C	<u>Unimplanted sample</u> : small steps on the surface introduced by thermal etching during the anneal of the sapphire crystal. <u>Implanted sample</u> : Roughened on a fine scale (few angstroms).
Cr ₂ O ₃ /Al ₂ O ₃ ZrO ₂ /Al ₂ O ₃	Kr, 475 keV 8 x 10 ¹⁶ ions- cm ⁻² 825°C and 20°C	<u>Unimplanted sample</u> : rough on a fine scale; steps on the surface introduced by thermal etching during the anneal of the sapphire crystal. <u>Implanted sample</u> : Bubbles formed by Kr ~2nm in diameter.
ZrO ₂ /Al ₂ O ₃	Thermal anneal 1h, 1450°C	Surface texture consistent with ZrO ₂ agglomeration present after anneal.

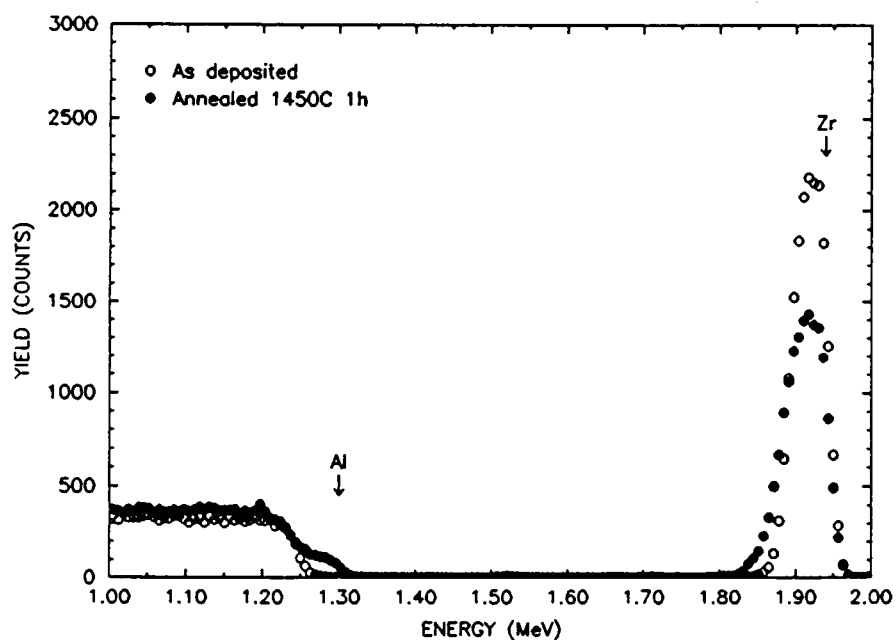


Fig. 13. Rutherford backscattering spectra from an as-deposited $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample, and one from a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample annealed for 1 h at 1450°C in flowing air.

Results from the thermal annealing experiments are presented first, because of their fundamental importance in this study. Two spectra are shown in Fig. 13; one from an as-deposited $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample, and one from a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample annealed for 1 h at 1450°C in flowing air. The substrates were cleaned and annealed at the same time, and the films were deposited at the same time, so the samples should have been identical before the anneal. As compared to the as-deposited sample, the Al edge in the annealed sample has moved to the surface (toward higher energy), and the Zr signal has broadened. This could be interpreted as either agglomeration and migration of the Zr during the anneal, or as loss of Zr via some other means, e.g. evaporation. The vapor pressure of ZrO_2 is 2.39×10^{-8} Pa (2.36×10^{-13} atm) [68], therefore no evaporation is expected.

In Figs. 14a-c, spectra from an unannealed $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample are compared with spectra from $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples annealed in air for 1 h at 1050 , 1150 , and 1450°C . As with the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ films discussed above, these samples should have been identical before the anneal. After the anneal at 1050°C , there is virtually no evidence of any change in the sample. After 1 h at 1150°C , the Al edge has shifted toward higher energy, and the Cr signal has decreased considerably. The trailing edge of the Cr signal decreases gradually as compared to that in the spectra from the as-deposited sample, indicating that the Cr has partially diffused into the Al_2O_3 . After 1 h at 1450°C , the Cr signal is only slightly higher than the background signal. This is indicative of a low level of Cr distributed deep into the sample after the annealing treatment. Since the vapor pressure of Cr_2O_3 is 9.2×10^{-3} Pa at 1450°C , no evaporation is expected. From the spectra, the substrate appears bare; the Al edge is at the surface. However, the background at energies higher than that where the Al edge appears is slightly higher than the background in the unannealed sample. The Cr has totally diffused into the Al_2O_3 . From RBS analysis, it not possible to know whether the Cr which has diffused in is bound as the metallic species, or as Cr_2O_3 . Results from experiments in which mixtures of Cr_2O_3 and Al_2O_3 powders were sintered at temperatures around 1450°C indicate that a solid solution is formed [51-53].

In Figs. 15a and b, spectra from as-deposited and implanted (320 keV Kr, to a fluence of 5×10^{16} ions- cm^{-2}) metal films on sapphire are presented. Spectra from the $\text{Cr}/\text{Al}_2\text{O}_3$ sample are shown in Fig. 15a. The implanted Kr appears at about 1.8 MeV; it overlaps the Cr signal on the high energy side. Comparing the spectrum from the as-deposited region to that from the implanted region, the Cr signal has decreased after implantation (the film thickness has decreased) and the Al edge has moved toward the surface, either due to sputtering of the film during implantation, or to due to mixing of the film and substrate. Figure 15b contains spectra from the $\text{Zr}/\text{Al}_2\text{O}_3$ sample. Again, the implanted Kr appears at

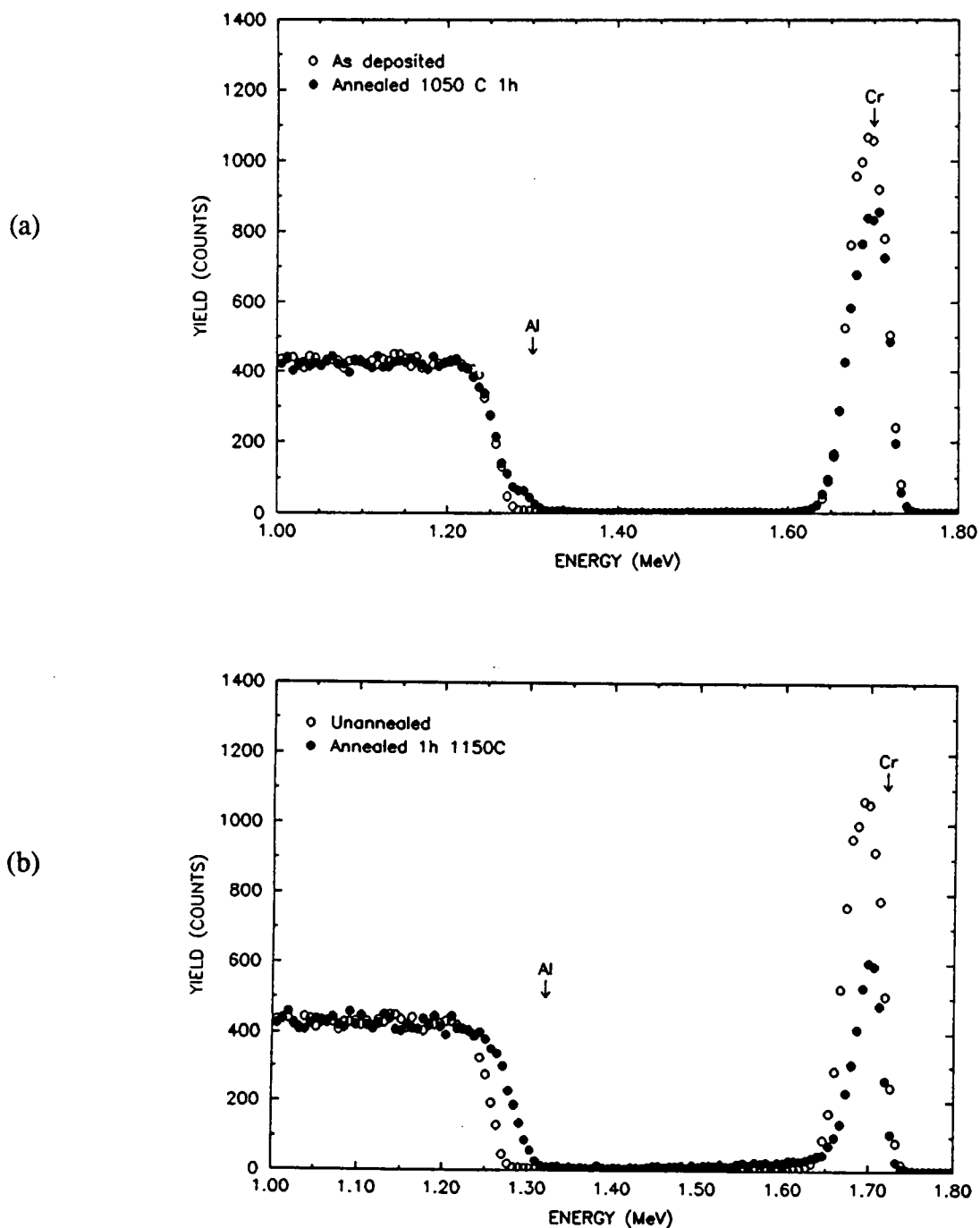


Fig. 14. Rutherford backscattering spectra from an unannealed $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample are compared with spectra from $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples annealed in air for 1 h at (a) 1050, (b) 1150, and (c) 1450°C.

(c)

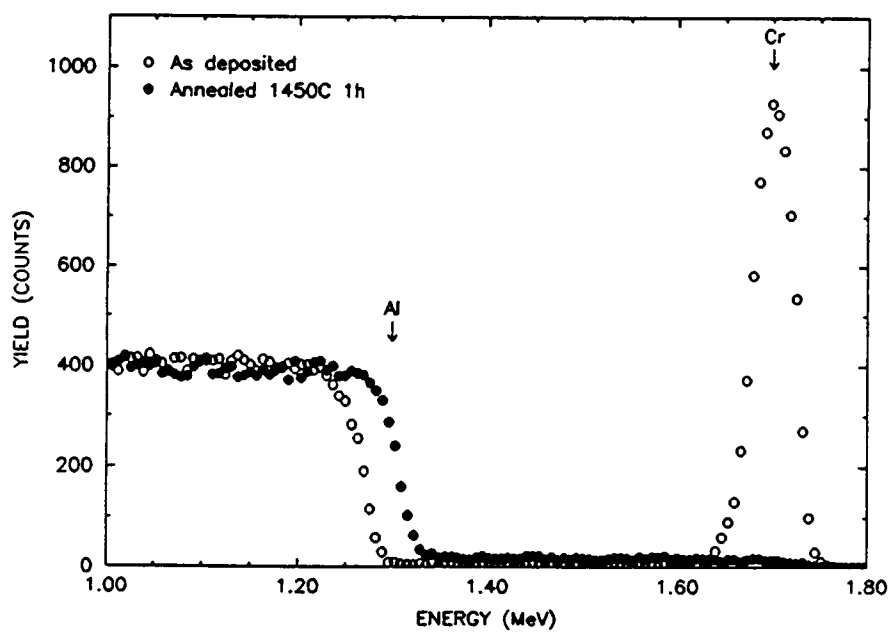


Fig. 14. Continued.

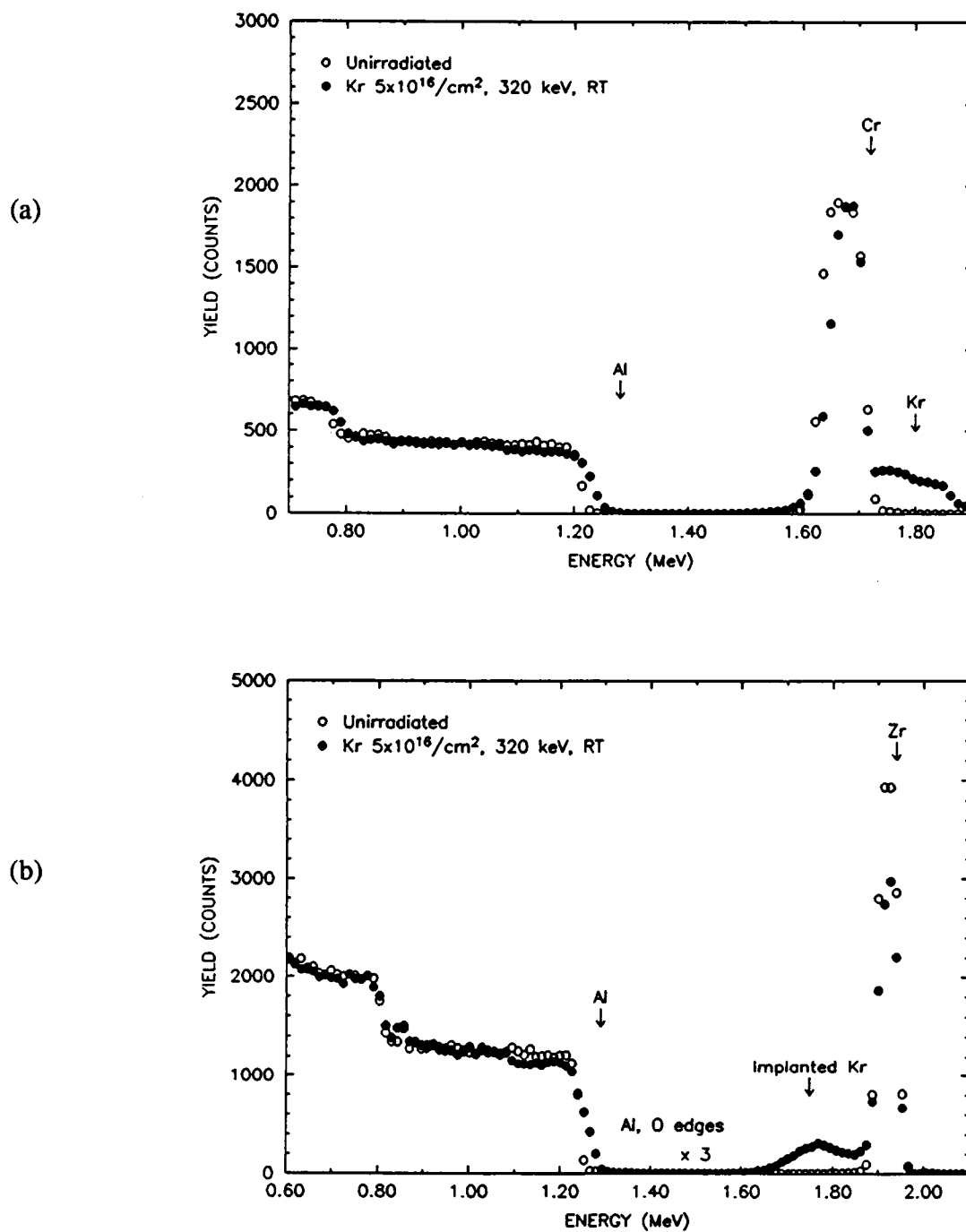


Fig. 15. Rutherford backscattering spectra from as-deposited and implanted (320 keV Kr, to a fluence of 5×10^{16} ions- cm^{-2}) metal films: (a) spectra from the Cr/ Al_2O_3 sample; (b) spectra from the Zr/ Al_2O_3 sample.

about 1.8 MeV, on the low energy side of the Zr signal. The Zr signal is significantly decreased after implantation. Also, the Al edge has shifted toward the surface, and appears to have a slight step. This is indicative of mixing, as reported in the literature (e.g. references 38, 76, and 77). Samples implanted with a higher fluence, 1×10^{17} ions-cm⁻², were examined by XPS. Backscattering spectra from these specimens are presented in Figs. 16a and b. They are basically the same as the spectra presented in Fig. 15a and 15b; the higher Kr concentration is apparent.

Figures 17a and b are RBS spectra obtained from the oxide films on Al₂O₃, before and after bombardment by 160 keV Cr ions to a fluence of 4×10^{16} ions-cm⁻² at room temperature. Spectra for the Cr₂O₃/Al₂O₃ sample are shown in Fig 17a; the spectra in Fig. 17b were obtained from the ZrO₂/Al₂O₃ specimen which received the same treatment. For both materials combinations, the Al edge and the trailing edge of the metal peak from the film have shifted toward higher energy after irradiation, suggesting some sputtering of the films. Neither irradiated specimen shows any significant evidence of mixing. Comparison of the Cr signal from the as-deposited film with the Cr signal from the irradiated film, after subtracting the signal from the implanted Cr, reveals that approximately 16% of the Cr₂O₃ film was sputtered off during this room temperature irradiation. Similarly, about 23% of the ZrO₂ film was sputtered away during the irradiation.

Figures 18a and b are the spectra for the Cr₂O₃/Al₂O₃ and ZrO₂/Al₂O₃ samples which were irradiated at 860°C. As in the experiments at room temperature, some sputtering of the films occurred. Approximately 12% of the Cr₂O₃ film was sputtered off during irradiation, while 17% of the ZrO₂ film was sputtered away. For both materials combinations, the slope of the Al edge is changed slightly after irradiation. This could be due either to surface roughening of the samples during irradiation, or to ballistic mixing.

The spectra for the oxide films implanted at liquid nitrogen temperature with Cr to a fluence of 5×10^{16} ions-cm⁻² are presented in Figs. 19a and b. Sputtering of the films during the implantation is apparent; 28% of the Cr₂O₃ film was lost, and 24% of the ZrO₂ film was lost. No mixing is detectable by RBS analysis.

The spectra from the ZrO₂/Al₂O₃ film bombarded at room temperature with 340 keV Cr to a fluence of 4×10^{16} ions-cm⁻² are presented in Fig. 20. In Fig. 21, the spectra from the ZrO₂/Al₂O₃ film bombarded at 900°C with Cr at the same energy and fluence are plotted. The oxide samples implanted under these conditions were chosen for the AEM investigations. These spectra are presented to illustrate that their main features appear virtually the same as those for the 160 keV Cr implants, shown in Figs 17b and 18b.

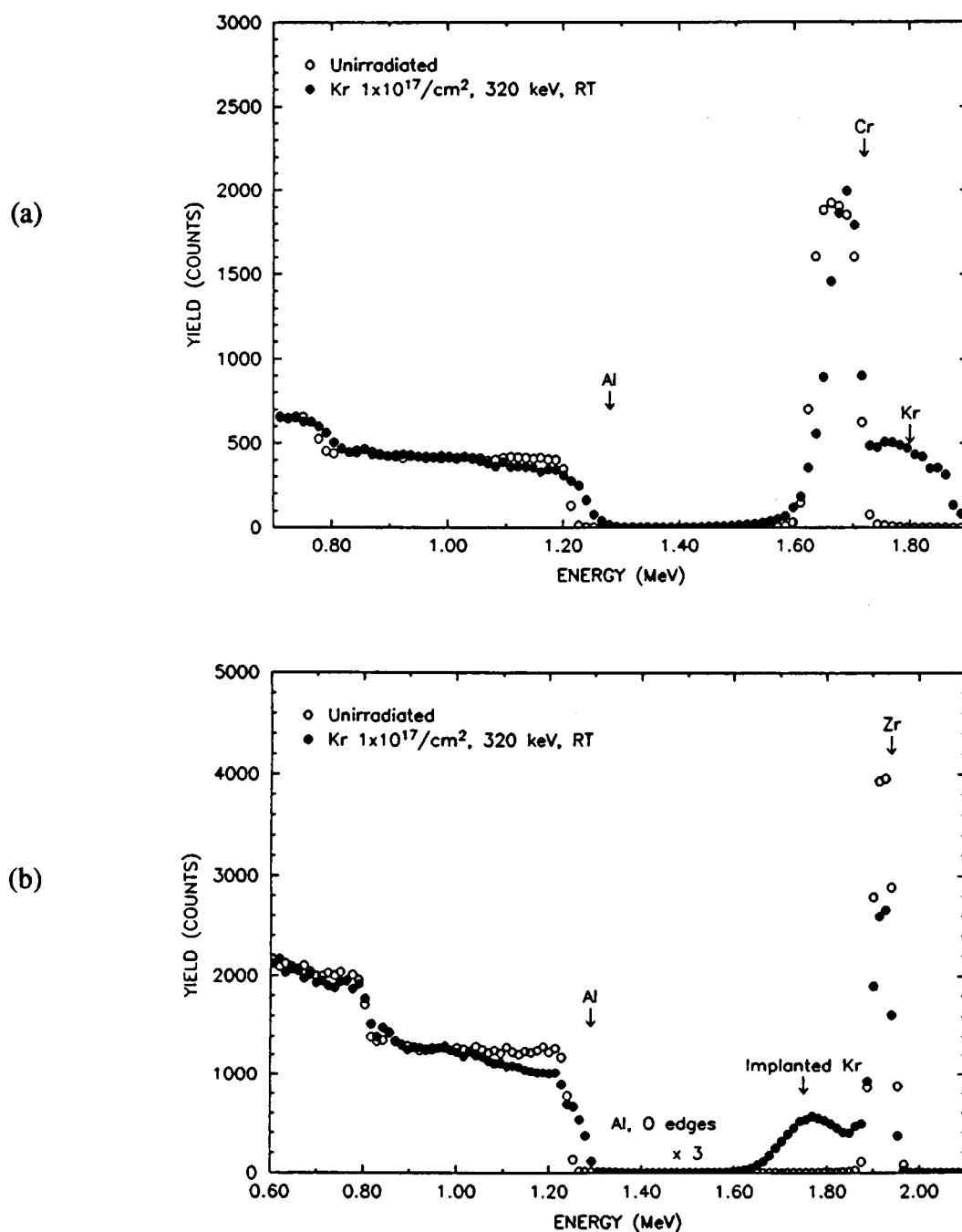


Fig. 16. Rutherford backscattering spectra from as-deposited and implanted (320 keV Kr, to a fluence of 1×10^{17} ions- cm^{-2}) metal films: (a) spectra from the Cr/ Al_2O_3 sample; (b) spectra from the Zr/ Al_2O_3 sample.

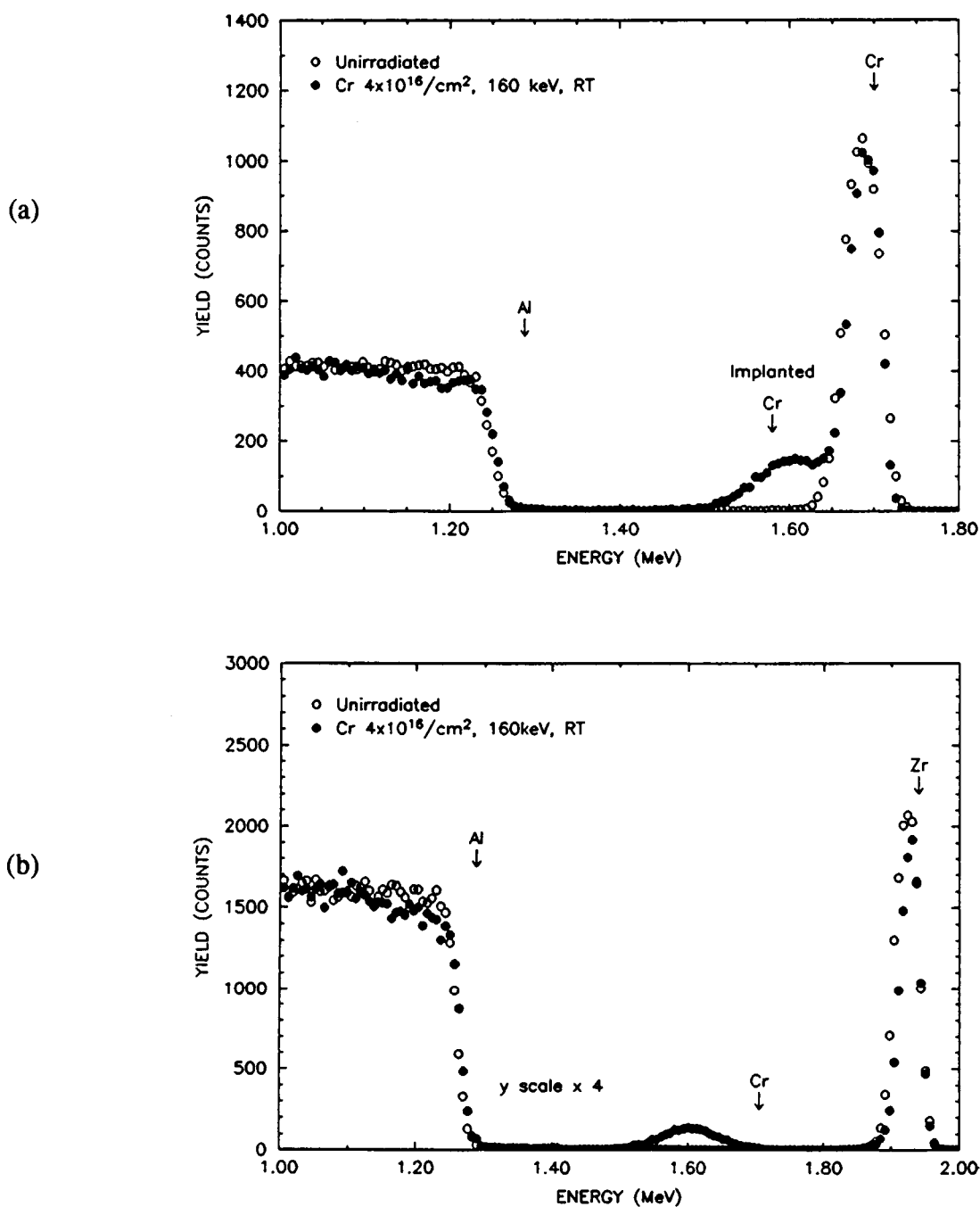


Fig. 17. The RBS spectra obtained from (a) Cr_2O_3 on Al_2O_3 and (b) ZrO_2 on Al_2O_3 , before and after room temperature bombardment by 160 keV Cr ions (4×10^{16} ions- cm^{-2}).

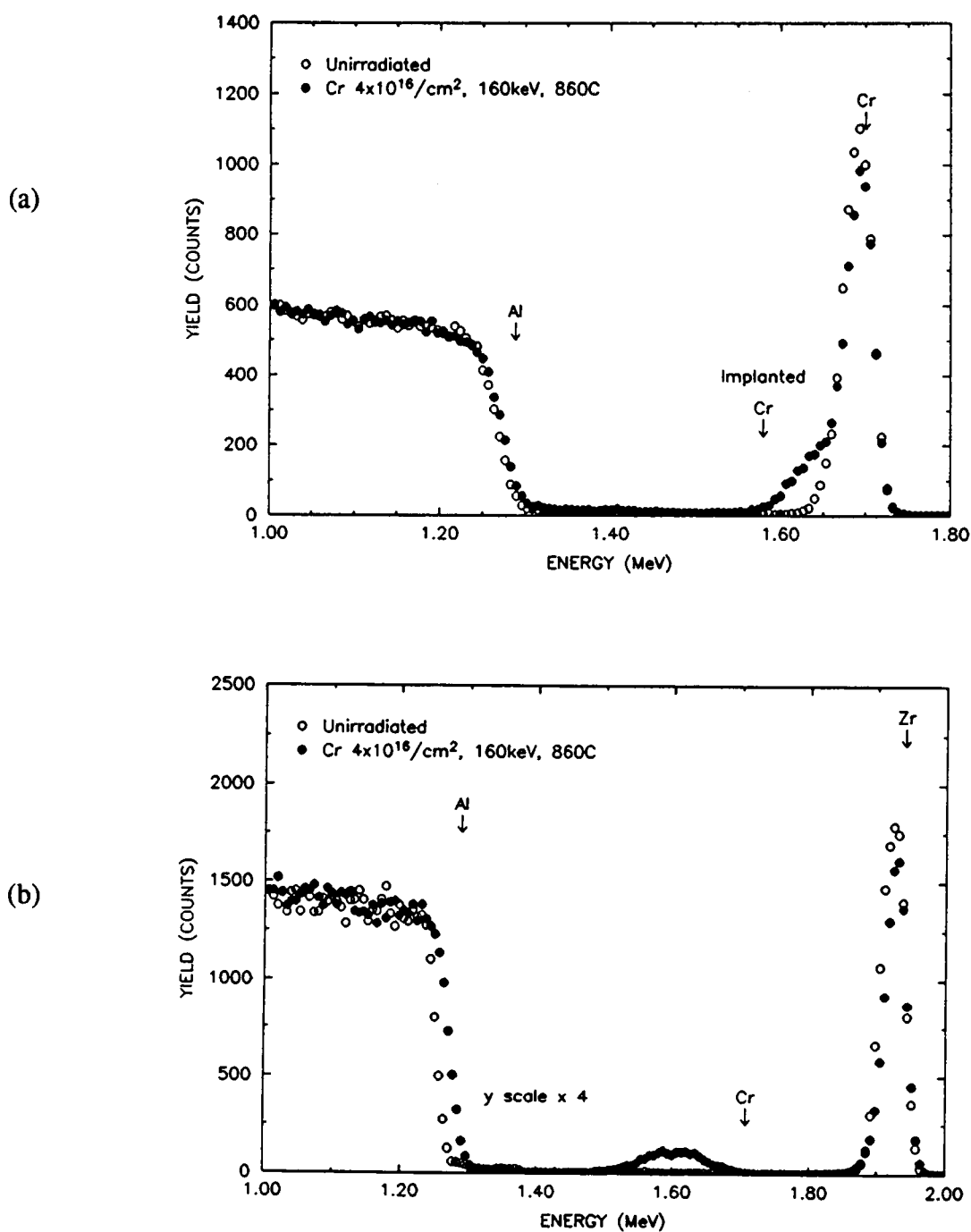


Fig. 18. Rutherford backscattering spectra for the (a) $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and (b) $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples irradiated at 860°C with 160 keV Cr ions (4×10^{16} ions- cm^{-2}).

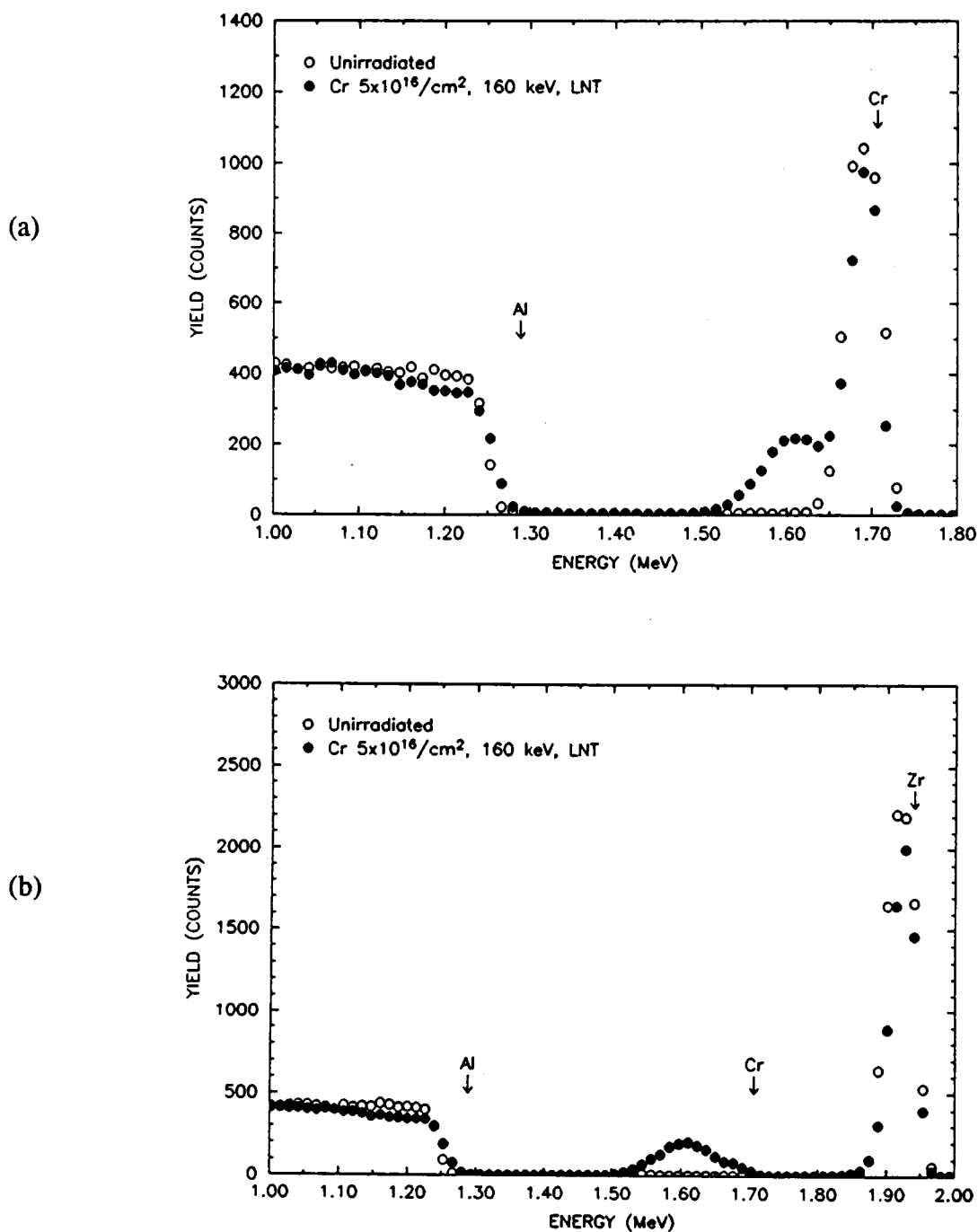


Fig. 19. Rutherford backscattering spectra for the (a) $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and (b) $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples implanted at liquid nitrogen temperature with Cr (5×10^{16} ions- cm^{-2}).

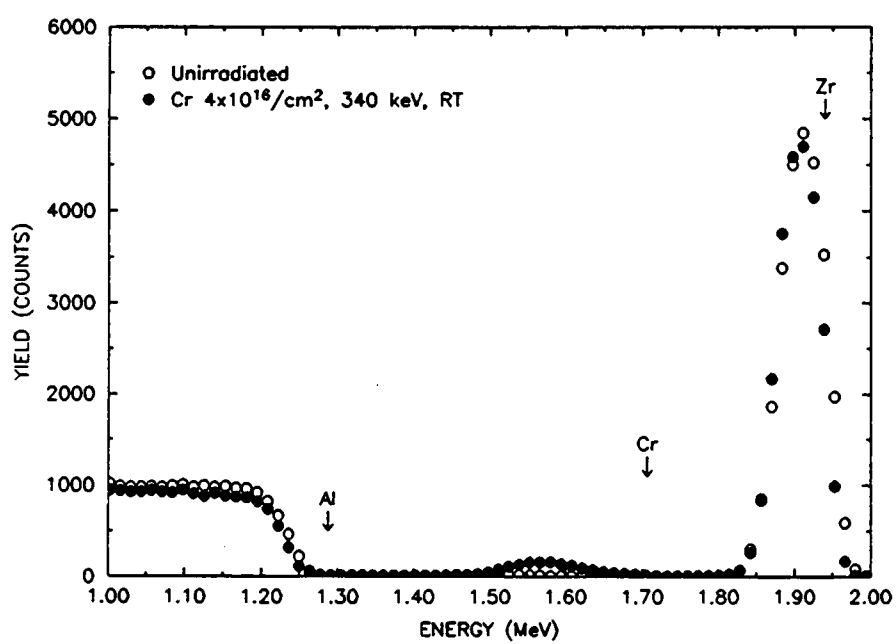


Fig. 20. The RBS spectra from the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ film bombarded at room temperature with 340 keV Cr to a fluence of 4×10^{16} ions- cm^{-2} .

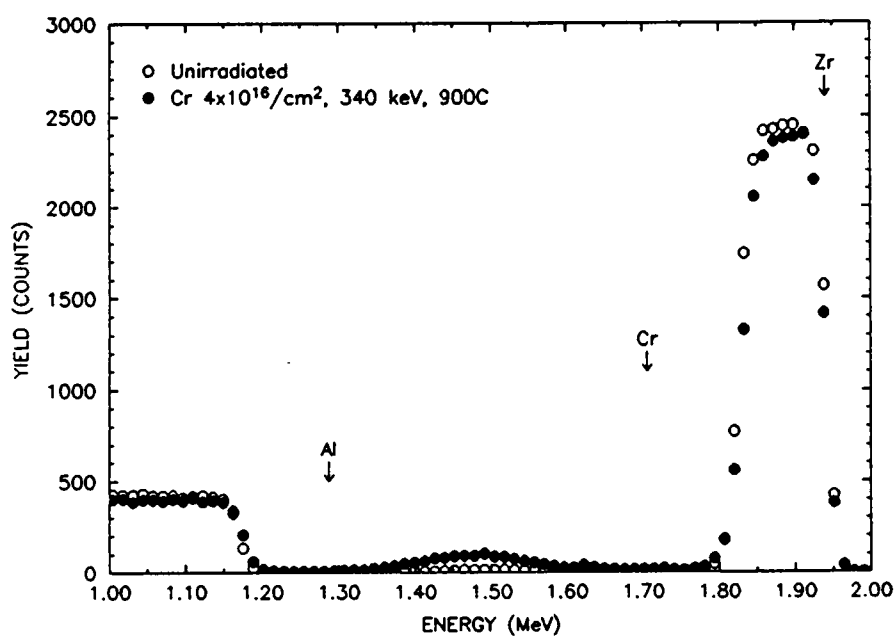


Fig. 21. Rutherford backscattering spectra from the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ film bombarded at 900°C with 340 keV Cr to a fluence of 4×10^{16} ions- cm^{-2} .

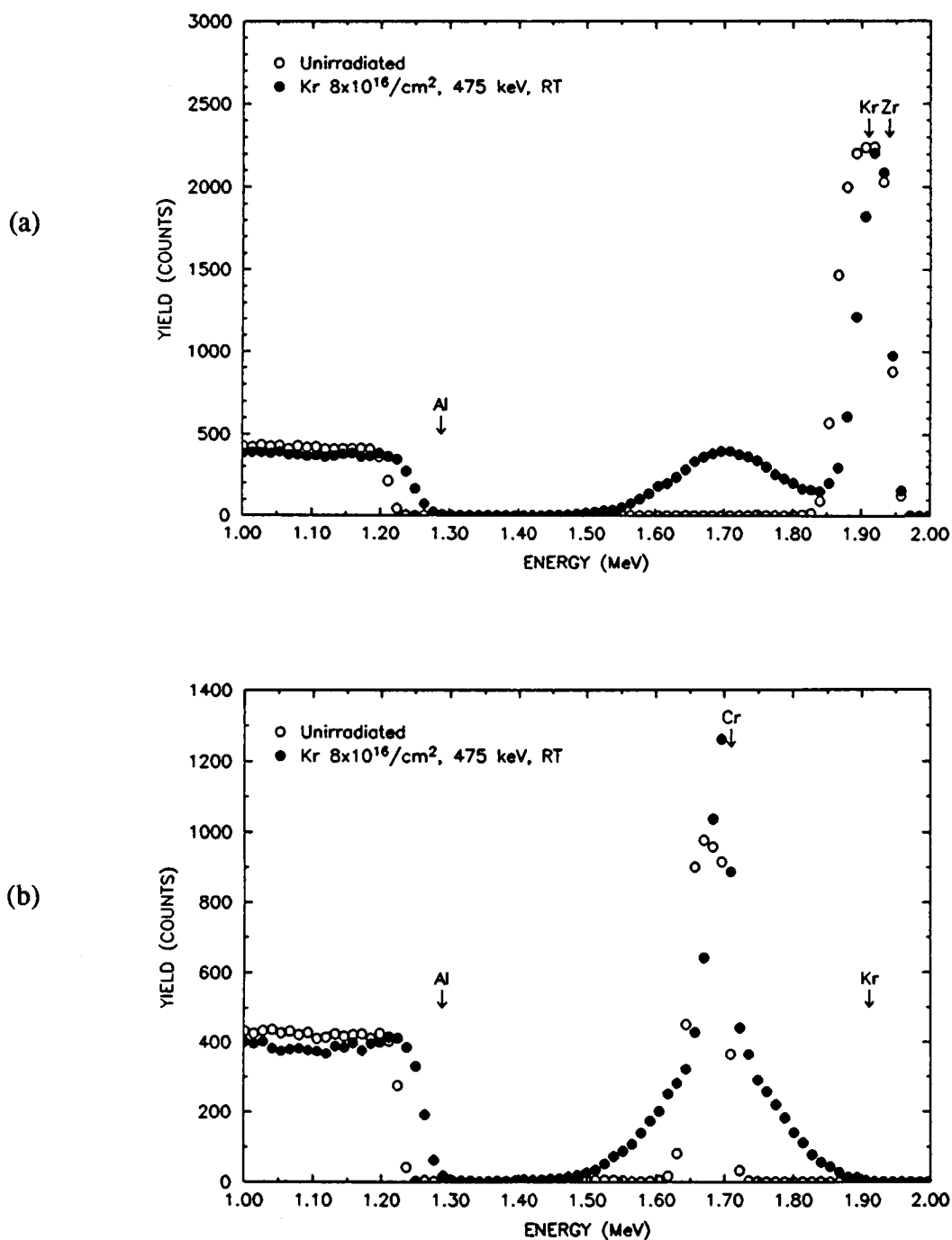


Fig. 22. The RBS spectra from (a) $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and (b) $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples implanted at room temperature with 475 keV Kr (8×10^{16} ions- cm^{-2}).

