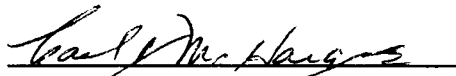


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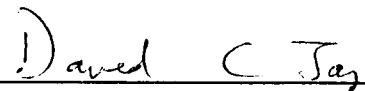
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Carl J. McHargue, Major Professor

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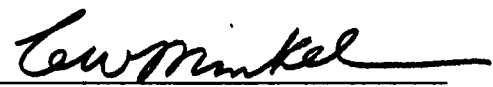








Accepted for the Council:


Associate Vice Chancellor
and Dean of the Graduate School

CHARACTERIZATION OF IRON IMPLANTED SAPPHIRE NANOCOMPOSITES

**A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville**

**Shelly Xinlei Ren
December 1995**

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ABSTRACT

Nanocomposites of iron in sapphire (α - Al_2O_3) were prepared by implantation of 160 keV Fe^{56} at room temperature with several fluences, and then annealed at selected temperatures between 700 and 1400°C in an Ar-4% H_2 atmosphere for 1 hour. The structure of these nanocomposites was characterized using Rutherford backscattering spectroscopy and high resolution transmission electron microscopy (TEM). Measurements showed that damage depth extended to about 300 nm and the embedded iron to approximately 200 nm. This region became amorphous when the fluence reached 2×10^{17} Fe/cm^2 , at which oriented precipitates with diameters of 2 to 3 nm were identified by TEM techniques as α -Fe. Thermal annealing restored crystallinity to the damaged near-surface region, formed metallic colloids, and coarsened the precipitates. Optical density and luminescence spectra were also determined. The predominant defects were F centers (an oxygen vacancy containing two electrons) indicated by an absorption peak of 200 nm. Hardness and elastic modulus were determined using the Nano-indenterTM. The results exhibited a radiation-induced softening and a decrease in modulus through the crystalline-to-amorphous transition, and also a radiation-induced hardening below the transition.

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CHAPTER I

INTRODUCTION

Ion implantation is an attractive technique for altering the near-surface properties of a wide range of materials since it is independent of many of the constraints associated with normal processing methods. Because of its ballistic nature, ion implantation allows excellent control over the number and distribution of atoms that can be injected [1].

Over the past several years, ion implantation has shown considerable promise in doping semiconducting materials for microelectronics applications [2-10] and implanting solutes into metals and alloys for surface treatment purposes (for increasing the hardness, corrosion resistance etc.) [4-11]. Recently, heavy metal ions have also been used to alter the physical, chemical, electrical, optical and mechanical properties of insulating materials at the near surface region [12-13].

The insulator materials are generally compounds composed of at least two sublattices that have different atomic masses. In the displacement cascade, one must deal with at least two sublattices that may have different displacement energy levels. The types of defects that can be produced are strongly influenced by the requirements of local electrical charge neutrality, the local stoichiometry, and the nature of the chemical bonding of the particular lattice. However, by applying ion beam implantation techniques, it is possible to introduce a desired elemental distribution in the near surface region due to its nonequilibrium process nature. Many of these insulator materials, and in particular sapphire ($\alpha\text{-Al}_2\text{O}_3$), are sensitive to the condition of the surface. For instance, tensile surface stresses can give rise to crack initiation and low fracture toughness, and surface hardness can affect the wear properties of ceramic or ceramic coated-tools. The very practical interest in surface and near surface properties of these materials has thus motivated the investigation of the effects

of irradiation on the hardness and fracture toughness of ion-implanted α -Al₂O₃, on the electrical and optical properties changes and its modified microstructure which produces these properties [14-19]. In addition, the solubility of most impurities in α -Al₂O₃ is vanishingly small; the properties of supersaturated solutions of α -Al₂O₃, which might result from ion implantation with almost any impurity, are therefore unknown and could be of general interest.

The purpose of this research is to conduct a systematic study of nanocomposites of iron-implanted sapphire, and thus, develop a model to verify the potentials of such materials for applications in high technology areas. For example, nanocomposites of iron implanted into sapphire may be used to make "smart" resistors which can give a reasonable leakage current for warning or controlling purposes at a threshold voltage before breakdown occurs. Iron implanted sapphire is also expected to be used as a candidate material to make computer disk by IBM if a magnetic layer could be formed underneath the surface to eliminate the corrosion problem.

In this study, a near surface layer of iron impurities was implanted into α -Al₂O₃ single crystal substrates which were then heat treated at different temperatures in a reducing environment for a certain period of time. The resulting microstructure changes which occurred at the near surface region due to the implantation and post-implant heat treatments were addressed in detail by Rutherford Backscattering Spectrometry (RBS) and Analytical Electron Microscopy (AEM). The resulting electrical, optical, and mechanical properties changes were investigated via galvanometric, spectrophotometric, and nanoindenter measurements respectively.

The specific concerns in this investigation included: (1) To determine how to control the size distribution of particles through annealing; (2) To determine the maximum volume fraction of metal particles that can be obtained by implantation at higher fluences; (3) To optimize the mechanical properties (hardness, elastic modulus) of such nanocomposites by

control of size, shape, and size distribution of the metallic component; and (4) To produce localized modification of electrical and optical properties of such materials.

The dissertation presented herein is based on this investigation and composed of four parts. The first part gives a brief literature review of some basic concepts and principles of ion beam analysis, ion implantation processes, the resulted damage accumulation, the properties of sapphire, and the previous study results on iron implanted sapphire. Part two is devoted to the description of some experimental procedures and techniques that were used in this investigation. The third part contains experimental results and discussion, which include the test data, the interpretation of the tables and figures, the correlation between the material structure and properties and some suggested future work. The last part is the summary and conclusions on this study.

CHAPTER II

LITERATURE REVIEW

2.1 Concepts and Principle of Ion Beam Analysis

2.1.1 Ion-atom Interactions

Ion-atom interactions during implantation are controlled by many parameters including ion velocity, ion implantation energy, ion size, atom size, atomic number and mass, and distance of the closest approach [20]. To understand the ion-atom interactions and the controlling factors, the dynamic process when an ion approaches sample atoms in the ion implantation is analyzed as follows.

As an ion approaches the sample, the ion interacts with the atoms in the solid. These interactions slow down the energetic ion and perturb its trajectory. The ion quickly loses its energy during this process. If the implanted ion has the energy of a non-relativistic energy level, the total energy loss can be conveniently divided into two independent processes, namely, electronic stopping (inelastic ion-atom collisions) and nuclear stopping (elastic ion-atom collisions). Each process is energy dependent and makes different contributions to the total energy loss along the ion's path. The nuclear stopping usually dominates at lower implantation energy level, while the electronic stopping dominates at higher energy level. Both processes make significant contributions to the total energy loss in the region typically of interest for ion implantation. The nuclear stopping is important in determining ion implantation depth, displacement damage, and sputtering processes. The electronic stopping is important for excitation phenomena which result in secondary electron emission and can produce defects in the implanted insulator materials.

During the implantation process, ions also undergo some other interactions with the sample atoms such as large angle scattering, atomic displacements, sputtering, inner shell ionization, or nuclear reaction. The results of these interactions are also dependent on the energy of the ion. For low energy ions, observable interaction products include scattered ions, sputtered ions and atoms, displaced atoms and de-excitation products such as photons and electrons, while in the high energy regime, the major processes are inner shell ionization (X-ray emission), elastic scattering and nuclear reactions. When the ion loses its energy in nuclear collisions with target atoms, many atoms are displaced from their normal locations. Target atoms recoiling from these collisions can carry enough energy themselves to cause additional displacements -- sometimes producing a collision cascade which affects many atoms at a distance from the original ion path.

2.1.2 Depth Profiling

When ions are implanted into a material, they penetrate to certain depth in the near surface region to form a certain pattern of radiation damage and ion distribution. This pattern or distribution is highly dependent on the implantation energy and has great influence on the structures and properties of the implanted material. Usually, the stopping power is used to calculate the total path length of an ion or, in other words, the depth of implantation, and the distribution of radiation damage along the path or the distribution of the implanted ion. Analytical techniques based on transport equations and Monte Carlo techniques are used to give the depth profile of deposited damage energy and the initial distribution of defects. Generally, the projected range relative to the incident direction is of more interest, since it describes the spatial distribution of implanted ions relative to the surface.

The profile of deposited energy as a function of penetration depth x can be evaluated by using the commercialized TRIM92 program [21], which requires the input data such as the

atomic weights of the implanted ion and substrate material, ion beam implantation energy, incident angle etc., and produces the output data such as projected range, spatial distribution of the implanted ion, the mean range and straggling etc..

2.1.3 Physical Concepts of Backscattering Spectrometry

As discussed above, the penetration is dependent on the energy of the ions. When an ion is implanted, it loses its energy along its path. Therefore, to calculate the penetration depth, x , the energy loss of the implanted ion, ΔE , is measured, and the concepts such as the kinematic factor K and the energy loss factor or S factor need to be introduced. In the following paragraph, the introduction of these factors and the calculation of the penetration depth are discussed through the analysis of the backscattering process of an implanted ion.

Along the path of its penetration, an implanted ion inevitably collides with the atoms of the material. If an elastic collision is assumed, the simple elastic collision of two masses M_1 and M_2 can be solved fully by applying the principles of conservation of energy and momentum. The dynamic process of an elastic collision is represented with a schematic as shown in figure 2.1 [22]. In this figure, M_1 , v_0 , and E_0 are the atomic mass, velocity, and the energy of a projectile before the collision, respectively, M_2 is the mass of the target atom at rest. After the collision, the velocities of the projectile and the target atom become v_1 , v_2 and their energy levels become E_1 , E_2 , respectively.

From the conservation of energy, we have

$$\frac{1}{2} M_1 v_0^2 = \frac{1}{2} M_1 v_1^2 + \frac{1}{2} M_2 v_2^2 \quad (2.1)$$

From the conservation of momentum parallel and perpendicular to the direction of incidence, the following expressed equations can be obtained:

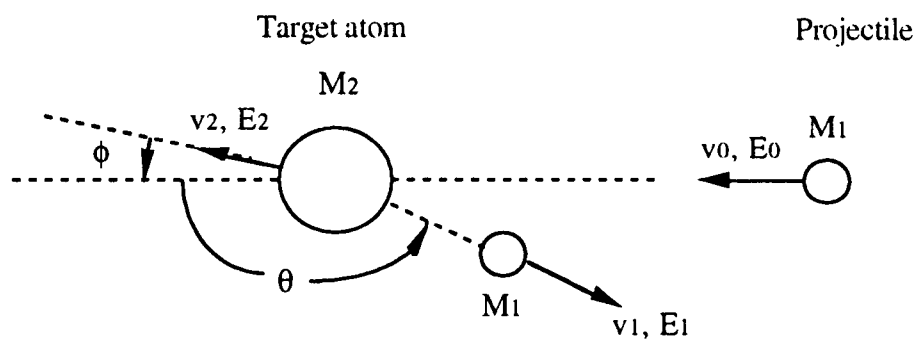


Figure 2.1 A schematic representation of an elastic collision [22].

$$M_1 v_0 = M_1 v_1 \cos \theta + M_2 v_2 \cos \phi \quad (2.2)$$

$$0 = M_1 v_1 \sin \theta - M_2 v_2 \sin \phi \quad (2.3)$$

Eliminating ϕ first and then v_2 , we have,

$$\frac{v_1}{v_0} = \frac{[\pm(M_2^2 - M_1^2 \sin^2 \theta)^{\frac{1}{2}} + M_1 \cos \theta]}{(M_2 + M_1)} \quad (2.4)$$

For $M_1 \ll M_2$, the plus sign holds. The ratio of the projectile energy after the elastic collision to that before the collision is now defined as the kinematic factor K,

$$K = E_1 / E_0 \quad (2.5)$$

From equation (2.4) we obtain

$$K_{M_2} = \left[\frac{(M_2^2 - M_1^2 \sin^2 \theta)^{\frac{1}{2}} + M_1 \cos \theta}{M_2 + M_1} \right]^2 \quad (2.6)$$

where, as a frequent practice, a subscript has been added to K to indicate the target mass M_2 for which the factor applies.

The energy E can be related to the length $x/\cos \theta_1$ of the incident path by

$$\frac{x}{\cos \theta_1} = - \int_{E_0}^E \frac{dE}{(dE/dx)} \quad (2.7)$$

where the negative sign arises because E is smaller than E_0 and dE/dx is taken as a positive quantity. Similarly, the path length $x/\cos\theta_2$ of the outward path is related to KE and E_1 by

$$\frac{x}{\cos\theta_2} = - \int_{KE}^{E_1} \frac{dE}{(dE/dx)} \quad (2.8)$$

If we assume a constant value for dE/dx along the inward and outward paths, the two integrals reduce to

$$E = E_0 - \frac{x}{\cos\theta_1} \frac{dE}{dx} \Big|_{in} \quad (2.9)$$

and

$$E_1 = KE - \frac{x}{\cos\theta_2} \frac{dE}{dx} \Big|_{out} \quad (2.10)$$

where the subscripts "in" and "out" refer to the constant values of dE/dx along the inward and outward paths. By eliminating E from these two equations, we have

$$KE_0 - E_1 = \left[\frac{K}{\cos\theta_1} \frac{dE}{dx} \Big|_{in} + \frac{1}{\cos\theta_2} \frac{dE}{dx} \Big|_{out} \right] \times x \quad (2.11)$$

The energy KE_0 is the edge of the backscattering spectrum and corresponds to the energy of particles scattered from atoms at the surface of the target. The energy E_1 is the measured value of a particle scattered from an atom at depth x . If we introduce the symbol ΔE for the energy difference between E_1 and KE_0 , i.e.,

$$\Delta E = KE_0 - E_1 \quad (2.12)$$

then we can write

$$\Delta E = [S] \times x \quad (2.13)$$

where

$$S = \frac{K}{\cos\theta_1} \left. \frac{dE}{dx} \right|_{in} + \frac{1}{\cos\theta_2} \left. \frac{dE}{dx} \right|_{out} \quad (2.14)$$

S is called the energy loss factor or S factor.

where

$$\left. \frac{dE}{dx} \right|_{in} = \left. \frac{dE}{dx} \right|_{E_0} \quad \text{and} \quad \left. \frac{dE}{dx} \right|_{out} = \left. \frac{dE}{dx} \right|_{KE}$$

These two parameters can be obtained from a sixth order semi-empirical stopping power equation with different sets of constants for different elements or compounds. K values for each element are listed in reference [23], and θ_1 and θ_2 are entry and exit angle respectively measured in the experiment.

Therefore, with known S for each element and the energy loss measured via backscattering spectrometry, the estimated impurities and lattice damage depth distribution could be computed using equation (2.13).

2.2 Ion Implantation Process and Damage Accumulation

The ion implantation process consists of bombarding the surface of a material in a vacuum chamber by an electrostatically accelerated beam of ions. The ions become embedded to a depth controlled by the incident ion energy for a given ion-target material combination. The range of the embedded depth is generally less than one micrometer. The ions come to rest by dissipating their kinetic energy in elastic collisions that displace target atoms (ions) from their normal lattice sites and by inelastic processes that may ionize target atoms. Large number of defects are produced before the ions come to rest as an impurity, dopant, or alloying element. The basic processes which directly result from ion bombardment are illustrated schematically in figure 2.2 [1].

In an insulator, elastic or nuclear collisions are dominant damage processes. For oxide materials, electronic processes can lead to changes in the charge state of dilute impurities such as Fe or Mn, but elastic or nuclear collisions are the dominant processes for producing vacancy-interstitial pairs. The displacement energies for aluminum and oxygen in Al_2O_3 are 18 and 72 eV respectively [24]. It is not clear whether this difference results in different rates of defect production in the two sublattices during ion implantation. Most studies of ion implantation damage suggest that the residual damage is stoichiometric in nature; that is, there are two Al displacements and three oxygen displacements. Pells and Stathopoulos [25] have observed stoichiometric dislocation loops that were faulted with respect to the cation sublattice after bombarding at high temperatures with electrons that had sufficient energy to displace aluminum ions but not enough to displace oxygen ions. The implanted cations are associated with point-defect configurations or segregate to form neutral metallic clusters.

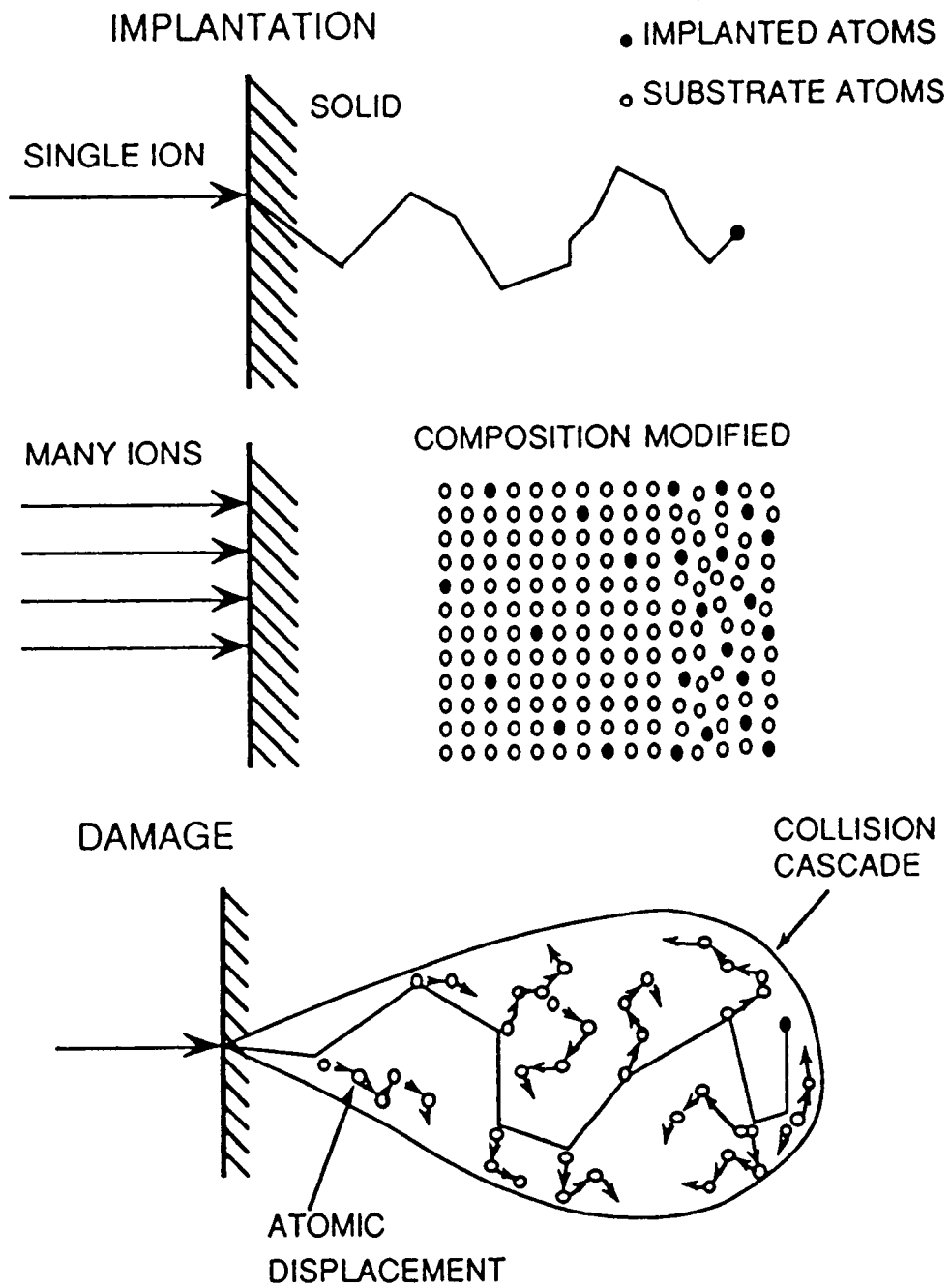


Figure 2.2. Schematic of ion implantation processes [1]

2.3 Previous Research Results on Iron Implanted Sapphire

Many research projects have been conducted in recent years on heavy metal implantation of insulating materials as a means of altering the mechanical, physical or chemical surface-related properties. Reference [13] reviewed the study of ion implantation and the following annealing of some crystalline oxides. The structure-property relationships in surface modified ceramics were given by reference [12]. In particular, the recent research results on iron implanted α -Al₂O₃ were presented in paper [16] and [17]. Results from the previous work are summarized as follows:

2.3.1 Sapphire Characterization

Sapphire (α -Al₂O₃) is routinely grown as relatively pure single crystals containing less than 10 ppm of impurities. The overall properties of α -Al₂O₃ from reference [26] etc. are given in table 2.1.

2.3.2 Microstructural and Chemical Characterization of Iron Implanted α -Al₂O₃

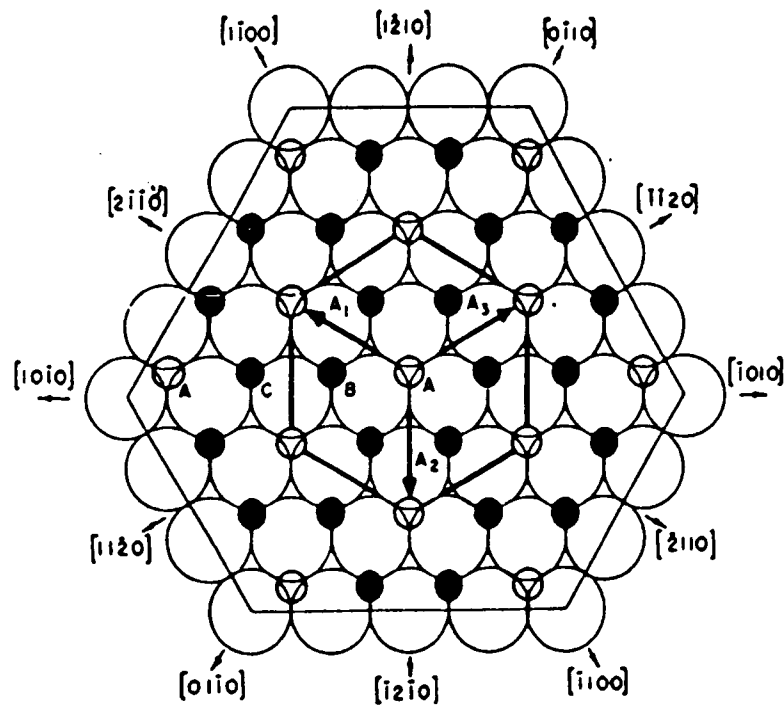
To understand the microstructural and chemical characteristics of iron implanted α -Al₂O₃, Rutherford backscattering (RBS)-ion channeling, transmission electron microscopy (TEM), and conversion electron Mössbauer spectroscopy (CEMS) were used to determine the structure of α -Al₂O₃ implanted with iron at room temperature. The preliminary observations are summarized as follows:

- Implantation of 160 keV Fe at room temperature produces a crystalline but damaged microstructure for fluences as high as 1×10^{17} Fe/cm².

Table 2.1 Properties of sapphire (α -Al₂O₃)

Structure	The lattice structure of sapphire is rhombohedral, and belongs to the space group $R\bar{3}c = D_3^6d$. The O ²⁻ anions are approximately hexagonal close-packed, and the Al ³⁺ cations are ordered, occupying 2/3 of the available octahedral sites (Figure 2.3 (a) and (b) [27]). Crystallographic and electron diffraction data for sapphire are presented by Lee et al [28] Dislocations are also observed as impurity-defect complexes [29].			
Applications	Generally used for structural and electrical applications			
Thermal and Mechanical Properties	Because of a strong bond strength between the Al and O ion, as expected from the value of heat of formation (400 Kcal/mol), α -Al ₂ O ₃ has outstanding physical stability, such as a high melting point (2050°C), the highest hardness among oxides, and high mechanical strength.			
	Modulus of Elasticity (GPa) 434 or from [30] (a-axis=403) (c-axis=499)	Poisson's ratio [31] 0.234	Hardness (GPa) [30] 30	Thermal Conductivity 0.43
Electrical Properties	Electrically insulating: the volume resistivity of high-purity ceramics with a low alkali concentration is more than 10 ¹⁵ Ω cm at room temperature.			
Optical Properties	Refractive index of 1.876. The principal point defects observed in α -Al ₂ O ₃ 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) [19]. Oxygen divacancy centers are also observed.			
Chemical Properties	Chemically stable and has high corrosion resistance. It is insoluble in water and very slightly soluble in strong acid and alkaline solution. It can be colored by the addition of impurities, thermal reduction, energetic electron, and neutron or ion beam irradiation.			

a



b

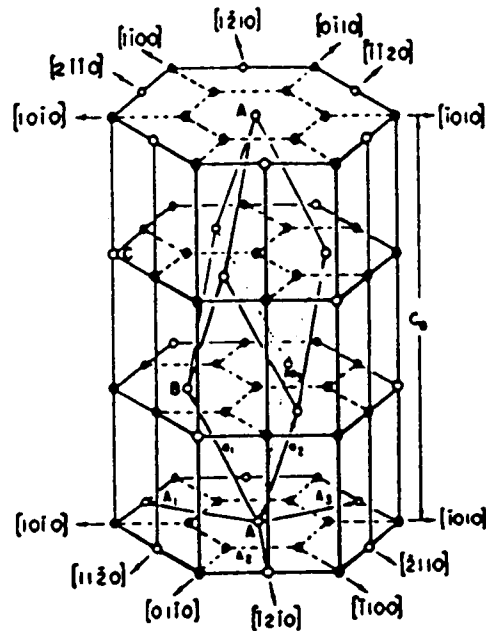


Figure 2.3 Schematic of the unit cell of sapphire. (a) Unit hexagonal lattice vectors in the basal plane. Large open circles represent underlying oxide ions, small open circles represent holes, and small filled circles represent aluminum ions. (b) Distribution of aluminum ions and holes on the simple hexagonal lattice [27].

- The iron resides in various local environments: three Fe^{2+} components, one Fe^0 component, and two Fe^{4+} components. Mössbauer parameters for components obtained by computer fitting of spectra taken at room temperature for $\alpha\text{-Al}_2\text{O}_3$ implanted with ^{57}Fe at room temperature are given in table 2.2,

where, IS = Isomer shift (mm/s)

QS = Quadruple splitting (mm/s)

W = Line width (mm/s)

R = Relative area.

- Mössbauer hyperfine parameters of components in CEMS spectra for samples implanted with $7 \times 10^{16} \text{ Fe/cm}^2$ and annealed for 1 h in Ar-4% H_2 are summarized in table 2.3,

where, HF = Magnetic Hyperfine Field (KOe)

A_2/A_1 = Relative areas of lines in sextet.

- Recovery of implantation-induced disorder in the Al- and O- are in one continuous stage for hydrogen-annealing. The end state for iron is Fe^{3+} for oxygen anneals and Fe^0 for hydrogen anneals. The precipitated phases observed are those to be expected from the equilibrium phase diagrams.

2.3.3 Optical Absorption, Luminescence and Electron Paramagnetic Resonance (EPR)

In general, cation impurities tend to form precipitates preferentially at strained regions in the oxides [19]. When oxide samples are heated in a reducing atmosphere, transition-metal impurity segregate and precipitate along dislocations and grain boundaries to form metallic precipitates, a process referred to as decoration. Optical measurements are useful in that the colloids give rise to characteristically broad extinction bands, attributed to Mie scattering [32]. Moreover, optical absorption and, especially, the luminescence technique have the unique features of highly sensitivity. Low concentrations of defects can be

Table 2.2 Mössbauer parameter for components for α -Al₂O₃ implanted with ⁵⁷Fe at room temperature (160 keV) [16].

Component		Fluence, ions/cm ²							
		10 ¹⁶	2 x 10 ¹⁶	3 x 10 ¹⁶	4 x 10 ¹⁶	5 x 10 ¹⁶	7 x 10 ¹⁶	10 x 10 ¹⁶	
Fe ²⁺ _{III}	IS	0.71	0.66	0.61	0.63	0.59			
	QS	1.90	1.86	1.92	1.95	1.88			
	W	0.63	0.63	0.60	0.55	0.58			
	R	0.45	0.56	0.39	0.33	0.16			
Fe ²⁺ _{II}	IS	1.07	1.18	1.20	1.12	1.30	1.38	1.45	
	QS	2.03	1.92	1.90	1.97	1.78	1.40	1.40	
	W	0.52	0.48	0.45	0.53	0.44	0.60	0.60	
	R	0.31	0.18	0.15	0.27	0.12	0.17	0.19	
Fe ²⁺ _I	IS	1.00	1.23	1.26	1.28	1.28	1.06	1.07	
	QS	1.04	1.30	1.22	1.19	1.16	1.18	1.28	
	W	0.44	0.53	0.56	0.61	0.64	0.67	0.72	
	R	0.23	0.21	0.24	0.22	0.28	0.24	0.18	
Fe ⁰	IS		0.00	-0.06	-0.10	-0.13	-0.15	-0.12	
	W		0.29	0.57	0.70	0.43	0.40	0.46	
	R		0.05	0.22	0.18	0.19	0.21	0.36	
Fe ⁴⁺ _{II}	IS					-0.12	-0.15	-0.10	
	QS					0.38	0.42	0.36	
	W					0.35	0.38	0.29	
	R					0.19	0.30	0.16	
Fe ⁴⁺ _I	IS					-0.12	0.00	-0.17	
	QS					0.70	0.51	0.65	
	W					0.34	0.30	0.36	
	R					0.06	0.08	0.11	

Table 2.3 Mössbauer parameter for components in CEMS spectra for α -Al₂O₃ implanted with 7×10^{16} ⁵⁷Fe/cm² at room temperature and annealed for 1 h in Ar-4%H[16].

Component		Annealing temperature				
		As- implanted	700°C	900°C	1100°C	4 x10 ¹⁶ , 1500°C
Fe ²⁺ _{II}	IS	1.38	1.10			
	QS	1.40	1.40			
	W	0.60	0.79			
	R	0.17	0.12			
Fe ²⁺ _I	IS	1.06	0.69			
	QS	1.18	0.66			
	W	0.67	0.73			
	R	0.24	0.15			
Fe ⁴⁺ _{II}	IS	-0.15				
	QS	0.42				
	W	0.38				
	R	0.30				
Fe ⁴⁺ _I	IS	0.00				
	QS	0.51				
	W	0.30				
	R	0.08				
Fe ⁰	IS	-0.15	-0.06	-0.05	-0.04	
	W	0.40	0.41	0.29	0.26	
	R	0.21	0.60	0.56	0.02	
Fe ³⁺	IS		0.33	0.36	0.35	
	QS		0.52	0.52	0.79	
	W		0.46	0.36	0.72	
	R		0.13	0.11	0.07	
α-Fe	IS			0.01	0.02	0.00
	HF			330	330	330
	W			0.29	0.27	0.33
	A ₂ /A ₁			1.33	1.06	1.33
	R			0.23	0.91	1.00

detected by using these methods. A model that assigns absorption and luminescence bands to specific charge states of anion divacancies has been proposed for neutron-irradiated sapphire [33]. The absorption and emission bands associated with single anion vacancies are given in references [34-37]. The absorption and emission bands associated with specific lattice defects for α -Al₂O₃ are plotted from the data of references [34-36, 38] and shown in figure 2.4.

Some recent work was reported for a study of point defects produced by 3.8 MeV Fe²⁺ ions at fluences of 0.5×10^{16} and 2×10^{16} cm⁻² in α -Al₂O₃ [39]. The experimental results are summarized as follows:

- The predominant defect was the F center, identified by an absorption peak at 6.2 eV (200 nm). F⁺ (absorbs at 4.8 eV or 260 nm) and F₂ centers were also present, identified by luminescence and, in the case of the paramagnetic F⁺ center, also by EPR, but in concentrations not detectable by optical absorption.