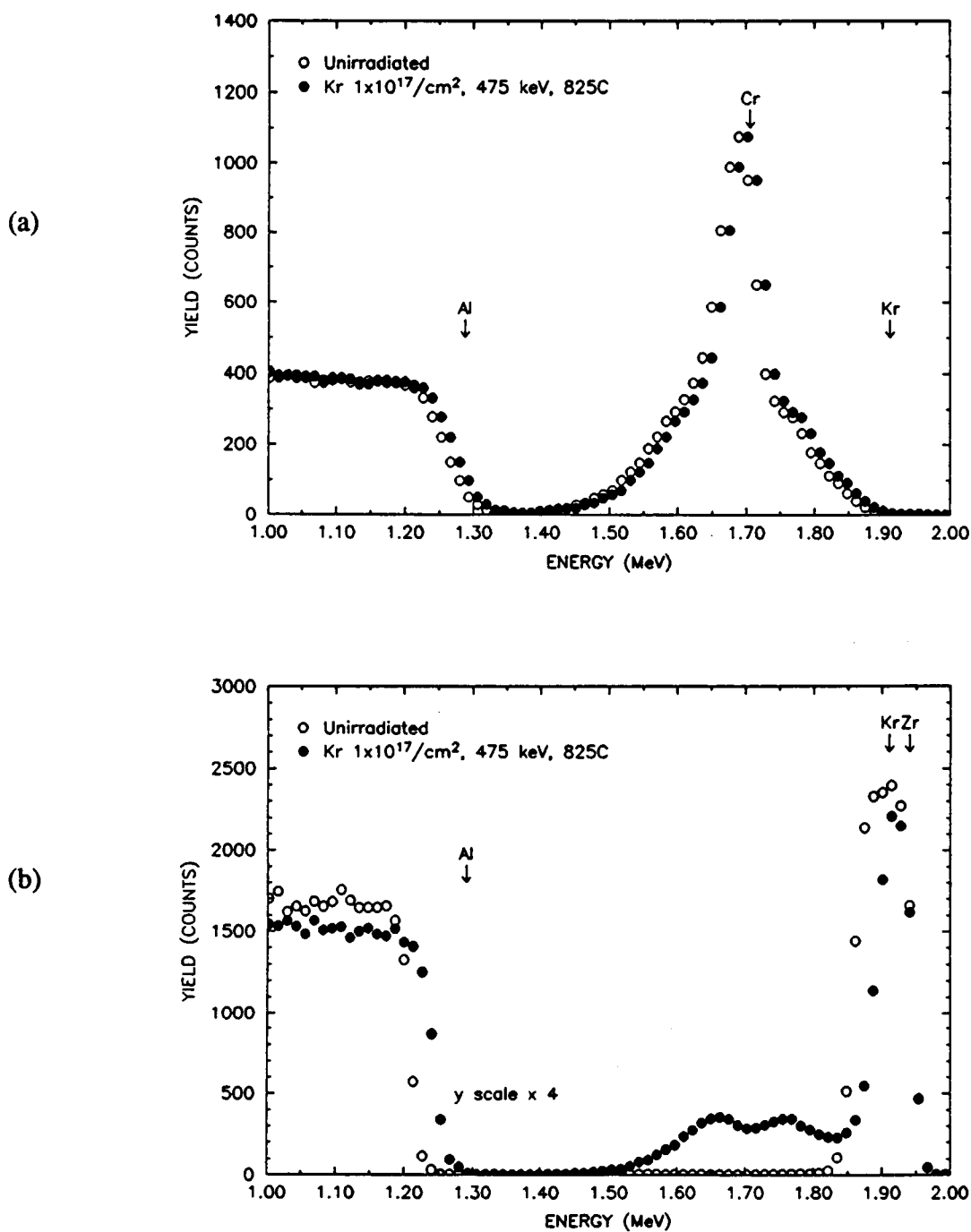


Fig. 23. The RBS spectra from (a) $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and (b) $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples bombarded at elevated temperature with 475 keV Kr (1×10^{17} ions- cm^{-2}).

Likewise, the spectra for the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ film implanted with 340 keV Cr at room temperature and 900°C (not shown) are similar to those plotted in Figs. 17a and 18a.

The RBS spectra from the oxide films implanted at room temperature with 475 keV Kr (8×10^{16} ions- cm^{-2}) are presented in Figs. 22a and b; Figs. 23a and b are spectra obtained from oxide films bombardment at elevated temperature (475 keV Kr, 1×10^{17} ions- cm^{-2} , 825°C). The spectra in Figs. 22a and 23a are from $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ specimens. The spectra in Figs. 22b and 23b are from $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples. In all these spectra, the implanted Kr appears at about 1.7 MeV. On the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample it overlaps the metal signals (between about 1.9 and 1.5 MeV). Significant sputtering of all the films has occurred. During both implantations (room temperature and 825°C), about 50% of the Cr_2O_3 film was lost, and 40% of the ZrO_2 film was lost. The amount of sputter loss precludes detection of any small amount of mixing via RBS analysis. Spectra from the samples implanted at both temperatures with the same energy Kr to a lesser fluence (4 or 5×10^{16} ions- cm^{-2}) appear essentially the same as those presented in Figs. 22 and 23.

Channeling spectra obtained from an uncoated sapphire substrate implanted with 340 keV Cr to a fluence of 4×10^{16} ions- cm^{-2} at room temperature and 900°C are shown in Fig. 24. Comparison of the random spectra and the aligned unimplanted spectra (from a portion of the sample which was masked during implantation) illustrate the effect of channeling of the He ions in the lattice: the yield is nearly zero. The aligned spectra from the implanted samples indicates the lattice damage caused by implantation. Note that the spectrum from the sample implanted at room temperature shows a slightly higher yield than the spectrum from the sample implanted at elevated temperature: defects in Al_2O_3 are mobile at 900°C, and recovery occurs even as the sample is being implanted.

The RBS results are summarized in Table 8.

4. X-ray photoelectron spectroscopy

Elemental analysis via XPS involves setting energy windows for the photoelectrons emitted from elements of interest. Spectra for each element are obtained by analyzing each energy window several times, then adding the yields of electrons in each window. Depth profiles are obtained by sputtering the sample for a set time, and performing this multiple pass analysis over each window before sputtering again. A common way of presenting the data from sputter depth profiling is as a profile of atomic concentration versus sputter time, which can be converted to distance into the sample if the sputter rate is known. The atomic concentrations are determined at any one depth in the sample by measuring the peak areas of each component for which spectra were collected, and normalizing each area by an

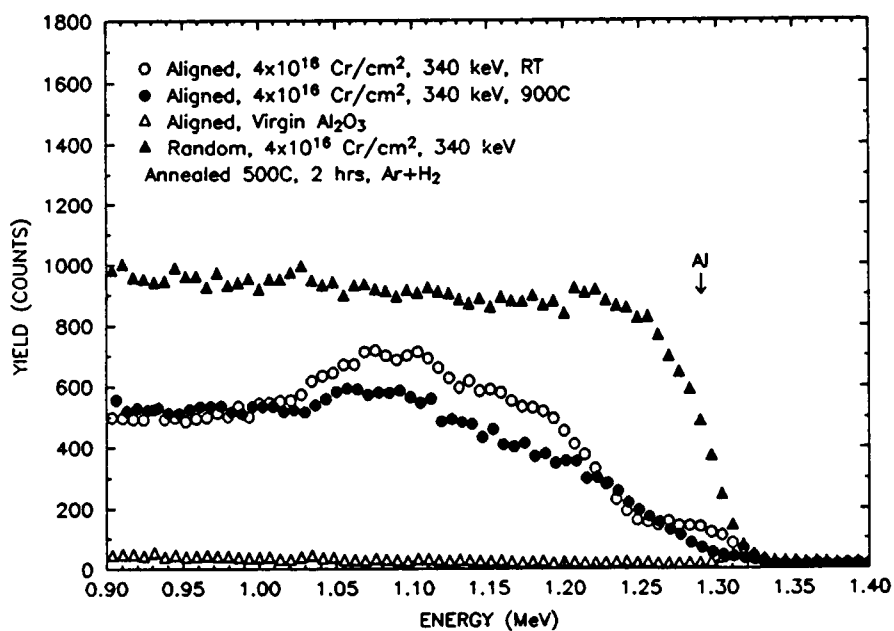


Fig 24. Channeling spectra obtained from an uncoated sapphire substrate implanted with 340 keV Cr to a fluence of 4×10^{16} ions-cm⁻² at room temperature and 900°C.

Table 8. Rutherford backscattering spectrometry results

Film/substrate combination	Treatment	RBS observations
ZrO ₂ /Al ₂ O ₃	Thermal anneal 1h, 1450°C	Evidence of agglomeration of the ZrO ₂ film after anneal.
Cr ₂ O ₃ /Al ₂ O ₃	Thermal anneal 1h, 1050, 1150 or 1450°C	After 1h at 1450°C, all of the Cr ₂ O ₃ film has diffused into the substrate. After 1h at 1150°C, partial diffusion of the film into the substrate has occurred.
Cr/Al ₂ O ₃	Kr, 320 keV 5 x 10 ¹⁶ ions- cm ⁻² 1 x 10 ¹⁷ ions- cm ⁻² 20°C	Some sputtering of the film during implantation.
Zr/Al ₂ O ₃	Kr, 320 keV 5 x 10 ¹⁶ ions- cm ⁻² 1 x 10 ¹⁷ ions- cm ⁻² 20°C	Some sputtering of the film during implantation; a small amount of mixing between the film and substrate.
Cr ₂ O ₃ /Al ₂ O ₃	Cr, 160 keV or 340 keV	Some sputtering of the films during implantation (16% of Cr ₂ O ₃ ; 23% of ZrO ₂ sputtered away). No evidence of mixing; surface roughness may interfere with the analysis.
ZrO ₂ /Al ₂ O ₃	4 x 10 ¹⁶ ions- cm ⁻² 20°C	

Table 8. (continued)

Film/substrate combination	Treatment	RBS observations
Cr ₂ O ₃ /Al ₂ O ₃	Cr, 160 keV or 340 keV	Some sputtering of the films during implantation (12% of Cr ₂ O ₃ ; 17% of ZrO ₂ sputtered away). Possible evidence for ballistic mixing only.
ZrO ₂ /Al ₂ O ₃	4 x 10 ¹⁶ ions-cm ⁻² 860-900°C	
Cr ₂ O ₃ /Al ₂ O ₃	Kr, 475 keV	Significant sputtering of the films during implantation (~50% sputter loss) precludes determination of amount of mixing via RBS.
ZrO ₂ /Al ₂ O ₃	4 -8 x 10 ¹⁶ ions-cm ⁻² 20 or 825°C	
Al ₂ O ₃ substrate only	Cr, 340 keV 4 x 10 ¹⁶ ions-cm ⁻² 20 or 900°C	RBS channelling measurements indicate that some recovery of the damage produced by implantation is dynamically recovered during implantation at elevated temperature.

experimentally determined sensitivity factor. The equation for the normalized peak area (NPA) is

$$\text{NPA} = \frac{\text{measured area}}{(\text{K.E.})^{(t.f.)} S(\text{K.E.})^{(e.d.f.)}} \propto I_i$$

where K.E. is the kinetic energy of the electrons, S is the Scofield sensitivity factor (values from reference 78), t.f. is the transmission factor function (an analyzer characteristic), and e.d.f. is the escape depth factor, generally taken to be 0.5 [63]. The NPA is proportional to the intensity of the signal from the element in question. To obtain the atomic concentration, the normalized area for each elemental component is divided by the sum of all the normalized peak areas, giving an atom fraction for each component.

For the profiles presented in this section, the atomic concentrations must be viewed as semiquantitative, since windows were set for the film and substrate components and usually for any implanted ion, but not for possible surface or bulk impurities such as carbon. In XPS, the time-consuming step is the multiple pass "building" of the spectra, therefore analysis is performed on as few windows as possible. The sputter rates are also somewhat imprecise. The original film thicknesses as determined by profilometry have a ± 5 nm error, and the thicknesses of the implanted films were determined from measurements of the percent sputter loss via RBS, which may lead to an error of a few percent. The sputter rates were determined from the XPS spectra themselves, by noting where the binding energy of the oxygen electrons shifts from its value in the film to the value in the Al_2O_3 . Commonly, the sputter rate is determined by measuring the depth of the sputtered crater via profilometry. Measurement of the crater formed by sputtering is not a trivial task on the materials in this study--all of the oxide samples are transparent, and determination of location of the crater is extremely difficult with the optics systems available in most profilometers.

Charging occurs on these oxide materials during the XPS process. Charge correction for individual spectra was accomplished by noting the measured binding energy of the oxygen electrons. The binding energies of oxygen 2p electrons in all of the materials of interest is known, so the difference between the measured value and the accepted value was taken as the charge shift for all of the elements at a particular depth in the sample. This is not a usual method for charge referencing. Several standard methods for charge referencing exist, none of which were suited to this work. For example, for surface analysis without sputter depth profiling, the carbon binding energy is monitored. For

depth profiling, a very thin layer of a gold is deposited on the sample after sputtering, and then the spectrum for gold 4f electrons is recorded along with a spectrum from the most important element in the sample. The shift in binding energy for the gold peak is assumed to be due to charging. Very little carbon is present in either the films or the sapphire samples examined in this study, and neither XPS system used in this work afforded a way of depositing any reference layer on the sample without removal of the sample from the system. Removal of the sample after each cycle of sputtering and analysis would cause sample contamination and allow straying from the original analysis area. All charge referencing methods assume that the samples are homogeneous. In real, heterogeneous systems, charging can vary even on the micrometer scale because particles of materials can charge to different extents [79].

Sputter depth profiling has many potential problems. Preferential sputtering may occur in the material of interest, giving false information about the chemical surroundings of the elemental components at a given depth. Erroneous data may also be obtained due to crater edge effects. Along the diameter of the crater formed by sputtering, differential amounts of film material are present--the center of the crater is deeper than the sides. For samples like those analyzed in this work, it is possible to be in the substrate at the center of the crater and still be in the film near the crater's edge. If the analysis spot is not centered in the area being sputtered, anomalous data concerning the sharpness of the interface, as well as erroneous peak widths due to differential charging may be obtained. This effect was a problem in this work. Some of the data suffering from crater edge effects are included here when they serve to make a point. They are clearly denoted.

It should be noted that the data taken from the two XPS systems used in this study differ in some ways. The first system, a V.G. ESCALAB II, was plagued with component failures, and many months elapsed between some of the data acquisitions. During this period of time, the position of the detector, x-ray source, and sputter gun were altered, as was the sputter gun current (not easily adjustable on this system). Because of this, the sputter rates are drastically different for some of the profiles. Also, the data processing software on the first system provided no method for plotting atomic concentration vs. depth; all of the plots were constructed manually from peak areas determined one by one using the existing software. Therefore, the depth profiles obtained from this equipment contain data taken at selected sputter cycles instead of data from each cycle (for some analyses, there were over 100 sputter cycles). The second system, a Perkin-Elmer Model 5600, was more dependable than the V.G. system, and the data processing software calculated the atomic concentration vs. depth profiles. However, the system was so new

that no depth profiling had been performed in it before, and the analysis spot and the sputter area were not well-aligned. Crater edge effects were a problem until the alignment was performed.

Plots of atomic concentration vs. either depth or sputter time for various film/substrate combinations and implantation conditions are presented in this section, along with some montages of the actual spectra and some specific spectra with curve fits to reveal the various chemical states present. Montages presented here are labelled as sputter "cycle" vs. binding energy (BE). When specific spectra are mentioned with reference to the montages, both depths and sputter cycles are mentioned. Depth profiles acquired on the V.G. system are presented as concentration vs. depth because of the sputter rate variance. Because of the problems with this system, only implanted samples were profiled. Depth profiles from the Perkin-Elmer (Phi) system are presented as sputter time versus depth since the sputter rates on this system were relatively constant; the rates are clearly indicated. All of the data were smoothed before curve fitting; smoothing was done over 9 points for relatively noiseless spectra (high intensity), and over up to 21 points for noisy spectra (low intensity, i.e. small concentrations). Curve fitting routines available in the XPS systems' manufacturer-supplied software were used for all curve fits. Both packages employ standard curve fitting routines as described in reference 63. Curve-fitted spectra from the VG system are presented as counts ($\propto$ intensity) vs. BE. Spectra obtained on the Phi system are displayed in terms of normalized counts $(N(E)/E)$, where E is the unit energy interval) vs. BE. All charge corrections were performed manually after curve fitting, by total relabelling of the x-axis. Charge correction was not always necessary for the metal films; the recorded BEs were within ± 0.3 eV of the literature values. Chemical state identifications were made by comparison to BE values found in the literature for the elements of interest (references 79-95). Tables 9, 10, and 11 are compilations of binding energies and values for full peak width at half maximum height (FWHM) reported in the literature for the various elemental components.

It should again be emphasized that the data presented here are semiquantitative and therefore cannot be used to determine exact stoichiometries. A table summarizing the results presented below is included at the end of this section.

Figure 25 is a depth profile taken on a Zr/Al_2O_3 sample implanted with 320 keV Kr to a fluence of 1×10^{17} ions-cm⁻². The film was around 33 nm thick after implantation. The sputter rate during this analysis was about 5 nm/minute. Each data point on this plot represents one sputter cycle. The surface of the sample is oxidized, as evidenced by the high oxygen concentration at the sample's surface. A small amount of oxygen is present

Table 9. X- ray photoelectron spectroscopy data for Cr and selected Cr oxides

Species		Peak, eV	FWHM, eV	O 1s Peak, eV	FWHM, eV	Ref.
$\text{K}_2\text{Cr}_2\text{O}_7$ (Cr^{6+})	2p _{3/2}	580.8	1.9			[80]
	2p _{1/2}	589.9				
	2p _{3/2}	579.4	1.9	529.8	2.1	[81]
	2p _{1/2}	588.7	2.4			
	2p _{3/2}	579.4				[79]
CrO_3 (Cr^{6+})	2p _{3/2}	578.2				[79]
CrO_2 (Cr^{4+})	2p _{3/2}	576.7				[82]
	2p _{3/2}	576.2				[79]
Cr_2O_3 (Cr^{3+})	2p _{3/2}	578.4	3.1			[80]
	2p _{1/2}	587.9				
	2p _{3/2}	576.6		530.1		[83]
	2p _{1/2}	586.2				
	2p _{3/2}	576.7		530.3		[84]
Cr metal (Cr^0)	2p _{3/2}	574.2				[79]
	2p _{1/2}	583.3				
	2p _{3/2}	574.2	2.0			[81]
	2p _{1/2}	583.5	2.2			
	2p _{3/2}	574.1				[79]
	2p _{1/2}	583.4				

Table 10. X-ray photoelectron spectroscopy data for Zr and selected Zr oxides

Species	Peak, eV		FWHM, eV	O 1s Peak, eV	FWHM, eV	Ref.						
ZrO ₂ (Zr ⁴⁺)	3d _{5/2}	182.2	1.8	530.7		[85]						
	3d _{3/2}	184.5										
	3d _{5/2}	182.3	1.8			531.2		[86]				
	3d _{3/2}	184.7										
	3d _{5/2}	183.3							[87]			
	3d _{3/2}	185.7										
	3d _{5/2}	182.3	1.7							[88]		
	3d _{3/2}	183.1										
	3d _{5/2}	182.8									[89]	
	3d _{3/2}	185.1										
	3d _{5/2}	182.3										[90]
	3d _{5/2}	182.3										
ZrO (Zr ²⁺)	3d _{5/2}	181.0	1.8									[85]
	3d _{3/2}	183.3										
	3d _{5/2}	182.3	1.8									[86]
	3d _{3/2}	183.1										
	3d _{5/2}	180.8										[87]
	3d _{3/2}	183.2										
	3d _{5/2}	183.2										[87]
	3d _{3/2}	185.6										
	3d _{5/2}	179.7	1.7									[88]
	3d _{3/2}	182.0										
	3d _{5/2}	180.7	1.7									[88]
	3d _{3/2}	183.0										

Table 10. (continued)

Species	Peak, eV	FWHM, eV	O 1s Peak, eV	FWHM, eV	Ref.
Zr (Zr ⁰)	3d _{5/2}	178.5	1.8		[86]
	3d _{3/2}	180.9			
	3d _{5/2}	179.3			[87]
	3d _{3/2}	181.7			
	3d _{5/2}	178.7	1.4		[88]
	3d _{3/2}	181.1			
	3d _{5/2}	178.5			[89]
	3d _{3/2}	180.9			
	3d _{5/2}	179.0			[90]
	3d _{3/2}	181.1			
	3d _{5/2}	178.7			[79]
	3d _{3/2}	181.1			

Table 11. X- ray photoelectron spectroscopy data for Al and selected Al oxides

Species		Peak, eV	FWHM, eV	O 1s Peak, eV	FWHM, eV	Ref.
Al ₂ O ₃ (Al ³⁺)	2p	74.5		531.6		[84]
	2p	76.3	2.25			[91]
	2p	74.7		531.6		[79]
	2p	74.7	3.0*	531.5	3.0*	[92]
	2s	119.4	2.5*			[92]
Al metal (Al ⁰)	2p	72.7				[79]
	2s	119				[79]

*Average of reported values

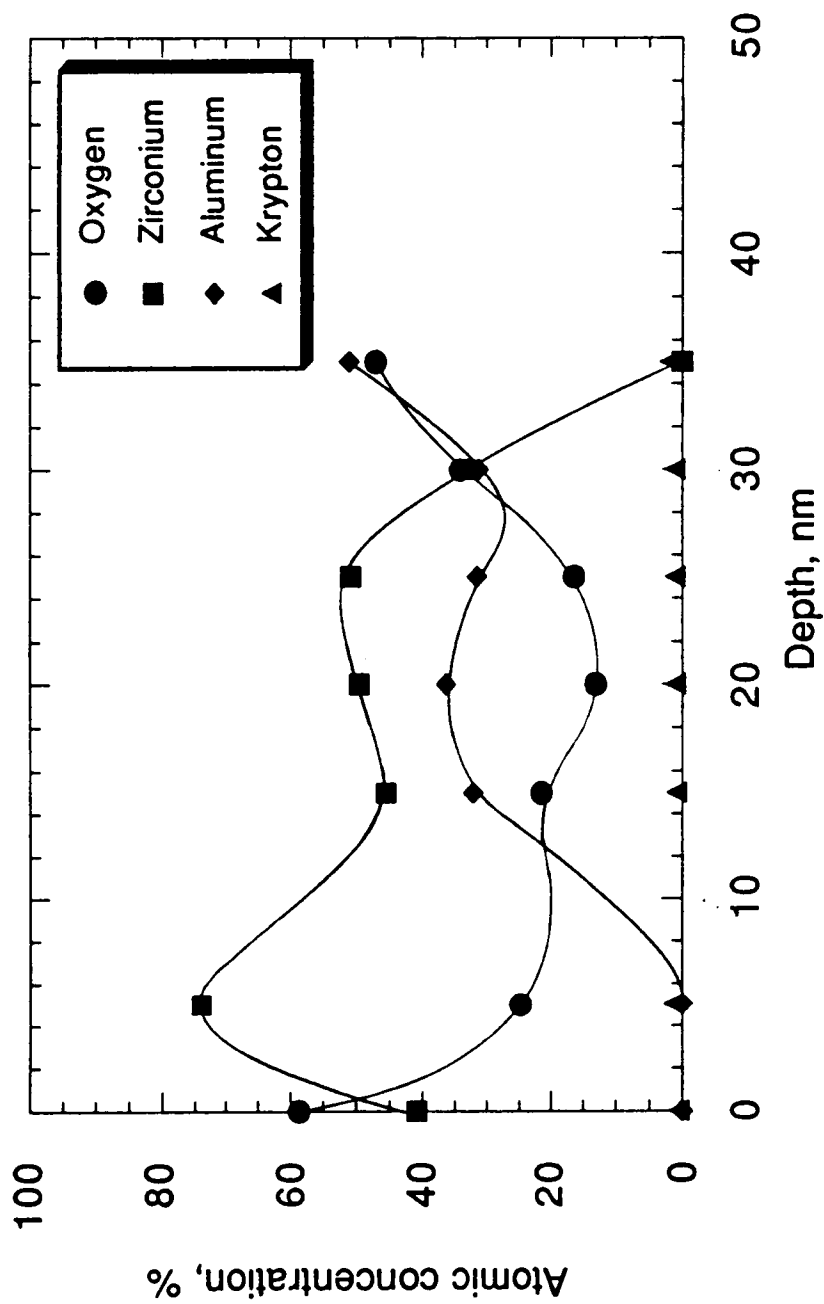


Fig. 25. A depth profile taken on a Zr/Al₂O₃ sample implanted with 320 keV Kr to a fluence of 1×10^{17} ions-cm⁻².

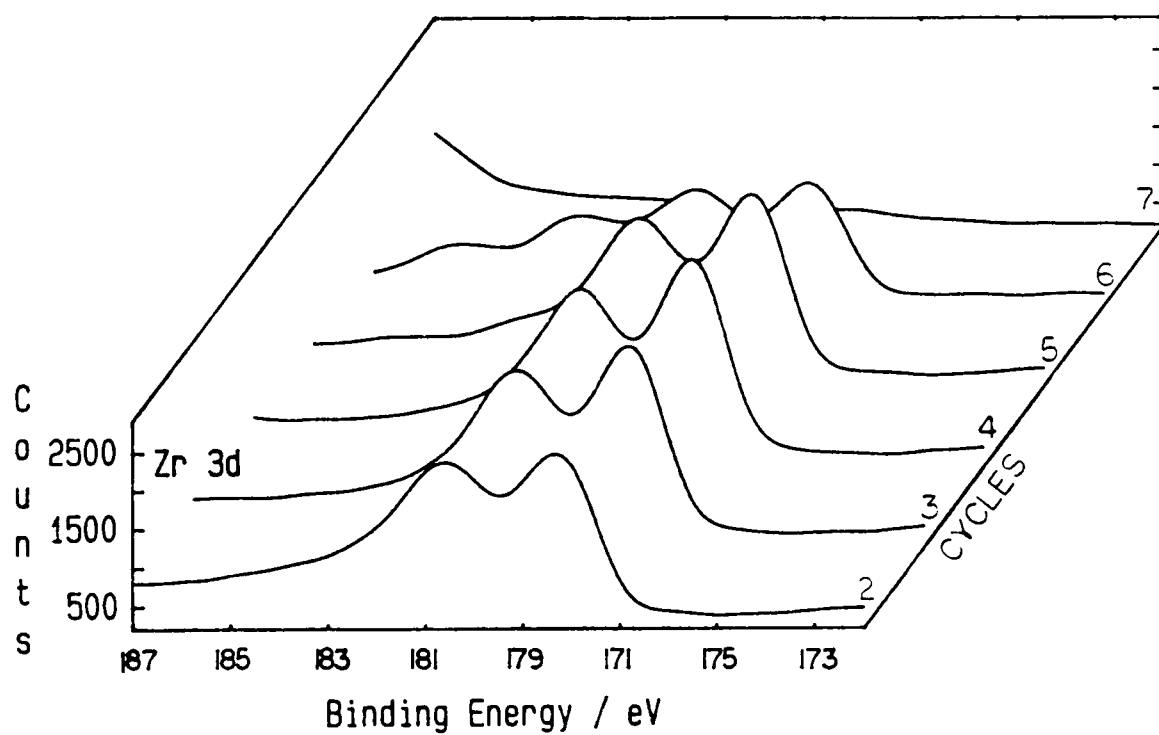


Fig. 26. A montage showing the Zr 3d peaks' evolution at various depths in the sample. At the interface (about 30 nm into the film; cycle 6), there is an apparent change in the chemical state of Zr.

throughout the film. Bare Al_2O_3 was reached after the last sputter cycle. Aluminum is detected 15 nm into the film, measured from the film's surface. Figure 26 is a montage showing the Zr 3d peaks' evolution at various depths in the sample. At the interface (about 30 nm into the sample; cycle 6), there is an apparent change in the chemical state of Zr. The curve fit of this spectrum, shown in Fig. 27, reveals the presence of Zr in the metallic state (Zr^0), as well as Zr^{4+} (ZrO_2). Figure 28 is a montage displaying the Al 2p peak evolution for various sputter times. Curve fits for the Al spectra at 15 nm, 31 nm, and 35 nm (cycles 5-7) are presented in Fig. 29a-c. The presence of both Al^0 and Al^{3+} (Al_2O_3) is indicated in these spectra. This could be interpreted as reduction of the Al_2O_3 by the Zr. Alternatively, some of the Al recoiling back into the Zr film may react with the excess oxygen in the film, while the rest remains in the metallic state.

Figure 30 is a depth profile from the unimplanted (masked) portion of the same sample as Fig. 25. This profile suffers from crater edge effects: the interface appears broadened, as evidenced by the Zr extending into the Al_2O_3 . Because of these effects, the sputter rate for this experiment is not known. However, montages of the spectra obtained during the profile provide some information on the point at which no more film is detected, that is, the point at which the crater is deep enough so that the analysis area is totally in bare Al_2O_3 . Figures 31a and b are montages of the spectra obtained for the Zr 3d peaks after each sputter cycle; the spectra are shown in reverse order in Fig. 31b to reveal the true shape of the peaks. The oxidation on the surface of the film is evident in the first few cycles. Oxidation was also evident on the surface of the implanted film, but the spectra from the surface are not shown in the montage (Fig. 26). After a few cycles, the oxide is no longer present in large amounts, the signal is primarily from Zr metal. However, oxygen is present at a low level throughout the film. Figures 32a and b are curve-fitted Zr 3d spectra from cycles 13 and 24; cycle 24 is the last cycle where a significant amount of Zr is present. No ZrO_2 is discernible in these spectra. The two small peaks visible at higher BE are not identifiable from data in the literature. They are probably due to differential charging in the specimen, an artifact due to crater edge effects. This assumption is supported by the Al and O spectra. A curve fit of the Al spectrum from cycle 24 is displayed in Fig. 33. Four peaks are present: 67.5 eV, 70.2 eV, 72.5 (possibly Al^0) eV, and 74.7 eV (Al^{3+}). The peaks at 67.6 eV and 70.2 eV are unidentifiable from values in the literature for oxides of aluminum. Peaks at 525 eV, 527.5 eV, 530 eV, and 531.5 eV are apparent in the O 1s spectrum for cycle 24 (Fig. 34). The BE for O 1s electrons in Al_2O_3 is generally taken to be 531.6 eV [79, 84]. For O 1s electrons in ZrO_2 , the BE is around 531.1 eV [88, 89]. None of the oxygen peaks in Fig. 34 are separated by 0.5 eV;

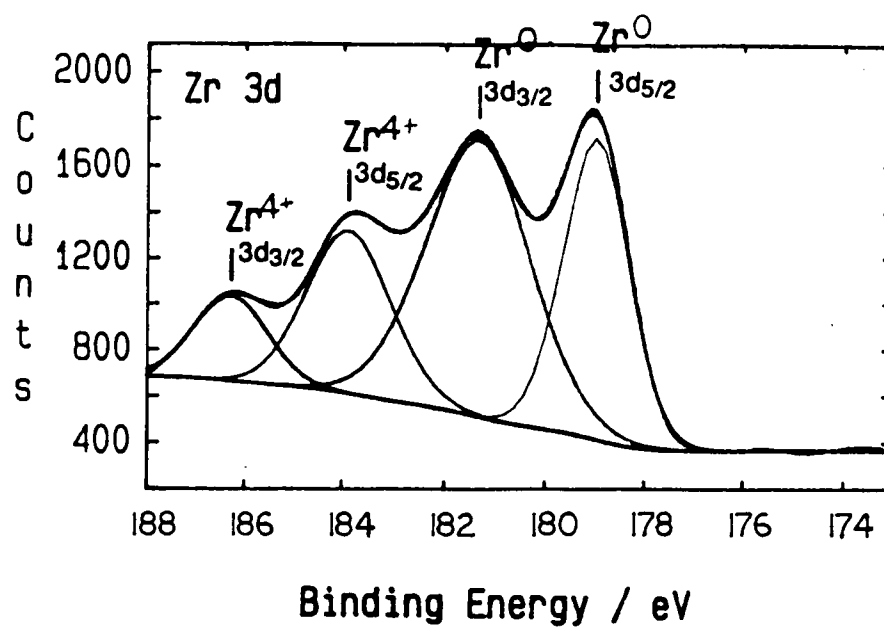


Fig. 27. A curve fit of the spectrum from cycle 6 in Fig. 26 (about 30 nm into the film).

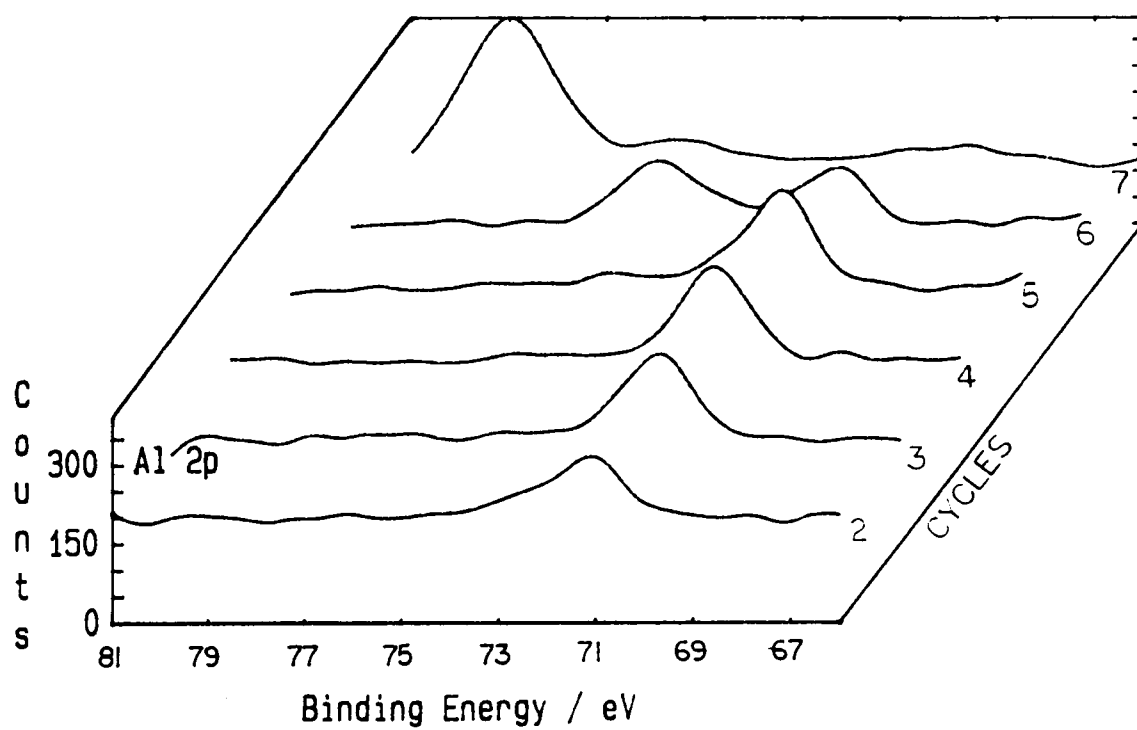


Fig. 28. A montage displaying the Al 2p peak evolution for various sputter times.

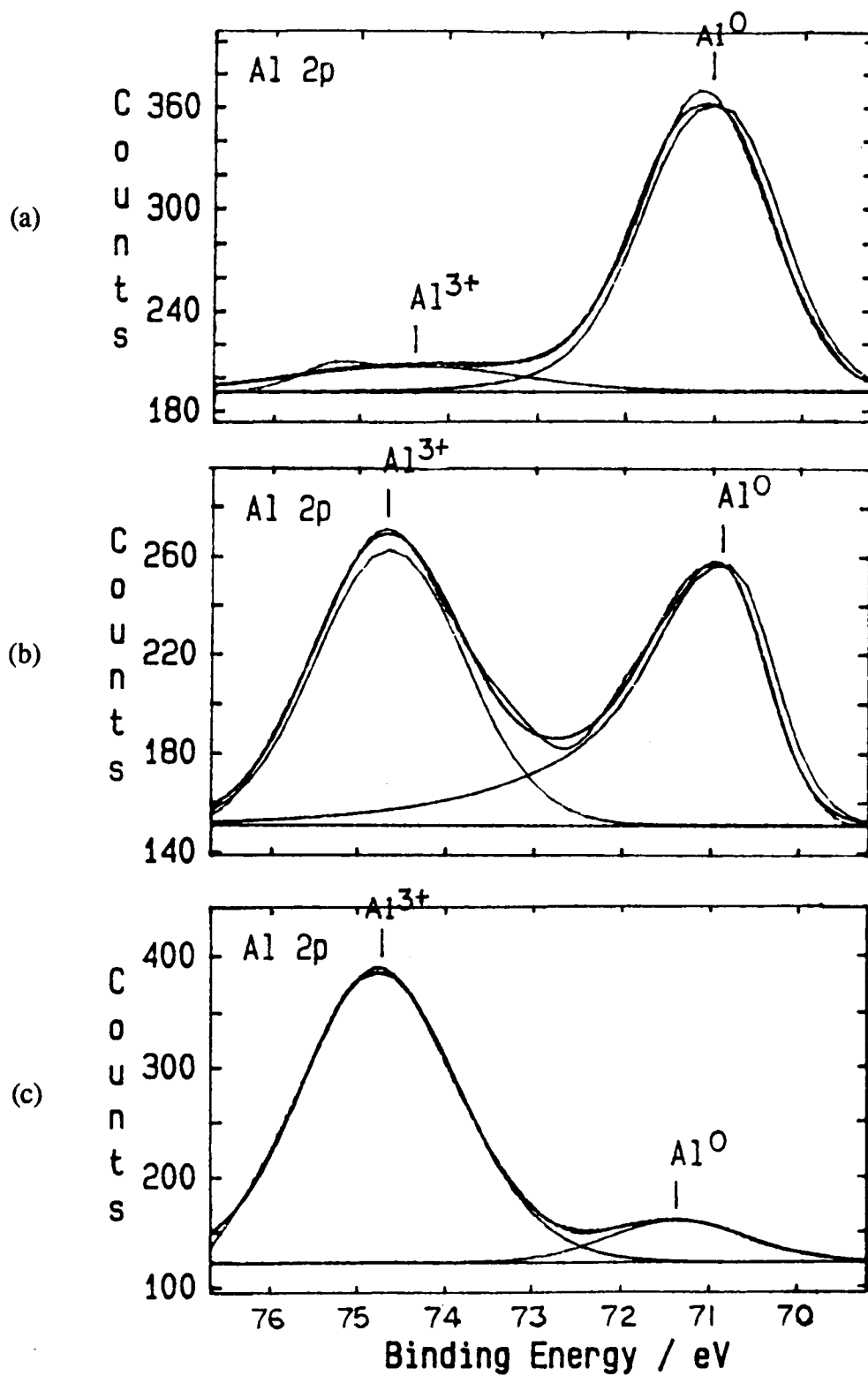


Fig. 29. Curve fits for the Al spectra at 15 nm, 31 nm, and 35 nm (cycles 5-7).

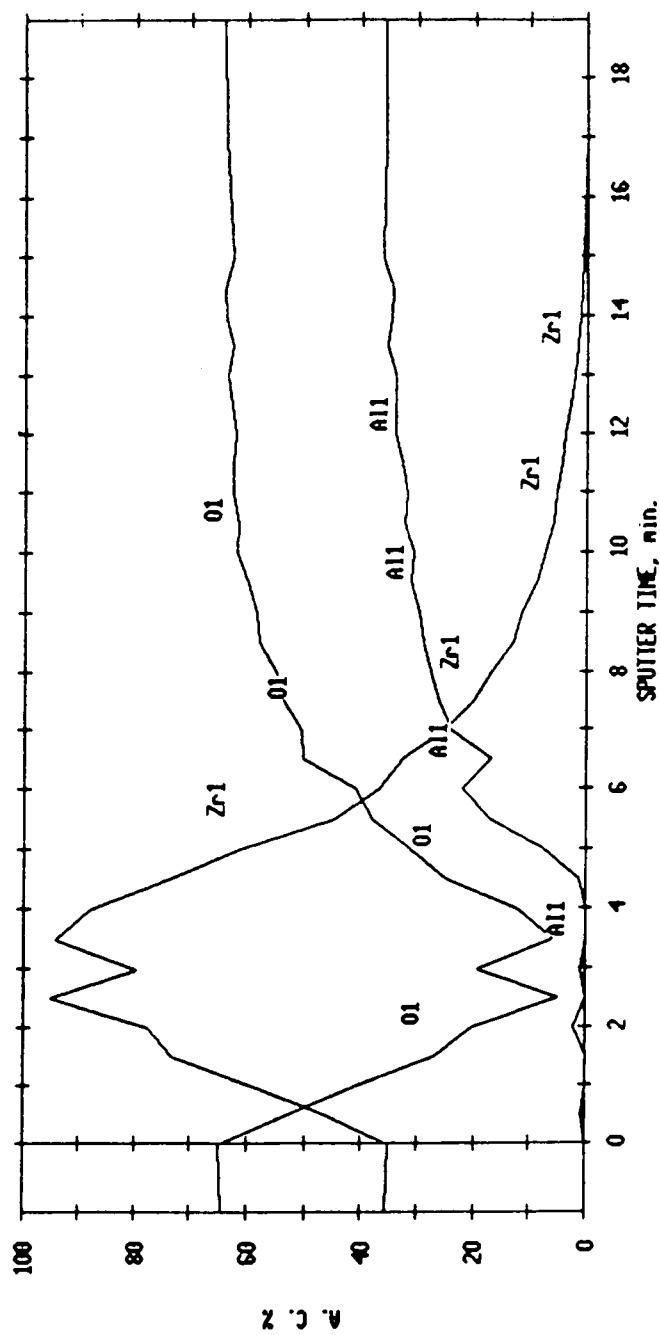


Fig. 30. A depth profile from the unimplanted (masked) portion of the same sample as Fig. 25. This profile suffers from crater edge effects.

Zr 3d

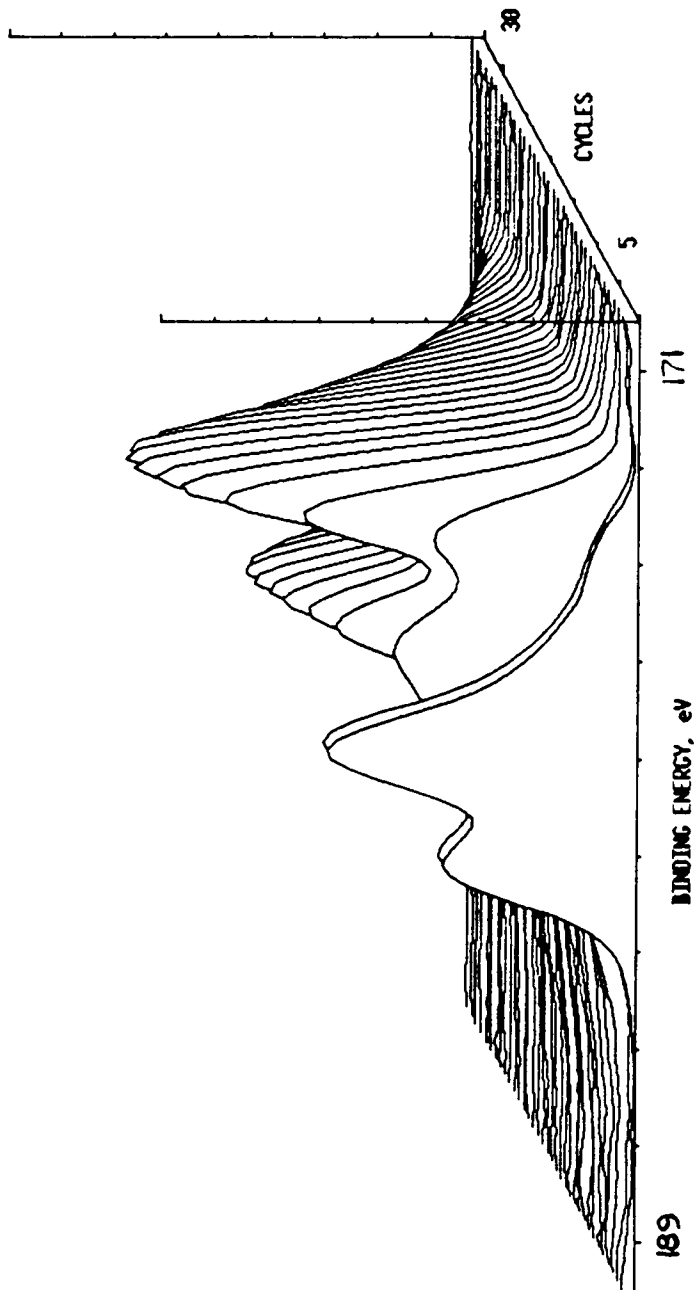


Fig. 31. Data obtained from the unimplanted Zr/Al₂O₃ sample (a) a montage of spectra obtained for the Zr 3d peaks after each sputter cycle; (b) the spectra in reverse chronological order, revealing the true shape of the peaks. The oxidation on the surface of the film is evident in the first few cycles.

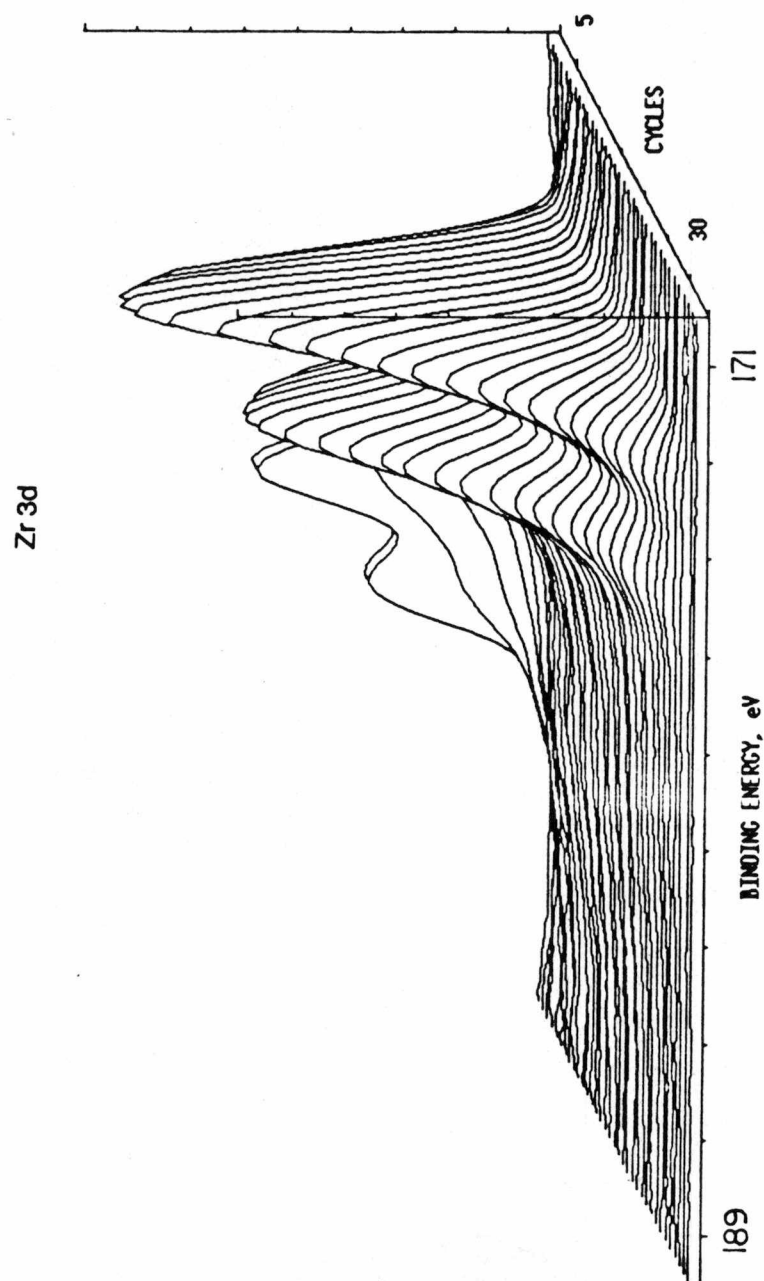


Fig. 31. (Continued).

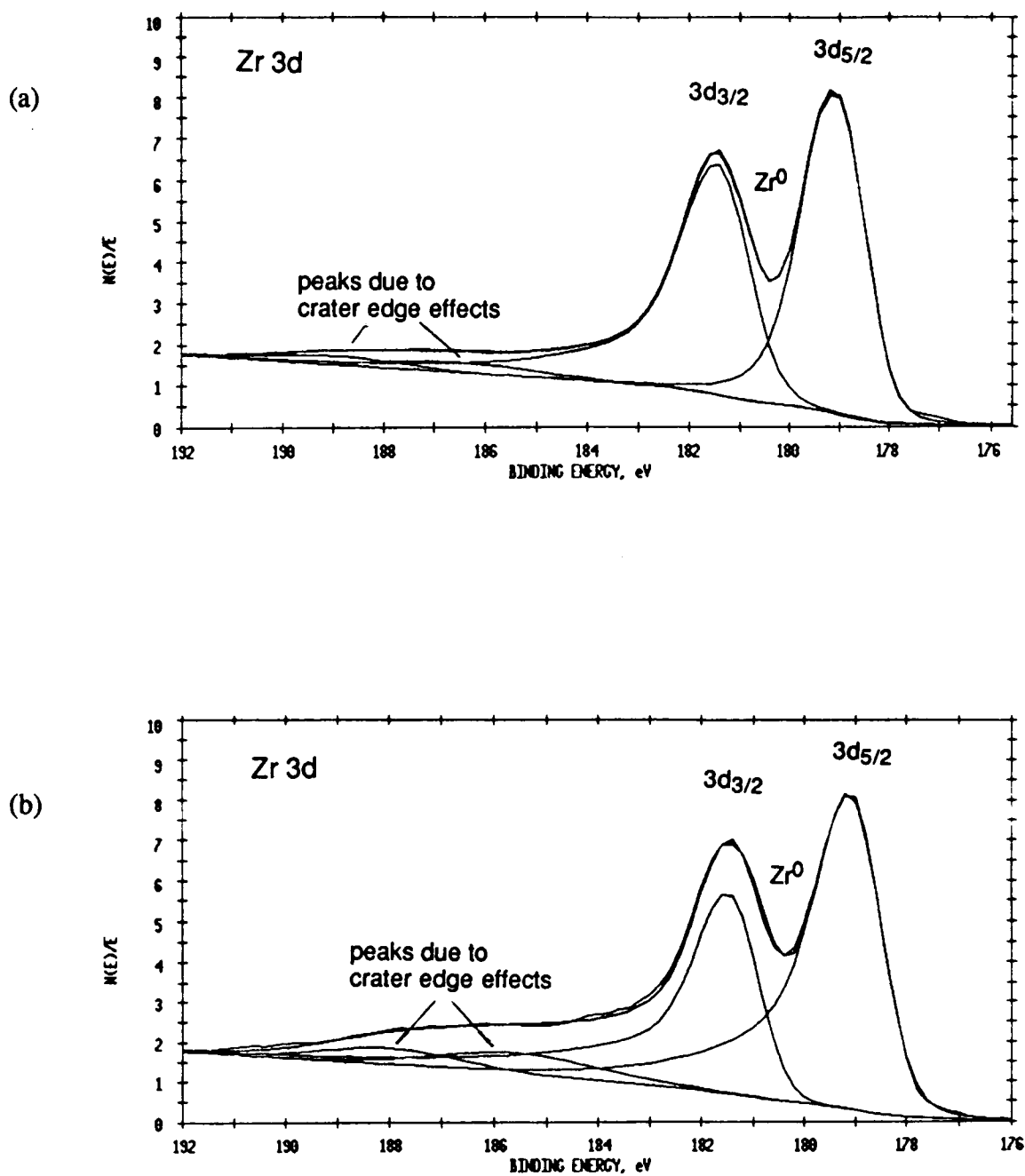


Fig. 32. (a) Curve-fitted Zr 3d spectra from cycle 13 and (b) cycle 24; cycle 24 is the last cycle where a significant amount of Zr is present (unimplanted Zr/Al₂O₃ specimen).

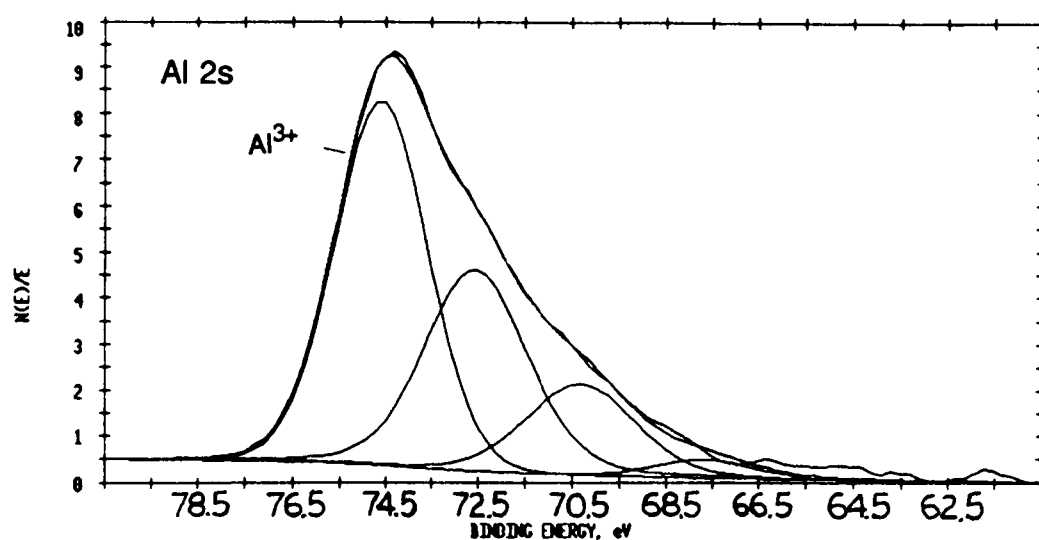


Fig. 33. A curve fit of the Al spectrum from cycle 24 (unimplanted Zr/Al₂O₃ specimen).

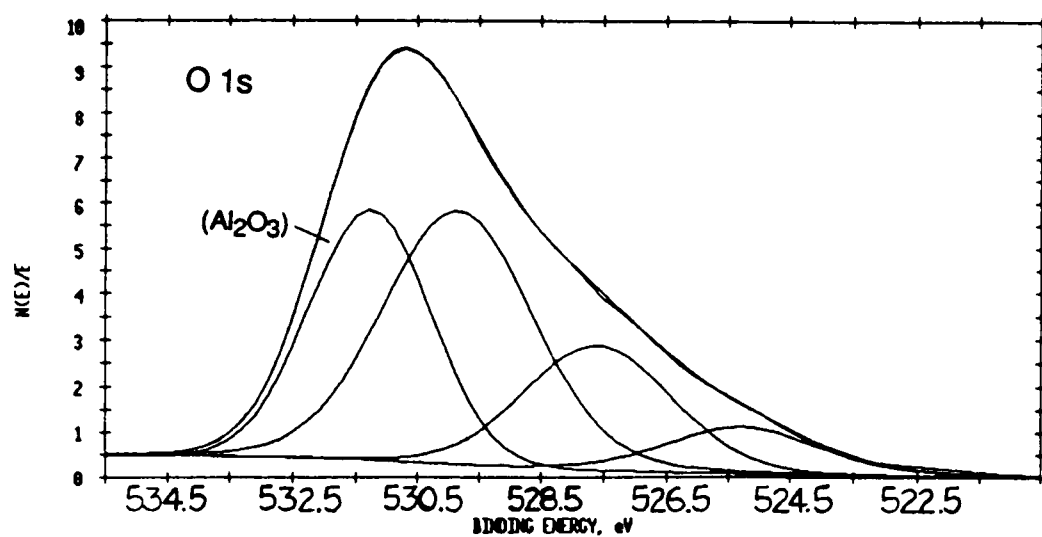


Fig. 34. A curve fit of the O spectrum from cycle 24 (unimplanted Zr/Al₂O₃ specimen).

the smallest separation is 1.4 eV. This suggests that much of the reduction of Al in this sample may be due to preferential sputtering of oxygen. The lack of evidence for ZrO_2 at this same position in the sample supports this idea. In any case, reduction of the Al is not as pronounced as in the Kr implanted portion of this specimen (Figs. 25-29).

Depth profiles from the Cr/ Al_2O_3 film which was implanted 320 keV Kr to a fluence of 1×10^{17} ions-cm⁻² are shown in Figs. 35 (unimplanted) and 36 (implanted). The sputter rate in these specimens was around 11 nm/min. No gross crater edge effects are apparent in the profile from the unimplanted specimen (note the expanded time scale). The decrease in thickness of the film after implantation is obvious. The implanted Kr was not monitored in this sample (its concentration is very small in the region of interest). Comparison of Figs. 35 and 36 shows that the interface has broadened after implantation (> 88 nm as opposed to ~ 44 nm before implantation), assuming that the relative position of the apparent interface (where the Cr and Al curves cross) remains in approximately the same position after the implantation. The Cr appears to extend over 60 nm into the Al_2O_3 substrate. Because of the existence of a Cr peak (Cr 3s; BE = 77 eV) near the Al 2p peak (BE ~ 74 eV), the Al 2s peak was monitored rather than the Al 2p. Examination of the spectra from the unimplanted portion of the specimen implies that there is reduction of the Al_2O_3 in the region near the interface: curve-fitted spectra for Cr at positions near the film/substrate interface (33, 44, and 55 nm) are displayed in Figs. 37a-c. These positions are in the film, on the film side of the interface and on the substrate side of the interface respectively. Curve-fitted spectra for Al and O at 44 nm are shown in Figs. 38a and b. The O spectrum indicates the presence of at least two distinct oxides, and probably more; the FWHM of the peaks are quite broad. The Al is present in several oxidation states. The lack of data in the literature for BEs of 2s peaks for oxides of Al precludes their identification here. In the implanted specimen, the changes in the chemical state of the Cr occur farther into the sample. Sputter loss during implantation of this sample left the ZrO_2 film about 45 nm thick. This is in agreement with the depth profile (Fig. 36), which shows the apparent film/substrate interface at 44 nm from the sample's surface. The Cr, Al, and O spectra taken at about 33 nm into the implanted sample are compared in Figs. 39a-c. This position is in the film approximately 10 nm from the apparent interface, corresponding to the 44 nm (4 minutes sputter time) in the unimplanted portion of the specimen. Here, the Cr is present as Cr^0 , while the Al exists in various states of oxidation, which are also apparent in the oxygen spectrum. In both the implanted and unimplanted samples, the existence of numerous Al oxidation states may be due to preferential sputtering of the oxygen, as discussed before.

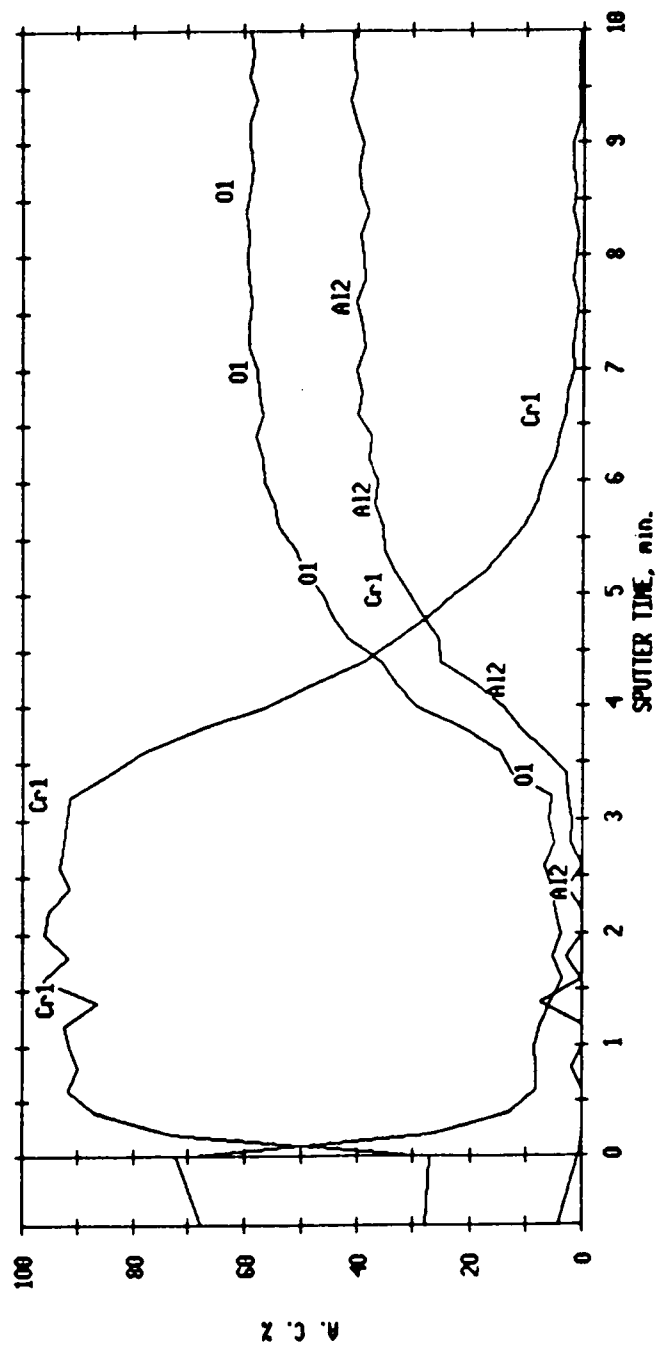


Fig. 35. A depth profile from an unimplanted (masked) portion of a Cr/Al₂O₃ sample.

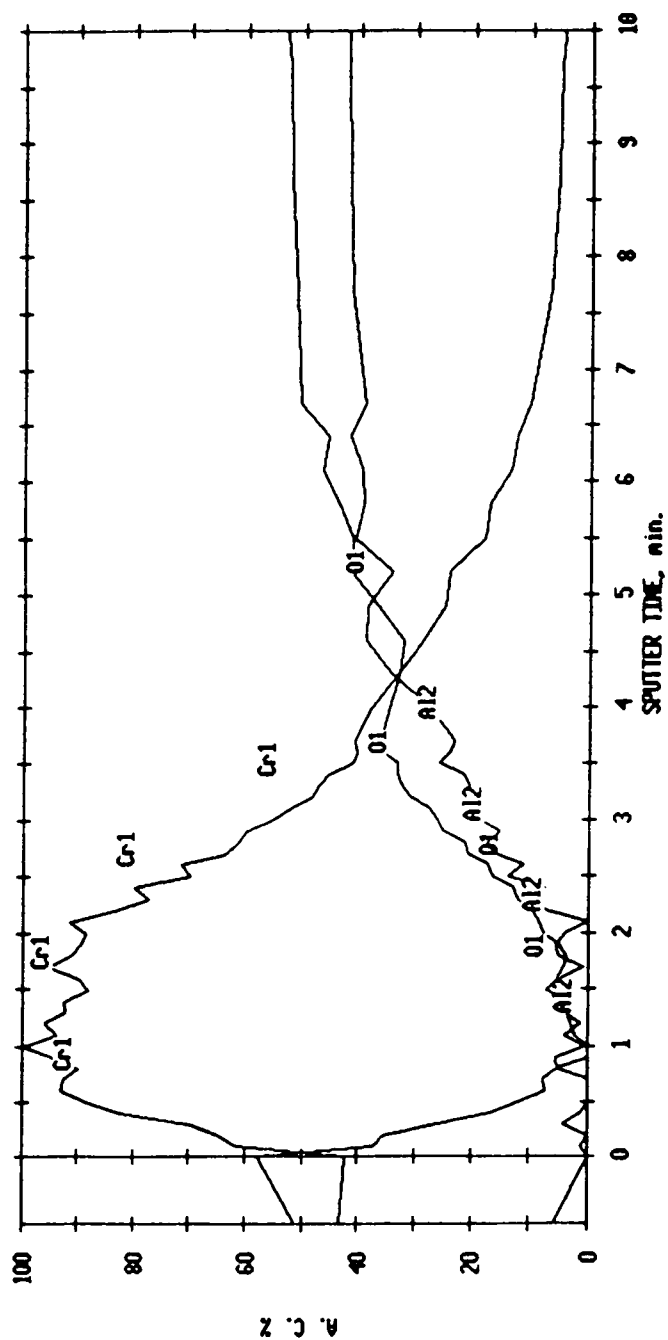


Fig. 36. A depth profile from the Cr/Al₂O₃ sample which was implanted with 320 keV Kr to a fluence of 1×10^{17} ions-cm⁻².

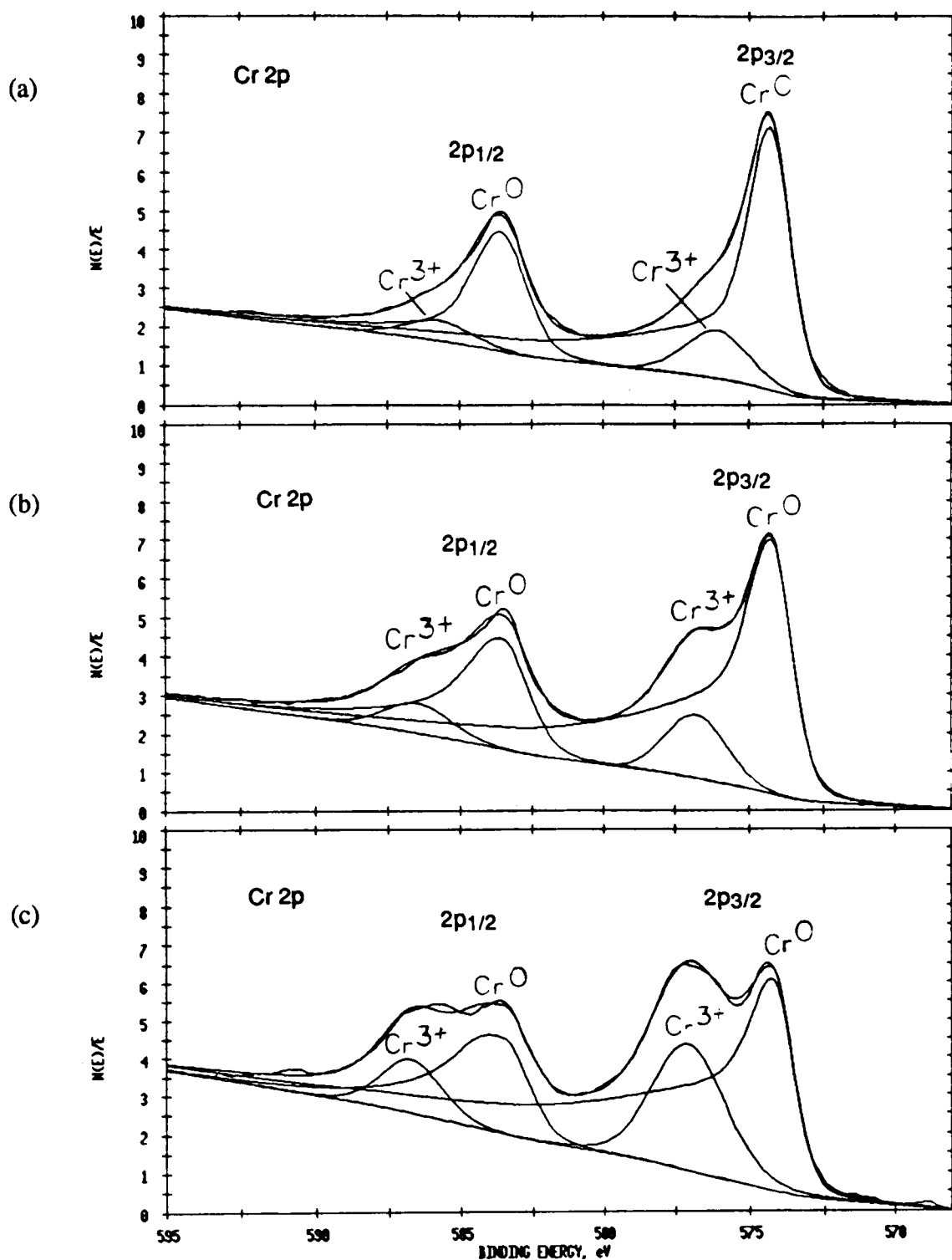


Fig. 37. Curve-fitted spectra for Cr from the unimplanted Cr/Al₂O₃ sample (a) 33, (b) 44, and (c) 55 nm. These positions are in the film, on the film side of the interface, and on the substrate side of the interface, respectively.

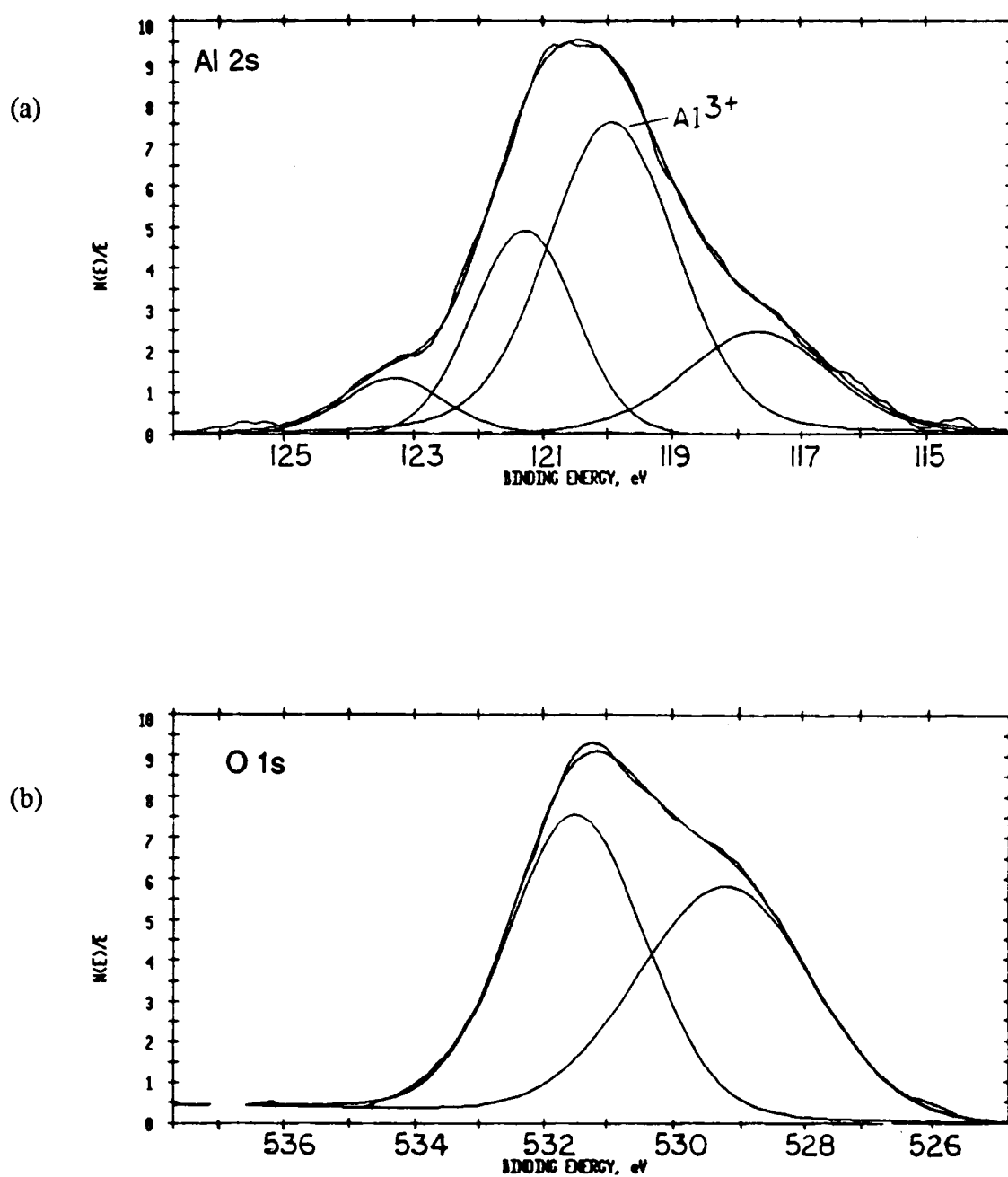


Fig. 38. Curve-fits of spectra for (a) Al and (b) O at 44 nm (unimplanted Cr/Al₂O₃ sample).

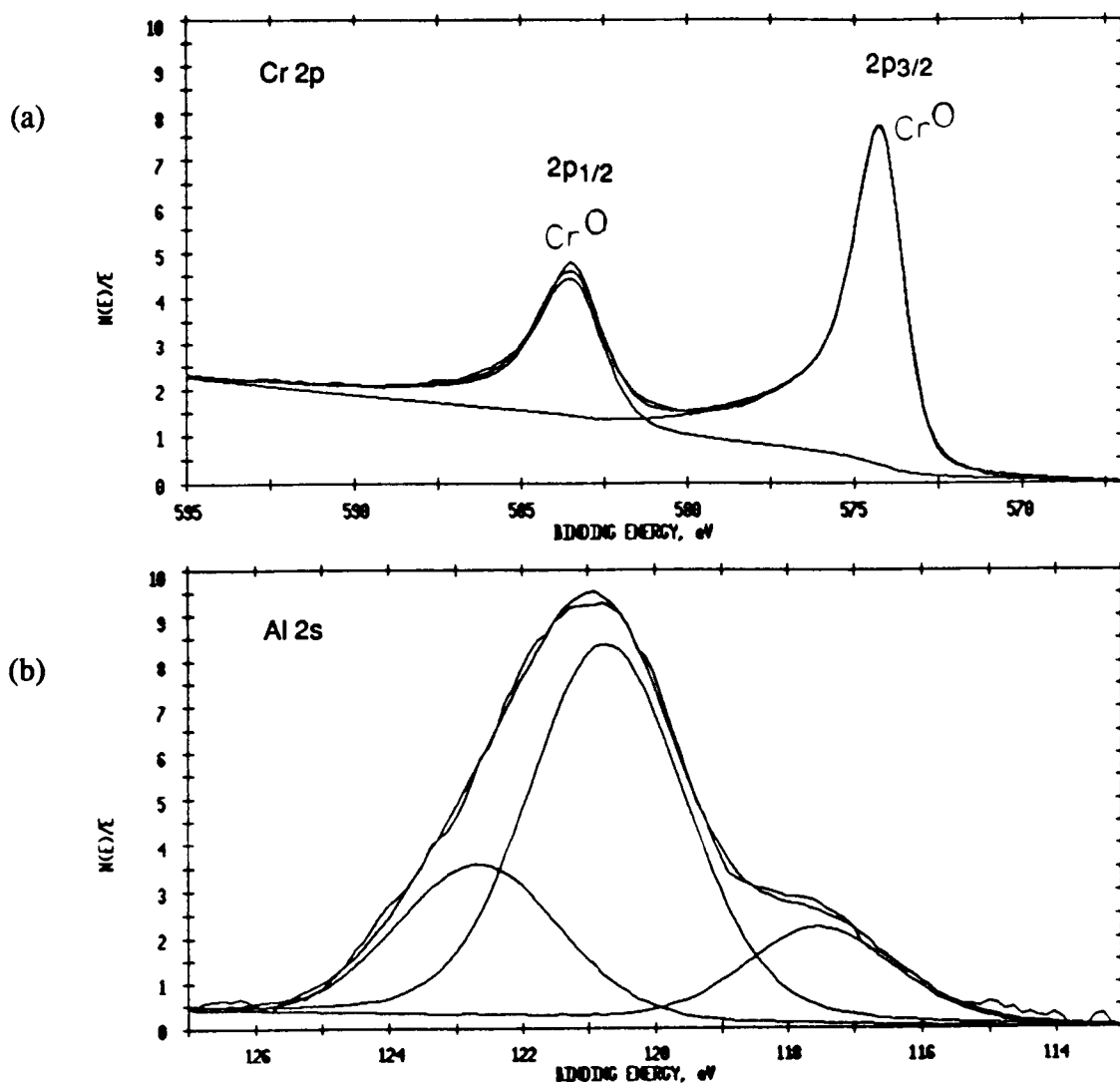


Fig. 39. (a) Cr, (b) Al, and (c) O spectra from about 33 nm into the implanted Cr/Al₂O₃ specimen. This position is in the film approximately 10 nm from the apparent interface.

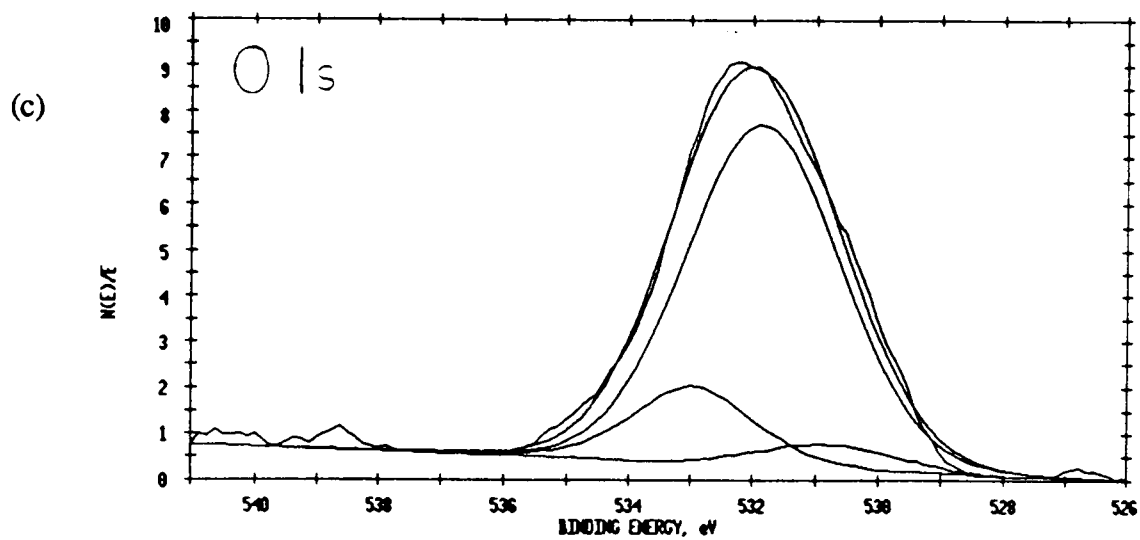


Fig. 39. (Continued).

Figure 40 is a depth profile from a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample implanted at room temperature with 160 keV Cr to a fluence of 4×10^{16} ions- cm^{-2} . There is a small amount of Al present at the sample's surface, and the Cr appears to extend at least 25 nm from the interface into the Al_2O_3 substrate. The sputter rate was approximately 0.5 nm/min in this sample. Curve-fitted spectra of Cr 2p and Al 2p peaks from 29, 43, and 53 nm into the sample (i.e., in the film, at the interface, and on the substrate side of the interface) are presented in Figs. 41 and 42. The Cr spectra indicate the presence of multiple charge states, from Cr^0 to Cr^{6+} . At 29 nm, the major contribution is from Cr metal; at 43 and 53 nm, Cr^{3+} is the major component, but the amount of Cr^0 is significant. In Fig. 42, near the Al 2p peaks, the Cr 3s peaks are evident, but Al appears to exist in just one charge state: Al^{3+} , as in Al_2O_3 . The Cr 3s peaks are not specifically identified here; data for these peaks corresponding to different Cr oxides are not common in the literature. The O spectra from the same positions as in Figs. 41 and 42 are displayed in Fig. 43. The spectra do not show the presence of multiple Cr oxides: the FWHM of the two peaks shown is within the normal range for Cr_2O_3 and Al_2O_3 (see Table 9). Any unresolved peaks must contribute to broadening of the peaks shown. Since the BE range of the O peaks for the various oxidation states of Cr is small, and the contributions of small amounts of O from different Cr oxides may very well be unresolvable. The presence of Cr metal is not apparent from a montage of the Cr spectra; due to the presence of the three Cr charge states and the fact that the normal FWHM of these peaks is about 3 eV, the peaks smear together, and do not appear as well-defined as Zr^0 and Zr^{4+} .