2.3.4 Mechanical Property Measurements and Analyses

Many attempts have been made over the past years to determine thin film and near-surface mechanical properties. The desire to improve the near-surface mechanical properties is one of the main driving forces for the study of ion beam implanted insulators [40,41]. Since the implanted layer is very thin, approximately a few tenths of a micron thick, conventional techniques for mechanical property measurements can not meet these requirements, and new testing techniques are needed to perform the characterization on very small scales.

A mechanical property microprobe (MPM) method has been developed to determine thin films and near-surface properties [42]. To introduce this technique, several examples of the testing procedures and results of MPM studies on thin films including implanted sapphire were presented. Based on this technique, an improved method for determining

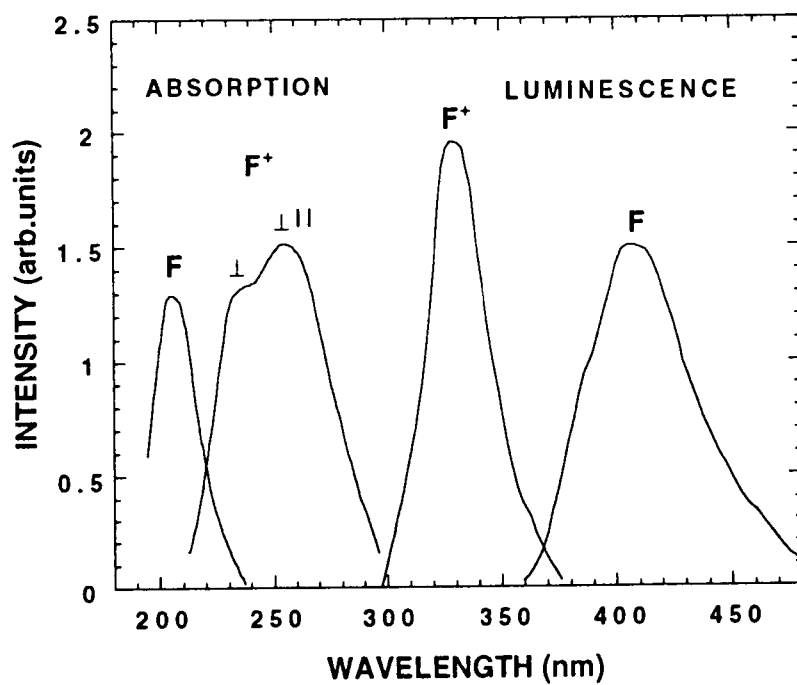
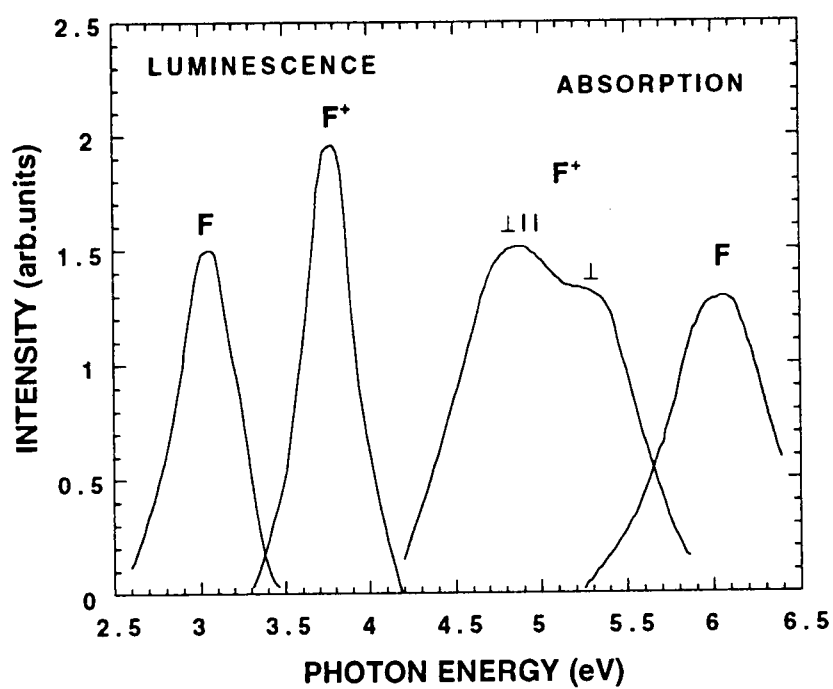


Figure 2.4 Absorption and emission bands associated with specific lattice defects.

hardness and elastic modulus using load and displacement sensing indentation experiments was established [30]. Values of the hardness and elastic modulus of six materials including sapphire were calculated using this analysis technique and compared with the values determined by independent means to access the accuracy of the method.

Moreover, several empirical models have been proposed to estimate the hardness or modulus values of thin films over the past years. The simplest technique was presented by Jonsson [43]. Hardness values of thin films which are too thin for direct microhardness measurements can be generated using this geometrical model. Given the film thickness t , the film hardness H_f can be solved directly after recording the composite hardness H_c and substrate hardness H_s at a given indentation depth D (or diagonal d) using the derived expression as follows:

$$H_f = H_s + \frac{H_c - H_s}{2Ct / D - C^2 (t / D)^2} \quad (2.15)$$

where, C = constant determined by the geometry of the film deformation;

$C = \sin^2 22^\circ$ for a thin film on a hard substrate,

$C = 2\sin^2 11^\circ$ for a hard or brittle film on a soft substrate.

A successful application of this technique requires:

- 1) a known film thickness greater than 200 nm.
- 2) a knowledge of the composite hardness.
- 3) a knowledge of the substrate hardness as measured at the same impression size as that of the composites.
- 4) diagonal $d > 7t$ (film thickness), for the best agreement between the experimental and calculated data.

Another empirical approach first proposed by Sargent [44] and then modified by Burnett [45,46] is called the law of mixtures. It applies to a soft layer on a harder substrate in order to predict the hardness variations arising from differing layer thicknesses and different indentation sizes. The effective hardness can be expressed as the contribution from both the film and the substrate hardness values:

$$H_{\text{effective}} = \frac{H_s V_s + H_f V_f}{V_s + V_f} \quad (2.16)$$

where, $H_{\text{effective}}$ = the resultant hardness
 H_s = substrate hardness value
 H_f = surface-layer/film hardness value
 V_s = deforming volumes of the substrate
 V_f = deforming volumes of the layer

H_s and H_f can be expressed as:

$$H_s = c d^{m-2} \quad (2.17a)$$

$$H_f = c' d^{m'-2} \quad (2.17b)$$

where, c, c' = constants
 m, m' = indentation size effect (ISE) index (e.g. $m=2$ when no ISE)
 d = indentation diagonal.

An even better fit is found by further incorporation of an empirical factor $V_s/(V_s+V_f)$ into the term of H_s to emphasize the substrate hardness, i.e.,

$$H_s V_s = c d^{m-2} \frac{V_s^2}{V_s + V_f} \quad (2.18)$$

Then the effective hardness can be given by:

$$H_{\text{effective}} = c d^{m-2} \frac{V_s^2}{(V_s + V_f)^2} + c' d^{m'-2} \frac{V_s}{(V_s + V_f)} \quad (2.19)$$

A third empirical model was given by Bhattacharya and Nix [47]. They have shown that the dependence of hardness and modulus on depth-of-penetration for a soft film on a hard substrate can be described by the equations of the form:

$$H_m = H_s + (H_f - H_s) \exp(-C h_c^2) \quad (2.20a)$$

$$E_m = E_s + (E_f - E_s) \exp(-C h_c^2) \quad (2.20b)$$

where, H_m = measured hardness

H_s = substrate hardness

H_f = film hardness

E_m = measured modulus

E_s = substrate modulus

E_f = film modulus

h_c = depth of the indent

C = a constant that is dependent on the film thickness and the relative properties of the film and substrate.

A nonlinear least-square analysis using the above equations was successfully used for lead implanted zircon [48] to determine the parameter C, film hardness and modulus values.

The study of elastic modulus of two-phase system has also been proposed for many cases where a dispersed phase has the dimensions of several micrometers [49]. In two-phase systems the overall modulus is intermediate between the high- and low-modulus components. An exact treatment of the problem requires specification of the mutual interaction of many second-phase inclusions. Such a treatment has not been effected, but a number of upper and lower bounds on the elastic moduli have been evaluated. The widest possible bounds are found by Voigt. This model assumes that the strain in each constituent is the same, whence the Young's modulus E_U of the composite becomes

$$E_U = V_2 E_2 + (1 - V_2) E_1 \quad (2.21)$$

where V_2 is the volume fraction of the phase with modulus E_2 , and E_1 is the modulus of the other phase. In this case, most of the applied stress is carried by the high-modulus phase.

The second (Reuss) model assumes that the stress in each phase is the same, whence the modulus of the composite E_L is

$$\frac{1}{E_L} = \frac{V_2}{E_2} + \frac{(1 - V_2)}{E_1} \quad (2.22)$$

The designation E_U and E_L indicate, respectively, the upper and lower bounds on the elastic moduli.

Therefore, after we obtained the elastic modulus of virgin sapphire using nanoindenter measurement, together with the volume fraction of the precipitates (α -Fe) from CEMS,

and the elastic modulus of α -Fe from literature, the upper and lower bounds of the elastic moduli can be calculated to compare with the measured composite modulus value.

Some other approaches such as exponential or smooth curve fitting by directly extrapolate the plot of hardness or modulus data versus contact depth to zero contact depth are also worth trying.

Previous mechanical property results (hardness and elastic modulus) measured on Cr or (Al + O) implanted sapphire suggested that a slight increase in hardness occurred with increasing ion fluence. The elastic modulus did not change for conditions which preserved the crystalline state. Both hardness and elastic modulus for the amorphous Al_2O_3 were significantly lower than for the crystalline Al_2O_3 [50].

There appears to be no previous study of the mechanical properties of ceramics containing nanometer size dispersions.

CHAPTER III

EXPERIMENTAL PROCEDURES AND TECHNIQUES

Since the purpose of this investigation is to systematically study the iron implanted sapphire nanocomposites and explore their potential applications in high technology areas, the iron implanted sapphire nanocomposite samples were prepared with parameters covering a wide ranges of conditions. The samples were prepared with three different implantation fluences and four different post-implant heat treatment temperatures. Then, these samples were characterized with Rutherford Backscattering Spectrometry (RBS) and Analytical Electron Microscopy (AEM) to reveal their microstructures and the relationships between the microstructures and the sample preparation conditions, and thus, provide a basis for an in-depth understanding of the properties of the material. Meanwhile, the electrical, optical and mechanical properties of the samples were studied to explore the potential applications of the material.

3.1 Ion Beam Implantation and Post-Implant Heat Treatment

High purity single crystal sapphire (α -Al₂O₃) disks (c-axis oriented) were used as matrix for ion beam implantation. These matrix discs were supplied with an optical-grade polish by the manufacturer (Crystal Systems, inc., Bedford, MA). Prior to implantation, they were ultrasonically cleaned, first in Micro® cleaning solution, followed by acetone and then ethanol and finally rinsed in distilled water. After that, they were annealed at 1350°C in flowing air for 120 hours to remove residual polishing damage and organic contamination of the surface.

The substrate specimens were implanted with 160 keV ^{56}Fe ions at fluences of 4×10^{16} , 1×10^{17} , 2×10^{17} Fe/cm² at room temperature in the Surface Modification and Characterization Research Center of Oak Ridge National Laboratory. The implantation was performed with the ion beam approximately 7° off-normal to minimize channeling effects. The as-implanted samples with each fluence level were then annealed for 1 hour in a mixture of Ar-4% H_2 atmosphere at 700, 900, 1100, and 1400°C respectively.

The TRIM92 program was employed in this investigation to approximate depth profile before implantation. With the ion beam implantation energy of 160 keV, TRIM92 calculations showed that the mean range, R_p , had a value of 759 Å, while the straggling, ΔR_p , had a value of 237 Å.

3.2 Microstructure Characterization

3.2.1 Rutherford Backscattering Spectrometry (RBS)

Rutherford Backscattering Spectrometry is an analytical method to determine the concentrations of various impurity elements as a function of depth beneath the surface of a sample. When RBS is employed to determine the profile of an element in the near surface region, the concentration of the element as a function of depth is detected by measuring the energy spectrum of the probe ions which are back-scattered from a beam directed at the surface [22].

The basic principle of RBS can be explained as follows: Typically when light ions of H^+ , He^+ or N^+ at 1-2 MeV are fired at a target, most ions lose their energy by electronic excitation and become only slightly deviated, however, a few ions will suffer direct nuclear collisions and elastic recoil. These reflected ions can be detected with an energy-sensitive detector such as a silicon barrier detector. The resultant charge pulse due to these reflected ions is proportional to the ion energy. The various pulses are sorted via a multi-channel

analyzer and hence an energy spectrum of the reflected particles is derived. Usually, in a real RBS analysis, the geometry of the measurement has a deflection angle of 150° or 170° , and approximately 10^{-6} of the incident ions are reflected.

When the materials investigated are single crystals, another phenomenon, the channeling of incident ions, can provide useful information in addition to the ion backscattering. In the case of a single-crystalline sample, the incident ions should easily penetrate the sample through the interstitial channels among the well-aligned lattice atoms. This is called the channeling effect. Since the channeling effect greatly depends on the alignment of the incident beam with the lattice direction of the single crystal, it produces strikingly large changes in the yield of back scattered particles as the orientation of the single-crystalline target is changed with respect to the incident beam. Channeling effect measurements have had three major applications in backscattering analysis:

1. Amount and depth distribution of lattice disorder.
2. Location of impurity atoms in the lattice sites.
3. Composition and thickness of amorphous surface layers.

Figure 3.1 shows schematically the interactions that take place when an incident beam of MeV He^{++} ions is aligned with a low-index axial direction of the single crystal. The shaded part represents the magnitude of the yield in the aligned spectrum.

In this investigation, Rutherford backscattering and ion channeling measurements were performed via Van De Graaff generator located at the Surface Modification and Characterization Research Center of Oak Ridge National Laboratory. All the measurements were conducted with a beam of 2.0 MeV He^{++} at near-normal incidence to the sample surface and scattering into a surface-barrier detector at 160° . The ion channeling spectra were obtained with the beam aligned along the c-axis, while in the case of random spectra,

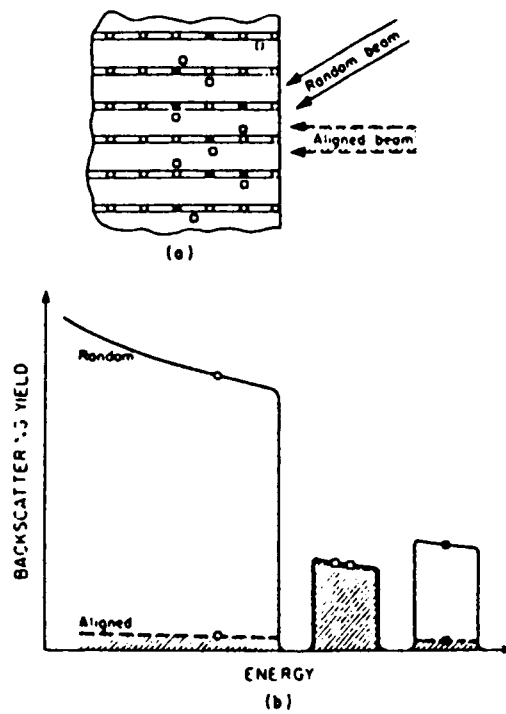


Figure 3.1 (a) Schematic and (b) backscattering spectra for random and aligned beams for MeV He^{++} ions incident on a crystal containing heavy impurities in the near-surface region. Substitutional site ($\bullet$), interstitial sites (o) and host lattice atoms(") [22]

the spectra were obtained by rotating the sample off axis. Both random and channeling RBS technique were performed on the as-implanted and post-implantation thermal annealed samples to show the microstructure changes of the matrix materials and variations in the amount and depth profiles of implanted iron atoms.

3.2.2 Analytical Electron Microscopy (AEM)

The microstructure investigation was carried out primarily to determine the distribution profiles of implanted impurities, the damage in the single crystal matrix caused by the ion-implantation, and the effects of annealing on the recovery of the damage and the re-distribution of implanted impurities.