A depth profile from a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample implanted at 860°C with 160 keV Cr to a fluence of 4×10^{16} ions- cm^{-2} is shown in Fig. 44. The sputter rate in this sample was around 2 nm/min. Again, a significant amount of Al is found near the sample's surface; however, the Cr extends only about 15 nm into the Al_2O_3 substrate. The amounts of Al shown at the surface in Fig. 44 is about 3% less than for the room temperature implant (Fig. 41). The Al concentration is noticeably less in the implanted specimen up to the interface. Figures 45 and 46 are curve-fitted spectra for Cr 2p and O 1s peaks at 12 nm, 34 nm, and 50 nm into the sample. These positions are in the film, on the film side of the interface region, and on the substrate side of the interface. At 12 nm, the Cr spectra shows the presence of several peaks, again indicating that Cr is present in various states of oxidation, as in the specimen implanted at room temperature. These peaks persist through the interface region, with the relative amounts changing slightly. The major contribution is from Cr^{3+} . The O spectra from the same positions show only one peak present, corresponding to O bound in Cr_2O_3 . The peaks corresponding to Cr^0 and Cr^{6+} are small,

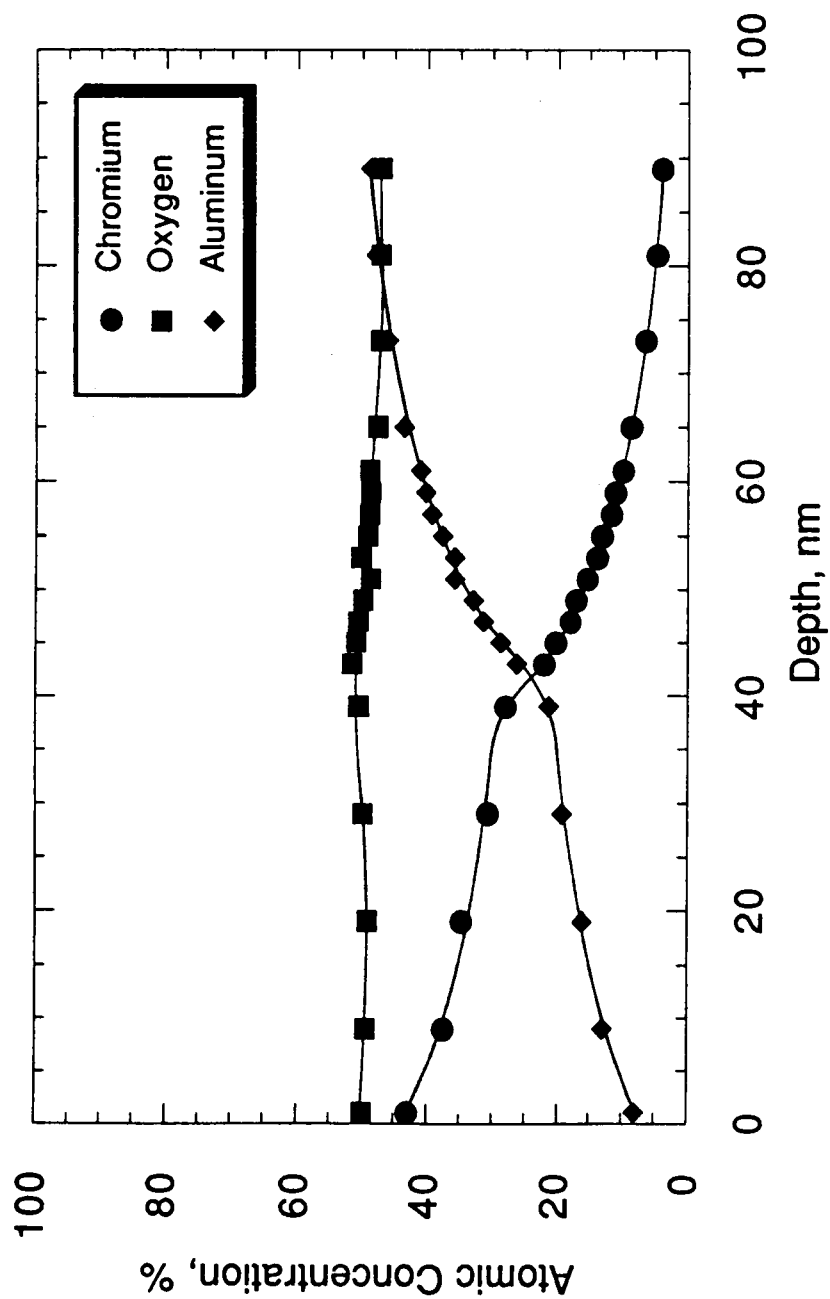


Fig. 40. A depth profile from a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample implanted at room temperature with 160 keV Cr to a fluence of 4×10^{16} ions- cm^{-2} .

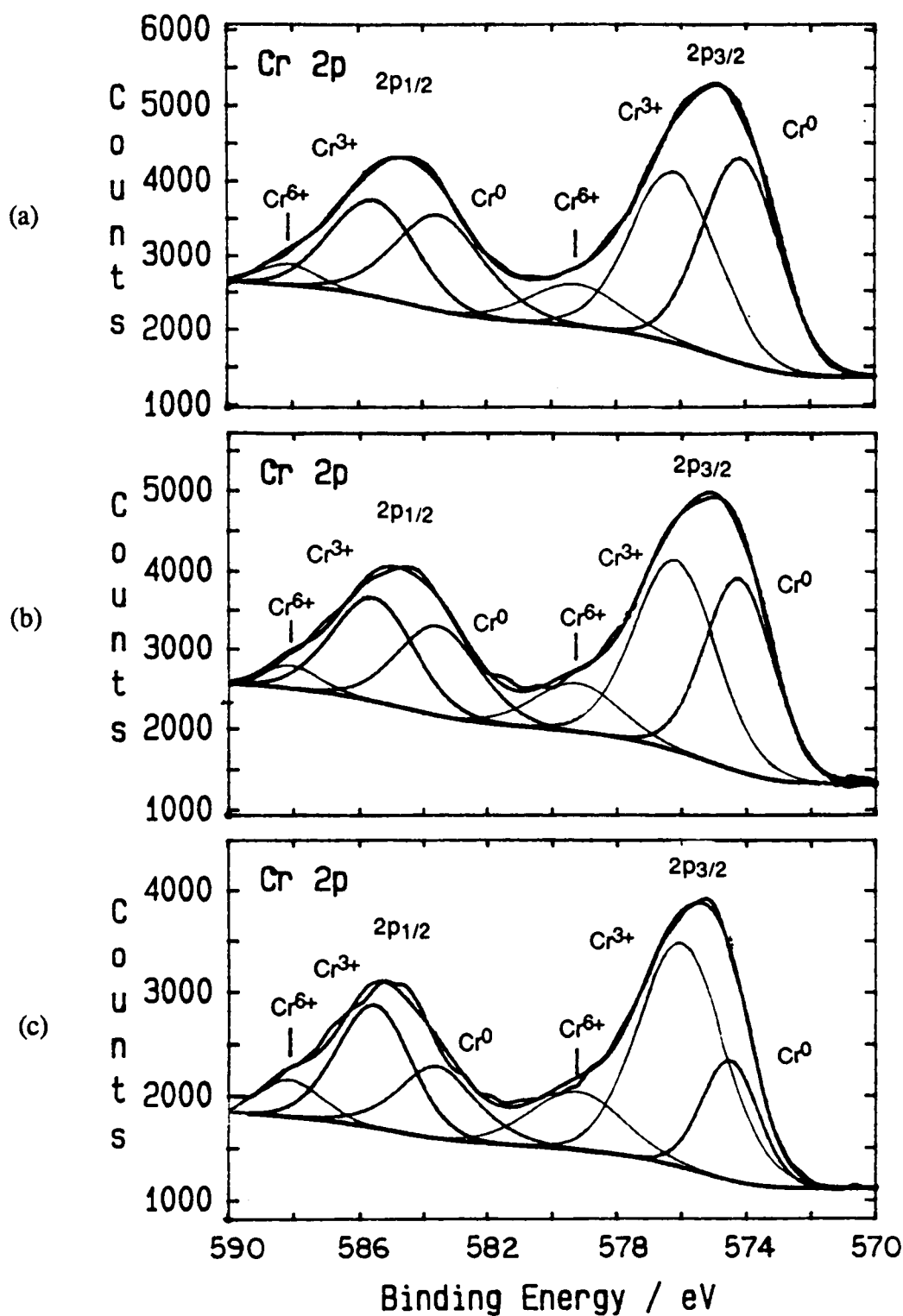


Fig. 41. Curve-fitted spectra of Cr 2p peaks from (a) 29, (b) 43, and (c) 53 nm into the implanted Cr₂O₃/Al₂O₃ sample (see Fig. 40). These positions are in the film, at the inter-face, and on the substrate side of the interface, respectively.

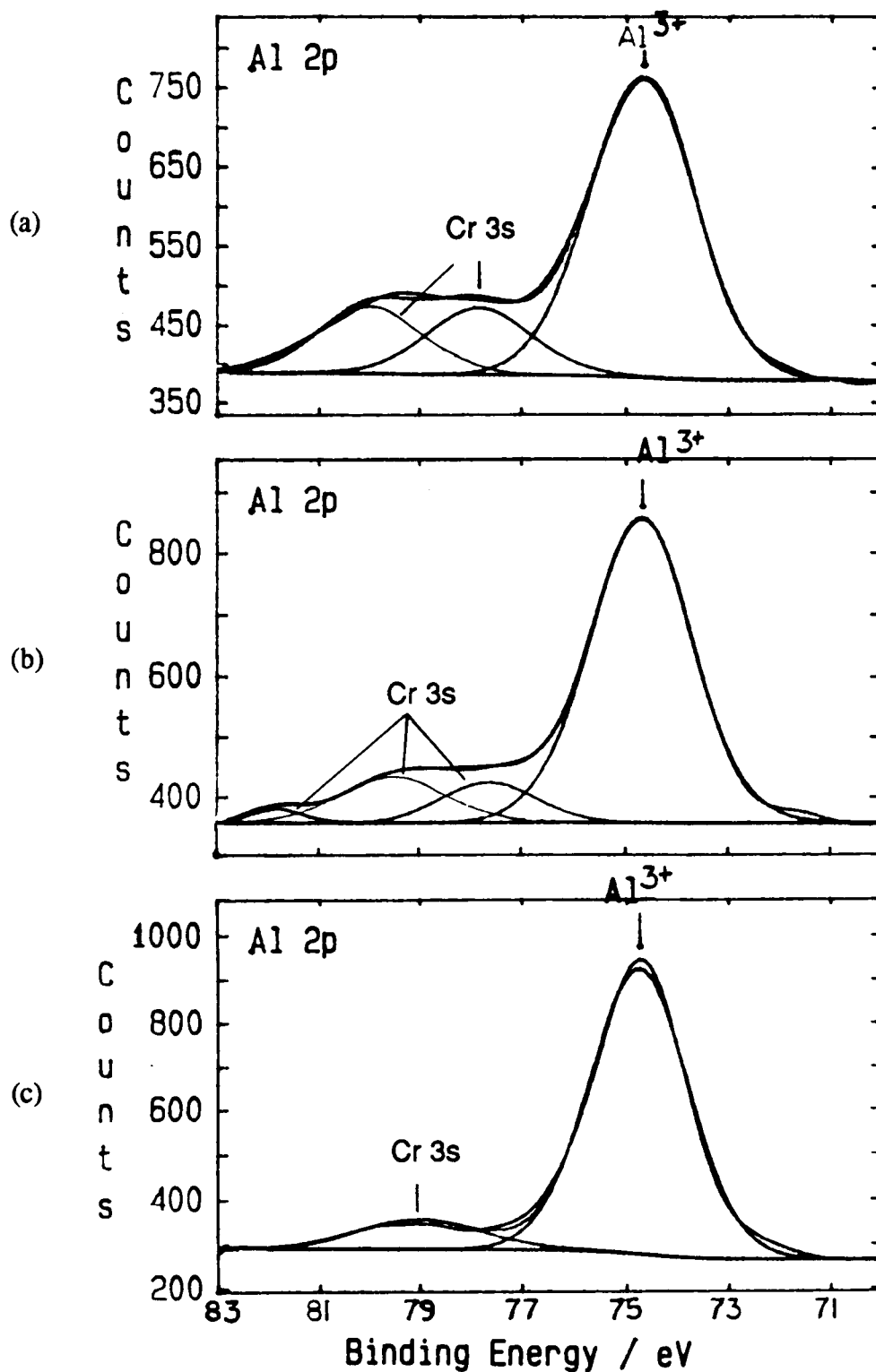


Fig. 42. Curve-fitted spectra of Al 2p peaks from (a) 29, (b) 43, and (c) 53 nm into the implanted $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample (see Figs. 40 and 41).

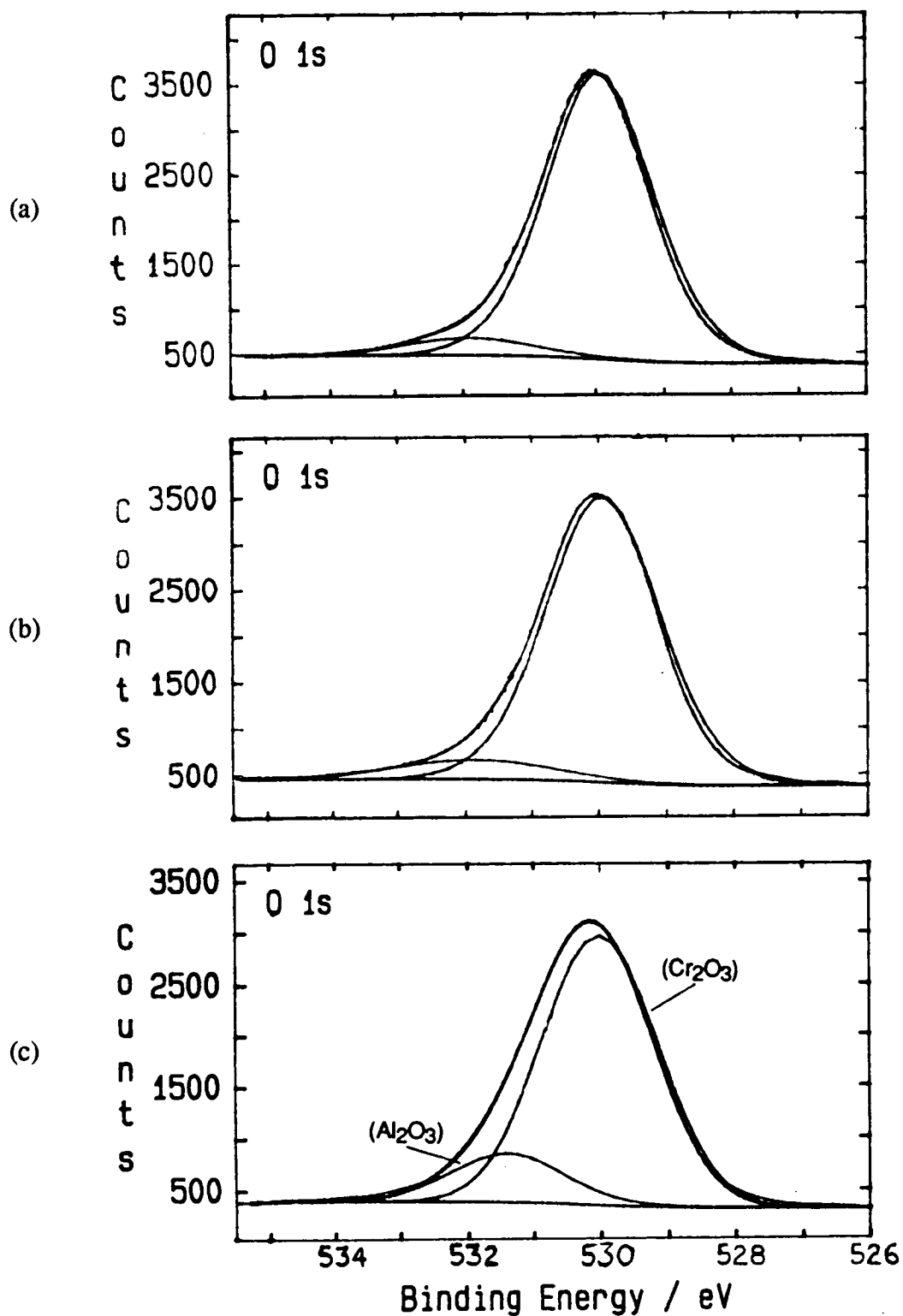


Fig. 43. The O spectra from the same positions as in Fig. 41.

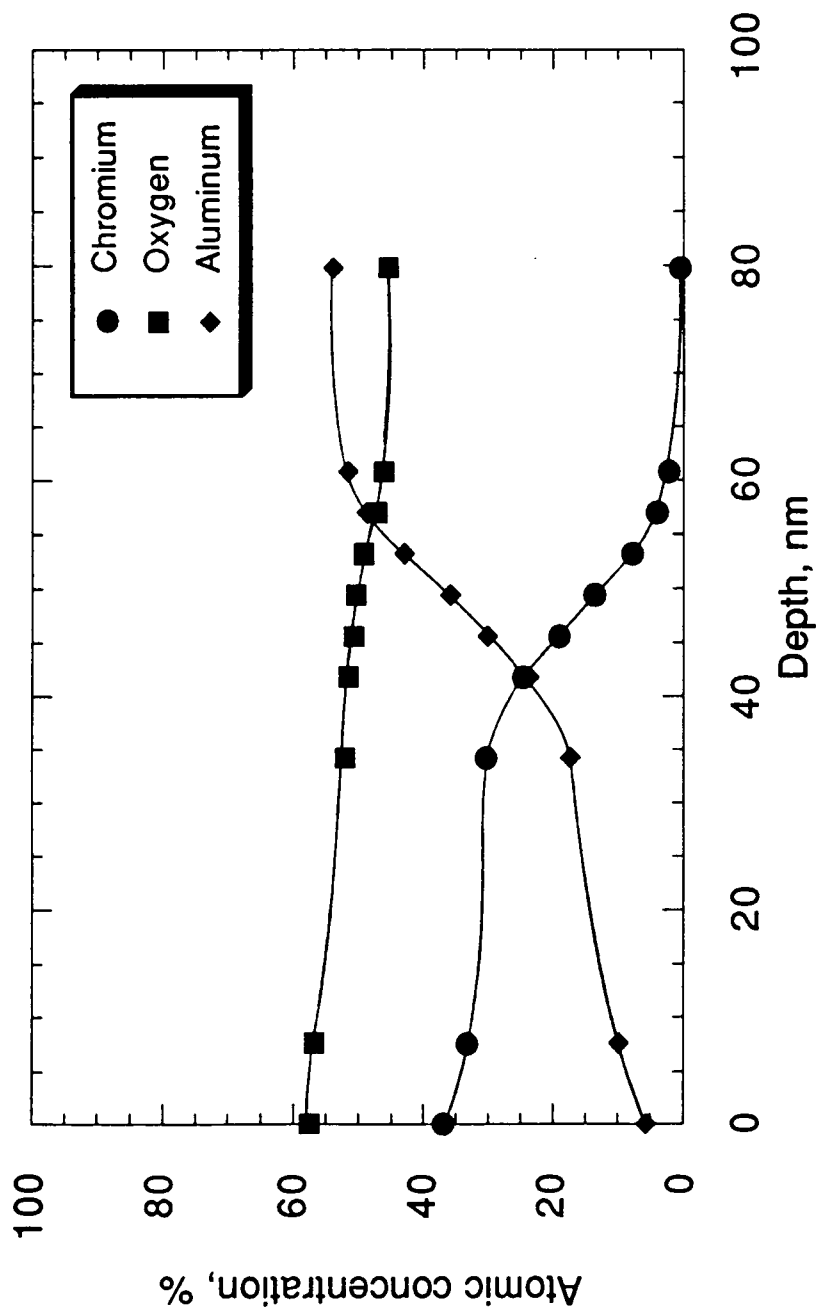


Fig. 44. A depth profile from a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample implanted at 860°C with 160 keV Cr to a fluence of $4 \times 10^{16}\text{ ions-cm}^{-2}$.

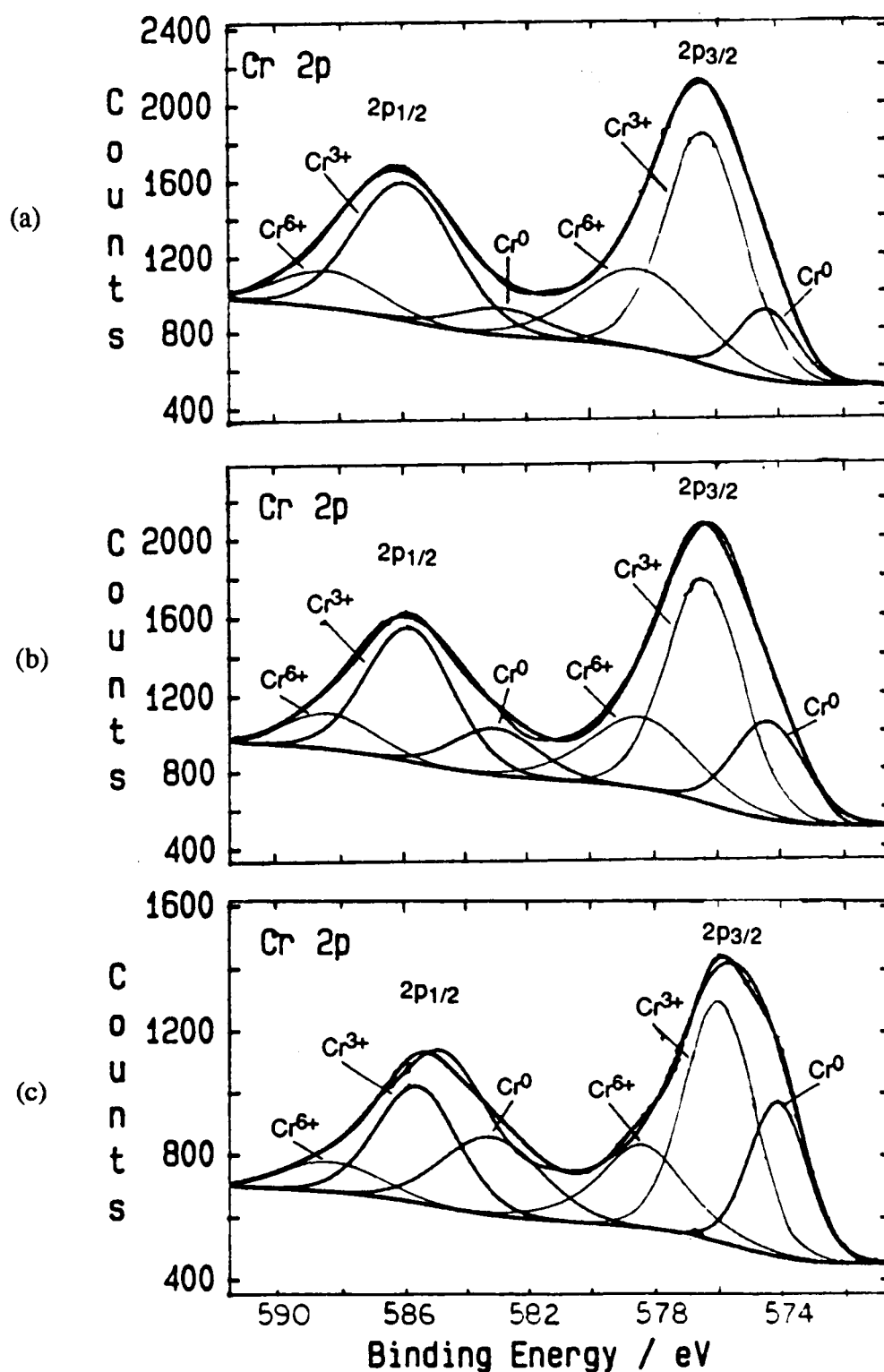


Fig. 45. Curve-fitted spectra for Cr 2p peaks taken at (a) 12 nm, (b) 34 nm, and (c) 50 nm into the sample (i.e. in the film, on the film side of the interface region, and on the substrate side of the interface, respectively).

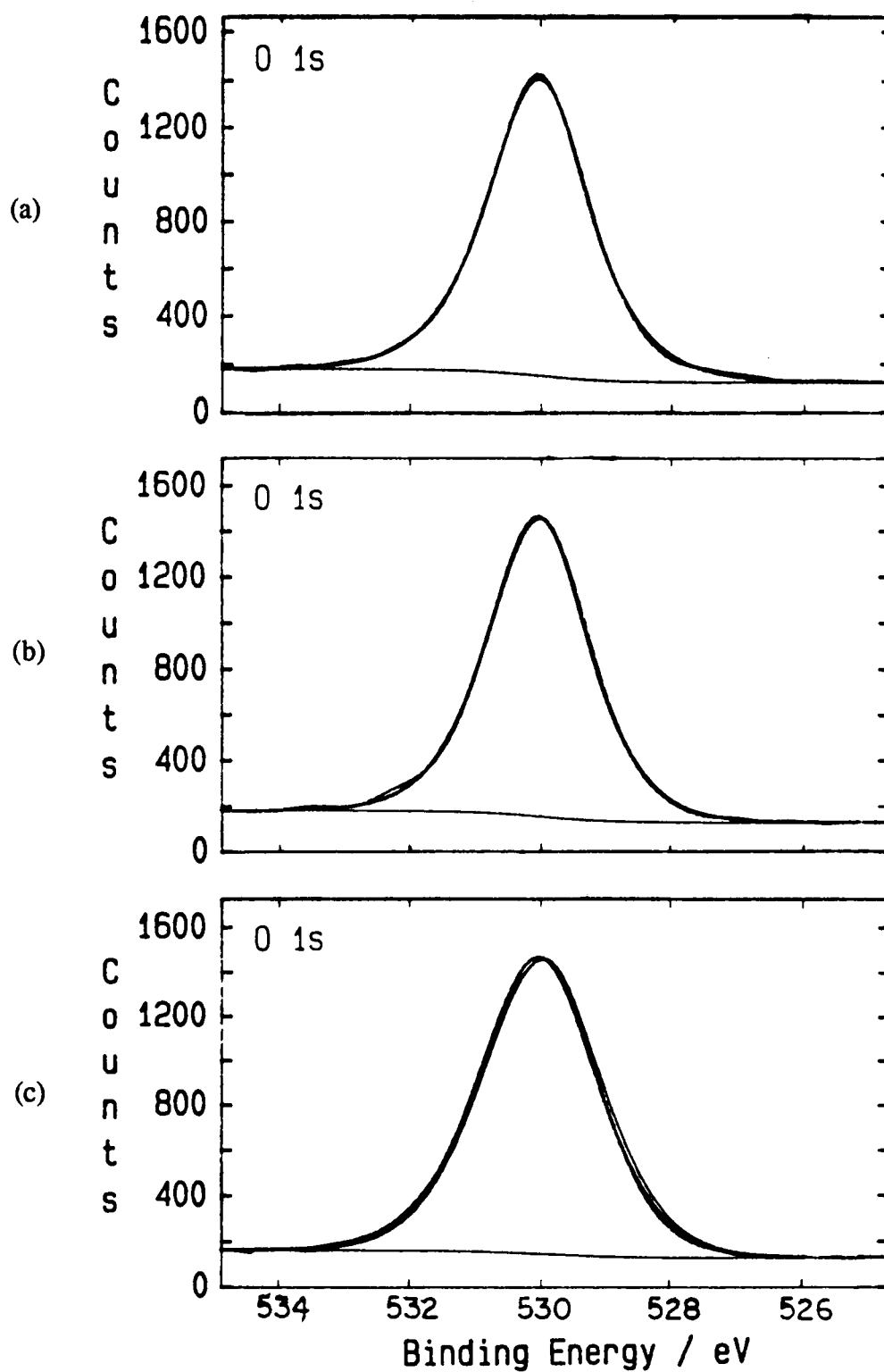


Fig. 46. Curve-fitted spectra for O 1s peaks obtained from (a) 12 nm, (b) 34 nm, and (c) 50 nm into the sample.

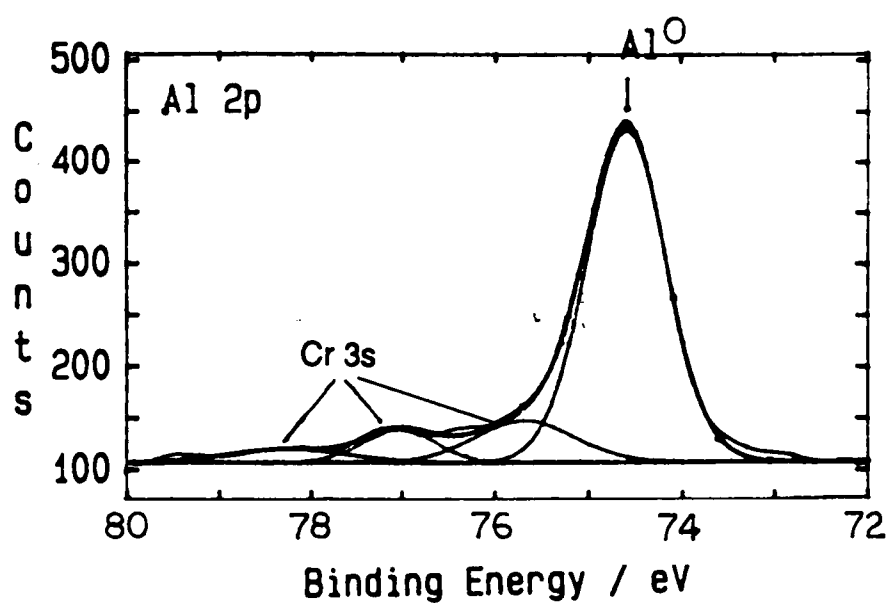


Fig. 47. An Al 2p spectra taken on the film side of the interface (34 nm).

so the change in the O 1s signal is probably not resolvable. An Al 2p spectra taken on the film side of the interface (34 nm) is shown in Fig. 47. The Al is present as Al^{3+} . No Al spectra from the surface of this specimen is shown; the intensity of the spectra is low enough so that a good curve fit was not obtainable.

Figure 48 is a depth profile from the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at room temperature with 160 keV Cr to a fluence of 4×10^{16} ions- cm^{-2} . The sputter rate in this sample was about 0.5 nm/min. There is no evidence of Al near the surface in this sample. However, the Zr appears to extend approximately 20 nm into the Al_2O_3 substrate. Montages of the Zr 3d and Al 2p peak evolution are displayed in Figs. 49 and 50. Each cycle except last corresponds to about 2.5 nm. The last cycle shown represents one 0.5 nm. The satellite peaks from the x-ray source have not been removed; they are clearly marked. Both the Al and Zr montages show the presence of at least two chemical species. Curve fits of spectra from both Zr and Al, taken at approximately 40 nm into the sample (at the interface), are presented in Fig. 51a and b. These spectra indicate the presence of Al^0 and Al^{3+} , Zr^0 and Zr^{4+} (refer to Table 9).

Figure 52 is a depth profile from a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at 860°C with 160 keV Cr to a fluence of 4×10^{16} ions- cm^{-2} . The sputter rate in this sample was approximately 1.5 nm/min. As in the sample implanted at room temperature, no Al is present at the sample's surface. The Zr extends around 15 nm into the substrate. Montages of the Zr 3d and Al 2p peak evolution are shown in Figs. 53 and 54. The Zr montage is shown in reverse chronological order to completely reveal the appearance of the peaks. Each cycle corresponds to ~2.8 nm. The montages reveal no evidence of reduction of either elemental species. Figures 55a and b are curve-fitted spectra from both Zr and Al taken in the substrate near the interface, at about 44 nm. No reduction of Al is apparent, however the Zr appears to exist in two states, Zr^{4+} and Zr^{2+} .

Depth profiles from the unimplanted and implanted portions of the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ film bombarded with 475 keV Kr (1×10^{17} ions- cm^{-2}) at room temperature are displayed in Figs. 56 and 57. The sputter rates were approximately 5 nm/min in these materials. The interface appears to be broader after implantation, with Al present within 15 nm of the sample's surface. A significant amount of Cr is found to about 50 nm into the substrate. Curve fits of Cr spectra taken in the unimplanted specimen at approximately 23 and 100 nm into the sample (i.e., in the film and in the substrate near the interface) are presented in Figs. 58a and b. In both positions, the Cr exists in several oxidation states, mostly as Cr^{3+} , but Cr^{6+} and Cr^0 are also present. Figures 59a and b are curve fits of Al spectra taken in the same sample at 100 and 143 nm. These positions are in the substrate near the

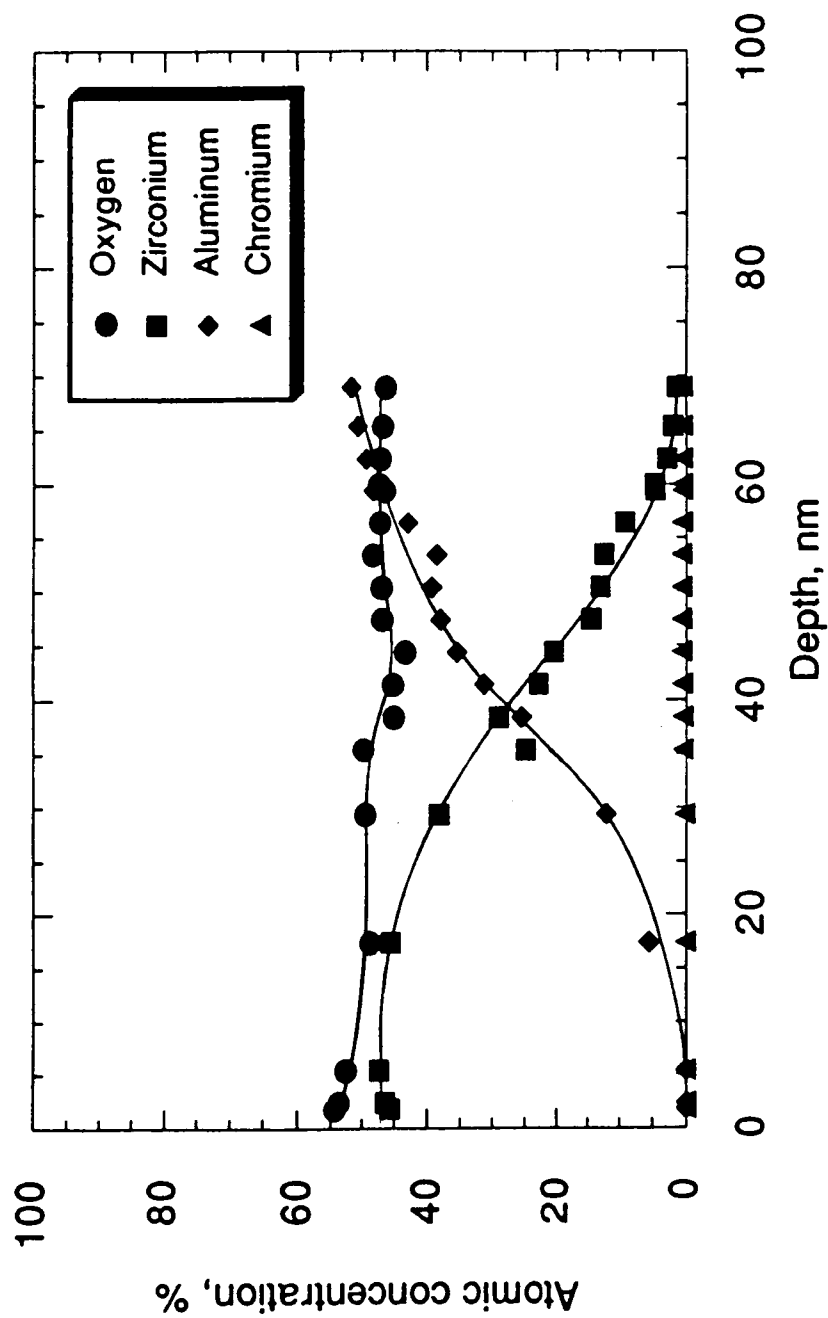


Fig. 48. A depth profile from the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at room temperature with 160 keV Cr to a fluence of $4 \times 10^{16} \text{ ions-cm}^{-2}$.

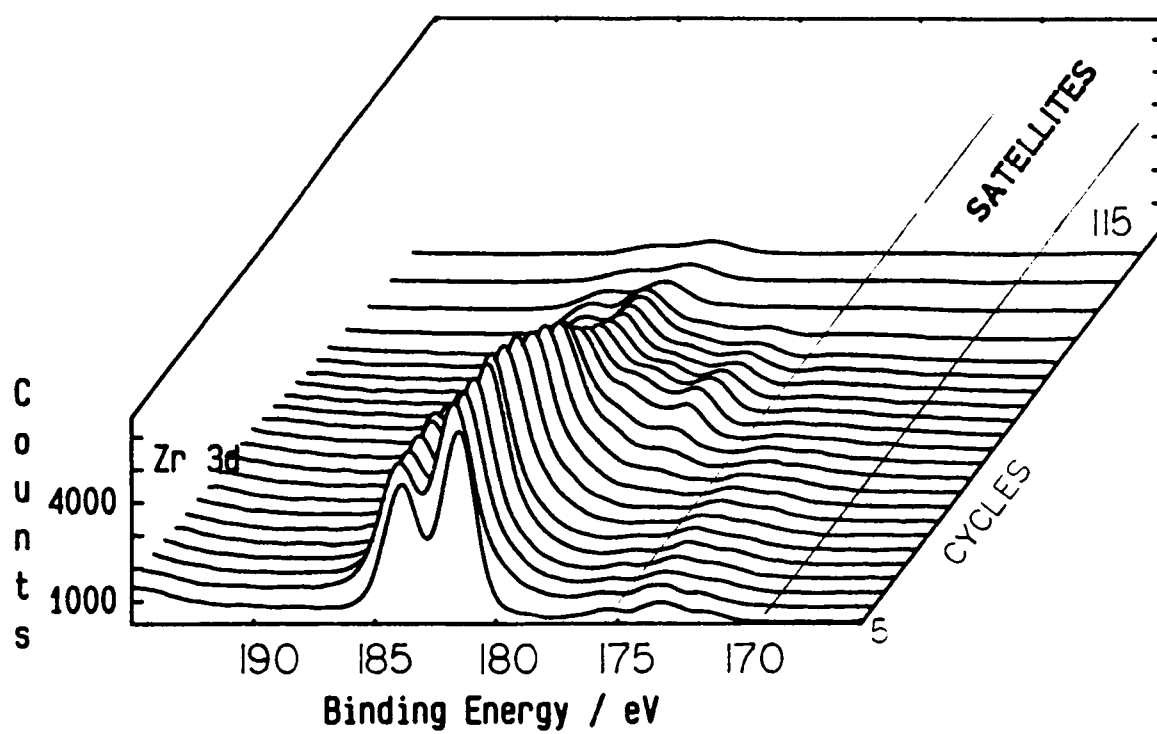


Fig. 49. A montage of the Zr 3d spectra from the same $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample as Fig. 48.

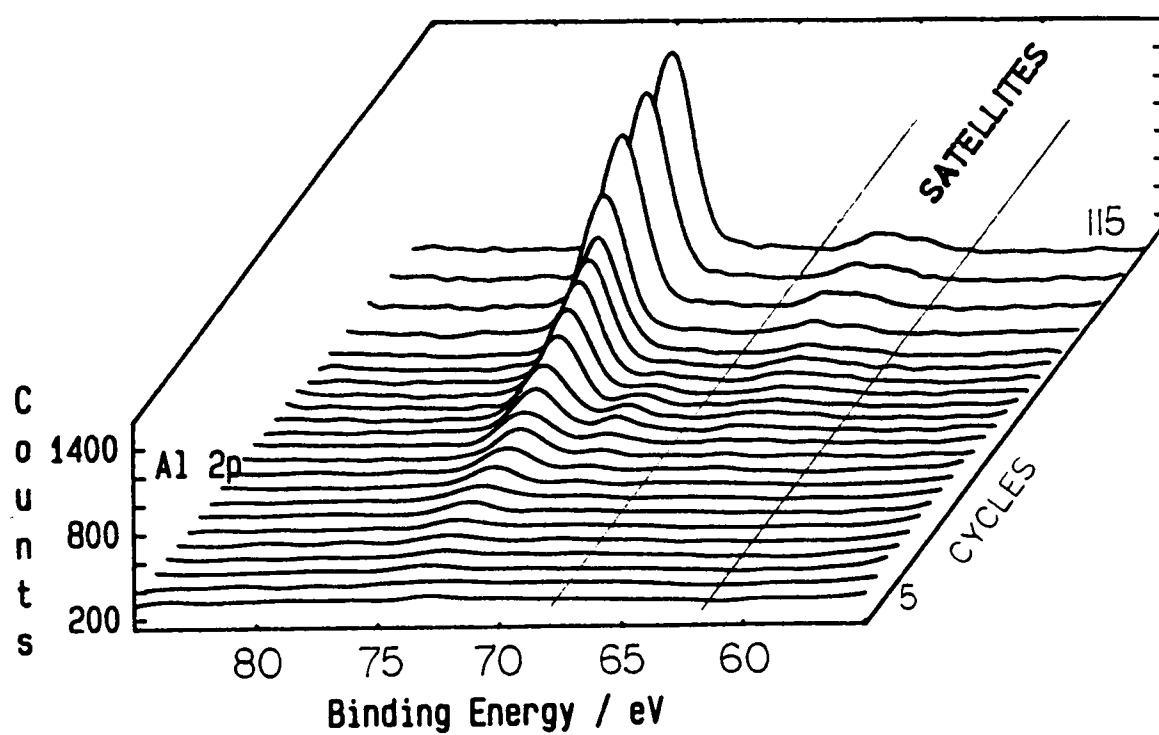


Fig. 50. A montage of the Al 2p spectra from the same $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample as Fig. 48.