The microstructural characterizations were mainly conducted on two modern transmission electron microscopes (TEM), i.e., a JEOL 2000FX analytical TEM and a Hitachi HF-2000 field-emission transmission electron microscope (FE-TEM). The JEOL 2000FX analytical TEM was utilized for the general studies, while the recently introduced Hitachi HF-2000 FE-TEM operating at 200 kV was utilized for the more advanced TEM specimen observations. This facility has the advantages of having high resolution images and an ultra-fine X-ray probe (about 1 nm) for energy dispersive spectroscopy (EDS) analysis, which are highly desirable for the present investigation.

In the Hitachi HF 2000 FE-TEM, the electron beam is generated from an electron gun consisting of a pointed cathode and two anodes [51]. The cathode is tungsten single crystal with its tip polished to 100 nm radius of curvature. Electrons are emitted from a $\langle 310 \rangle$ oriented tungsten tip when a high voltage (V_1) is applied across the cathode and the first anode. Another high voltage (V_2) is applied across the cathode and the second anode. The first and second anode voltages (V_1 and V_2) constitute an electrostatic lens which focuses the electrons and forms a beam having an apparent ("virtual") source about 3 nm in diameter. The cold field-emission electron source is built in a compact gun, maintained at a

vacuum of the order of 10^{-11} torr to ensure stable operation. In the HF 2000 FE-TEM, the electron beam is accelerated in a 6-stage ceramic accelerator up to 200 keV. The cold field-emission electron gun yields a brightness of approximately 7×10^8 amps/cm²/sr. The actual illuminating optics composed of a pair of condenser lenses and a condenser-objective lens forms a demagnified image of the condenser aperture at the specimen plane, filling a small beam area with nearly parallel illumination, i.e., for an illuminated area 2 nm in diameter the effective total illumination angle is measured to be 5 micro-rads. The objective lens has a spherical aberration coefficient $C_s = 1.2$ mm and chromatic aberration coefficient $C_c = 1.49$ mm. By a combination of intermediate lenses and projection lenses at suitable excitations the magnification of the image could be varied from 50x to 1,500,000x.

Cross-sectioned TEM specimens [52] are particularly well suited to the study of near surface details since they make it possible to determine the depth dependence of the composition and microstructural features. However, the preparation of such single crystal ceramic specimens is extremely difficult because of the brittle nature and small size of the specimens. In this study, a modified technique for preparing cross-sectioned TEM specimens of brittle single crystals was developed, which minimized cracking during the thinning processes, and is illustrated in figure 3.2. In this new method, two pieces of 1 x 2 x 6 mm slices of the ion-implanted single crystal sapphire were mechanically cut from the implanted specimens by using a diamond saw lubricated with lapping oil, then, the two slices were glued with the implanted surfaces face-to-face using M-bond type 610 adhesive epoxy to form a sandwich shaped specimen. The freshly glued cross sections were squeezed in a vise so that the glue thickness was minimized. The epoxy was allowed to cure by leaving the glued specimen at 80°C in an oven overnight. After a strongly bonded interface was formed between the glued implanted surfaces, the glued specimen was sliced perpendicularly to the glued interface, resulting in a specimen with a thickness of approximately 400-500 μ m. Then, one side of this specimen was mechanically polished

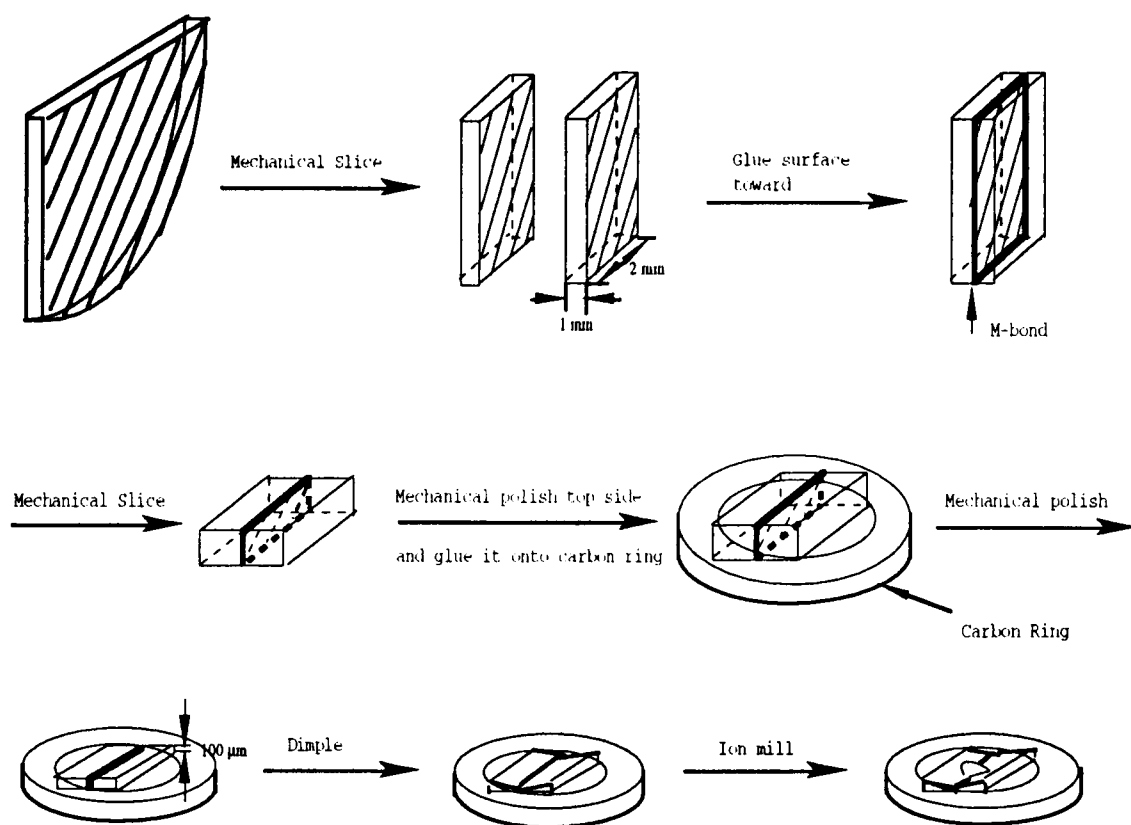


Figure 3.2 A schematic diagram illustrating the steps of the cross-sectioned TEM sample preparation.

with 6 μm followed by 3 μm diamond pastes. To minimize possible rupture caused by the crack initiation during subsequent processes, and also to help fit the sample into the TEM sample holder, the polished side was glued onto a carbon ring. With the carbon ring glued on one side, the specimen was ground on the other side to a thickness of 100 μm by using 6 μm diamond paste, and then dimpled to a thickness of approximately 20-25 μm . The last polishing process was conducted with 1 μm diamond paste. The final step in this preparation process was to reduce the thickness of the specimen at an atomic scale until a small hole at the interface could barely be observed with naked eyes. This was accomplished on an ion mill machine by taking off atom layers with ion beams to form the hole. The edge of the hole consisted of two ion implanted surfaces. Because it was very thin and electron-transparent, it provided the area for TEM observation.

Because this specimen was a typical insulator, it had the problems associated with most insulators when subjected to SEM and TEM observations. Usually, insulating specimens in electron microscopy tend to build up an electron charge under exposure to the electron beam. This trend causes distortion of the image, and in many cases a reflection of the incident electrons from the highly charged surface. Observations can become very difficult or even impossible when this happens. To overcome the charging effect, insulator samples need to be coated with a thin layer of a conducting material to drain away the surface charge which would otherwise accumulate. In this investigation, carbon was used to form the conducting thin layer because it has a low atomic number and causes little interference with the image or with X-ray analysis [21]. The coating was deposited by leaving the ion-milled specimens in a carbon atmosphere produced with an electrical arc between two carbon electrodes in a vacuum container. The coating thickness was controlled by adjusting the coating time and current.

3.3 Property Characterization

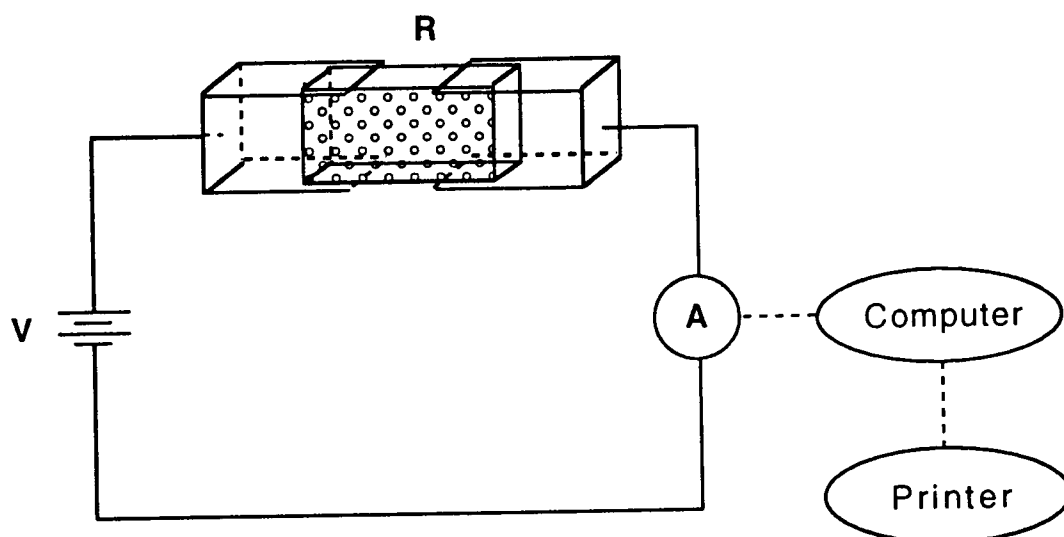
3.3.1 Electrical Property Measurements

The effect of iron implantation on the electrical conductivity in sapphire has attracted great interest in the electronic engineering industry because the improved electrical conductivity of the sapphire induced by ion implantation provides great potentials for sensor applications. A previous study of Nb implanted sapphire indicated that the electrical conductivity of the implanted samples was several orders of magnitude greater than that of the virgin sample [18]. The current study attempted to use the same experimental technique to determine the metallic precipitates might cause similar increase in the conductivity.

Since the electrical resistance of sapphire is extremely high, regular Volt-Ohmmeters can not be employed to measure its electrical conductivity with satisfactory accuracy. Under such circumstances, a method using the electrical field theory is usually employed to obtain accurate electrical properties of elements with high resistance in a DC electrical circuit [53]. In this method, the electric field is used for surface integration in order to determine the current between electrodes in terms of electric field intensity. Several devices, including the Wheatstone bridge, voltage divider, RC circuit and electrometer, have been used to measure the current of high-resistance materials.

The system employed for measuring the resistivity of ion-implanted sapphire specimen in this investigation is shown in figure 3.3. It consisted of the measured specimen, two electrodes, a Keithley Model 247 high voltage and high stability DC power supply, a Keithley Model 617 high accuracy multi-use electrometer, a computer and a printer. The Keithley Model 617 programmable electrometer was specifically designed to interface the computer for multiple data collection.

Because the resistivity of a high resistance material is very sensitive to its surroundings [54] such as temperature, moisture, light and electrical field, measurements have to be



V: High voltage power supply (Keithley Model 247)

R: Sample and sample holder.

Note that the shaded area refers to the implantation surface

A: Multi-use electrometer (Keithley Model 617)

Figure 3.3 Schematic illustration of the electrical circuit for measuring the resistivity of the ion implanted insulating specimens

taken to minimize the possible effects of these factors on the results. In this investigation, a closed sample test chamber was employed to strictly control the temperature and relative humidity. The temperature in this sample chamber was controlled by immersing the entire chamber in a large container filled with water whose temperature was maintained constant with an immersion heater. The actual ambient temperature was kept at 22°C with the chamber temperature of 27°C and surrounding water at 25°C. The relative humidity around the specimen was kept constant by using a sulfuric solution on the bottom of the chamber [54,55]. In order to monitor the temperature and humidity, several transducers were placed inside the sample chamber. After the equilibrium condition was reached, the temperature and humidity could be controlled in the range of $\pm 0.1^\circ\text{C}$ and $\pm 0.5\%$ R.H., respectively.

To shield the apparatus from external electrical field interference described by the Gauss's law, the entire chamber was covered by metal which functioned as a Faraday cage, and all the connections in the system were using coaxial cable for transmission shielding. The metal lip could also be used as the light controller.

In this investigation, sapphire specimens in three different material conditions were examined. All the specimens examined had a rectangular shape with a size of 38 x 5 x 2.5 mm. The three materials were the virgin sapphire, sapphire implanted with 2×10^{17} Fe/cm² and sapphire implanted with 2×10^{17} Fe/cm² followed by annealing at a temperature of 1000°C for 1 hour in a reducing atmosphere. In addition to the normal relative humidity measurements, the one which was annealed was also examined at low relative humidity condition. The normal relative humidity had a value of approximate 67% and the low relative humidity had a value of near 0%.

In each measurement, the specimen was first mounted on the electric circuit and then subjected to a voltage ranging from 100 to 1000 volts at room temperature, and when an essentially equilibrium condition was reached after approximately 72 to 120 hours, the system was ready for the computer to collect data. Electric current was measured one time

every ten minutes for a period of 1000 minutes. To exclude any other possible affecting factors, it was observed that the disturbance of light and electric field didn't show any significant effects on the measurements.

In order to compare the electrical properties of the specimens in different material conditions, the bulk and the regional properties need to be determined respectively. For the bulk property, the average electric current which represents the total current through a bulk specimen was determined and converted into the current by a specific applied voltage. For the regional property, the electrical resistivities of the matrix sapphire and the ion-implanted sapphire surface layer were estimated separately. When a specimen was inserted into the measuring system, it was assumed that the matrix sapphire and the ion-implanted sapphire surface layer had resistance values of R_1 and R_2 , respectively, and the equivalent circuit of the specimen was a typical parallel circuit as shown in figure 3.4.

The relationship among the applied voltage, the average current and the resistance is:

$$R = \frac{U}{I} = \frac{R_1 * R_2}{R_1 + R_2} \quad (3.1)$$

where, R = average resistance (Ω)

U = applied voltage (V)

I = average electrical current (A)

Since the resistance of each part could be determined from its resistance and geometry as:

$$R_i = \rho_i \frac{L_i}{A_i} \quad (3.2)$$

where, i = subscript representing 1 or 2.

ρ_i = resistivity of part i (the matrix or the layer) (Ωcm)

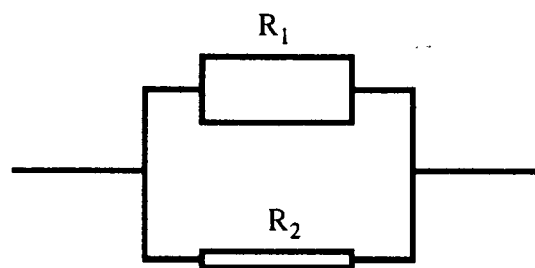


Figure 3.4 The equivalent electrical circuit for estimating the resistivities of the matrix sapphire and the ion-implanted sapphire surface layer.

A_i = cross-sectional area of part i given by the multiplication of width and thickness (cm^2)

L_i = length of specimen (cm)

Because the resistance and thus the resistivity of the matrix sapphire could be obtained from the virgin sapphire, and since the matrix and the ion-implanted sapphire surface layer had the same length and width but different thicknesses, the resistivity of the ion-implanted sapphire surface layer was estimated by substituting equation (3.2) into (3.1) such that:

$$\rho_2 = \frac{UW\rho_1 t_2}{(IL\rho_1 - UWt_1)} \quad (3.3)$$

where, ρ_1 = resistivity of the unimplanted matrix (Ωcm)

ρ_2 = resistivity of the ion-implanted sapphire surface layer (Ωcm)

W = width of the specimen (cm)

L = length of the specimen (cm)

t_1 = thickness of the unimplanted matrix (cm)

t_2 = thickness of the ion-implanted sapphire surface layer (cm)

3.3.2 Optical Property Measurements

The radiation damage produced by the implantation was investigated using optical absorption and luminescence techniques. Previous research showed the presence of point defects, predominantly in F centers, generated by implantation of 3.8 MeV with fluences ranged from 0.5×10^{16} to 2×10^{16} Fe/ cm^2 in $\alpha\text{-Al}_2\text{O}_3$ [39]. The current study attempted to verify the argument proposed by McHargue [16] that the presence of Fe^{2+} in Mössbauer spectra was due to the formation of iron-vacancy complexes to preserve the electro-neutrality, and the calculation made by Catlow et al. [56] that the most energetically

favorable configuration for a 2+ impurity in α -Al₂O₃ is the complex of Fe²⁺ -- oxygen vacancy -- Fe²⁺.