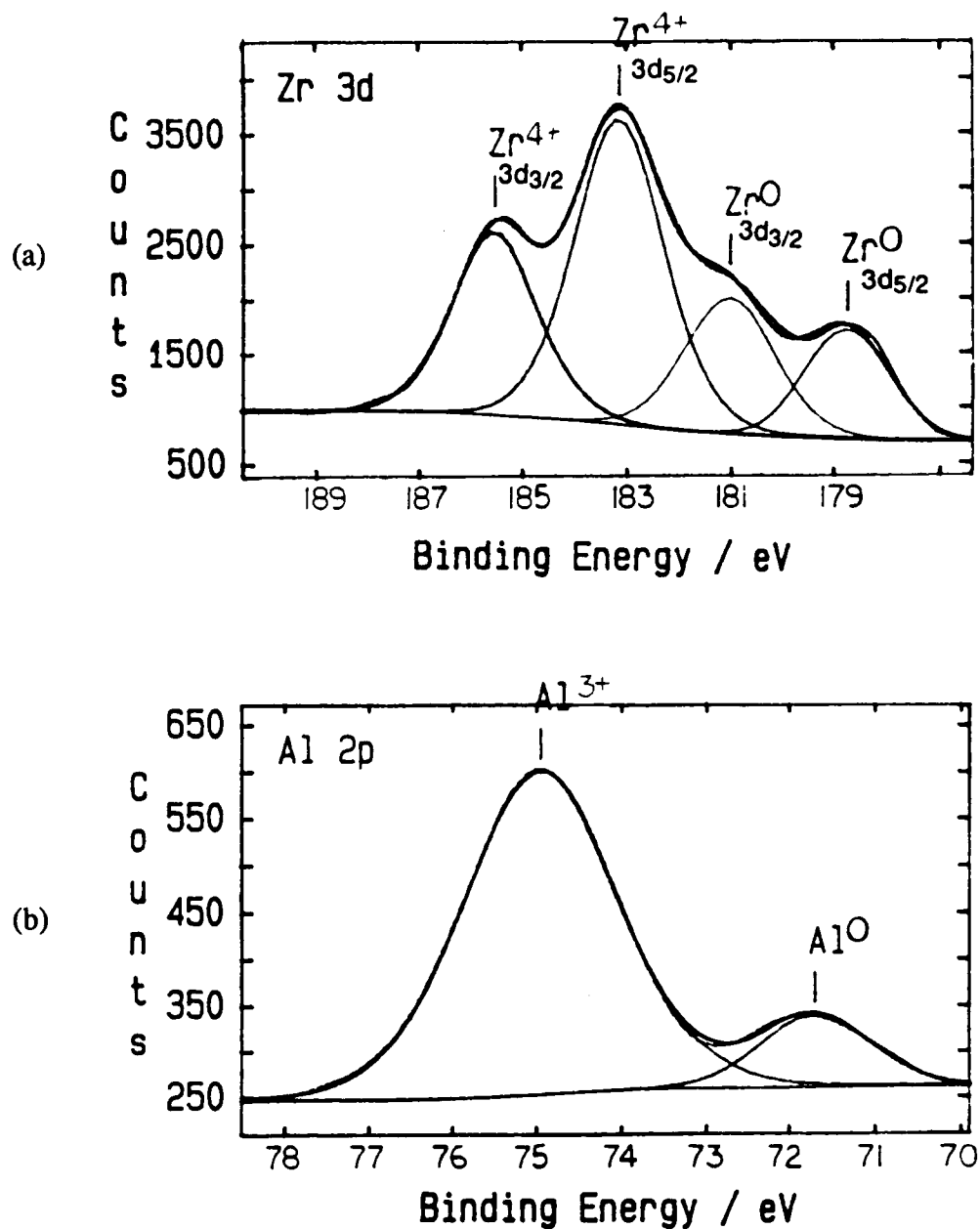


Fig. 51. Curve fits of spectra from (a) Zr and (b) Al, taken at approximately 40 nm into the sample (at the interface).

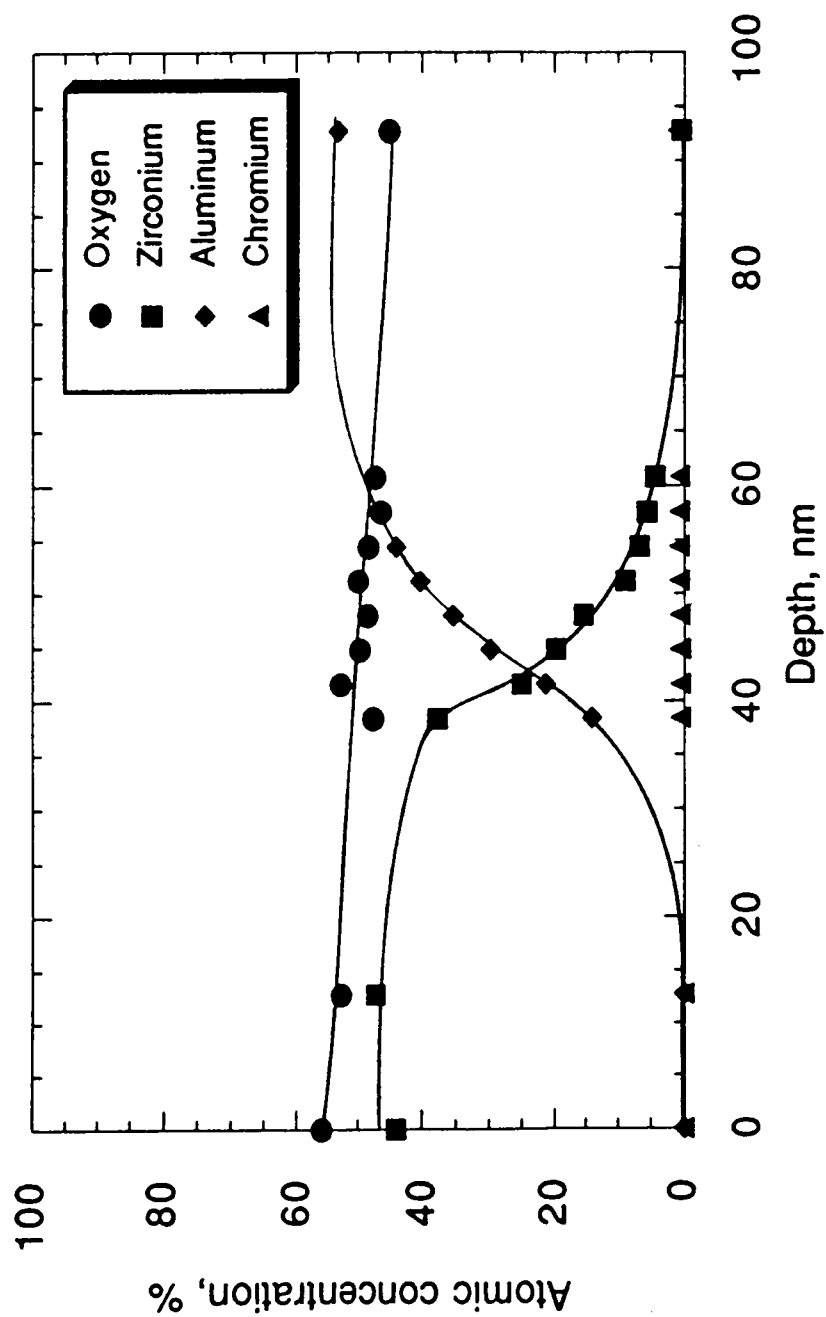


Fig. 52. A depth profile from a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at 860°C with 160 keV Cr to a fluence of $4 \times 10^{16}\text{ ions-cm}^{-2}$.

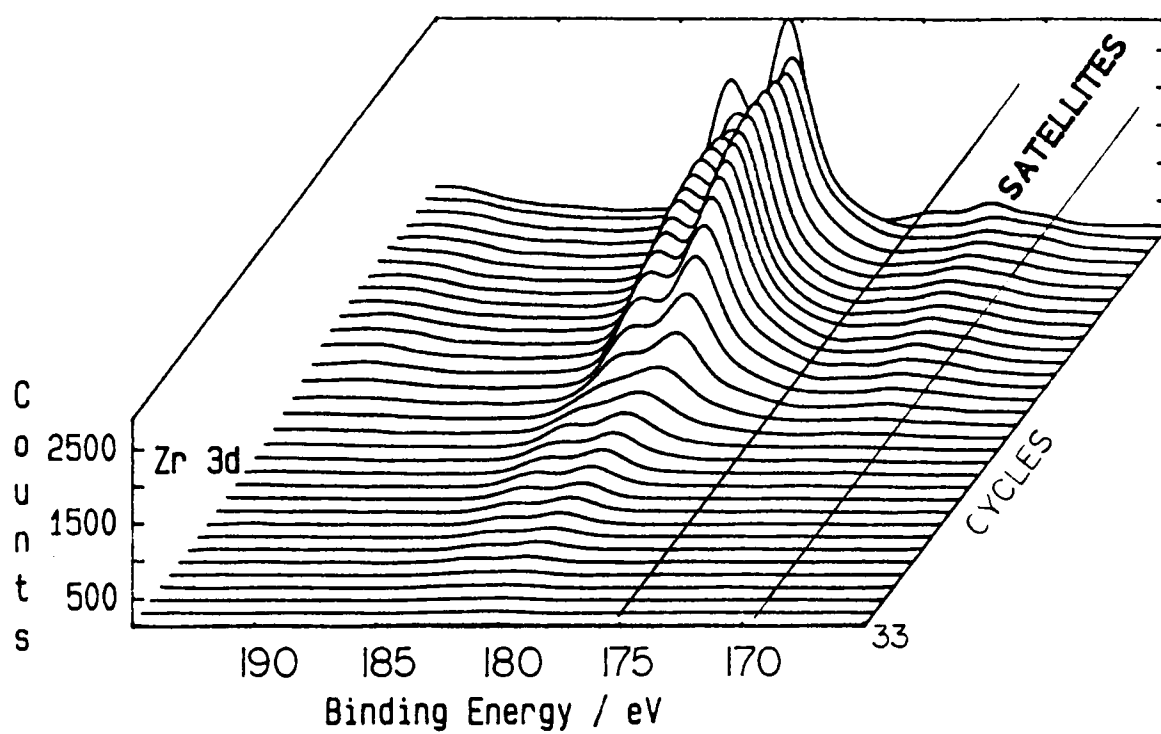


Fig. 53. A montage of the Zr 3d spectra from the same sample as Fig. 52.

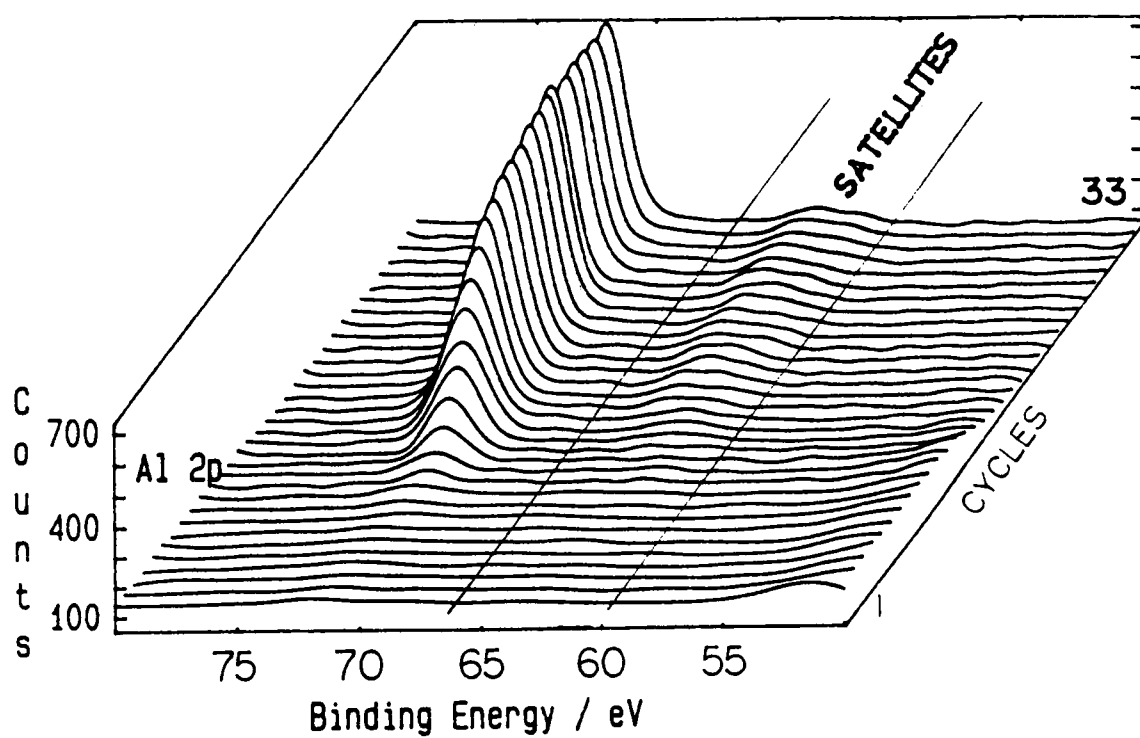


Fig. 54. A montage of the Al 2p spectra from the same sample as Fig. 52.

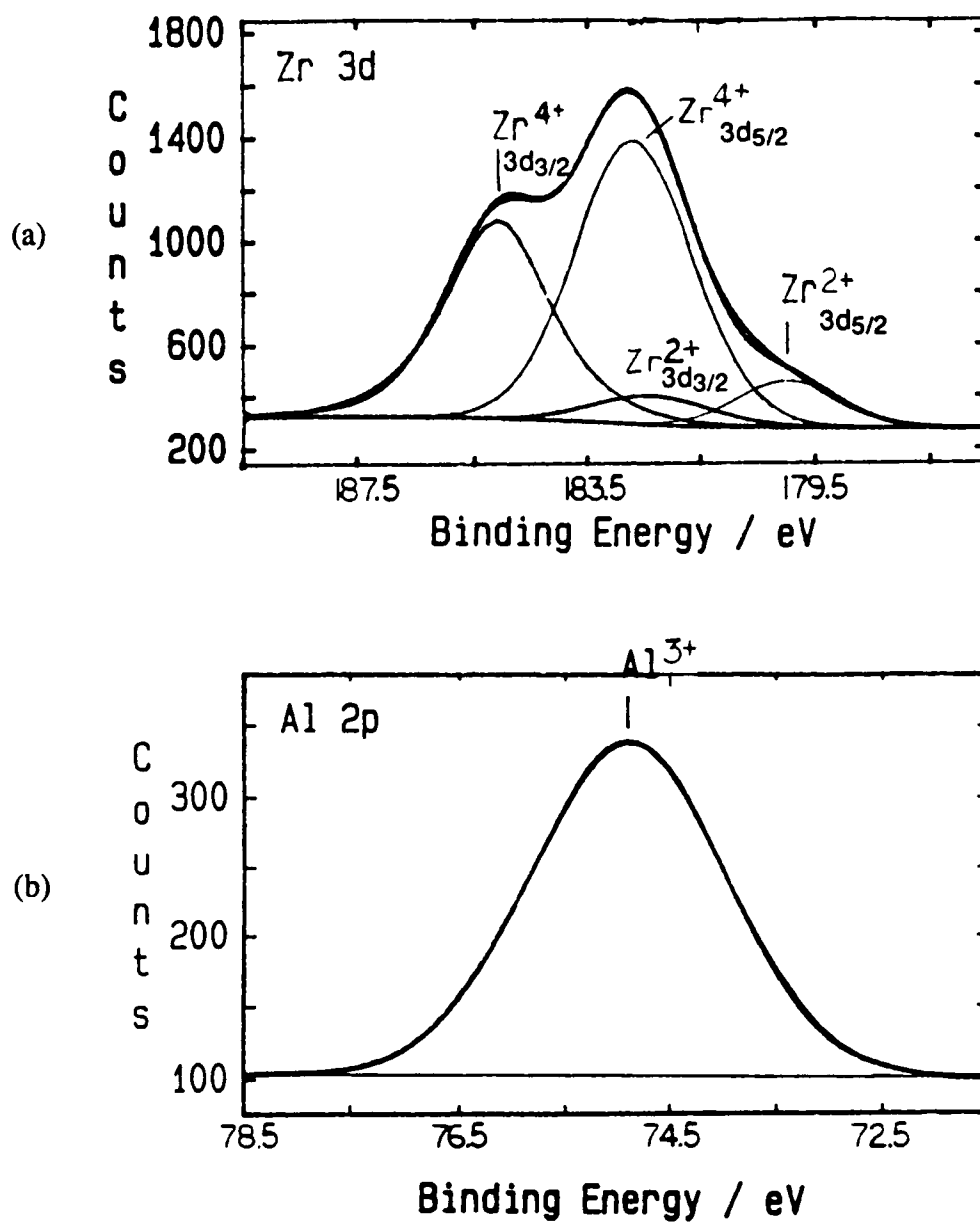


Fig. 55. Curve-fitted spectra from (a) Zr and (b) Al taken in the substrate near the interface.

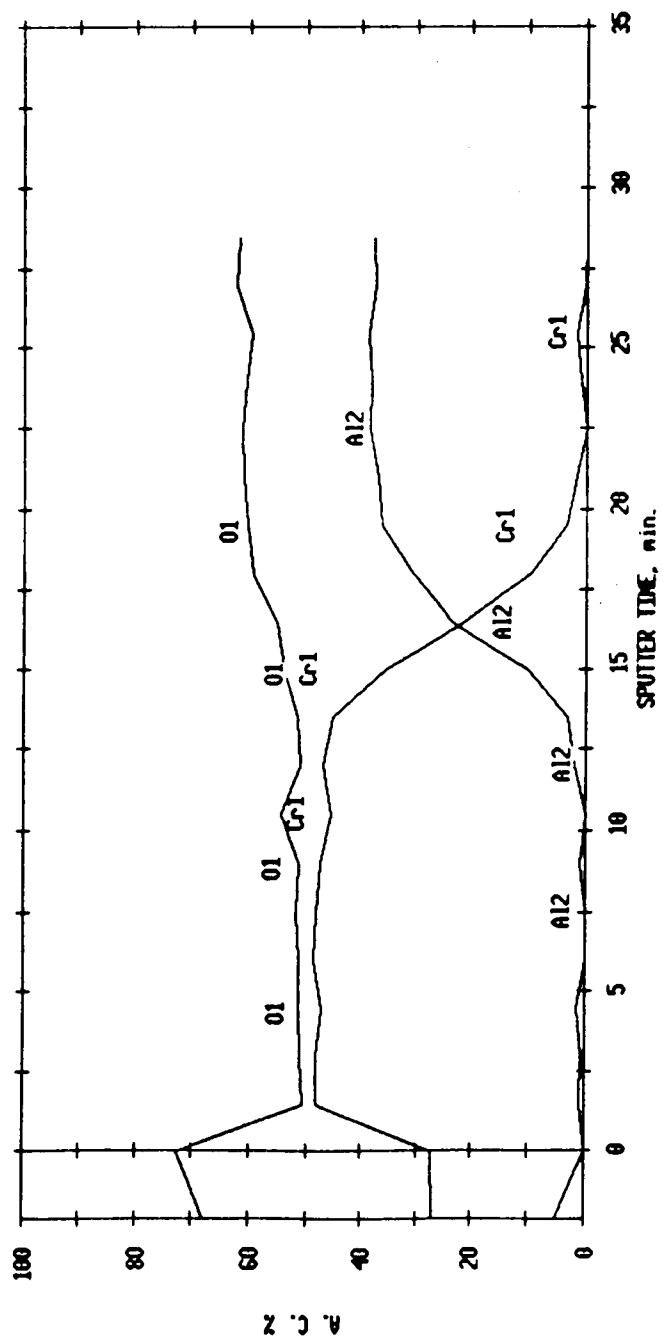


Fig. 56. A depth profile from the unimplanted (masked) portion of a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ film.

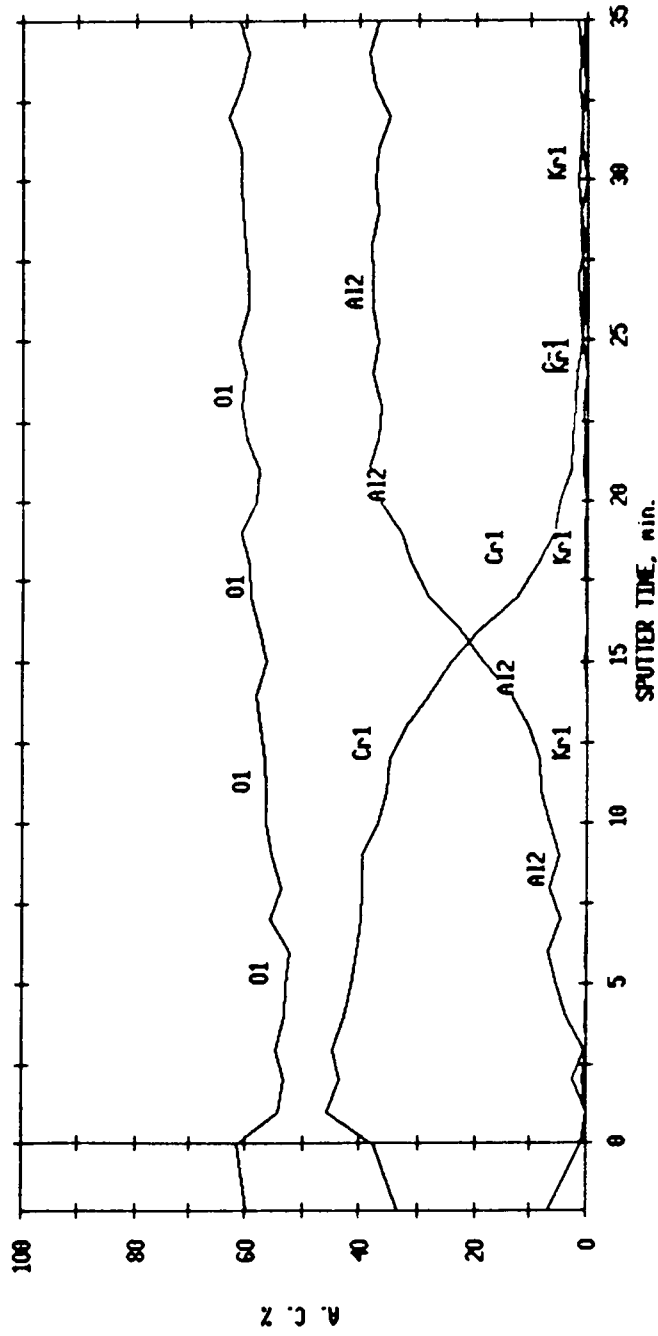


Fig. 57. A depth profile from a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ film implanted at room temperature with Kr (475 keV ; $1 \times 10^{17} \text{ ions-cm}^{-2}$).

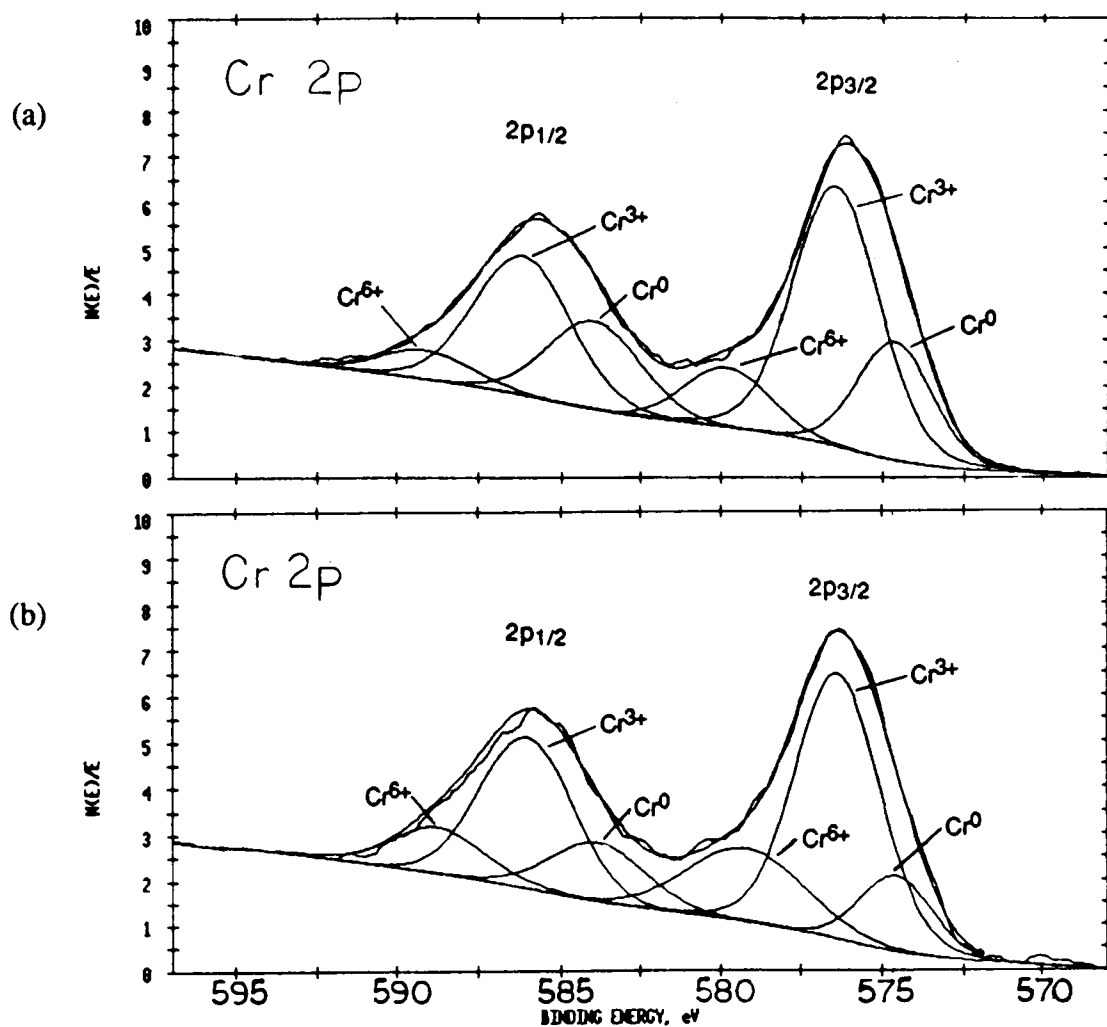


Fig. 58. Curve fits of Cr spectra taken in the unimplanted $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ specimen at approximately (a) 23 and (b) 100 nm into the sample (i.e., in the film and in the substrate near the interface).

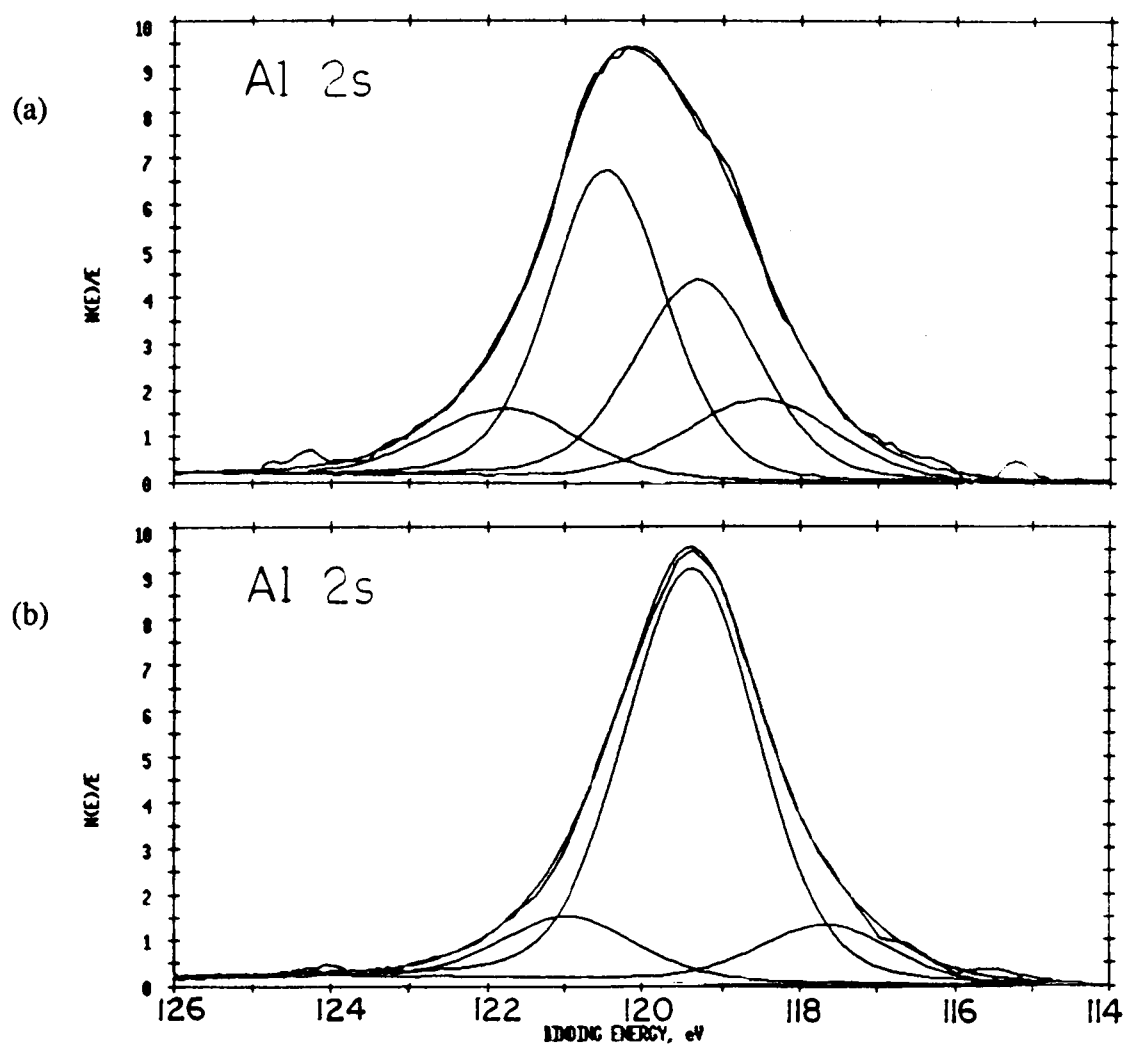


Fig. 59. Curve fits of Al spectra taken in the unimplanted $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample at (a) 100 and (b) 143 nm into the sample. These positions are in the substrate near the interface, and in the substrate far from the interface.

interface, and in the substrate far from the interface). The Al is present in multiple charge states at both positions. Again, since data on Al 2s peaks for various Al compounds is not common in the literature, no identification of these peaks is attempted here. Spectra from the implanted specimen indicate similar results for the charge states of Cr and Al: curve-fitted Cr and Al spectra from 65 and 160 nm into the sample (i.e. in the film and in the substrate) are shown in Figs. 60a-b and 61a-b. The signal from Cr at 160 nm is weak, and the peaks are not well-resolved. The Cr is probably present as Cr^{3+} and Cr^0 .

Depth profiles from the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ film bombarded with 475 keV Kr (1×10^{17} ions- cm^{-2}) at room temperature are displayed in Figs. 62 (unimplanted) and 63 (implanted). The sputter rate in these samples was around 2.5 nm/min. Implantation has apparently induced somewhat more extensive mixing in this sample than that observed after the other implantations. After implantation, the Zr extends at least 120 nm (~ 45 min sputter time) into the Al_2O_3 substrate. The position of the actual interface is not easily determined from the depth profile because of the extent of mixing, so this estimate of maximum depth of the Zr is not completely accurate. Figures 64 and 65 are montages of the Zr, Al, and O spectra from these specimens. The sample is markedly changed after implantation. It is important to note that the unimplanted specimen is unlike the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ specimens implanted with Cr. Close examination of spectra from the unimplanted " ZrO_2 " film reveals that the Zr is not Zr^{4+} as in ZrO_2 , but is mostly intermediate oxides (Fig. 66). Most of the states are not readily identifiable for two reasons: first, charge correction is not possible because the O signal was to be used for determining the level of charging in the specimen, and the absolute O BE is not known for the intermediate oxides, and second, the spread of BE values for " ZrO " in Table 10 is unusually large. Because of these problems, no attempt is made here to identify the charge states. Curve fits of Zr spectra from 1, 16, and 95 nm into the implanted sample are presented in Figs. 67a-c. These depths correspond to cycles 3, 18, and 90 (the first two are in the film; the last is at the interface). The amounts of Zr in the different states is obviously different. The presence of multiple oxidation states is revealed in a spectra from Al at 95 nm (Fig. 68); one is probably Al^{3+} , the other is probably an intermediate oxide. The montage in Fig. 63 indicates that yet another Al state is present after about 20 cycles (~ 18 nm).

Figures 69 and 70 are depth profiles from the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at 825°C with 475 keV Kr to a fluence of 1×10^{17} ions- cm^{-2} . The sputter rate was around 3 nm/min in this sample. Montages of the spectra from the unimplanted and implanted portions of this sample are presented in Figs. 71 and 72. In all four spectra, the decrease in the ZrO_2 thickness due to sputter loss is obvious. Comparison of Figs. 71 and 72

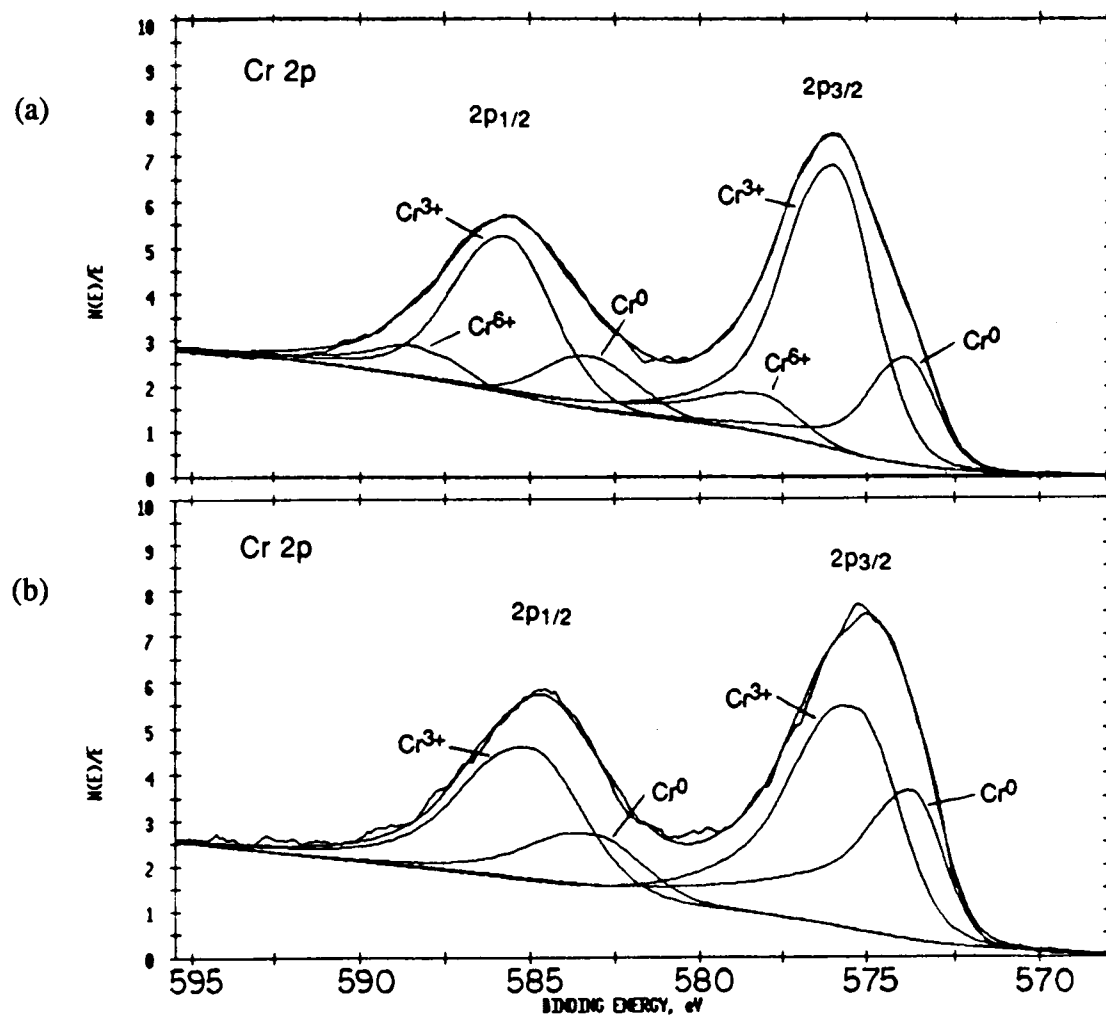


Fig. 60. Curve-fitted Cr spectra from the implanted $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ specimen (Fig. 57) (a) 65 and (b) 160 nm into the sample. The first position is in the film; the second is in the substrate.

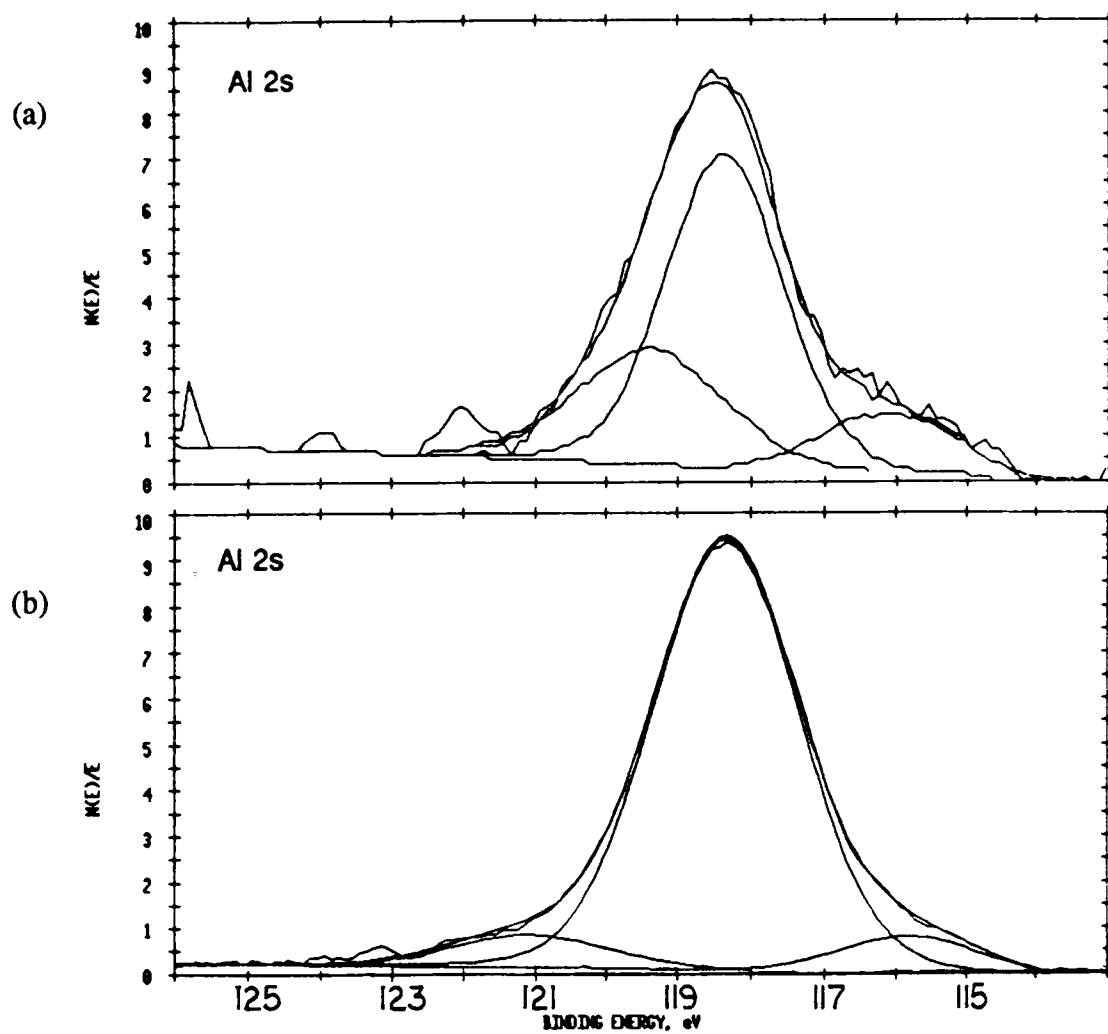


Fig. 61. Curve-fitted Al spectra from the implanted $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ specimen (Fig. 57) (a) 65 and (b) 160 nm into the sample.

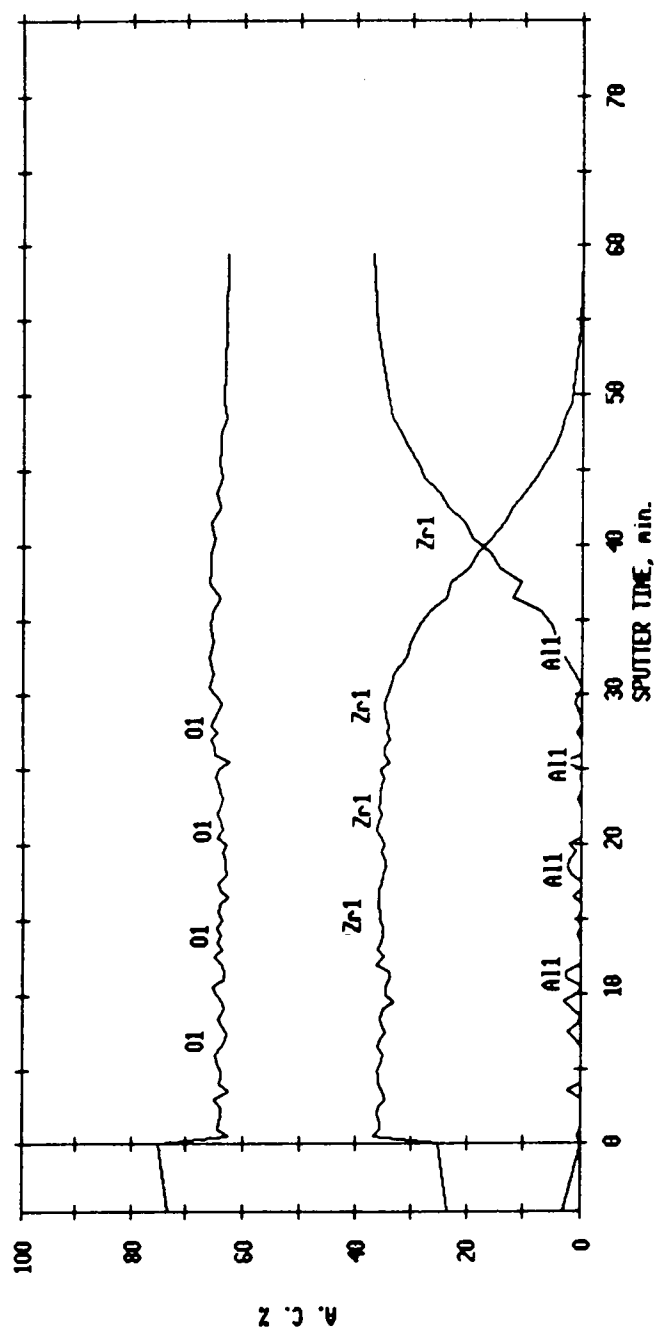


Fig. 62. A depth profile from an unimplanted $\text{ZrO}_2/\text{Al}_2\text{O}_3$ film.