Using absorption technique, optical properties were determined by measuring the optical absorption as a function of wavelength. Different wavelength ranges were employed to measure specimens, held at 25°C, with a Perkins-Elmer lambda 9 spectrophotometer in the uv, visible, and infrared range.

Using luminescence technique, optical properties were determined by measuring the luminescence intensity as a function of wavelength. A Spex Industries Model F212 was used for the luminescence measurements [19].

3.3.3 Mechanical Property Measurements

The desire to change the near-surface mechanical properties of the materials has been one of the main driving forces behind the resurgence of interest in ion beam modification of insulators. Ion implantation may alter the mechanical properties of a material at the near surface region by defect strengthening, solid solution or second-phase strengthening, or as a result of the phase transformation from crystalline to amorphous structure [12].

Because the implanted layer is very thin, conventional mechanical measurements can only determine the combined properties of the composite implanted layer/substrate region. Fortunately, the development of ultra-low load micro-indentation hardness testers has made possible the measurement of the elastic modulus and hardness of implanted layers. By using the ultra-low load micro-indentation hardness measuring technique, the load displacement curves were obtained from loading-unloading cycles on the ion-implanted sapphire specimens, the elastic modulus and hardness of the ion-implanted sapphire was then determined from these load-displacement curves [50].

Hardness and modulus tests in this investigation were performed using a Nano-indenter® (Nano Instruments, Inc., Knoxville, TN) at the Oak Ridge National Laboratory,

a schematic illustration of the equipment is shown in figure 3.5 [42]. The system has a load and displacement resolutions of 0.3 μN and 0.16 nm, respectively. A Berkovich indenter, i.e., a three-sided pyramid, was used in all the experiments. The experiments were performed using a load-time sequence as shown in figure 3.6.

The indenter was first loaded and unloaded three times in succession at a constant rate of loading with each of the unloadings terminated at 10% of the peak load to assure that contact was maintained between the specimen and the indenter. The reason for performing multiple loadings and unloadings was to examine the reversibility of the deformation and thereby make sure that the unloading data used for analysis purposes were mostly elastic.

Each specimen was probed ten times in a 2 x 5 array. The loading and unloading for each indentation was applied to three depths (26, 56 and 110 nm) in all the as-implanted and post implant annealed samples. The load-displacement curves were recorded. An analysis technique as shown in reference [30] was adopted to establish the contact area at peak load through the conjunction of depth and indenter shape function. The hardnesses and elastic modulus were then computed from indentation load-displacement data.

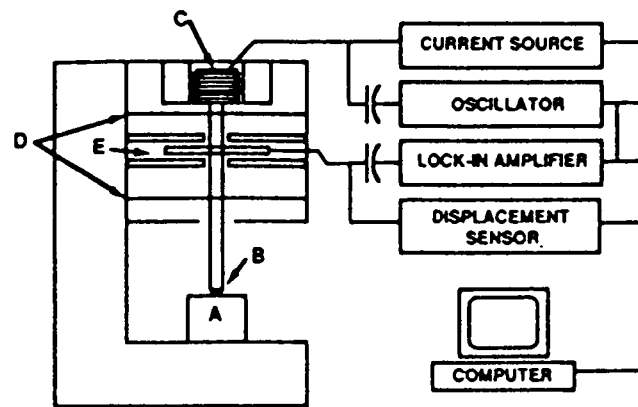


Figure 3.5 A schematic representation of the experimental apparatus used to perform the indentation experiments: (A) sample; (B) indenter; (C) load application coil; (D) indentation column guide springs; (E) capacitive displacement sensor [42].

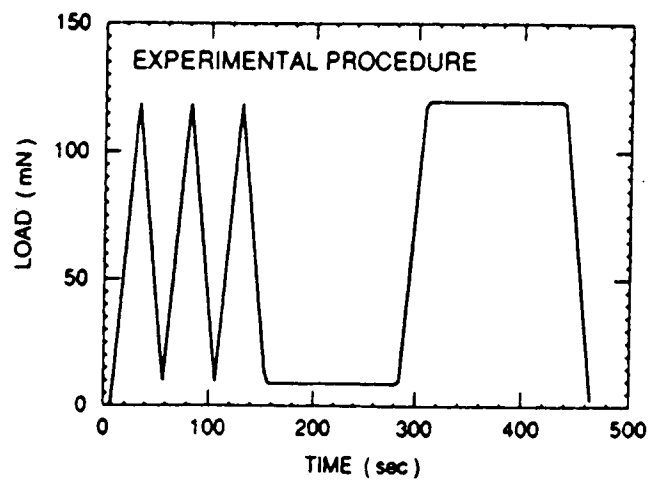


Figure 3.6 A typical load-time sequence; peak load =120 μ N [30]

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Rutherford Backscattering Spectrometry

As was discussed in section 2.1.3, with the known energy loss factor or S factor by equation (2.14) and energy loss measured via backscattering spectrometry, the estimated impurities and lattice damage depth distribution could be computed using equation (2.13). The correlations among ΔE , S factor and the depth distributions of Al, O, and Fe are given in table 4.1.

Random and channeled RBS spectra for virgin $\alpha\text{-Al}_2\text{O}_3$ are shown in figure 4.1 (a). The low ratio of channeled and random yield indicates that the crystal has very low defect content, which manifests a good quality of the crystallinity. Figure 4.1 (b) shows random and channeled RBS spectra of $\alpha\text{-Al}_2\text{O}_3$ implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ at 160 keV at room temperature. At this fluence, the damage peak in the channeling spectrum has not reached the random level indicating a highly damaged but crystalline implanted region. The implanted ions were embedded to a maximum depth of about 200 nm with a Gaussian distribution centered around 100 nm. Most of iron occupied interstitial sites as shown by the lack of channeling for the iron signal. The lattice damage extended to about 300 nm with a peak at about 150 nm. Theoretical models of ion-solid interactions also predict that the peak defect concentration should occur at a greater depth than the peak implanted ion concentration, which is in good agreement with RBS observation.

Figure 4.2 (a) shows random and channeled RBS spectra for $\alpha\text{-Al}_2\text{O}_3$ implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ and annealed for 1 h in an Ar-4% H_2 atmosphere at 700°C. A small increase of the gap between the channeling and random spectra indicates that lattice damage

Table 4.1 Calculated results of Al, O, and Fe depth distribution from the surface

For Sapphire: $dE/dX=437 \text{ KeV}/\mu\text{m}$ @ $E_0=2\text{MeV He}$						
Lab Data: $\theta_1=\theta_2=10^\circ$						
$[S] = \left[\frac{K}{\cos\theta_1} \frac{dE}{dx} \right]_{\text{in}} + \frac{1}{\cos\theta_2} \frac{dE}{dx} \Big _{\text{out}}$						
$\Delta E = [S] \times x$						
Element	Kinetic Factor K	dE/dX @KE (KeV/ μm)	Energy Loss Factor S Factor	ΔX (Depth) (nm)	ΔE (Energy Loss) (MeV)	
Al	0.56	539	796	300	239	
O	0.37	566	739	200	148	
Fe	0.76	492	837	200	167	

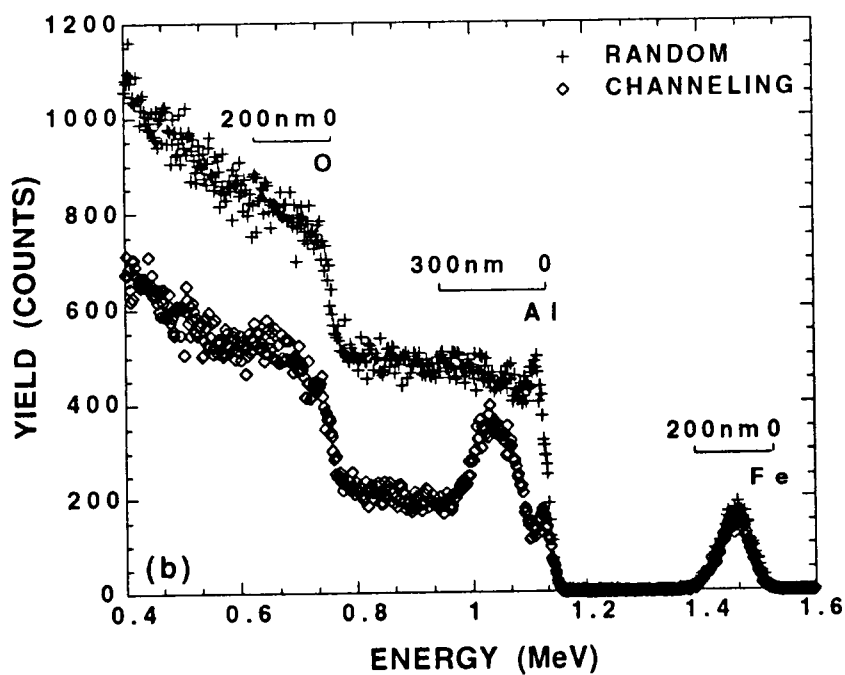
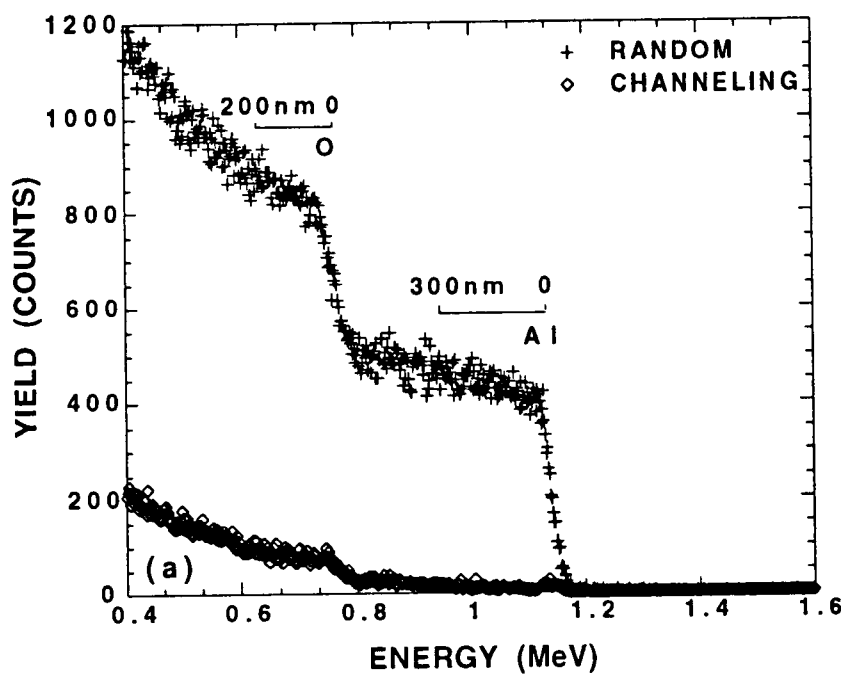


Figure 4.1 RBS spectra for α - Al_2O_3 (a) virgin, and (b) implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ at 160 keV at room temperature.

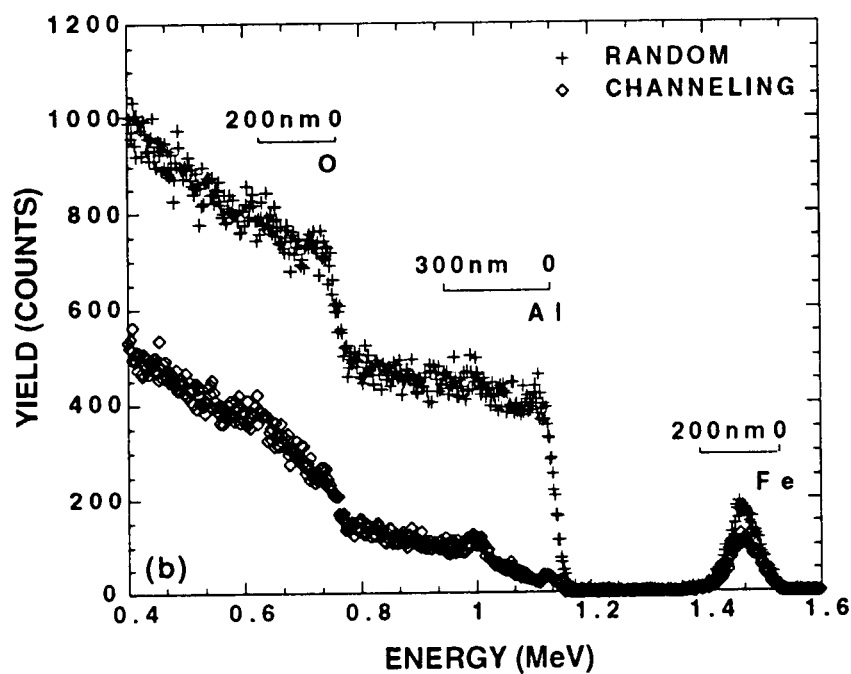
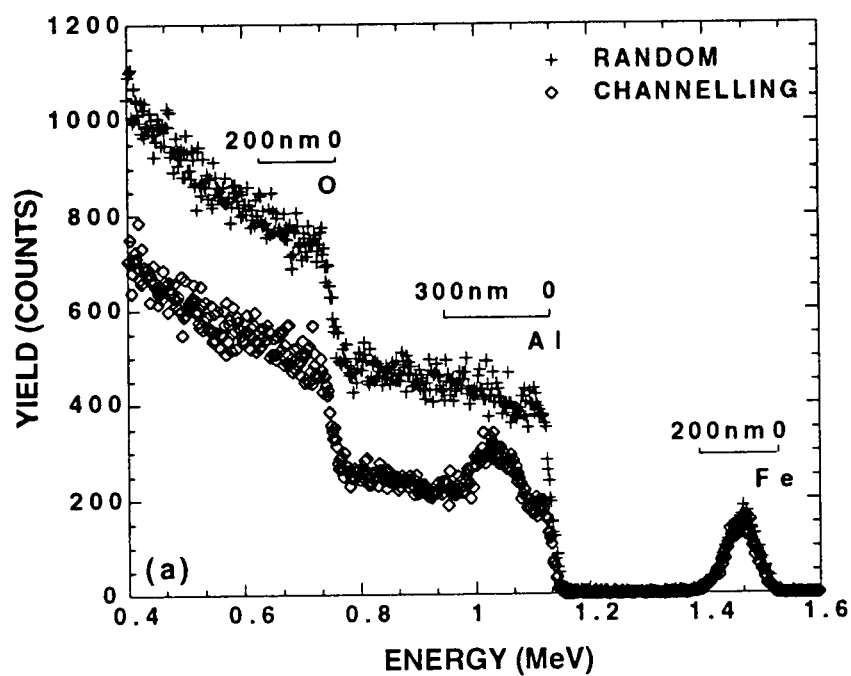


Figure 4.2 RBS spectra for α - Al_2O_3 implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ and annealed for 1 hour in an Ar-4% H_2 atmosphere at (a) 700 (b) 900 (c) 1100, and (d) 1400°C

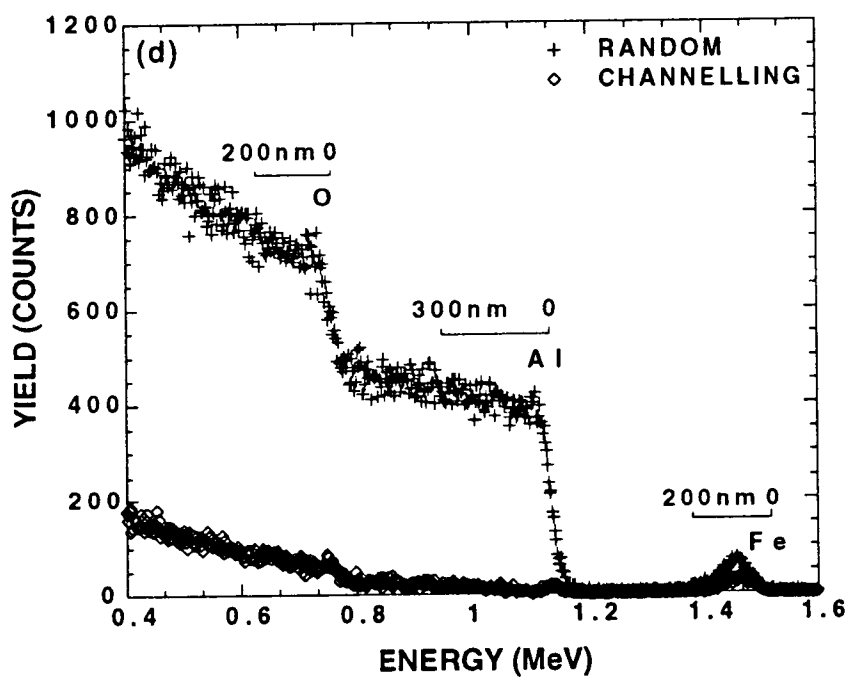
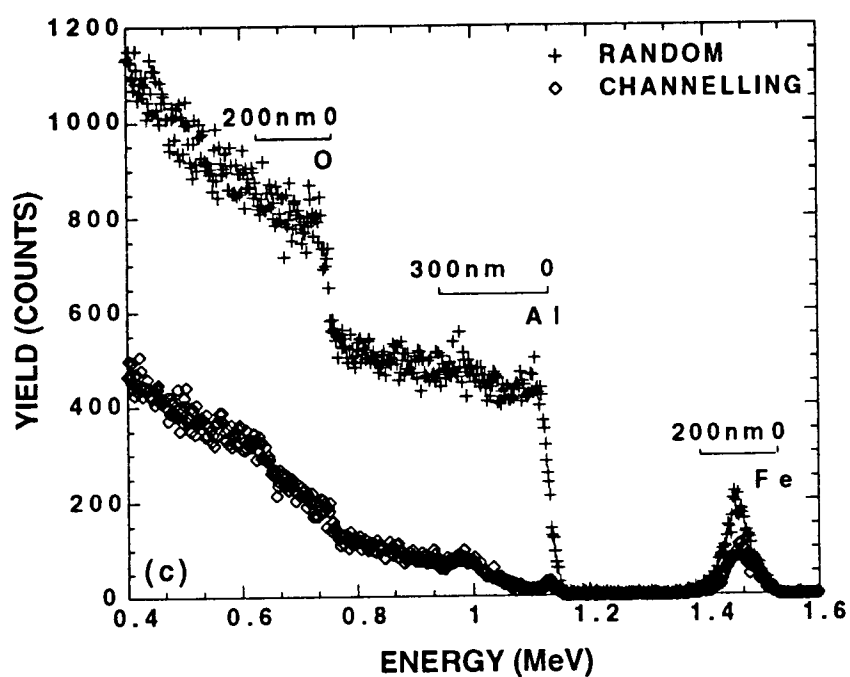


Figure 4.2 Continued

recovery has just started in the damaged region. However, consistent with the CEMS results shown in table 2.3, the amount of recovery or impurity rearrangement is relatively small at this temperature. More lattice damage was recovered after annealing at 900°C as shown in figure 4.2 (b). The reduced iron peak could be considered as either the diffusion of some iron from interstitial to substitutional sites or the formation of oriented iron precipitates. The small peak at approximately 1 MeV arises from the "end-of-range" damage. The origin of this increased amount of defects has not been uniquely determined. It is thought to arise from the range of secondary knock-ons and/or dislocations created from the residual stresses generated in the implanted zone. Lattice damage was almost recovered after annealing at 1100°C as shown in figure 4.2 (c). The increased channeling in the iron spectrum, i.e. a reduction of about half at the iron peak, shows that more precipitates were formed due to annealing, which was also shown in CEMS measurements [16]. Moreover, precipitates were closer to the surface than the as-implanted peak concentration of iron. Annealing the sample at 1400°C causes more iron to diffuse toward the surface where much of it gradually evaporates as shown in figure 4.2 (d).

Random and channeled RBS spectra for α -Al₂O₃ implanted with 1×10^{17} Fe/cm² are shown in figure 4.3. More ions were implanted to this specimen so that the iron peak is higher than that in the lower fluence implantation spectra shown in figure 4.1. Note that the damage peak in the channeling spectrum is very close but doesn't reach the random level indicating more damage was introduced, but amorphization has not occurred in the implanted region. The dip in the Al portion of the random spectrum is caused by the dilution effect of high fluence implantation. The other features such as implantation depth, peak implanted iron concentration, and lattice damage extension in the implanted region are similar to α -Al₂O₃ implanted to the lower fluence.

A partial recovery of the lattice damage was observed when α -Al₂O₃ implanted with 1×10^{17} Fe/cm² and annealed for 1 h in an Ar-4%H₂ atmosphere at 700°C as shown in figure

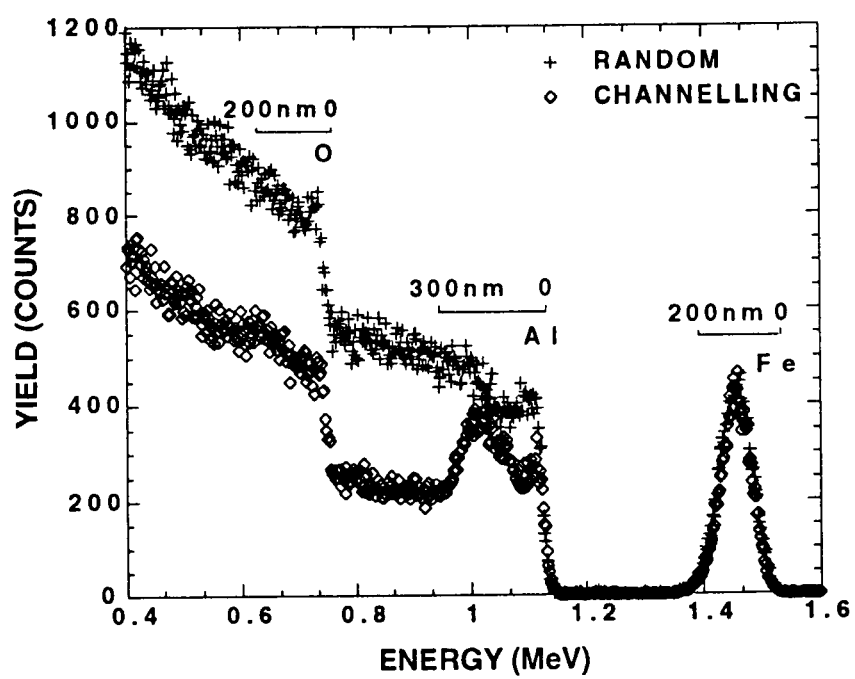


Figure 4.3 RBS spectra for α -Al₂O₃ implanted with 1×10^{17} Fe/cm².

4.4 (a). More and more lattice damage was recovered after annealing at higher temperature as shown in figure 4.4 (b), (c) and (d). Oriented iron precipitates might be formed as shown by the increased channeling effect in the iron spectrum. More precipitates diffused toward the surface region and finally evaporated from the surface for the annealing temperatures above 1100°C. As in the sapphire implanted with the lower fluence, the end-of-range damage recovered at a slower rate than the damage closer to the surface.

Random and channeled RBS spectra for α -Al₂O₃ implanted with 2×10^{17} Fe/cm² are shown in figure 4.5. At this fluence the damage peak in the channeling spectrum has reached the random level indicating that the matrix became either amorphous or microcrystalline in the implanted region. Rutherford backscattering-channeling can not distinguish between microcrystalline and amorphous structures and TEM is required to establish the phase structure. Again, the maximum implantation depth and lattice damage extent were the same as those of the lower fluence implantation since these parameters are mainly determined by the implantation energy, which was held constant.

Figure 4.6 (a) shows random and channeled RBS spectra for α -Al₂O₃ implanted with 2×10^{17} Fe/cm² and annealed for 1 h in an Ar-4%H₂ atmosphere at 700°C. The overlap between the channeling and random spectra represents that the matrix remained amorphous or microcrystalline, which indicates that the associated thermal energy was not large enough to overcome the potential free energy or activation energy to reach the relative stable state of a crystalline atomic structure at this annealing temperature.

A partial recovery of lattice damage occurred after annealing at 900°C as shown in figure 4.6 (b) and almost all the lattice damage was recovered after annealing at 1100°C as shown in figure 4.6 (c). The shape of the spectra indicates that epitaxial regrowth of the α -substrate into the amorphous layer was not occurring. Rather, the results are consistent with the earlier studies [16] of (Al+O) implanted sapphire wherein the amorphous layer first crystallized into the γ -Al₂O₃ phase at the lower annealing temperature. At $T > 1100^\circ\text{C}$,

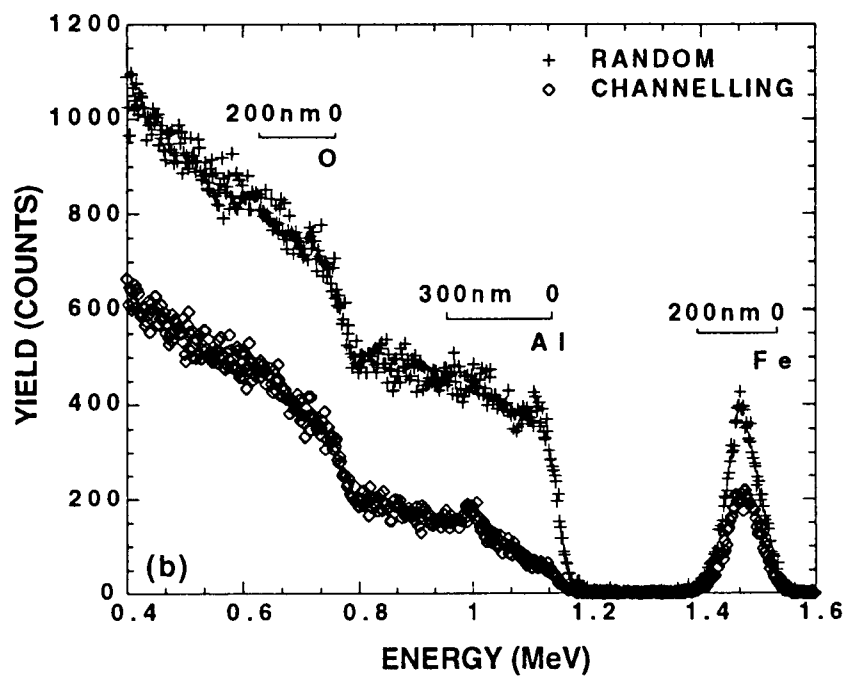
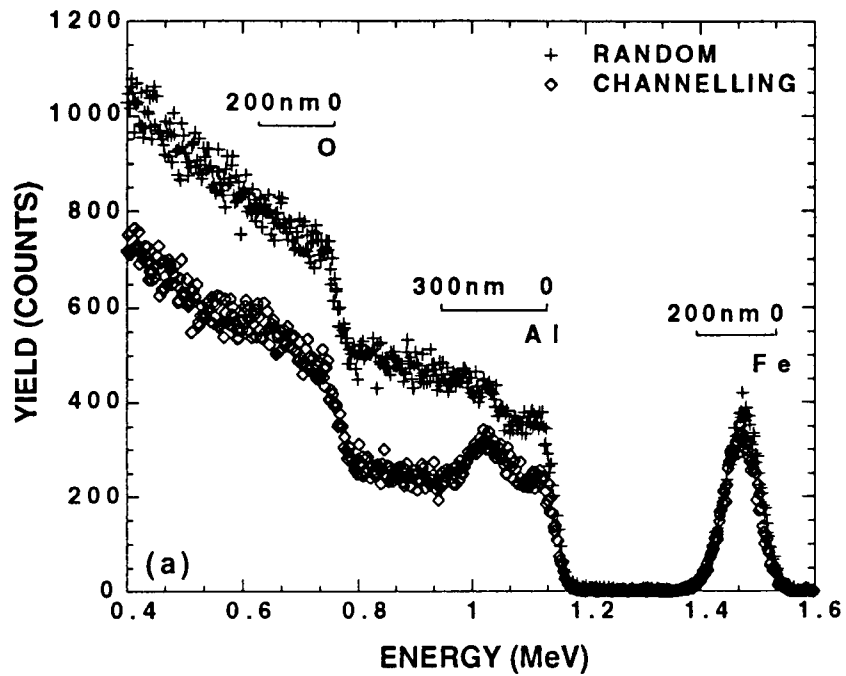


Figure 4.4 RBS spectra for α - Al_2O_3 implanted with $1 \times 10^{17} \text{ Fe/cm}^2$ and annealed for 1 hour in an Ar-4% H_2 atmosphere at (a) 700, (b) 900, (c) 1100, (d) 1400°C

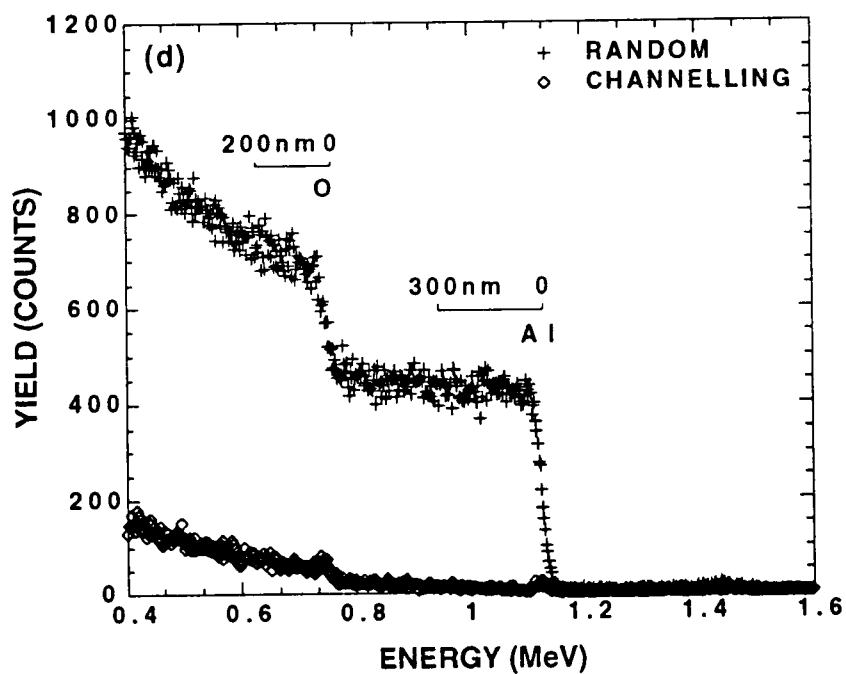
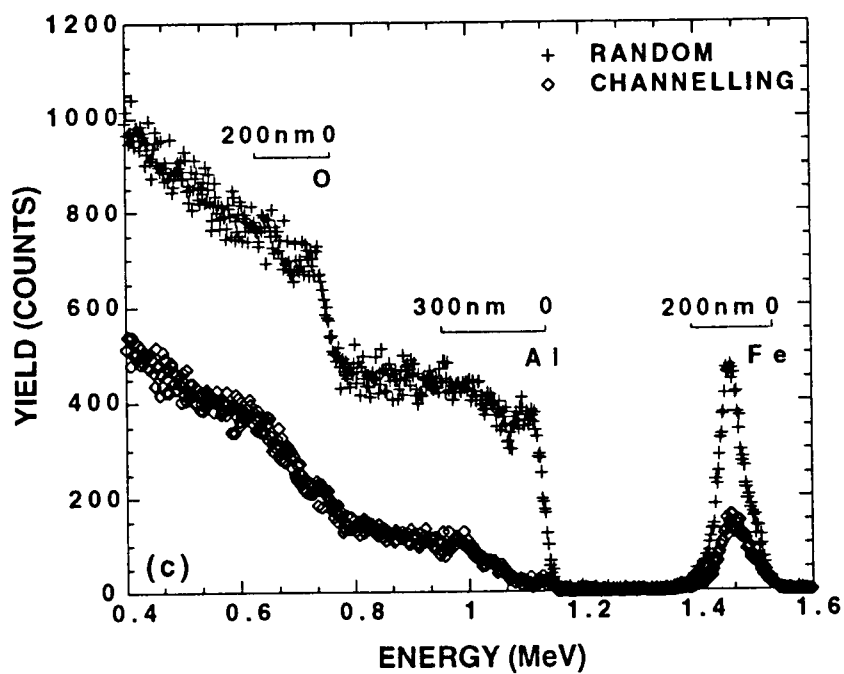