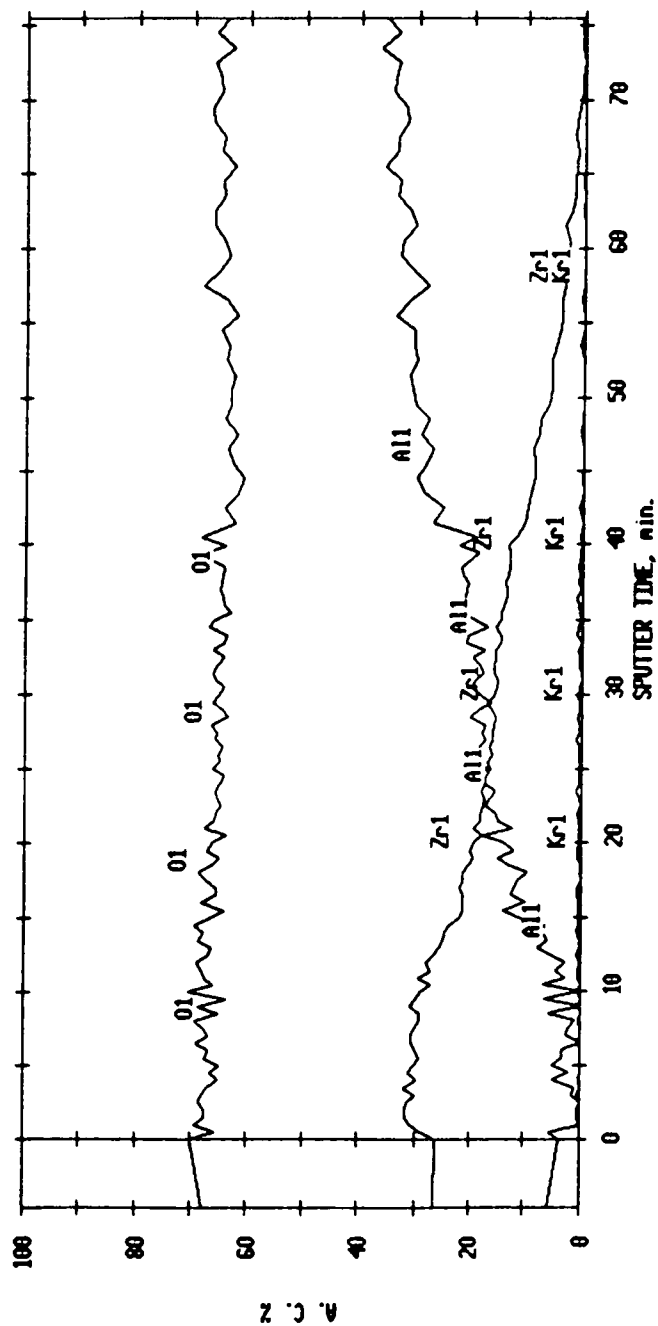


Fig. 63. A depth profile from a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ film bombarded at room temperature with $475 \text{ keV Kr } (1 \times 10^{17} \text{ ions-cm}^{-2})$.

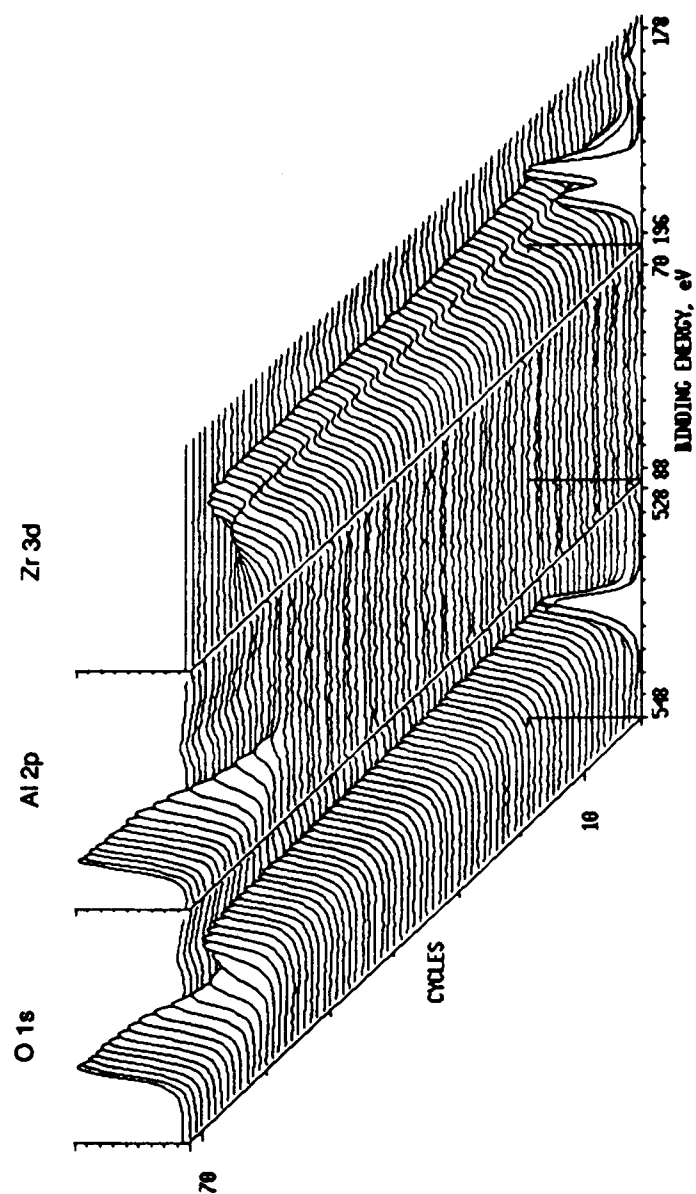


Fig. 64. A montage of the Zr, Al, and O spectra from the unimplanted $\text{ZrO}_2/\text{Al}_2\text{O}_3$ specimen.

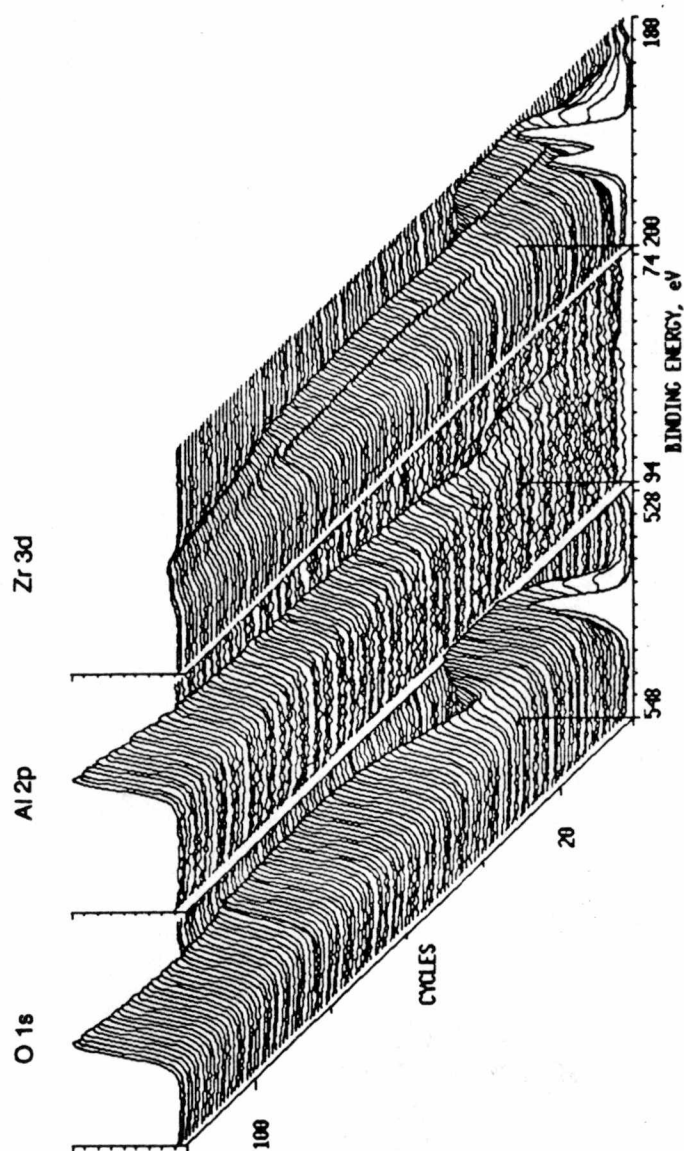


Fig. 65. A montage of the Zr, Al, and O spectra from the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ specimen implanted with 475 keV Kr (1×10^{17} ions- cm^{-2}). The sample is markedly changed after implantation.

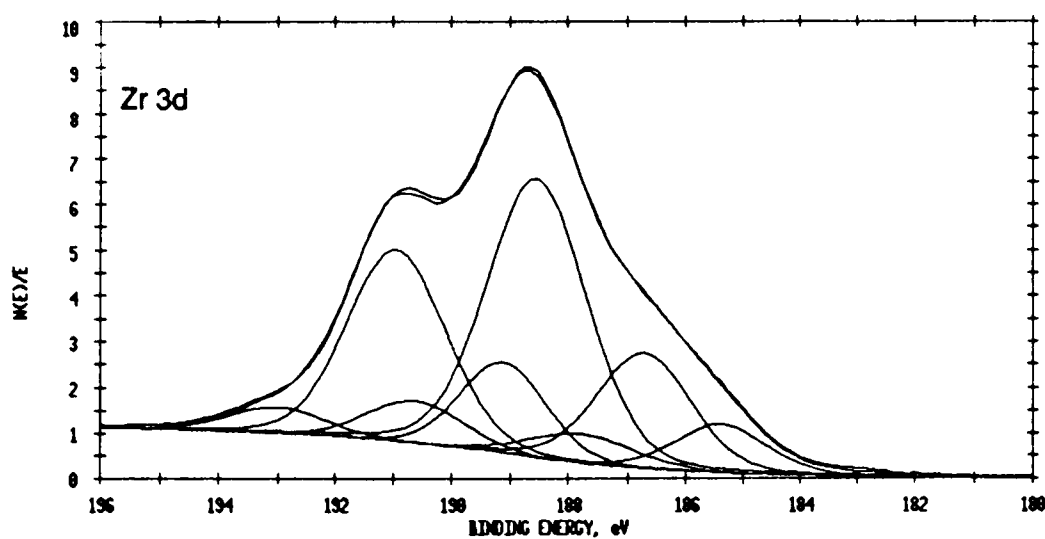


Fig. 66. A curve fit of a Zr spectra obtained in the unimplanted ZrO_2 film (the profile of this film was presented in Fig. 62). Close examination of spectra reveals that the Zr is present mostly as intermediate oxides.

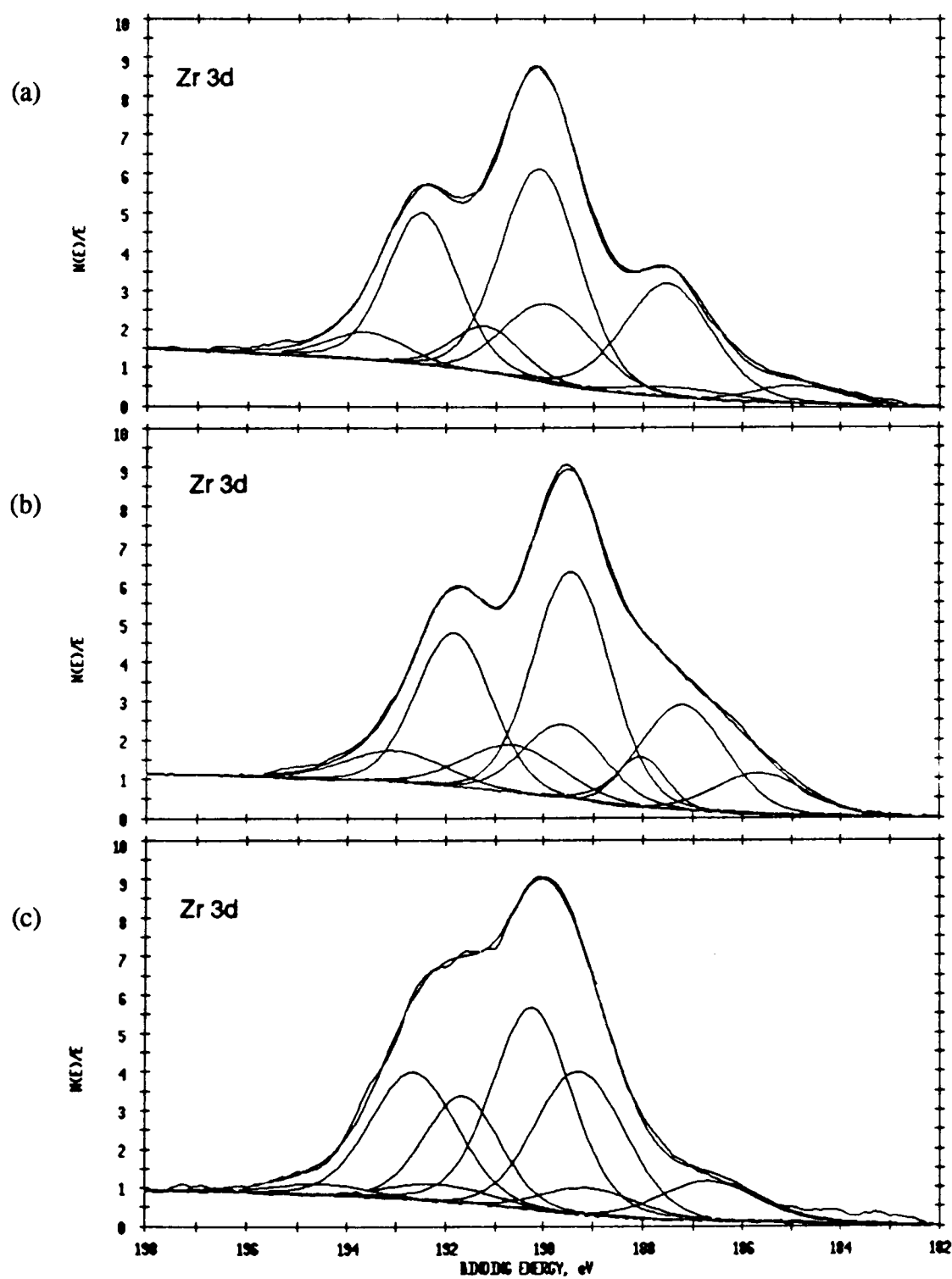


Fig. 67. Curve fits of Zr spectra from (a) 1, (b) 16, and (c) 95 nm into the implanted sample. These depths correspond to cycles 3, 18, and 90 (the first two are in the film; the last is at the film/ substrate interface).

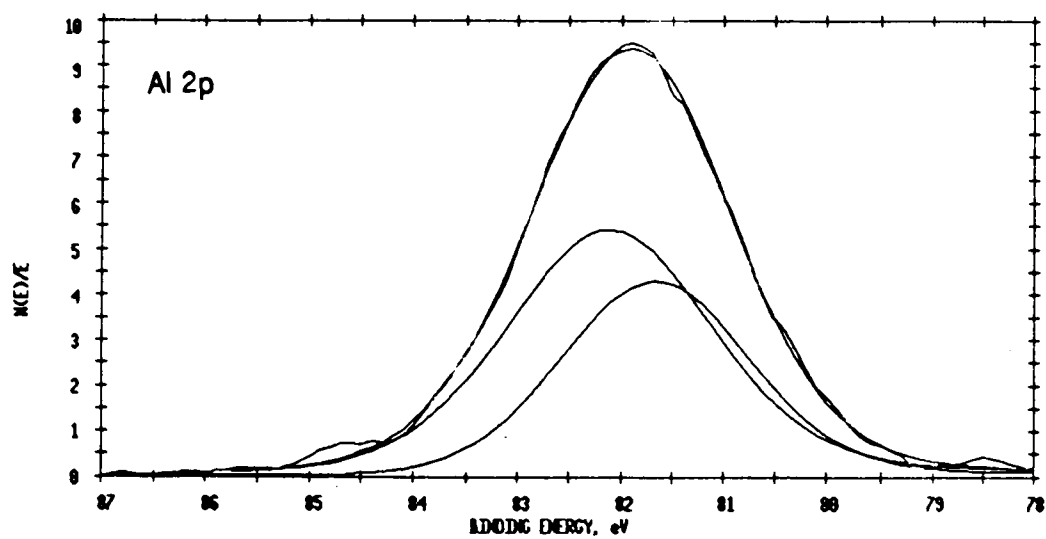


Fig. 68. A spectra from Al at 95 nm into the implanted sample.

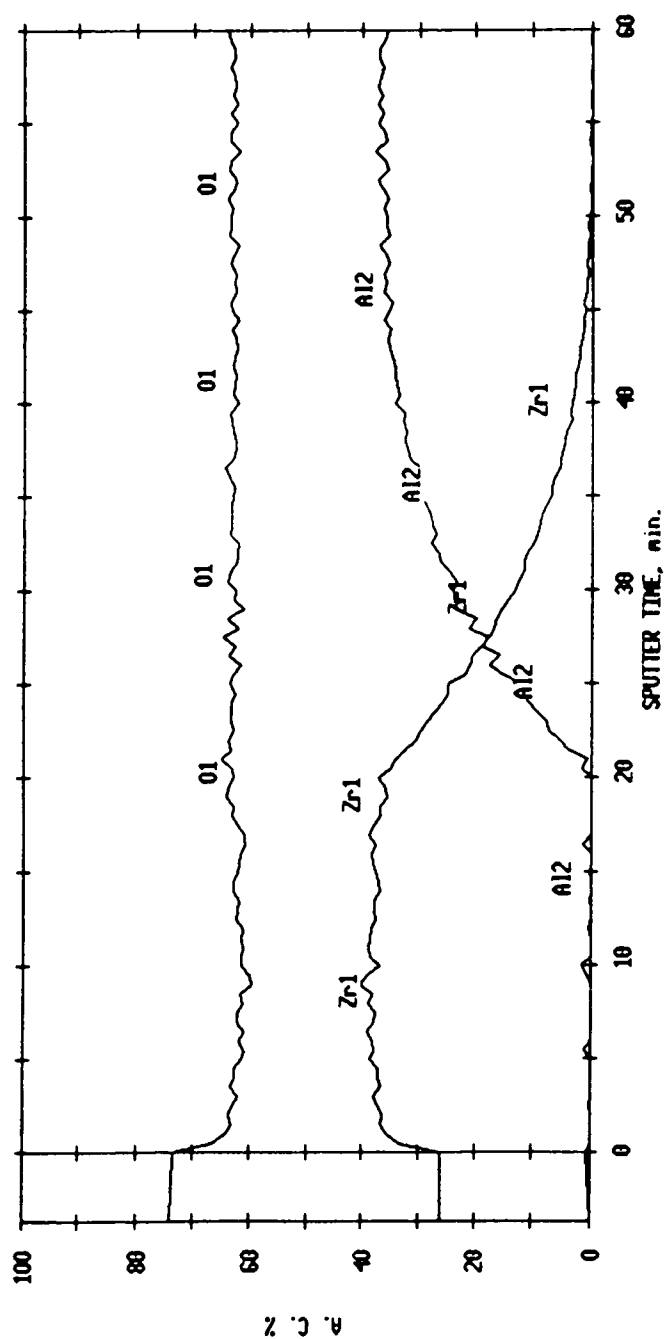


Fig. 69. A depth profile from the masked portion of the ZrO₂/Al₂O₃ sample implanted at 825°C with 475 keV Kr.

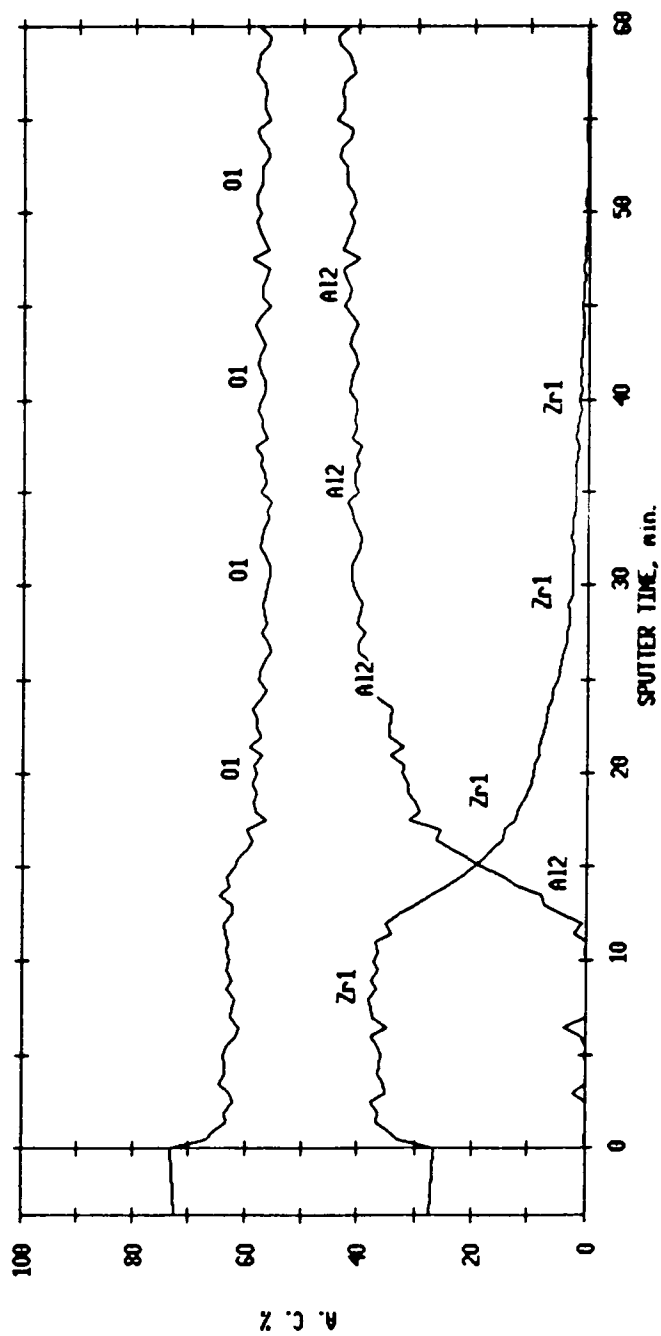


Fig. 70. A depth profile from the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted to a fluence of 1×10^{17} ions- cm^{-2} .

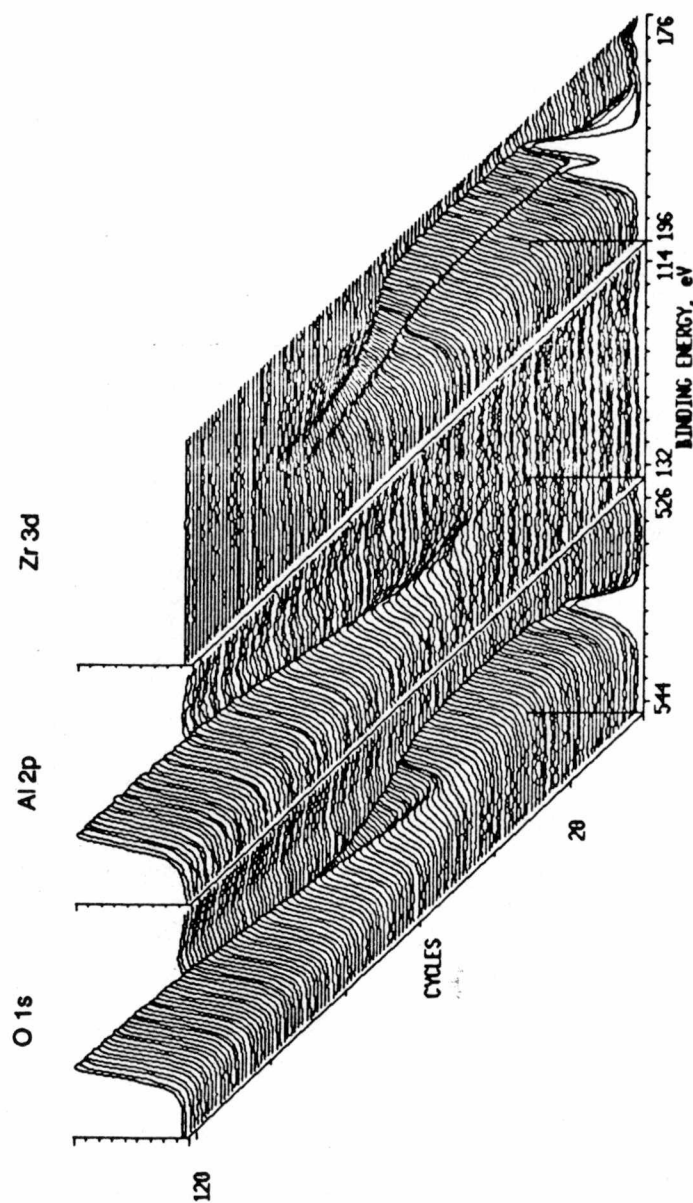


Fig. 71. A montage of the spectra from the unimplanted portions of this same $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample (profile shown in Fig. 69).

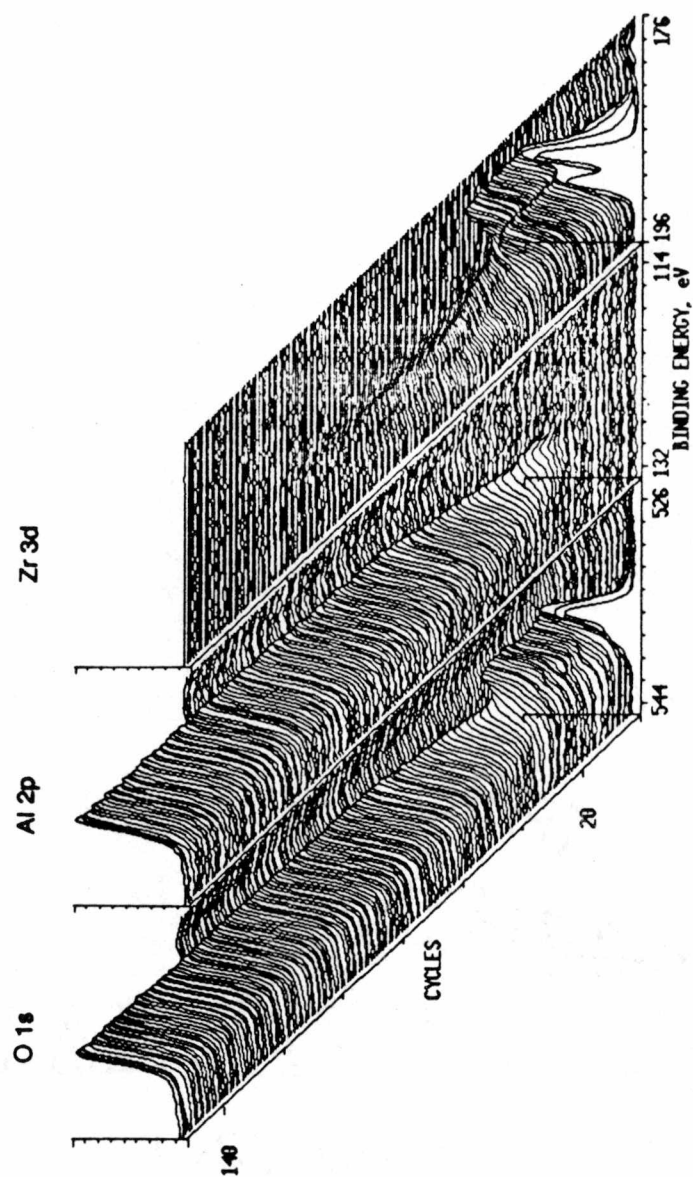


Fig. 72. A montage of the spectra from the implanted portions of the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample (profile shown in Fig. 70).

confirms that the Zr extends farther into the substrate after implantation, as shown in the depth profiles (75 nm into the substrate vs. 55 nm before implantation). The montage of spectra from the implanted portion of this specimen (Fig 70) is radically different from the montage from the specimen implanted with Kr at 825°C (Fig.65). In the specimen implanted at 825°C, there appear to be fewer chemical changes with increasing depth into the sample. Figure 73 is a Zr spectrum taken 35 nm into the unimplanted sample (at the interface: cycle 25). The presence of several oxidation states in the film is apparent. It is similar to the spectrum shown in Fig. 66, taken from the masked portion of the sample which was bombarded at room temperature with Kr. Both samples were treated in the same manner before implantation and both show this result in the unimplanted film. It is likely that the anneal in 96% Ar-4% H₂ was not performed properly, so that the stoichiometry of the Zr oxide was off. However, this does not explain the disparate results after the implantations at different temperatures.

Table 12 is a summary of XPS results.

5. Transmission electron microscopy

5.1. Crystalline state of the as-deposited oxide films

Selected area electron diffraction (SAD) patterns, as well as TEM micrographs were taken from oxide film specimens deposited on NaCl, floated off, and caught on Pt grids. Figure 74 is a SAD pattern from an as-deposited ZrO_{2+x} film (note that this film was not annealed in 96% Ar - 4% H₂). The film is microcrystalline, as evidenced by the "spotty" ring SAD pattern. A bright field micrograph of the sample is shown in Fig. 75. While the micrograph is slightly out of focus, crystallites are discernable. Energy dispersive analysis was also performed on the sample, confirming that all of the NaCl was washed off of the sample, and therefore that the SAD pattern was indeed from the ZrO_{2+x} film. Figure 76 is a SAD pattern from another ZrO_{2+x} sample deposited at a different time than the first. It is also microcrystalline.

In all of these experiments with grid-supported films, charging was a problem, as was destruction of the film from beam heating. To combat these problems, the films were sandwiched between platinum grids to allow charge (and heat) dissipation. Figure 77 is a micrograph of a Cr₂O_{3+x} film sandwiched between grids. Pieces of film can be seen in the holes.

A SAD pattern from an as-deposited Cr₂O_{3+x} film is shown in Fig. 78. The diffuse ring pattern indicates that the film is amorphous. Figure 79 is a SAD pattern from the same film after incrementally heating to 520°C and holding for 10 minutes. The film is

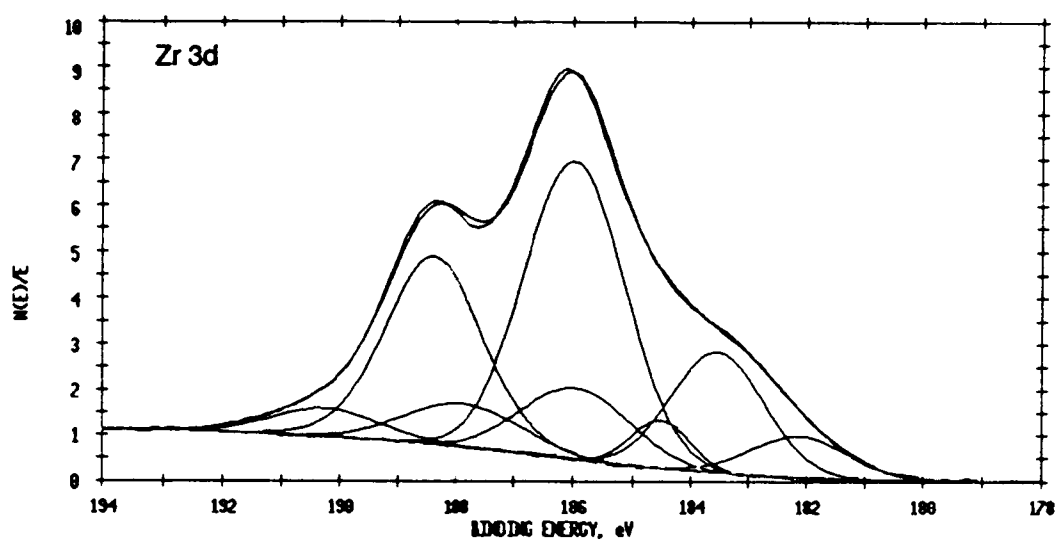


Fig. 73. A Zr spectrum taken 35 nm into the unimplanted sample (at the interface: cycle 25).

Table 12. X-ray photoelectron spectroscopy results

Film/substrate combination	Implantation conditions	XPS results
Zr/Al ₂ O ₃	Kr, 320 keV 1 x 10 ¹⁷ ions-cm ⁻² 20°C	<u>Unimplanted sample</u> : Crater edge effects evident. ZrO ₂ present at sample surface; Zr ⁰ present to film/substrate interface; small amounts of ZrO ₂ present at interface. Evidence for Al ⁰ , possibly due to preferential sputtering. <u>Implanted sample</u> : Aluminum present in Zr film: Zr ⁰ , Zr ⁴⁺ , Al ⁰ , Al ³⁺ present 30 nm into sample.
Cr/Al ₂ O ₃	Kr, 320 keV 1 x 10 ¹⁷ ions-cm ⁻² 20°C	<u>Unimplanted sample</u> : Some deoxidation of Al ₂ O ₃ ; possibly due to preferential sputtering. <u>Implanted sample</u> : Interface broader than in unimplanted sample: Cr extends into the substrate >60 nm past apparent film/substrate interface.
Cr ₂ O ₃ /Al ₂ O ₃	Cr, 160 keV 4 x 10 ¹⁶ ions-cm ⁻² 20°C	<u>Implanted sample</u> : Al present at sample's surface. Cr present ~25 nm into Al ₂ O ₃ substrate. Cr in film present as Cr ⁰ , Cr ³⁺ , Cr ⁶⁺ . Majority is Cr ³⁺ , but Cr ⁰ present in significant amounts. Through film and interface region, Al present as Al ³⁺ only.
Cr ₂ O ₃ /Al ₂ O ₃	Cr, 160 keV 4 x 10 ¹⁶ ions-cm ⁻² 800°C	<u>Implanted sample</u> : Interface sharper than in sample implanted at 20°C. Cr present ~15 nm into substrate. Cr in film present in several oxidation states; Cr ³⁺ is majority. Al ⁰ present in film and in interface region.

Table 12. (continued)

Film/substrate combination	Implantation conditions	XPS results
ZrO ₂ /Al ₂ O ₃	Cr, 160 keV 4 x 10 ¹⁶ ions-cm ⁻² 20°C	<u>Implanted sample</u> : Zr present to ~20 nm into substrate. Zr ⁰ , Zr ⁴⁺ , Al ⁰ , Al ³⁺ present in interface region.
ZrO ₂ /Al ₂ O ₃	Cr, 160 keV 4 x 10 ¹⁶ ions-cm ⁻² 800°C	<u>Implanted sample</u> : Zr present ~15 nm into substrate. Zr ⁴⁺ , Zr ²⁺ , Al ³⁺ present in interface region.
Cr ₂ O ₃ /Al ₂ O ₃	Kr, 475 keV 1 x 10 ¹⁷ ions-cm ⁻² 20°C	<u>Unimplanted sample</u> : Cr present in multiple charge states in the film, and Al present in multiple charge states in the substrate. <u>Implanted sample</u> : Al present within 25 nm of sample's surface. Cr present ~20 nm into substrate. Cr and Al present in multiple charge states throughout.
ZrO ₂ /Al ₂ O ₃	Kr, 475 keV 1 x 10 ¹⁷ ions-cm ⁻² 20°C	<u>Unimplanted sample</u> : Multiple Zr charge states in film. <u>Implanted sample</u> : Multiple Zr charge states in film; marked mixing into the substrate (Zr extends ~120 nm into the Al ₂ O ₃); several changes in chemical surroundings for all components.
ZrO ₂ /Al ₂ O ₃	Kr, 475 keV 1 x 10 ¹⁷ ions-cm ⁻² 825°C	<u>Unimplanted sample</u> : Multiple Zr charge states in film. <u>Implanted sample</u> : Zr extending into substrate ~75 nm. No evidence of changes in chemical surroundings of the components as found in the sample implanted at 20°C.

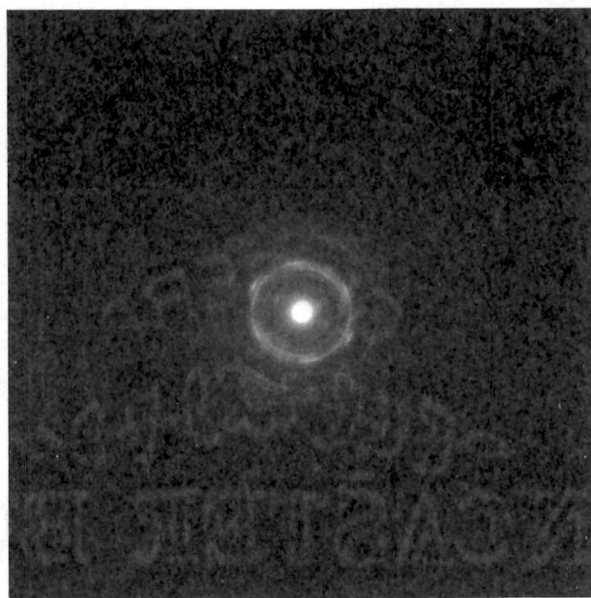


Fig. 74. A SAD pattern from an as-deposited ZrO_2 film. The film is microcrystalline.

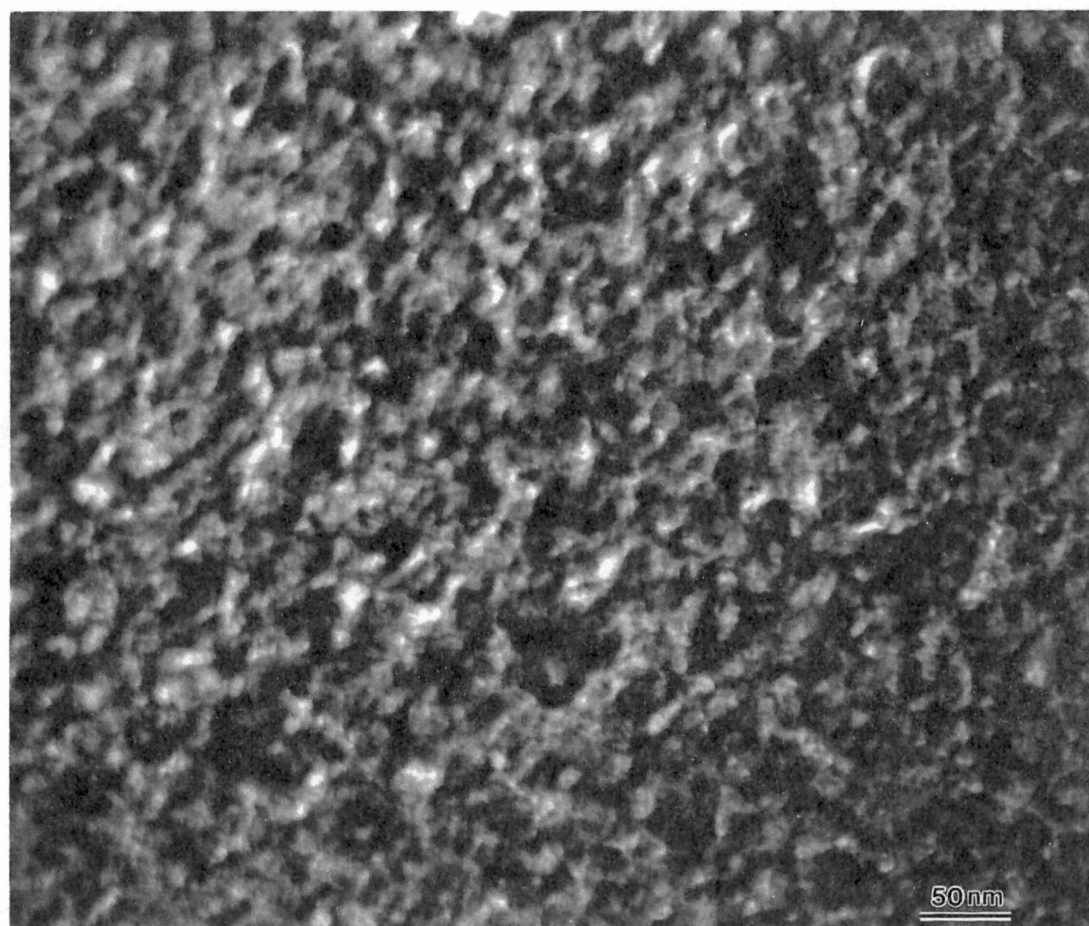


Fig. 75. A bright field TEM micrograph of the same as-deposited ZrO_2 film as Fig. 74.