Figure 4.4 Continued

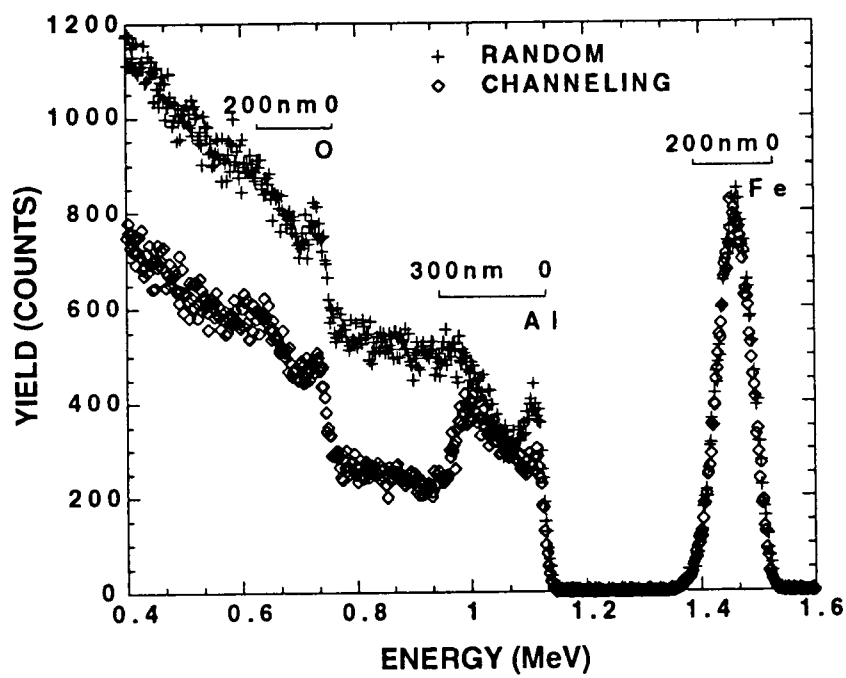


Figure 4.5 RBS spectra for α - Al_2O_3 implanted with $2 \times 10^{17} \text{ Fe/cm}^2$.

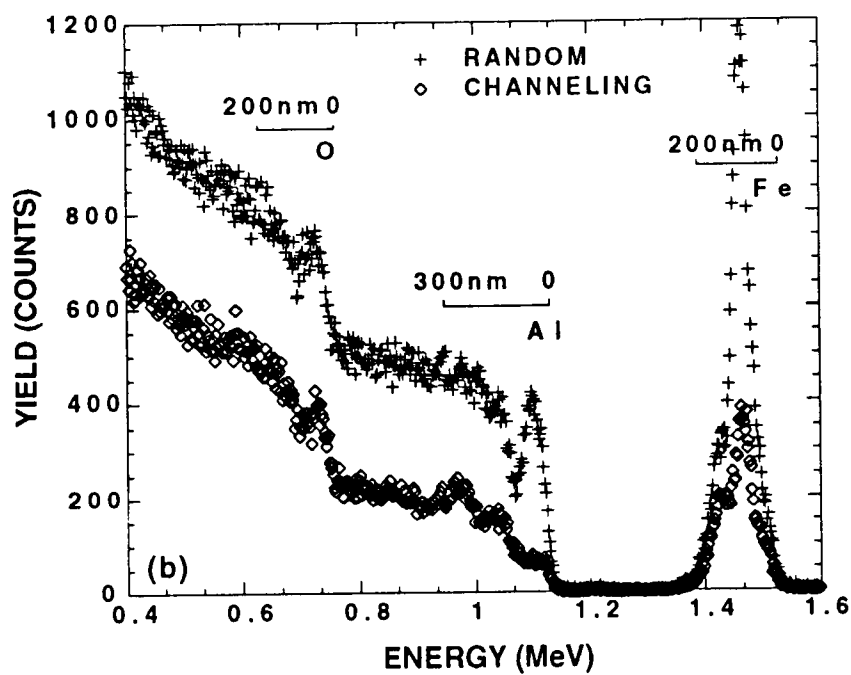
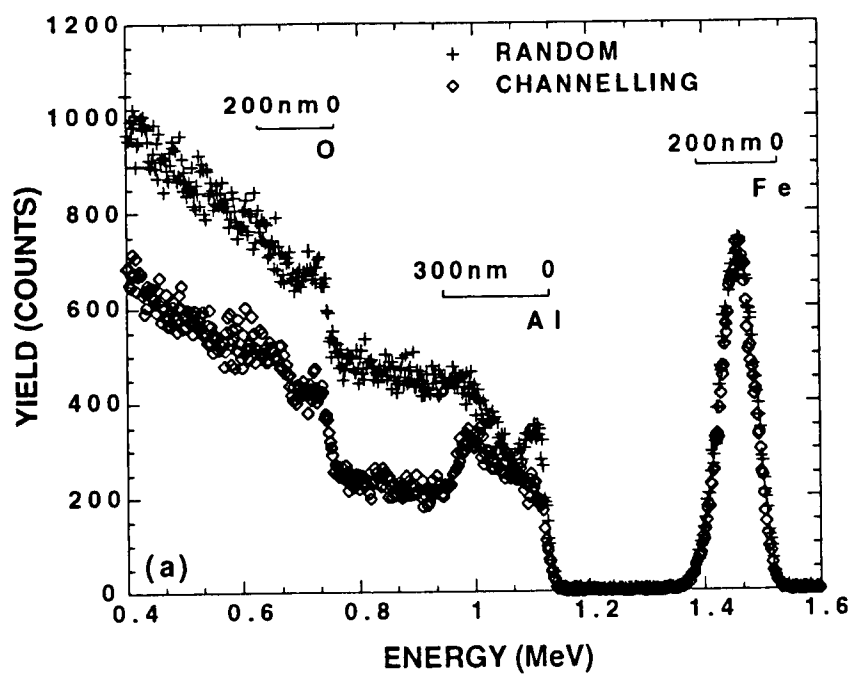


Figure 4.6 RBS spectra for α - Al_2O_3 implanted with $2 \times 10^{17} \text{ Fe/cm}^2$ and annealed for 1 hour in an $\text{Ar-4\%H}_2$ atmosphere at (a) 700, (b) 900, (c) 1100, (d) 1400°C

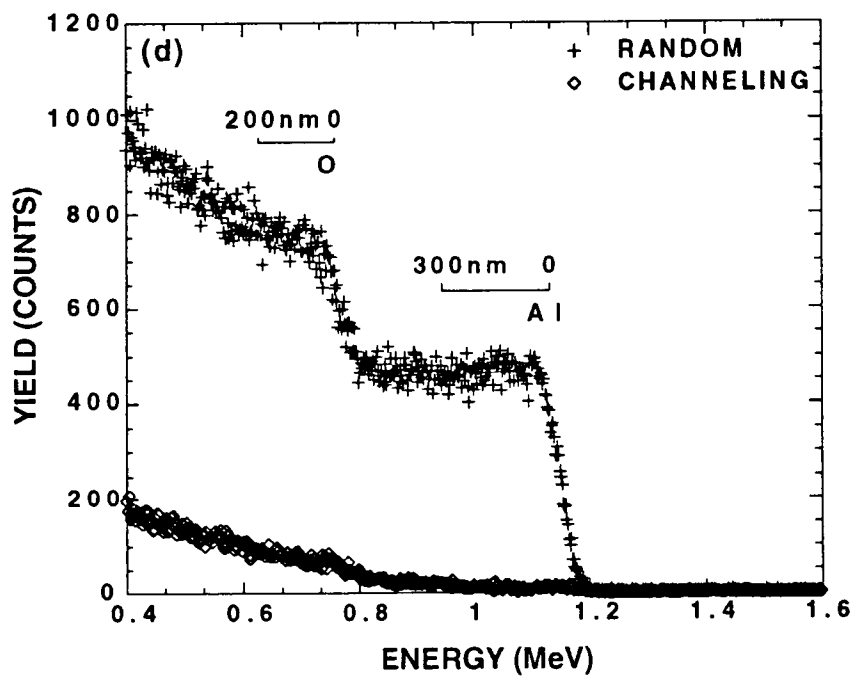
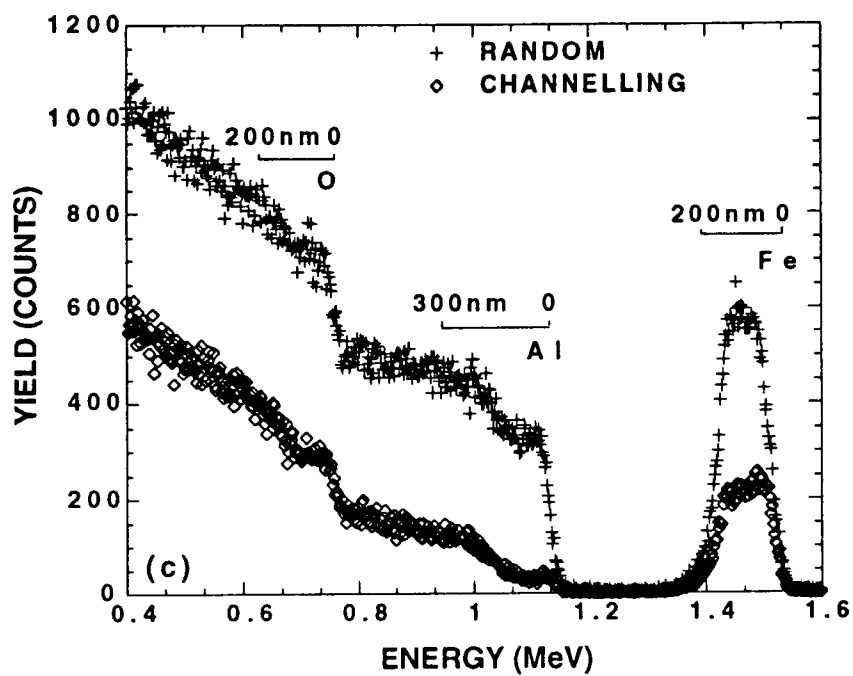


Figure 4.6 Continued

epitaxial growth occurred: the α -phase of the substrate consumes the γ -phase. These results indicated that the sufficient thermal energy was applied so that a stable state could finally be approached.

It was also found that all the iron impurities diffused toward the surface region and finally evaporated from the surface at high temperature annealing. The iron peak was diminished after 1400°C annealing as shown in figure 4.6 (d). Since iron is soluble in γ - Al_2O_3 but not in α - Al_2O_3 , all iron would be pushed toward surface by the moving of α/γ interface during the epitaxial growth. Therefore, the iron peak is absent in the spectrum of $2 \times 10^{17} \text{ Fe/cm}^2$ implantation followed by 1400°C annealing. On the other hand, the iron peak still exists, although reduced in counts, in the spectrum of $4 \times 10^{16} \text{ Fe/cm}^2$ implantation followed by 1400°C annealing. This is because no amorphous film was formed at this fluence implantation and thereby no phase transformation such as amorphous Al_2O_3 to γ - Al_2O_3 to α - Al_2O_3 ever took place.

4.2 Analytical Electron Microscopy

Figure 4.7 (a) shows a micrograph of the cross-sectioned specimen of α - Al_2O_3 implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ at 160 keV at room temperature. The implanted iron produced a damage layer extending to at least 300 nm in the $\langle 0001 \rangle$ direction below the specimen surface. Previous conversion electron Mössbauer spectroscopy measurements indicated that about 0.18 of the implanted iron existed as Fe^0 (about 2% volume fraction), and about 0.82 as Fe^{2+} [16]. This low volume fraction of metallic iron precluded the probability of imaging discrete particles at this fluence. The presence of the amorphous glue region is not clear at low magnification but is very distinct in the high resolution micrograph shown in figure 4.7 (b). The sharp lattice fringes in figure 4.7 (b) provide strong evidence that the implanted layer remained crystalline although damaged. These

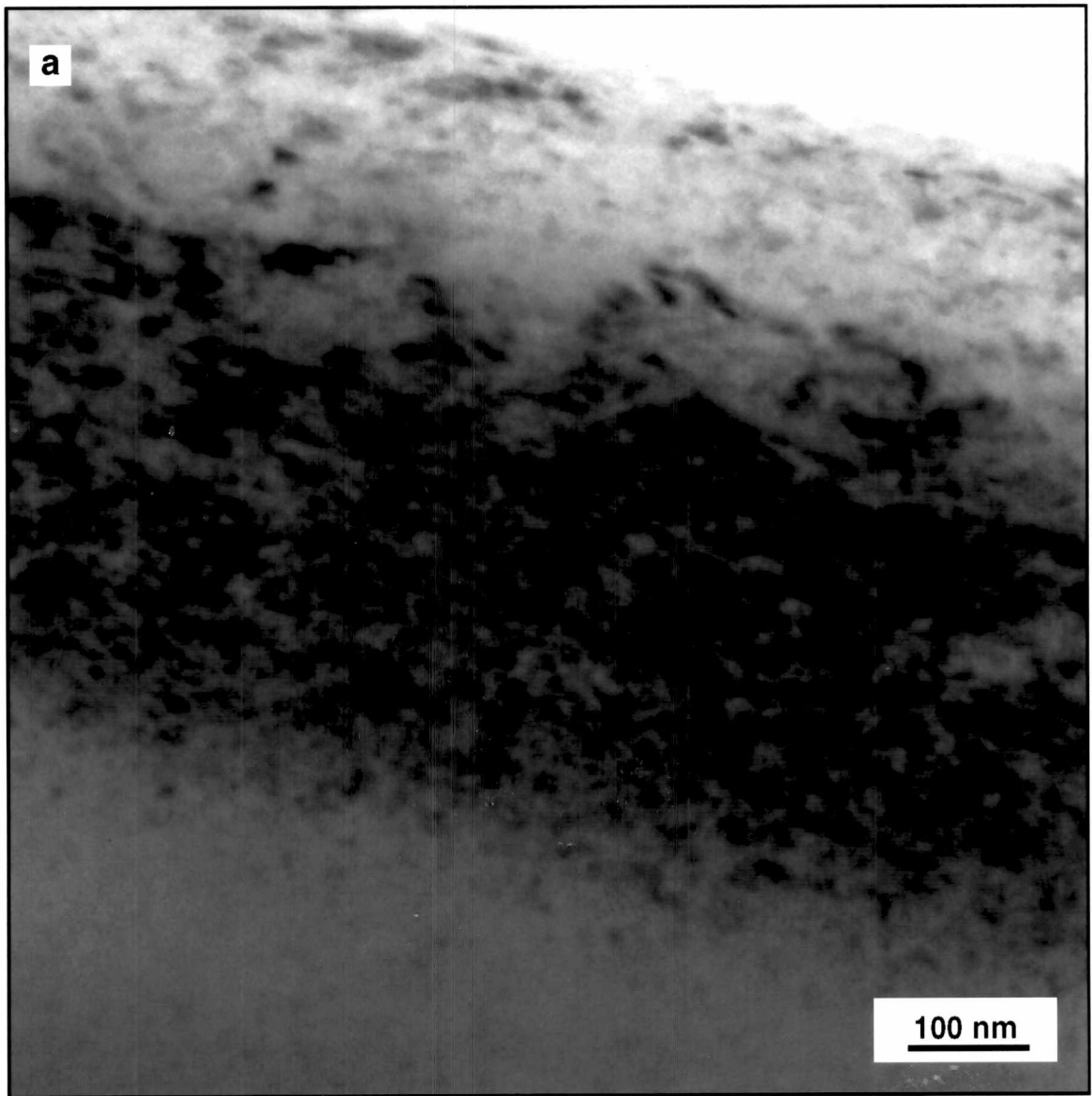


Figure 4.7 Micrograph of cross-sectioned specimen of α -Al₂O₃ implanted with 4×10^{16} Fe/cm². (a) Low magnification and (b) High resolution