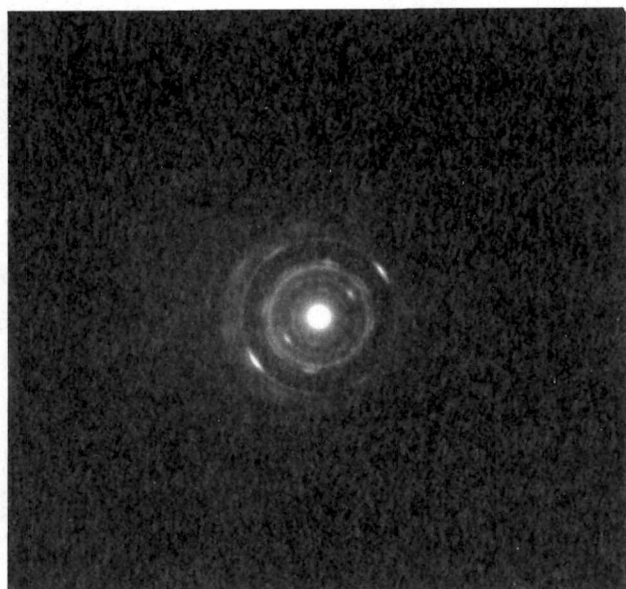


Fig. 76. A SAD pattern from another ZrO₂ sample deposited at a different time than that shown in Figs. 74 and 75. It is also microcrystalline.

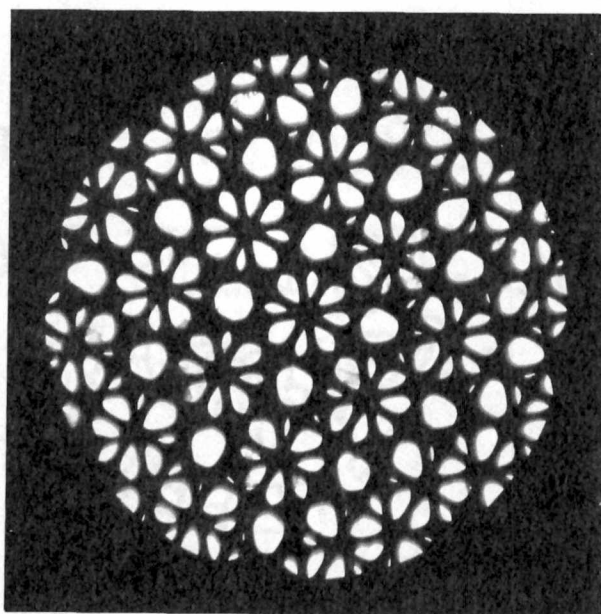


Fig. 77. A TEM micrograph of a Cr₂O₃ film sandwiched between grids. Pieces of the film can be seen in the holes.

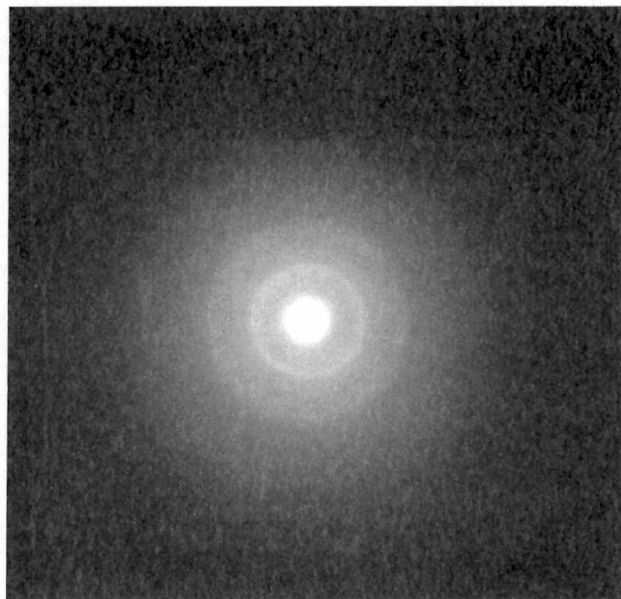


Fig. 78. A SAD pattern from an as-deposited Cr_2O_3 film. The film is amorphous.

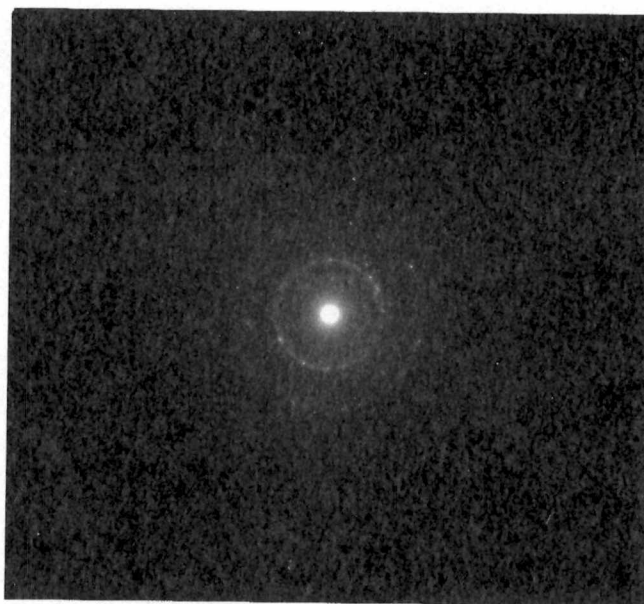


Fig. 79. A SAD pattern from the same Cr_2O_3 film after incrementally heating to 520°C and holding for 10 minutes. The film is crystallizing.

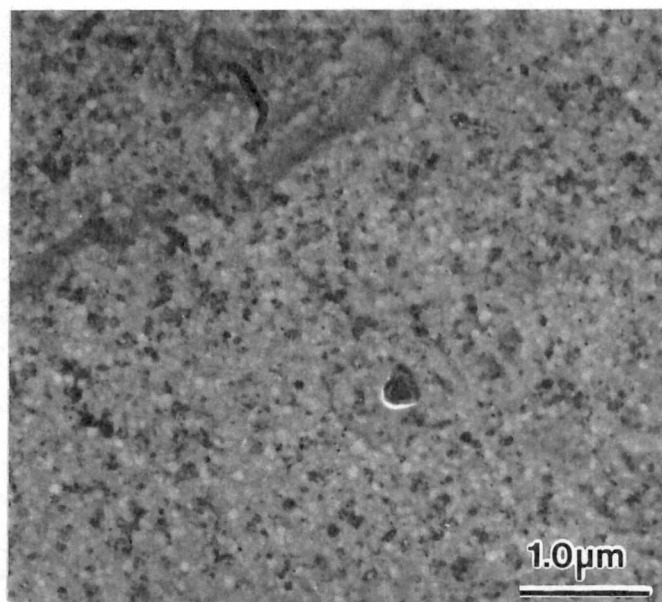


Fig. 80. A bright field micrograph of the Cr_2O_3 film taken just after the SAD pattern (Fig. 79).

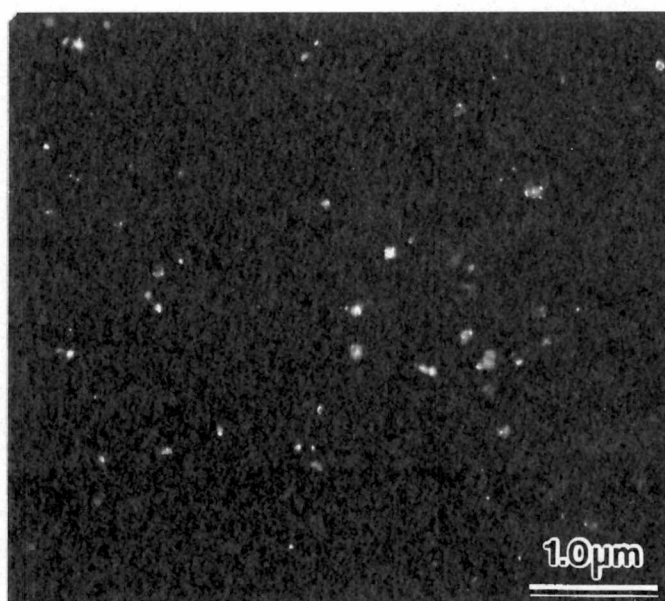


Fig. 81. A dark field micrograph of the same area as in Fig. 79. Differences in orientation of the crystallites are revealed.

crystallizing. There was no evidence of crystallization below 500°C. A bright field micrograph of the film taken just after the SAD pattern is shown in Fig. 80; Fig. 81 is a dark field micrograph of the same area in which differences in orientation of the crystallites are revealed. A SAD pattern taken after the sample was held at 695°C for 10 minutes is shown in Fig. 82. The crystallites have increased in size, and most of the film is crystalline. Figures 83 and 84 are dark field micrographs of the sample taken just after the SAD pattern (Fig. 84 is higher magnification). The crystallites are larger than those in Fig. 80.

To ensure that the Cr_2O_3 film is crystalline after the 2 h anneal in 96% Ar + 4% H_2 at 500°C, one of the grid-supported films was annealed in this manner and then examined in the TEM. Figure 85 is a SAD pattern taken from this film. The film is microcrystalline. A dark field micrograph confirmed the presence of crystallites.

5.2. Analytical electron microscopy of $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples

Because the XPS analysis indicated that significant chemical changes occurred in the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ system after bombardment, analytical electron microscopy (TEM with small spot EDS analysis) was performed on $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples only. The EDS data were converted to atomic percent by the program NEDQNT2 [96-100], a standard package for this purpose. The conversion is analogous to that for XPS, in that atomic sensitivity factors accounting for relative peak intensities are applied to the raw EDS data. On all plots of the EDS line scans presented here, at least three distinct areas are denoted: the Al_2O_3 substrate, the ZrO_2 layer, and the hole in the TEM specimen.

Figure 86 is a micrograph of a cross section specimen from an unimplanted sample, taken before any EDS scans were performed. The film is about 50 nm thick at its widest point. The thickness is nonuniform due to sputter loss during ion milling of the specimen. The film/substrate interface is distinct. Figure 87 is a micrograph of the same specimen, in the area where the EDS line scans were performed. The white areas denoted by arrows are the lines scanned--the sample was destroyed by the concentrated electron beam in those areas. The results of a line scan beginning at area A (in the Al_2O_3) on the micrograph is plotted in Fig. 88. The data indicate that the Zr extends into the Al_2O_3 about 20 nm; however, the interface does not appear diffuse in the micrograph. One possible explanation for the data is that secondary K_α X-rays are generated from the Al due to fluorescent excitation by L_α X-rays emitted from the Zr, and this is affecting the results. Another possibility is that a surface film of Al was deposited on the ZrO_2 during the ion milling step of the TEM sample preparation.

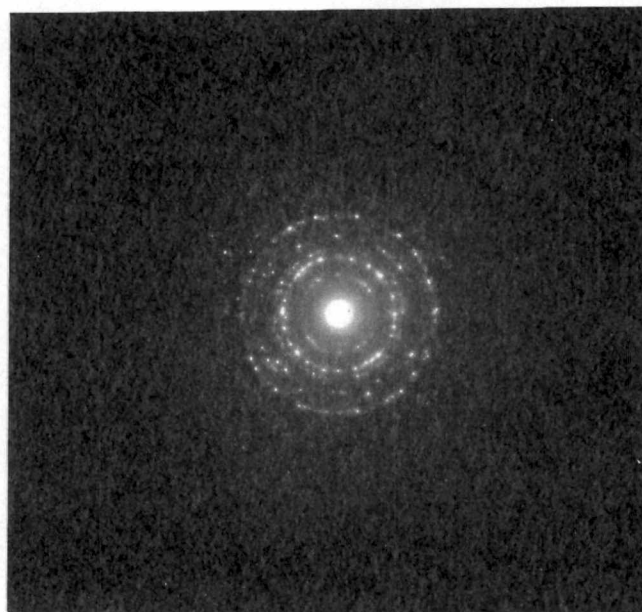


Fig. 82. A SAD pattern taken after the Cr_2O_3 sample was held at 695°C for 10 minutes. The crystallites have increased in size, and most of the film is crystalline.

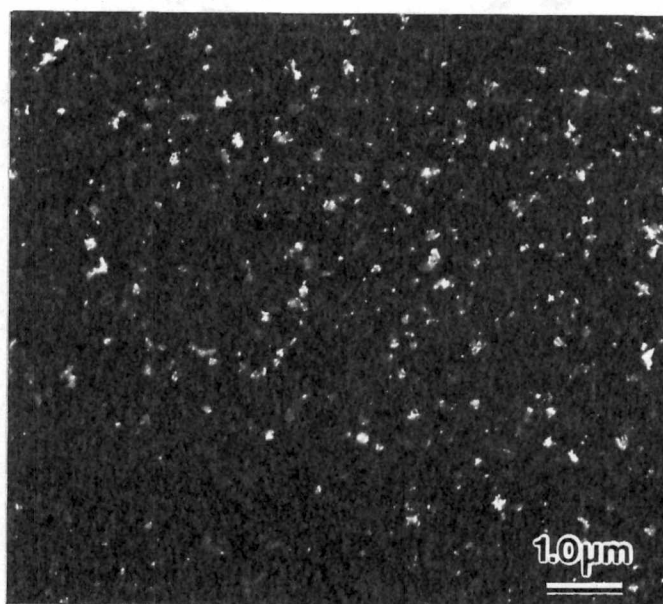


Fig. 83. A dark field micrograph of the Cr_2O_3 sample taken just after the SAD pattern in Fig. 82.

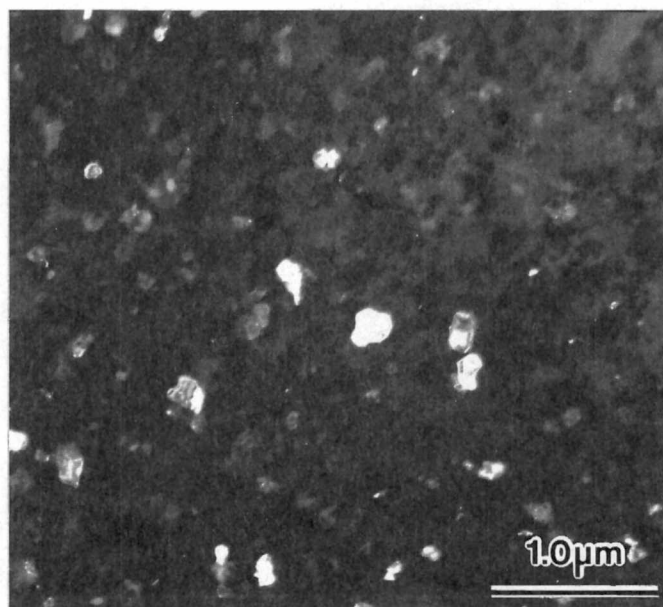


Fig. 84. A higher magnification dark field micrograph of the Cr_2O_3 sample taken just after the SAD pattern in Fig. 82. The crystallites are larger than those in Fig. 80.

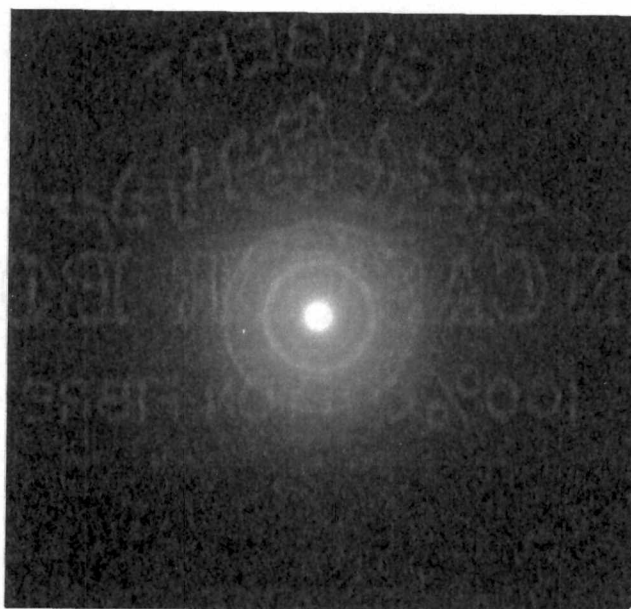


Fig. 85. A SAD pattern taken from a Cr_2O_3 film annealed for 2 h in 96% Ar + 4% H_2 at 500°C . The film is microcrystalline.

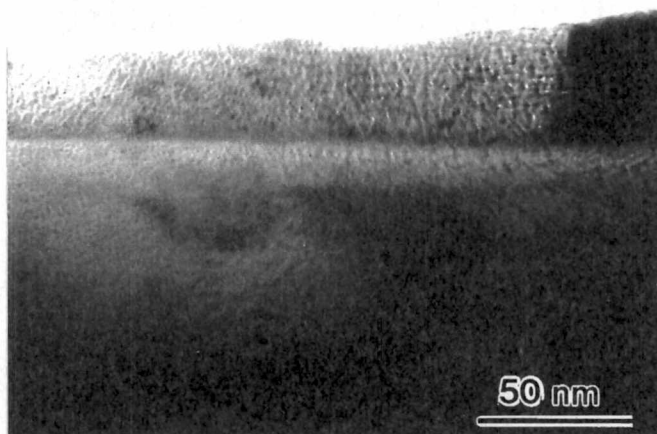


Fig. 86. A TEM micrograph of a cross section specimen from an unimplanted $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample, taken before any EDS scans were performed.

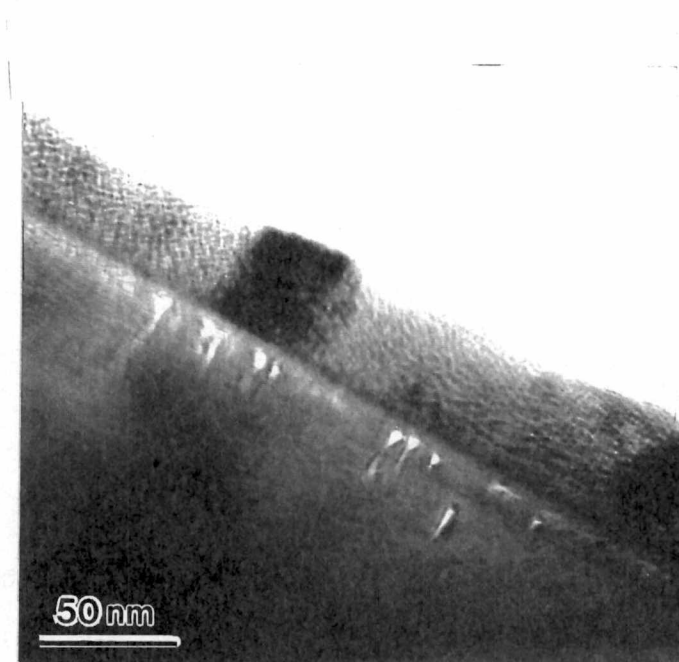


Fig. 87. A micrograph of the same specimen as in Fig. 86, in the area where the EDS line scans were performed. The white areas denoted by arrows are the lines scanned--the sample was destroyed by the concentrated electron beam in those areas.

In order to determine whether fluorescence is a problem in these samples, EDS spectra were taken from the same spot on a sample, but with varying tilts toward the detector. Changing the specimen tilt increases the X-ray path length through the material (i.e., different thicknesses of the specimen are sampled). The peak ratios, Zr/Al, were compared as a function of angle. The ratio increases with increasing angle (Fig. 89). This is characteristic of the X-ray fluorescence phenomena [101]. The existence of a fluorescence problem can interfere with data interpretation because it masks the existence of the true interface. Corrections for x-ray fluorescence effects is not trivial [98-100]; and are not attempted here. The EDS data presented here should be viewed with this in mind.

A micrograph of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at room temperature with 140 keV Cr to a fluence of 4×10^{16} ions- cm^{-2} is shown in Fig. 90. The film (area A) is roughly 85 nm thick here. Just below the film there is a layer of distinctly different appearance (area B), and below that, a third layer (area C). The EDS spectra obtained in these three positions indicate that area A is the ZrO_2 film. Areas B and C are in the Al_2O_3 , but are markedly different. The EDS spectra obtained from region B indicate that the layer is mostly Al_2O_3 , with a small amount of Zr. This layer extends from the film/substrate interface to about 35 nm into the Al_2O_3 . This distance is comparable to the projected range, R_p , of the implanted Cr. The simulations presented in Table 3 (Chapter 3) indicate that the ion range should be 119 nm from the sample's surface. For a film originally 80 nm thick, the distance past the interface would be 39 nm. The visible portion of layer C extends about 116 nm into the sapphire, and possibly farther because the thickness of the sample parallel to the electron beam increases rapidly in the Al_2O_3 , and thus the electron-transparent region is limited in the sapphire. From Table 4 (Chapter 4), the range of the oxygen recoils from the interface region is about 239 nm, and the range of the Zr recoils is about 78 nm. Figures 91a-c are SAD patterns from the three areas. Area A is polycrystalline, while area B is amorphous. Area C still exhibits the diffraction pattern for c-axis single crystal sapphire, but appears damaged. An EDS line scan from this sample is plotted in Fig. 92. The fact that the Al concentration remains at a relatively high, constant level for a distance into the ZrO_2 layer and then increases close to the hole is indicative of a surface film of Al. The thickness of the TEM specimen itself decreases rapidly near the hole. The EDS signal for a thin, relatively uniform layer of Al on the sample would begin to match the signal for the decreasing amount of Zr near the hole. This EDS line scan began past the R_p for the Cr ions. Comparison of the EDS line scan from the unimplanted $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample (Fig. 88) and the EDS scan from this sample reveals that the Zr

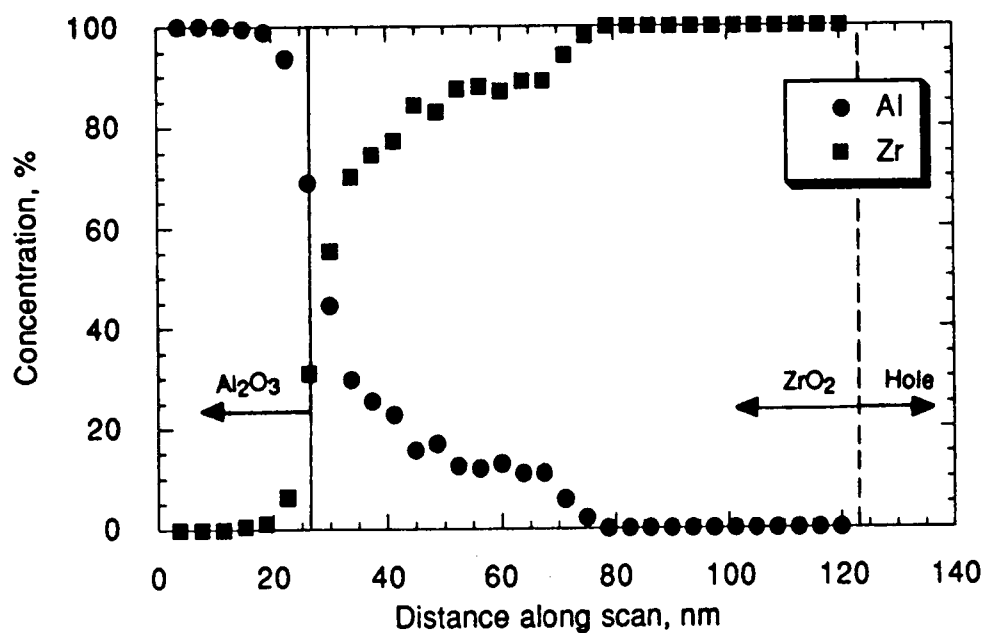


Fig. 88. The results of a line scan beginning at area A (in the Al_2O_3) on the micrograph in Fig. 87.

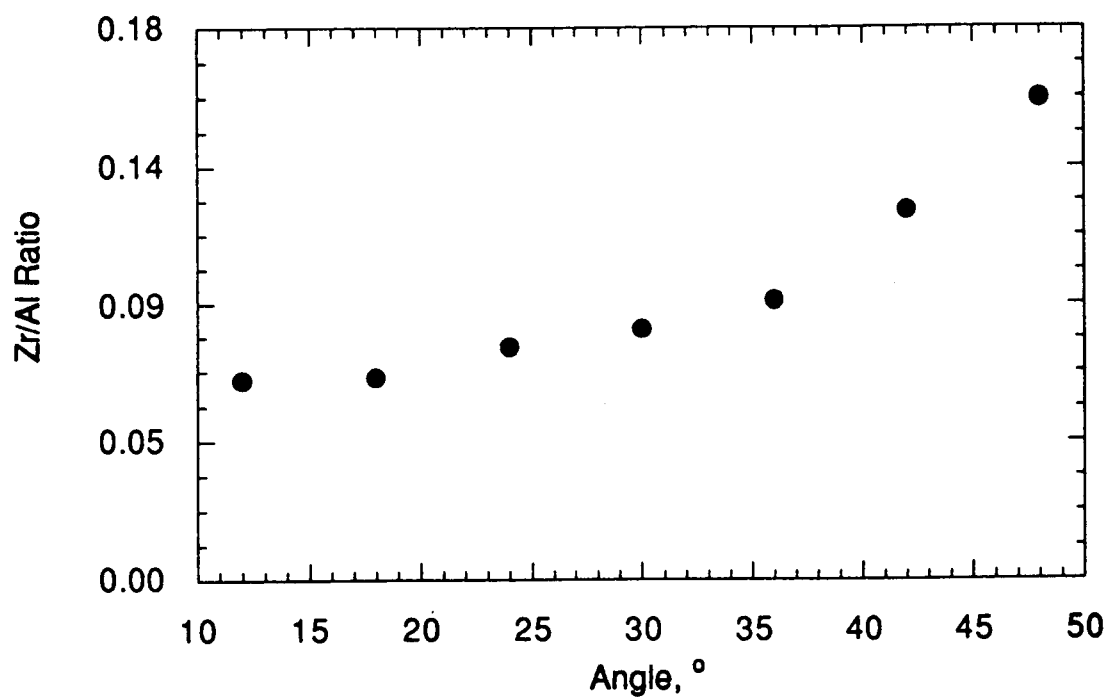


Fig. 89. The peak ratios, Zr/Al, plotted as a function of angular tilt toward the x-ray detector.

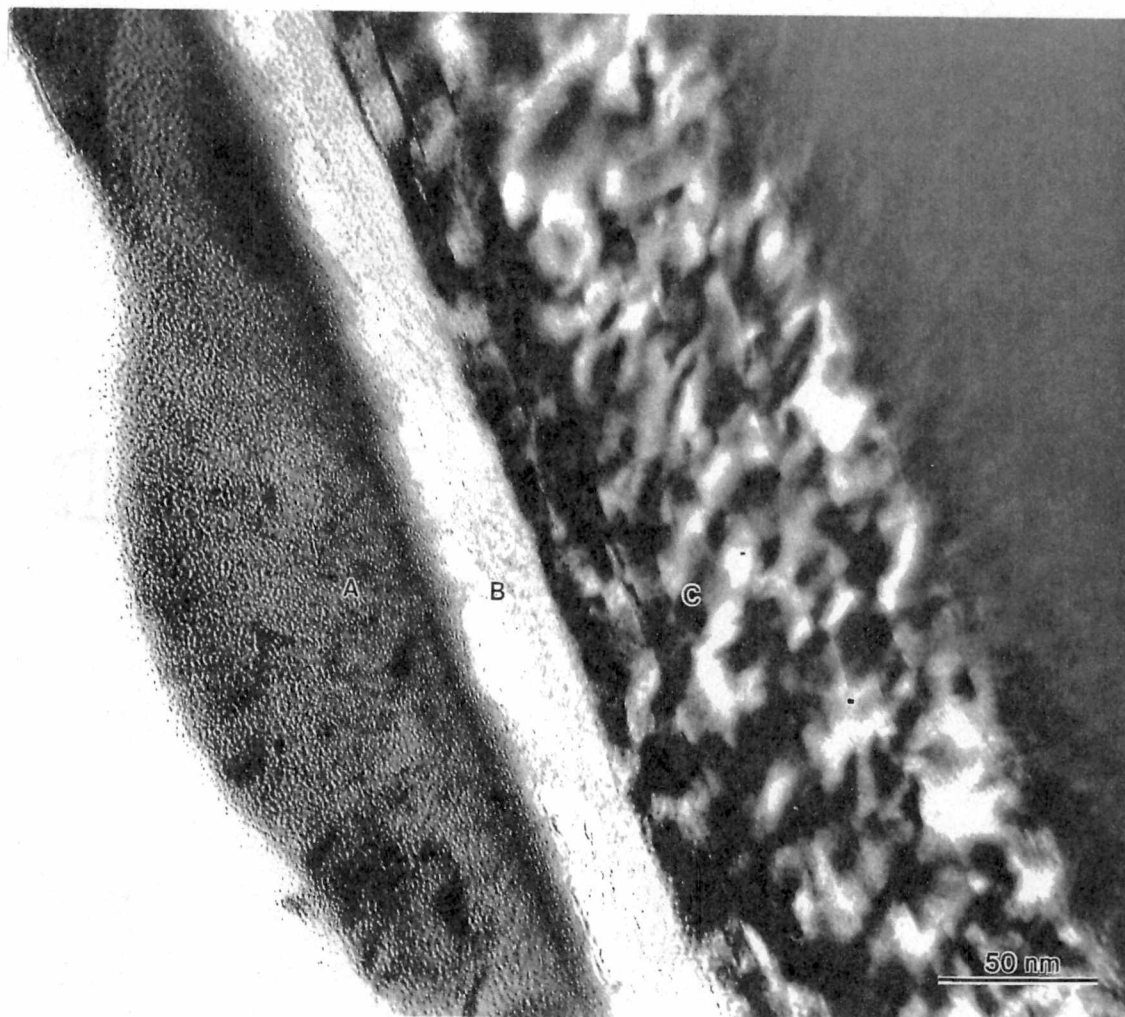


Fig. 90. A micrograph of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at room temperature with 140 keV Cr to a fluence of 4×10^{16} ions- cm^{-2} . Three different areas in the sample are denoted (A, B, and C).

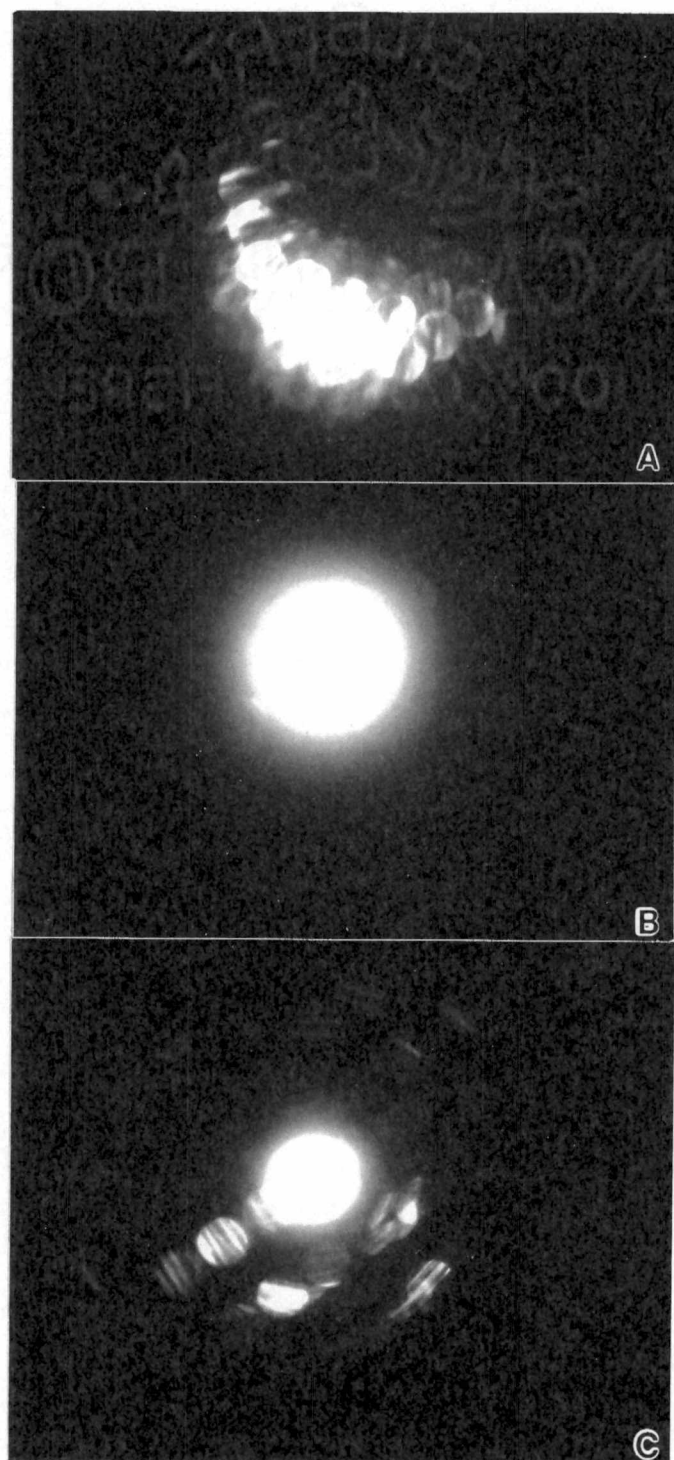


Fig. 91. The SAD patterns from the three areas (A-C) denoted in Fig. 90. Area A is polycrystalline, while area B is amorphous. Area C still exhibits the diffraction pattern for c-axis single crystal sapphire, but appears damaged.

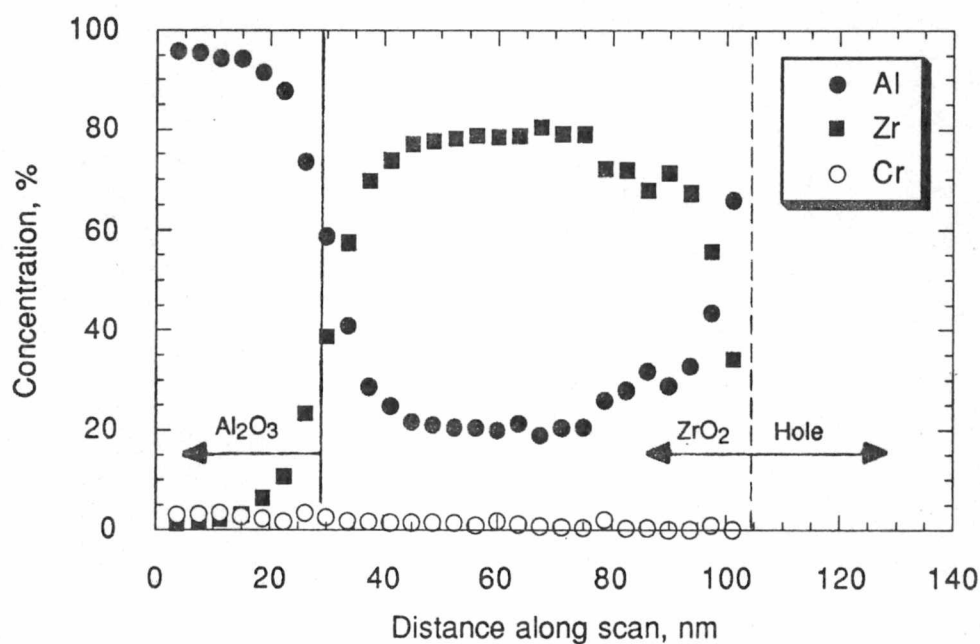


Fig. 92. An EDS line scan from the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample (140 keV Cr; 4×10^{16} ions- cm^{-2} ; 20°C).



Fig. 93. A micrograph of a sample implanted at 900°C with 340 keV Cr (4×10^{16} ions- cm^{-2}). A piece of glue which held the cross section together during sample preparation can be seen in the photograph (denoted with an arrow).

concentration in the sapphire below the apparent film/substrate interface is about the same as the concentration in the unimplanted sample.

A micrograph of a sample implanted at 900°C with 340 keV Cr (4×10^{16} ions-cm⁻²) is shown in Fig. 93. A piece of glue which held the cross section together during sample preparation can be seen in the photograph (denoted with an arrow). The ZrO₂ film is about 70 nm thick. The film/substrate interface appears to be relatively sharp. Figure 94 is a plot of data from a line scan performed on this sample in a region where the film is thinner (toward the lower part of the micrograph). The R_p of the implanted Cr is apparent in this graph; it is about 30 nm past the apparent film/substrate interface. This is relatively good agreement between the calculated and observed ranges. Analysis of the line scan from this sample indicates that the Zr level in the sapphire below the apparent film/substrate interface is about the same as compared to the unimplanted sample.

Figures 95 and 96 are micrographs from the ZrO₂/Al₂O₃ sample implanted with 475 keV Kr (4×10^{16} ions-cm⁻², room temperature). There are three obvious regions in this sample. Region A is the ZrO₂ film; it is about 75 nm thick at its widest point. Regions B and C are in the Al₂O₃. An EDS measurement taken in region B revealed the presence of a small amount of Zr. Region B appears to be about 45 nm thick. Another distinctly different region located between the film and the substrate is discernable in Fig. 96; it is marked "D." Region D is around 18 nm thick. The R_p of the Kr ions is around 155 nm from the sample's surface, or 75 nm past the film/substrate interface. Diffraction patterns from the different areas are shown in Figs. 97-100. Figure 97 is a SAD from region A, the ZrO₂ film. The film is polycrystalline. Figure 98 is from region D; this region is crystalline, and the area is not near a zone axis. Figure 99 is a SAD from region B. The interplanar angles match α -Al₂O₃; however the interplanar spacings are 10% greater than for α -Al₂O₃. The SAD in Fig. 100 is from region C; it is α -Al₂O₃, with zone axis 2110. Figure 101 is a plot of EDS line scan data from this sample. The climb in Kr concentration associated with the projected range (155 nm from the sample's surface) is evident. Comparison of the EDS scan for the unimplanted ZrO₂/Al₂O₃ specimen (Fig. 88), and the scan for this sample shows that the Zr/Al ratio is higher in the Kr-implanted specimen up to a distance of about 20 nm into the Al₂O₃ substrate. Figure 102 is a micrograph of the sample showing the tracks left by the electron beam during the line scans.

All TEM results are summarized in Table 13.

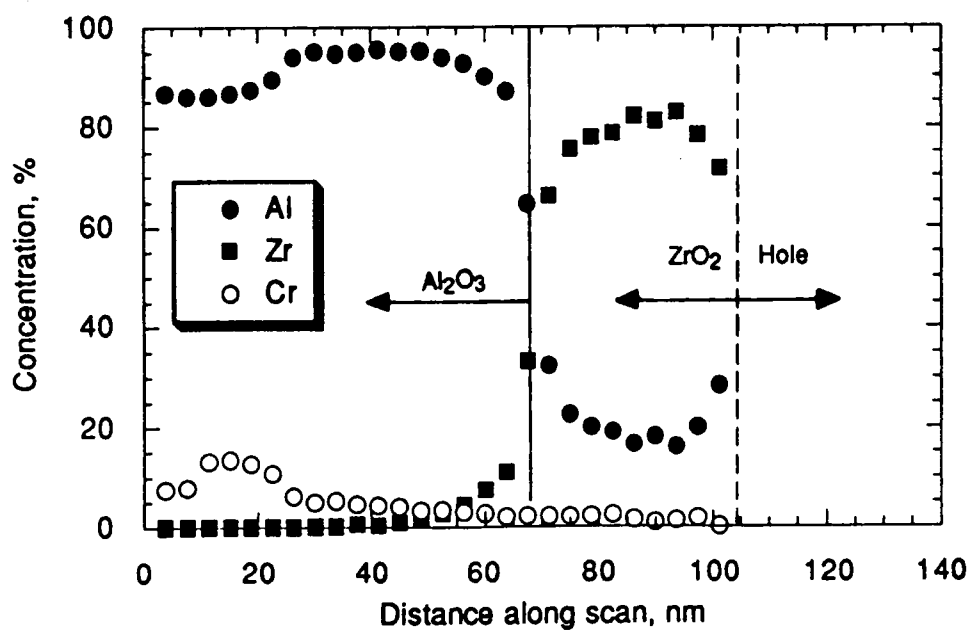


Fig. 94. A plot of EDS data from a line scan performed on the sample in an area toward the lower part of the micrograph in Fig. 93.

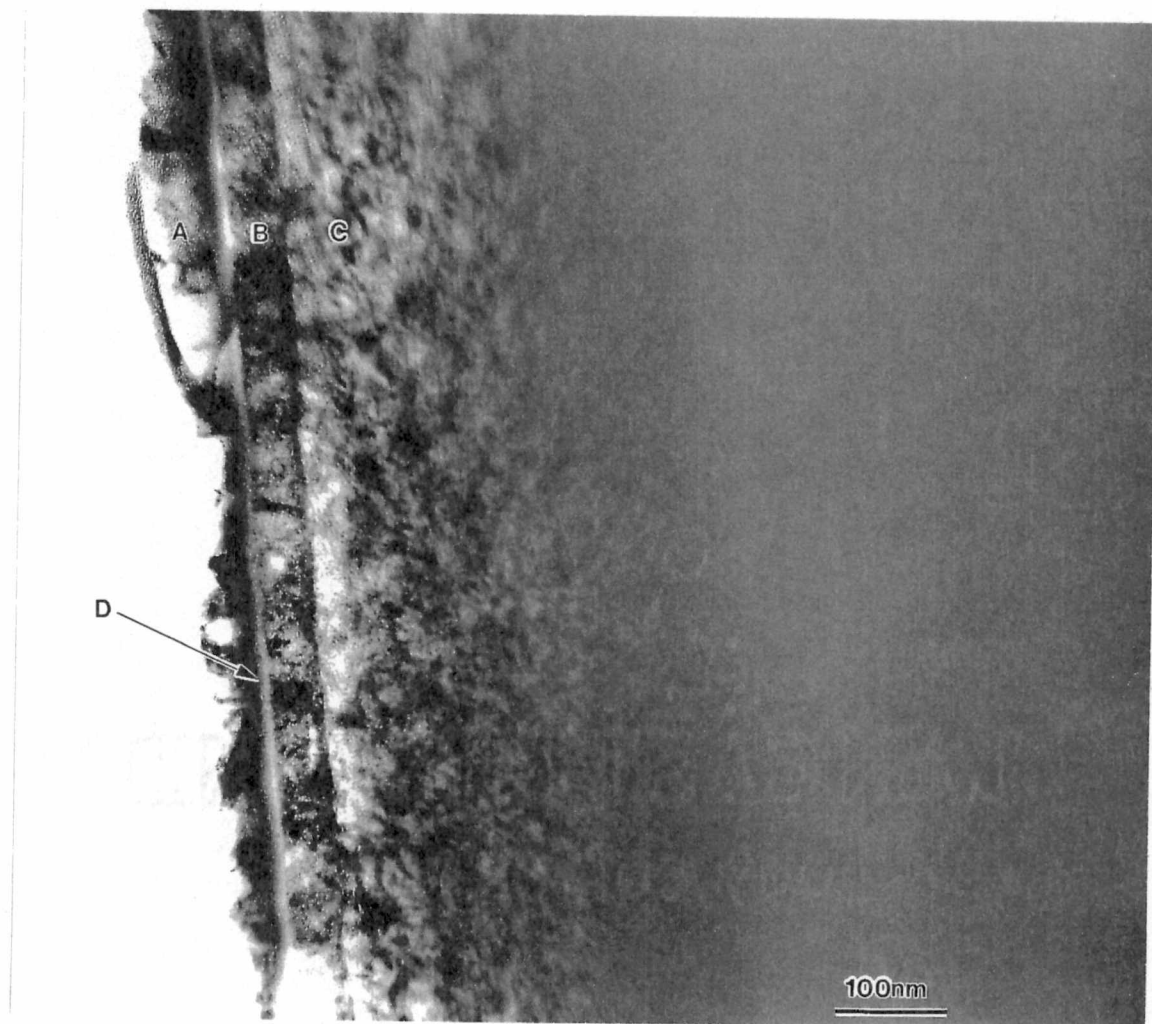


Fig. 95. A micrograph from the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted with 475 keV Kr (4×10^{16} ions- cm^{-2} , 20°C). Four different regions of the sample are denoted, A-D.

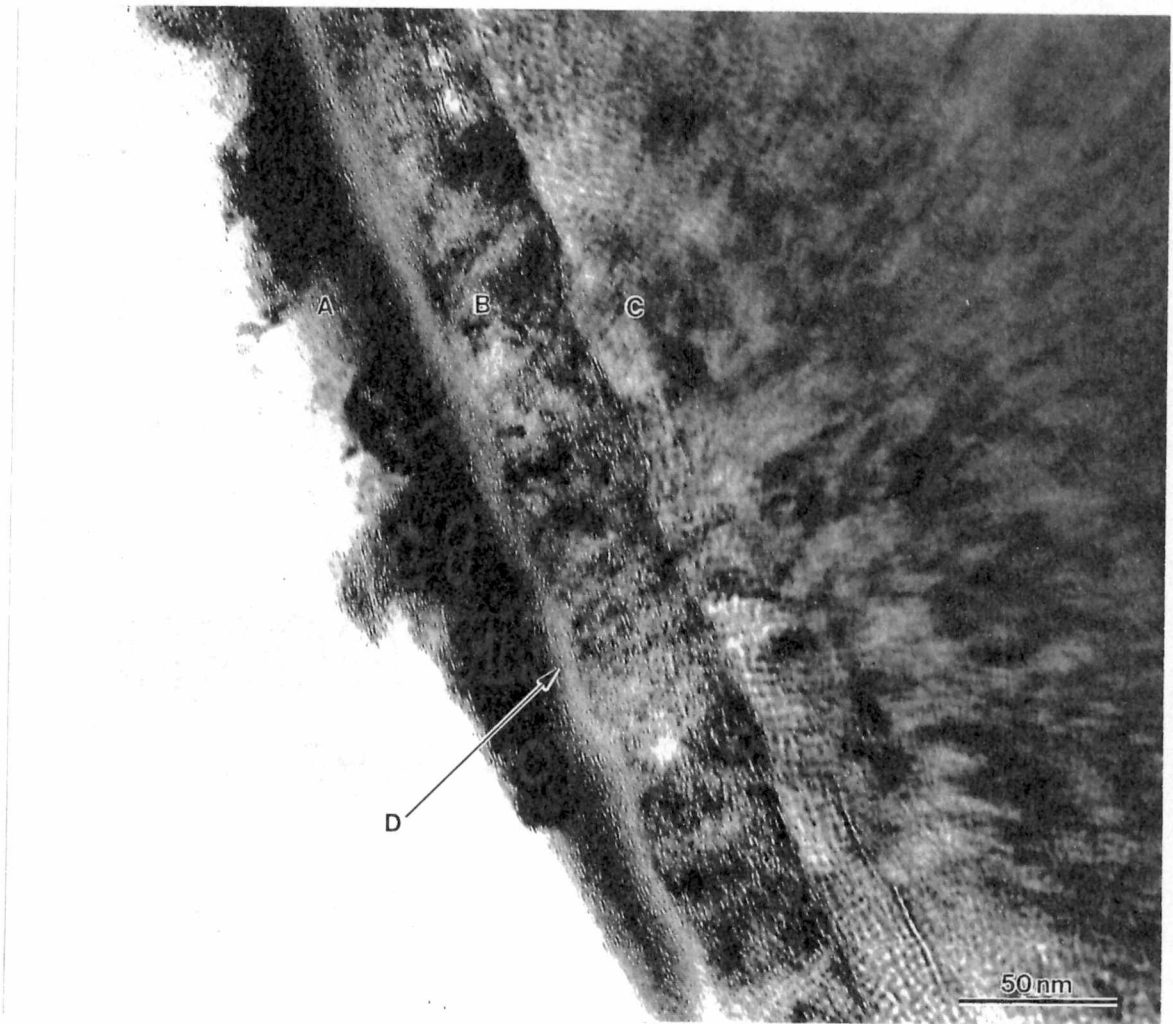


Fig. 96. A higher magnification micrograph of the same sample as Fig. 95. Four different regions of the sample are denoted, A-D.

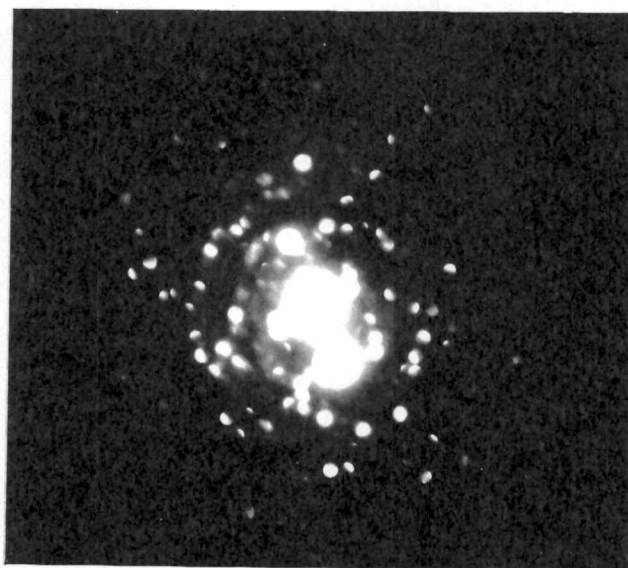


Fig. 97. A SAD from region A (Figs. 95 and 96), the ZrO₂ film. The film is polycrystalline.

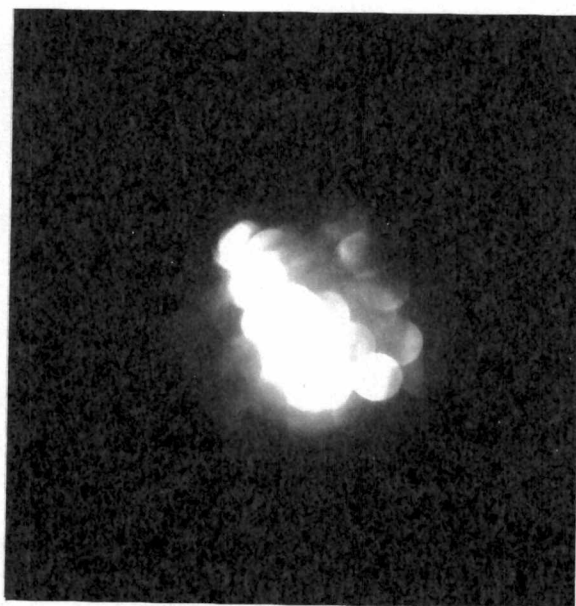


Fig. 98. A SAD from region D (Figs. 95 and 96); this region is crystalline, and the area is not near a zone axis.

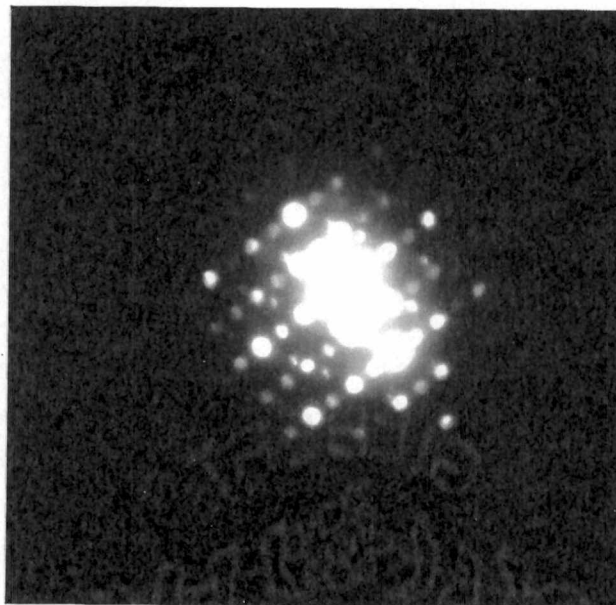


Fig. 99. A SAD from region B (Figs. 95 and 96). It is α -Al₂O₃.

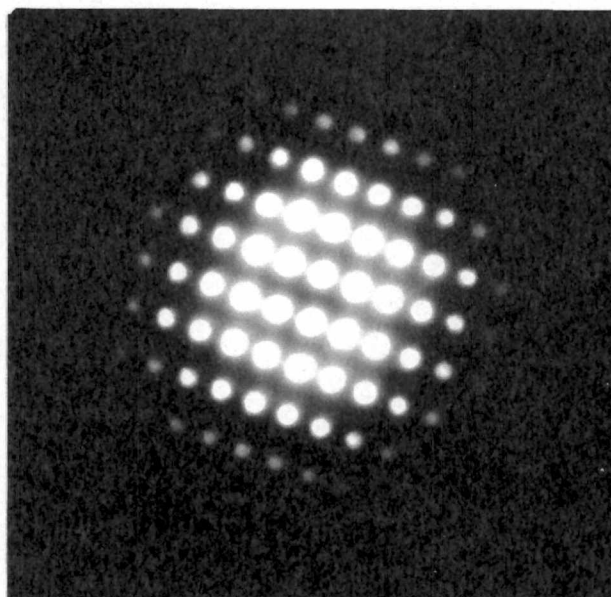


Fig. 100. A SAD from region C (Figs. 95 and 96). It is also α -Al₂O₃.

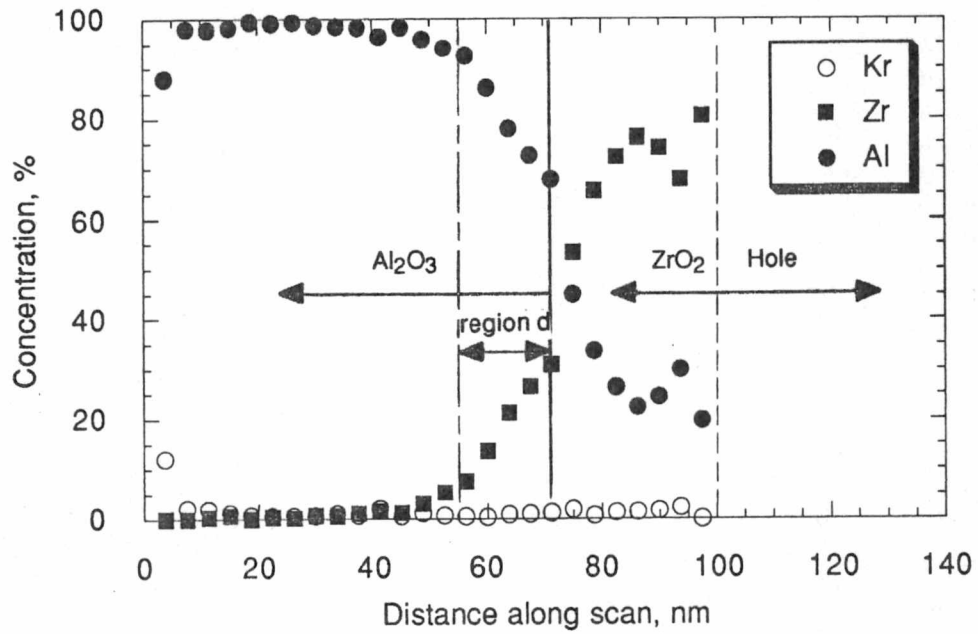


Fig. 101. An EDS line scan from the ZrO₂/Al₂O₃ sample implanted at room temperature with 475 keV Kr (4×10^{16} ions-cm⁻²).

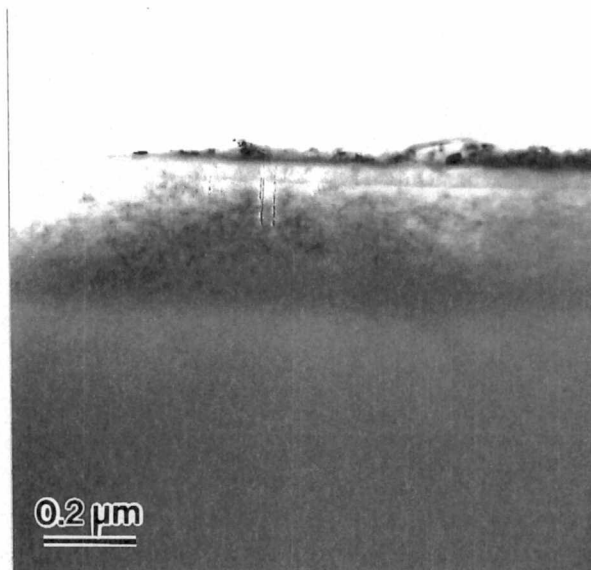


Fig. 102. A micrograph of the same sample as Fig. 101, showing the tracks left by the electron beam during the line scans.

Table 13. Transmission electron microscopy results

System and Implantation Conditions	Results
ZrO ₂ /Al ₂ O ₃ unimplanted	Distinct film/substrate interface.
ZrO ₂ /Al ₂ O ₃ Cr, 340 keV 4 x 10 ¹⁶ ions-cm ⁻² , 20°C	Three distinct layers observed in the sample; the ZrO ₂ film; an amorphous layer in the Al ₂ O ₃ which extends to the R _p of the Cr ions (~35 nm past the film/substrate interface), and contains a small amount of Zr; and a damaged Al ₂ O ₃ layer which extends at least 116 nm below the amorphous layer.
ZrO ₂ /Al ₂ O ₃ Cr, 340 keV 4 x 10 ¹⁶ ions-cm ⁻² , 900°C	Relatively sharp film/substrate interface. No obvious changes in structure of the kind observed in the sample implanted at room temperature.
ZrO ₂ /Al ₂ O ₃ Kr, 475 keV 4 x 10 ¹⁶ ions-cm ⁻² , 20°C	Four distinct regions apparent in the sample: the ZrO ₂ film; a very thin (about 15 nm thick) diffuse region just below the film; a region of Al ₂ O ₃ of different orientation or crystal structure than the original c-axis α -Al ₂ O ₃ , and which extends about 30 nm past the apparent film/substrate interface; and c-axis α -Al ₂ O ₃ . The total width of the two regions between the ZrO ₂ film and the α -Al ₂ O ₃ substrate roughly correspond to the projected range of the Kr ions.

6. Discussion summary

The extent of mixing in the systems studied in this work falls within the range of predicted recoil mixing. The predicted extent of the mixed region including both sides of the interface (Table 3, Chapter 4), is no greater than 60 nm for any of the ion/ion energy/target material combinations studied here. The recoil ranges of the metal atoms near the interface, as calculated by modelling the recoils as implanted atoms into sapphire (Table 4, Chapter 4) are never much more than 150 nm for any of the combinations. One system (Kr-Cr₂O₃/Al₂O₃), exhibited less mixing into the substrate than the ballistic models imply. The Cr₂O₃/Al₂O₃ systems seem to exhibit more mixing of the Al back into the film than expected. For example, from Fig. 5b, significant numbers of Al atoms (e.g. 10²¹ atoms-cm⁻², or about 9 atomic percent in the film) should recoil no more than 10 nm back into the film, as measured from the film/substrate interface. The XPS data indicate that Al is present in about these concentrations at the sample's surface in the Cr₂O₃/Al₂O₃ samples mixed with Cr at both temperatures (Figs. 40 and 44). These films are around 40 nm thick.

There is no evidence for the existence of thermal spikes under the conditions of these mixing experiments, even in the metal-sapphire systems for which Chen's mixing model involving the cohesive energies of the compounds predicted that thermal spikes could occur (Table 6, Chapter 4). Calculations employing Sigmund's parameters (Table 5, Chapter 4) indicate that the deposited energy density, θ_d , is never high enough for spike conditions to exist under the experimental conditions employed in this work. The deposited energy density is always less than 1 eV/atom; a few eV/atom are required for spike behavior (melting, surface evaporation, etc.).

The recoil ranges calculated by taking the films' component species to be implanted ions (Table 4, Chapter 4) define the worst-case scenario. To help illustrate this, the ion ranges and these calculated recoil ranges for each of the materials systems and film thicknesses employed in this work are graphically represented in Fig. 103. The predicted recoil range of the Cr in the Cr₂O₃/Al₂O₃ systems is always considerably greater than the recoil range observed by XPS; for example, in the sample implanted with Cr at room temperature, the predicted recoil range is 55 nm, while the observed recoil range is ~25 nm. The difference between the predicted recoil range and the observed recoil range is more pronounced in the Cr₂O₃/Al₂O₃ sample implanted with Kr: the predicted Cr recoil range is 155 nm, while the observed range is about 20 nm. However, the Cr concentration never quite reaches zero over the rest of the XPS profile; the Cr could possibly extend at a very low level to a greater depth in the Al₂O₃.

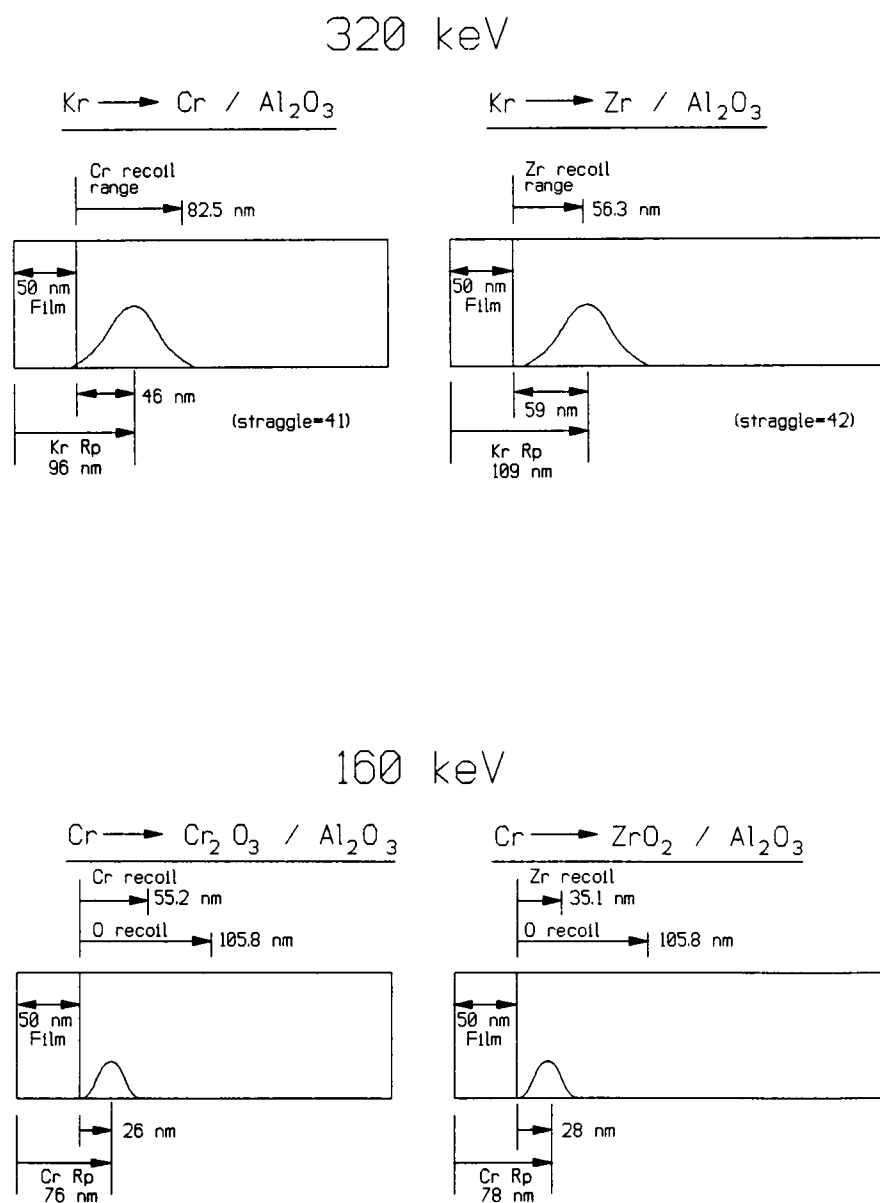
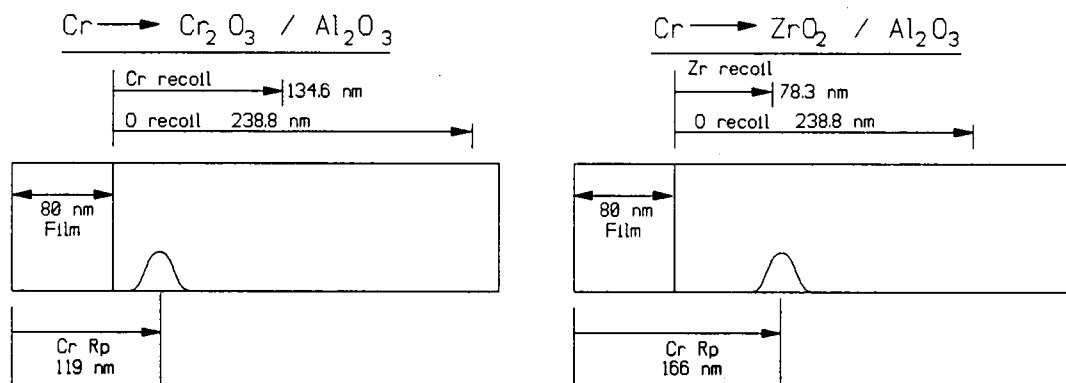


Fig. 103. Graphic representations of the ion ranges and calculated recoil ranges (Table 4) for each of the materials systems and film thicknesses employed in this work.

340 keV



475 keV

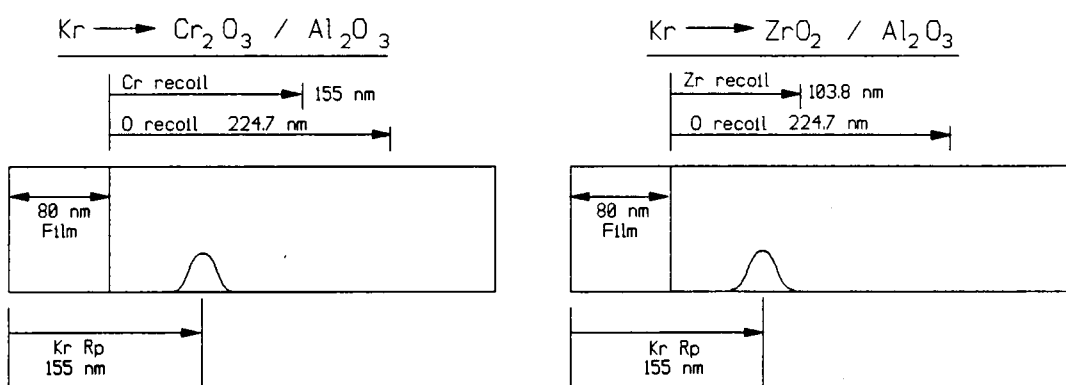


Fig. 103. Continued.

If long-range mixing (chemical effects, radiation-enhanced diffusion or segregation, thermal spikes, etc.) were involved in mixing phenomena in these oxide-sapphire systems, the extent of mixing should increase with increasing temperature and/or fluence. Within the limits of detection of the various techniques used in the present study, no such variation was detected. Instead, as will be discussed, samples irradiated at elevated temperatures may show evidence for demixing: the width of the "mixed" zone is less at temperatures near 900°C than at 20°C. From equilibrium thermodynamic considerations, long-range diffusion and solid solution formation would be expected for the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample irradiated at elevated temperature. In the absence of irradiation, interdiffusion and solid solution formation was detected in similar couples heated for 1 h at 1150°C and complete interpenetration was observed after 1 h at 1450°C. Such interdiffusion does not occur during irradiation of these samples.

According to the XPS analysis, changes in the charge states of the various elemental constituents occur after implantation of the samples. This is not an unexpected result; in order to maintain overall charge neutrality, the bonding of the various species in these systems must be changed to accommodate both the introduction of foreign atoms (the implanted species), and the defects produced during the implantation. The changes in charge state are less extensive in the samples implanted at elevated temperature than they are in the specimens implanted at room temperature. The latter samples exhibit reduction of the metal species in both oxide films to the metallic states; however, the Al_2O_3 is reduced to Al^0 only in the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ specimens implanted at room temperature. In the samples implanted at elevated temperature, the damage in the Al_2O_3 has time to at least partially recover during the high temperature implantations. This is not unreasonable, because it was demonstrated in this work that lattice disorder produced by irradiation of Al_2O_3 recovers at temperatures near 900°C. In other work, it was shown that the F-type color centers (oxygen vacancies containing trapped electrons) produced by ion bombardment in Al_2O_3 begin to anneal at 600°C and are generally removed by annealing for 1 h at 800-900°C [102]. These irradiation-produced defects need to migrate only short distances to be annihilated at irradiation-produced sinks. At 860°C, some demixing appears to occur in both the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ systems, as evidenced by the slight decrease in the distance into the substrate at which the film's metallic species is detected (via XPS). Arguments suggesting that long-range mixing should occur in soluble systems as implied by equilibrium thermodynamics are not applicable to the mixing phenomena observed in these systems because the mixing observed here is ballistic in nature: the oxide films are not knocked into the sapphire as molecules, but rather as individual ions, metal and

oxygen. Generally, impurities have negligible solubility in sapphire. The film components recoiling into the sapphire during room temperature bombardment are not mobile at room temperature. At elevated temperature, the possibility for diffusion of impurities back toward the film/substrate interface exists. White et al. [103] showed that much recovery occurs in the near surface region of Al_2O_3 during elevated implantation, implying that the surface is a sink for irradiation-produced defects as well as a source of oxygen and vacancies. In the specimen configuration used in the work presented here, the interface between the two oxides may serve as the sink/source. Although it has been shown that implanted ions (e.g. Cr) do not diffuse in sapphire except in oxygen-rich environments at temperatures above 1300°C [104], the presence of extra oxygen in the Al_2O_3 (knocked in from the film) may allow the process to occur at somewhat lower temperatures, since the oxygen does not have to diffuse into the sample from its surface.

Enthalpy considerations do explain some of the nature and extent of the chemical changes in these specimens. The enthalpy of reaction for the reduction of Al_2O_3 by Zr is very nearly zero; the literature contains both slightly positive and slightly negative values. Thus the reaction appears to be possible. In the case of Zr/ Al_2O_3 , elemental Zr is in contact with Al_2O_3 , and Zr atoms are recoiled into the substrate. Examination of the implanted Zr/ Al_2O_3 film via XPS revealed the presence of Zr^0 , Zr^{4+} , Al^0 , and Al^{3+} within the ballistic region. This reaction apparently occurs during the short period of the displacement cascade. The limited mobility of the components during this time confines the region over which reactions occur, thus equilibrium cannot be reached. The affected region in the substrate contains excess cations (due to the recoiled Zr), and there is insufficient oxygen available to react with all of the Zr and the displaced Al^{3+} . This leads to a mixture of Zr^0 , Zr^{4+} , and Al^0 with the Al_2O_3 matrix.

Because the recoil range of Zr ions is less than half that of the oxygen ions (Table 4, Chapter 4), the mixing experiments between Zr/ Al_2O_3 and $\text{ZrO}_2/\text{Al}_2\text{O}_3$ are essentially the same in the mixed region. Since the ZrO_2 is not knocked into the sapphire as molecules, but rather as component elemental ions, several charge states are again present in the ballistic zone. Because of the straggling of both Zr and O ions, the region is not as oxygen deficient in the case of $\text{ZrO}_2/\text{Al}_2\text{O}_3$ as in the Zr/ Al_2O_3 case. The XPS data can be interpreted as indicating the presence of nonstoichiometric oxides of both Zr and Al. The $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples implanted with Kr showed evidence of another problem entirely: nonstoichiometry of the as-deposited films. This problem appears to have been isolated to these specimens; the other $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples did not show the presence of so many suboxides.

In the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples, the presence of Cr^0 , Cr^{3+} and Cr^{6+} in the implanted samples can be explained by similar arguments concerning the relative recoil ranges of the Cr and the O ions. The recoil range of the O ions is about twice that of the Cr ions, so an oxygen deficient region is created in which a range of nonstoichiometric oxides are formed. The fact that more Cr^0 is present in the sample implanted at room temperature is related to kinetic effects. While oxygen can diffuse back into the film during the elevated temperature implant, it is immobile at room temperature.

In the unimplanted specimens, changes in charge state of the elemental species may be mostly due to preferential sputtering of oxygen, a problem inherent in sputter depth profiling. Preferential sputtering may also contribute to the chemical changes in the implanted specimens; however by comparison of results from XPS and Conversion Electron Mossbauer Spectroscopy (CEMS), van Hassel [85] determined that preferential sputtering was not a problem in Fe-implanted ZrO_2 . He found that the charge state of the implanted Fe as observed by XPS after sputtering appeared to differ markedly from the state determined by CEMS (no sputtering is involved in this technique). However, the amount of Zr present as Zr^{4+} (ZrO_2) detected via XPS did not change significantly after Ar sputtering. The fact that multiple charge states were observed in the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ specimens before and after implantation implies that preferential sputtering may be a problem in both Cr_2O_3 and Al_2O_3 .

To summarize, the presence of several charge states in the implanted films can be explained by (1) the introduction of oxygen deficiency due to the differential recoil ranges of the metal and oxygen ions, (2) preferential sputtering of oxygen during depth profiling, and (c) nonstoichiometry of the as-deposited films.

The TEM observations reveal that a 35 nm thick amorphous layer exists in the Al_2O_3 beneath the ZrO_2 film in the sample implanted with Cr at room temperature, and that a thin (15 nm) layer discrete in appearance and crystallographic orientation from either the ZrO_2 or the Al_2O_3 exists in the sapphire in the Kr implanted specimen. A distinct damaged region exists in the Al_2O_3 underneath this thin layer. No obviously damaged layer exists in the sample implanted with Cr at elevated temperature. The amorphous layer may be due to introduction of Zr into the Al_2O_3 via the recoil mechanism. Experiments by White et al. indicate that Al_2O_3 can be amorphized at room temperature by a critical concentration of implanted Zr [105, 106]. In those experiments, the Al_2O_3 exhibited a subsurface amorphous region corresponding to a Zr/Al ratio of around 0.065, as determined by EDS line scans. The determination of a reliable Zr/Al ratio was not possible in the work presented here. The absence of an amorphous layer in the sample implanted at elevated

temperature implies that a critical composition of Zr is not sufficient for amorphization of the sapphire; a certain level of damage is required. The Zr apparently stabilizes the damage against dynamic recovery during implantation at room temperature. The fact that no amorphous region is found in the sample implanted with Kr at room temperature implies that the presence of Cr may also have some stabilizing effect.

The AEM results and the XPS results are in agreement concerning the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples implanted with Kr at room temperature. The samples examined by the two techniques were identical except for the Kr fluence; the TEM specimen received 4×10^{16} $\text{Kr}\cdot\text{cm}^{-2}$, while the XPS sample received 1×10^{17} $\text{Kr}\cdot\text{cm}^{-2}$. The differences in fluence produce differences in the as-implanted film thickness; the specimen implanted with the higher fluence is thinner because more material is sputtered away. The XPS spectra montage in Fig. 65 shows a chemically altered region extending from approximately 25 cycles to 80 cycles. Each cycle represents 0.5 minutes of sputtering, and the sputter rate in the sample was about 2.5 nm/min. This corresponds to a thickness of around 70 nm. The Al signal is just beginning to rise at cycle 25; this is the film/substrate interface. From the TEM micrograph, the thickness of the diffuse layer (18 nm) and the region of different orientation below the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interface is about 63 nm. The change is also identifiable in the EDS line scan for this sample. As compared to the EDS scan for the unimplanted $\text{ZrO}_2/\text{Al}_2\text{O}_3$ specimen (Fig. 88), the Zr/Al ratio is higher in the Kr-implanted specimen (Fig. 101) up to a distance of approximately 15 nm below the film/substrate interface.

Comparison of the AEM and XPS results for the Cr-implanted $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples is not so straightforward, because the films are not the same thickness (80 nm for TEM vs. 50 nm for XPS) and the ion energies are not the same (340 keV vs. 160 keV). The range of the Cr in the thicker sample is roughly twice that in the thinner sample. Based on this, it is reasonable to assume that the amorphous layer in the sample examined using XPS would be roughly half the thickness that it is in the sample examined by TEM, 35 nm. Examination of the XPS depth profile for this sample (Fig. 49) reveals that the Zr extends about 20 nm into the sapphire, a little over half the expected distance. The montages of XPS spectra from the Zr and the Al (Figs. 49 and 50) reveal that a chemical change, the reduction of the oxides to their metallic states, has occurred in this region of the sample. The EDS data from this sample (Fig. 92) reveals that the Zr concentration in the sapphire below the apparent film/substrate interface is slightly elevated as compared to the unimplanted sample. This elevated Zr concentration extends to a depth of at least 10 nm into the substrate, the depth at which the scan was started. At this depth, the Zr concentration has not reached zero; it appears to be present at about the same concentration

as the implanted Cr. Because the scan does not provide data for depths greater than 10 nm, no further correlations can be made with the XPS results.

The AEM and XPS results for the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples implanted with Cr at elevated temperature (around 900°C) are in agreement. The TEM micrographs of the sample which received this treatment indicate that there are no obviously damaged layers in the sapphire underneath the film in this sample, as there were in the sample implanted at room temperature. The montage of Zr spectra obtained by XPS (Fig. 53) shows no apparent chemical changes, i.e. no reduction of either the ZrO_2 or the Al_2O_3 to the metallic states, which was observed in the sample implanted at room temperature. The EDS line scan from this sample (Fig. 94) indicates that the Zr level is still somewhat elevated as compared to the unimplanted sample, up to a depth of approximately 12 nm below the film/substrate interface.

No comparison of the results from either XPS or AEM analysis to the RBS results is possible. The detection of such small amounts of mixing (small concentrations over small distances) in these materials using RBS analysis is difficult. The effects of sample charging during analysis, and the effects of surface roughening during implantation, even on the fine scale observed here, prevent detection of the small concentrations of material moved across the original interface.

CHAPTER 5

CONCLUSIONS

The extent of mixing in the systems studied in this work falls within the range of predicted recoil mixing. There is no evidence for the existence of thermal spikes under the conditions of these mixing experiments. The deposited energy density, θ_d , is always < 1 eV/atom; a few eV/atom are required for spike behavior (melting, surface evaporation, etc.).

No increase in the extent of mixing in these systems was observed with increasing temperature, therefore the mixing phenomena studied here do not involve long-range mixing effects such as chemical reactions or radiation-enhanced diffusion or segregation. Rather than exhibiting increased mixing with increasing temperature, samples irradiated at elevated temperatures showed evidence for demixing. In the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples, although long-range diffusion and solid solution formation would be expected according to equilibrium thermodynamics, such interdiffusion does not occur during irradiation of these samples. However, interdiffusion was detected in similar couples heated for 1 h at 1150°C ; complete interpenetration was observed after 1 h at 1450°C .

Because the mixing observed here is ballistic in nature, arguments suggesting that long-range mixing should occur in soluble systems as implied by equilibrium thermodynamics are not applicable to the mixing phenomena observed in these systems. The film components recoiling into the Al_2O_3 during room temperature bombardment are immobile at room temperature; however, impurities may diffuse back toward the film/substrate interface during implantation at elevated temperature. The damage in the Al_2O_3 has time to partially recover during the high temperature implantations. These irradiation-produced defects need to migrate only short distances to be annihilated at irradiation-produced sinks.

The XPS analysis showed that changes in the charge states of the various elemental constituents occur after implantation of the samples. The bonding of the various species in these systems must be changed in order to maintain overall charge neutrality when foreign atoms (the implanted species), and defects are introduced during the implantation. The samples implanted at room temperature exhibit reduction of the metal species in both oxide films to the metallic states; however, significant amounts of metallic Al are found only in the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples.

Enthalpy considerations explain some of the nature and extent of the chemical changes in these specimens. The enthalpy of reaction for the reduction of Al_2O_3 by Zr is very nearly zero; thus the reaction may be possible. In the Kr-implanted $\text{Zr}/\text{Al}_2\text{O}_3$ specimen, Zr^0 , Zr^{4+} , Al^0 , and Al^{3+} are present within the ballistic region, implying that the Zr has reduced the Al_2O_3 . The reaction must occur during the short period of the displacement cascade (10^{-13} to 10^{-11} s), therefore equilibrium is not reached because the limited mobility of the components during this time.

The recoil range of Zr ions is less than half that of the oxygen ions, therefore the mixing experiments between $\text{Zr}/\text{Al}_2\text{O}_3$ and $\text{ZrO}_2/\text{Al}_2\text{O}_3$ are essentially the same in the mixed region. Because of this difference in recoil ranges, an oxygen deficient region is created in which a range of nonstoichiometric oxides are formed.

The $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples implanted with Kr showed evidence of another problem entirely: nonstoichiometry of the as-deposited films. This problem appears to have been isolated to these specimens; the other $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples did not show the presence of so many suboxides.

The presence of Cr^0 , Cr^{3+} and Cr^{6+} in the implanted $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples can be explained by similar arguments concerning the relative recoil ranges of the Cr and the O ions. The fact that more Cr^0 is present in the sample implanted at room temperature is related to kinetics effects. While oxygen can diffuse back into the film during the elevated temperature implant, it is immobile at room temperature.

In the unimplanted specimens, changes in charge state of the elemental species may be mostly due to preferential sputtering of oxygen, a problem inherent in sputter depth profiling.

To summarize, the presence of several charge states in the implanted films can be explained by (1) the introduction of oxygen deficiency due to the differential recoil ranges of the metal and oxygen ions, (2) preferential sputtering of oxygen during depth profiling, and (c) nonstoichiometry of the as-deposited films.

An amorphous layer exists in the Al_2O_3 beneath the ZrO_2 film in the sample implanted with Cr at room temperature. In the Kr implanted specimen, a thin layer of different crystallographic orientation from either the ZrO_2 or the Al_2O_3 exists in the sapphire; beneath this layer, a distinct damaged region exists in the Al_2O_3 . No obviously damaged layer exists in the sample implanted with Cr at elevated temperature. The amorphous layer may be due to introduction of Zr into the Al_2O_3 via the recoil mechanism. The absence of an amorphous layer in the sample implanted at elevated temperature implies that a critical composition of Zr is not sufficient for amorphization of the sapphire; a certain level of

damage is required. The Zr apparently stabilizes the damage against dynamic recovery during implantation at room temperature. The presence of Cr may also have some stabilizing effect.

The AEM results and the XPS results are in agreement concerning the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples examined via XPS.

The detection of such small amounts of mixing (small concentrations over small distances) in these materials using RBS analysis is difficult. The effects of sample charging during analysis, and the effects of surface roughening during implantation, even on the fine scale observed here, prevent detection of the small concentrations of material moved across the original interface.

Experimental work involving ion mixing processes should always include at least two analysis techniques. Transmission electron microscopy is particularly important because it provides information on the structure of the implanted samples which cannot easily be obtained by other techniques because of the sample configuration and microcrystallinity of the oxide films studied in this work. The RBS and XPS cannot be relied upon on their own because of the problems inherent in examination of insulators.

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