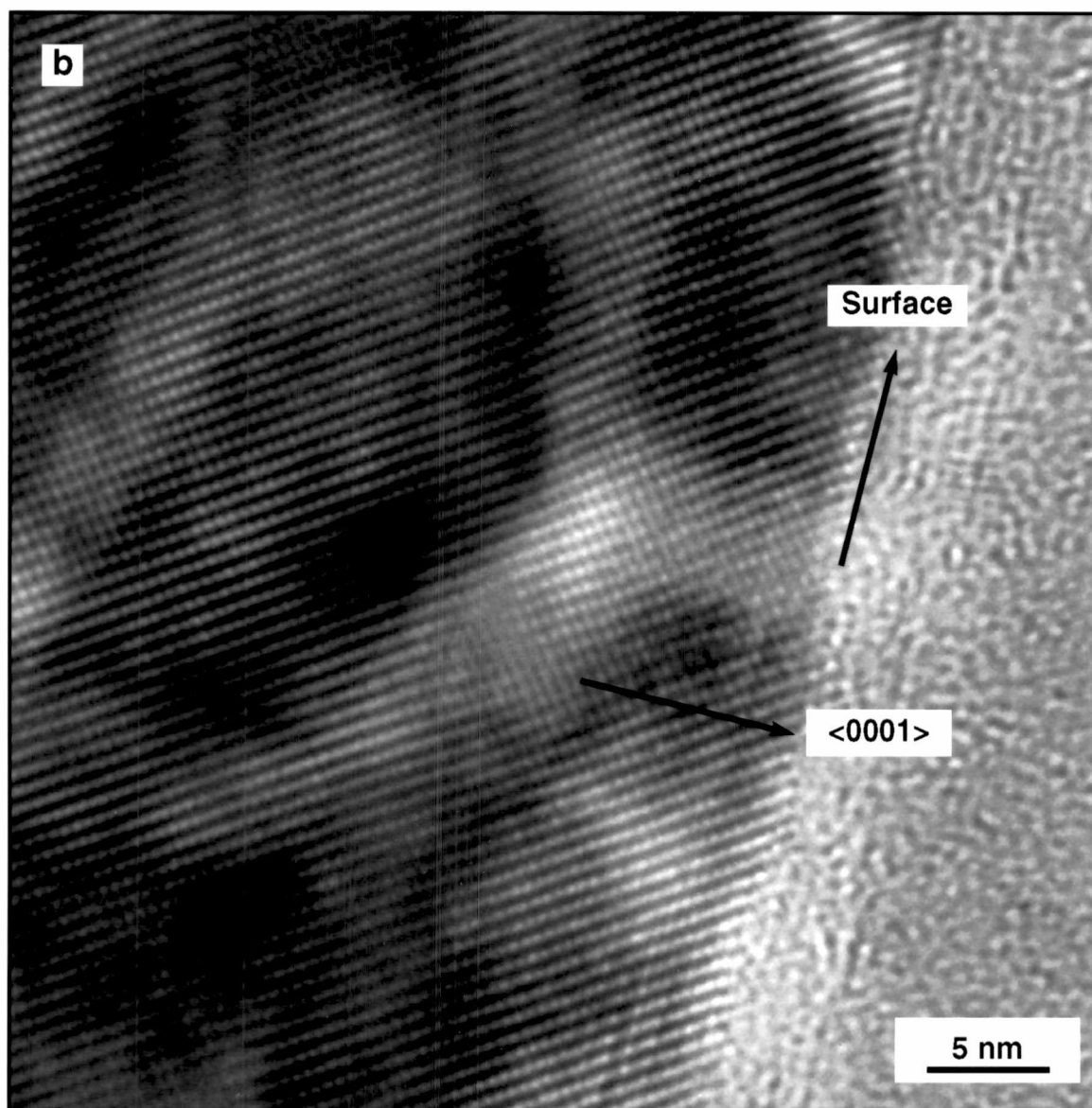


Figure 4.7 continued

direct observations are consistent with RBS measurements as shown in figure 4.1 (b). If we take a close look at an oblique angle along the lattice fringe direction, we can see that some fringes are slightly bent and deflected. These distortions are related to the strain caused by point defect clusters produced by the irradiation damage and/or clusters of iron atoms. Note that the dark areas at the subsurface region of high resolution micrograph do not necessarily indicate the location of the iron as such effects could be caused by radiation damage as well. In order to determine if ion milling could cause the similar appearance of the microstructure, a virgin sapphire crystal was prepared. A high resolution micrograph of a cross-sectioned specimen of this virgin α -Al₂O₃ is shown in figure 4.8. It also revealed the different shades of gray at the subsurface area, which is thought to be caused by the radiation effect during ion milling. Further studies to determine the nature of this variation in contrast might involve annealing to determine if argon gas bubbles form in the lighter appearing regions, EDS measurement to detect argon, and in situ heating to determine if interstitial dislocation loops form.

Since the recent installation of the digital camera system on the Hitachi HF-2000, convergent beam electron diffraction pattern could not be recorded at the time of this study because of inadequate shutter speeds. A selected area diffraction pattern of the same area as shown in figure 4.7 (a) gave a sharp sapphire diffraction pattern because of the relative small volume amount of the implanted iron. In addition, the implanted layer is only 200 nm thick, while the aperture covers a region more than 0.6 μ m in diameter.

Annealing at 700°C for 1 hr in an Ar-4% H₂ atmosphere produced few changes in the microstructure as shown in figure 4.9. The implanted layer has almost the same features as discussed above for the as-implanted specimen. It indicates that annealing at this stage did not provide enough energy to reorder the structure of the material on a microscopic scale, consistent with the CEMS and RBS results. Impurities were still resided in the interstitial sites of the crystalline α -Al₂O₃ as discussed for the as-implanted sample. It was also

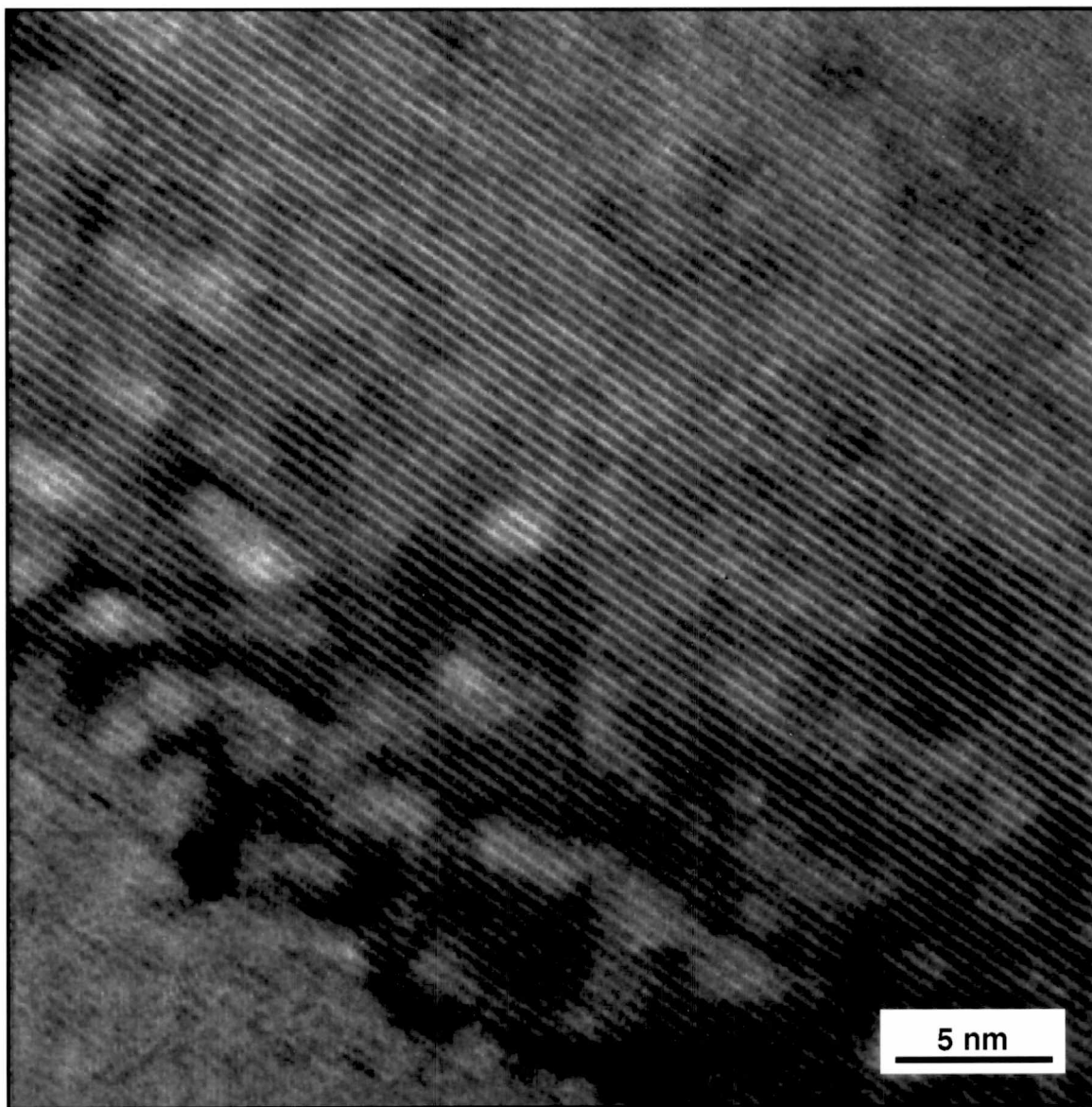


Figure 4.8 Micrograph of cross-sectioned specimen of α - Al_2O_3

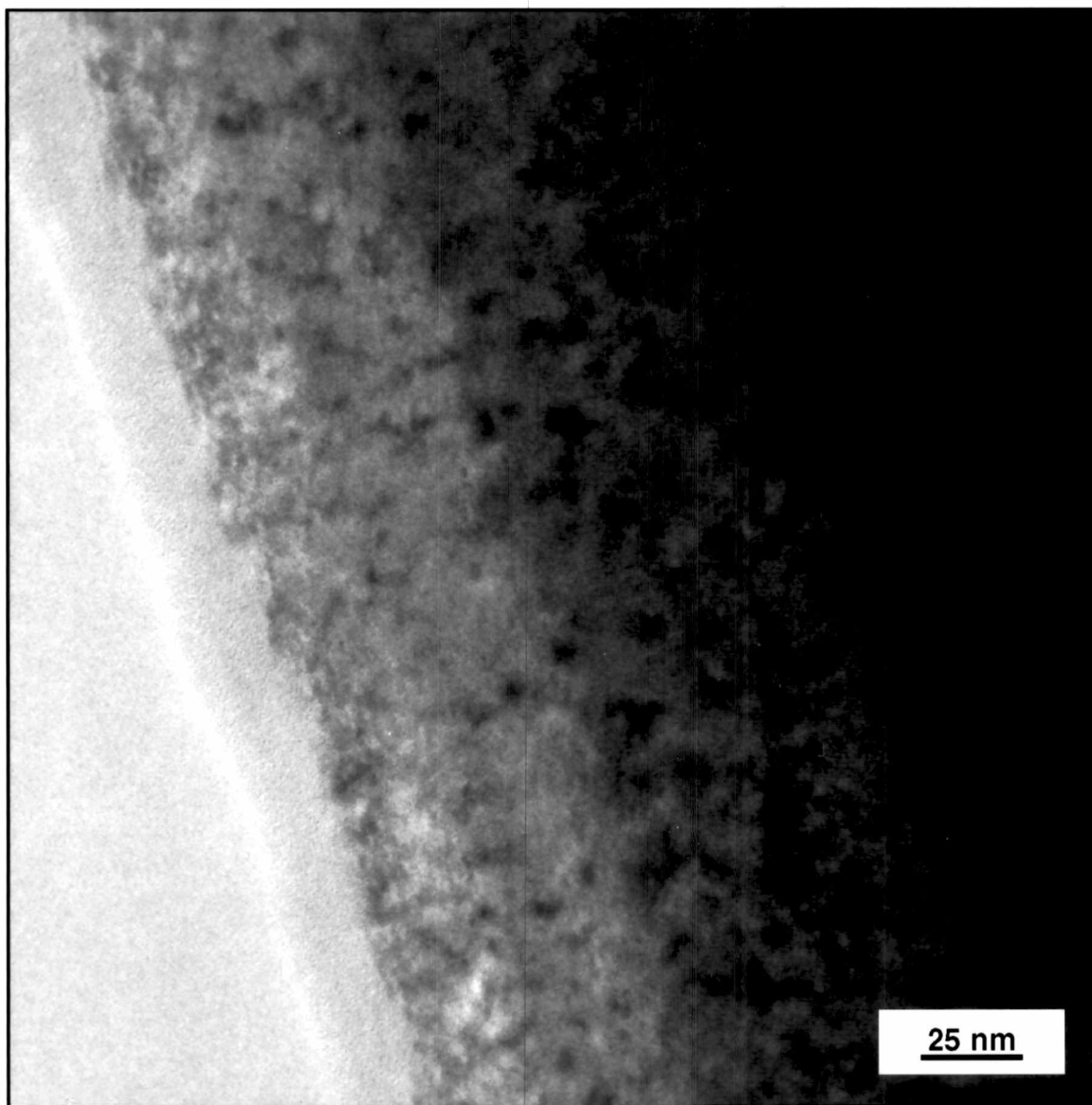


Figure 4.9 Micrograph of cross-sectioned specimen of α -Al₂O₃ implanted with 4×10^{16} Fe/cm² and annealed at 700°C.

found that there was no significant microstructure change due to 700°C annealing even for those specimens implanted with higher fluences.

Figure 4.10 (a) and (b) shows micrographs after 900°C annealing in which most precipitates were in the range of 3 to 23 nm in diameter. The largest particles appear to be located near the position of the maximum iron concentration. Some of the precipitates exhibit a tendency to form faceted surfaces, figure 4.10 (b). Using an image processing program, provided by a software from the National Institutes of Health (NIH "image"), the particle distribution obtained from several micrographs taken at different locations of the same specimen is shown in figure 4.11. There are several size groups: (a) the smallest particles are similar to the as-implanted size ($< 3\text{ nm}$); (b) the largest fraction lie in the 6-10 nm size range; (c) there is a small group in the 12-16 nm range, and (d) a larger fraction centered at 20 nm. It was calculated that the minimum ratio of minor axis to major axis of the precipitates is 0.36, while the maximum ratio of minor axis to major axis of the precipitates is 1. This indicates that the precipitates are in shapes ranging from elliptical to round. Moreover, the long axis is parallel to the surface in all cases.

More round precipitates were found following annealing of sapphire implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ at 1100°C for 1 h in an Ar-4% H_2 atmosphere shown in figure 4.12. Generally, small particles were found close the surface, while those larger ones were near the position of maximum implanted concentration of iron. Many of the precipitates appeared to be associated with voids, suggesting that mechanisms such as coalescence and then Ostwald ripening could have occurred. Studies on colloid formation in NaCl during annealing after the addition of excess Na were modeled by the migration of Na-vacancy clusters [29]. The CEMS studies showed that large fraction of the implanted iron presented as Fe^{2+} . McHargue et al [16] argued that the charge compensation was due to Fe^{2+} -oxygen vacancy configurations. Migration of these complexes could produce microstructures such as observed in this study. Particle and void distributions measured from micrograph 4.12

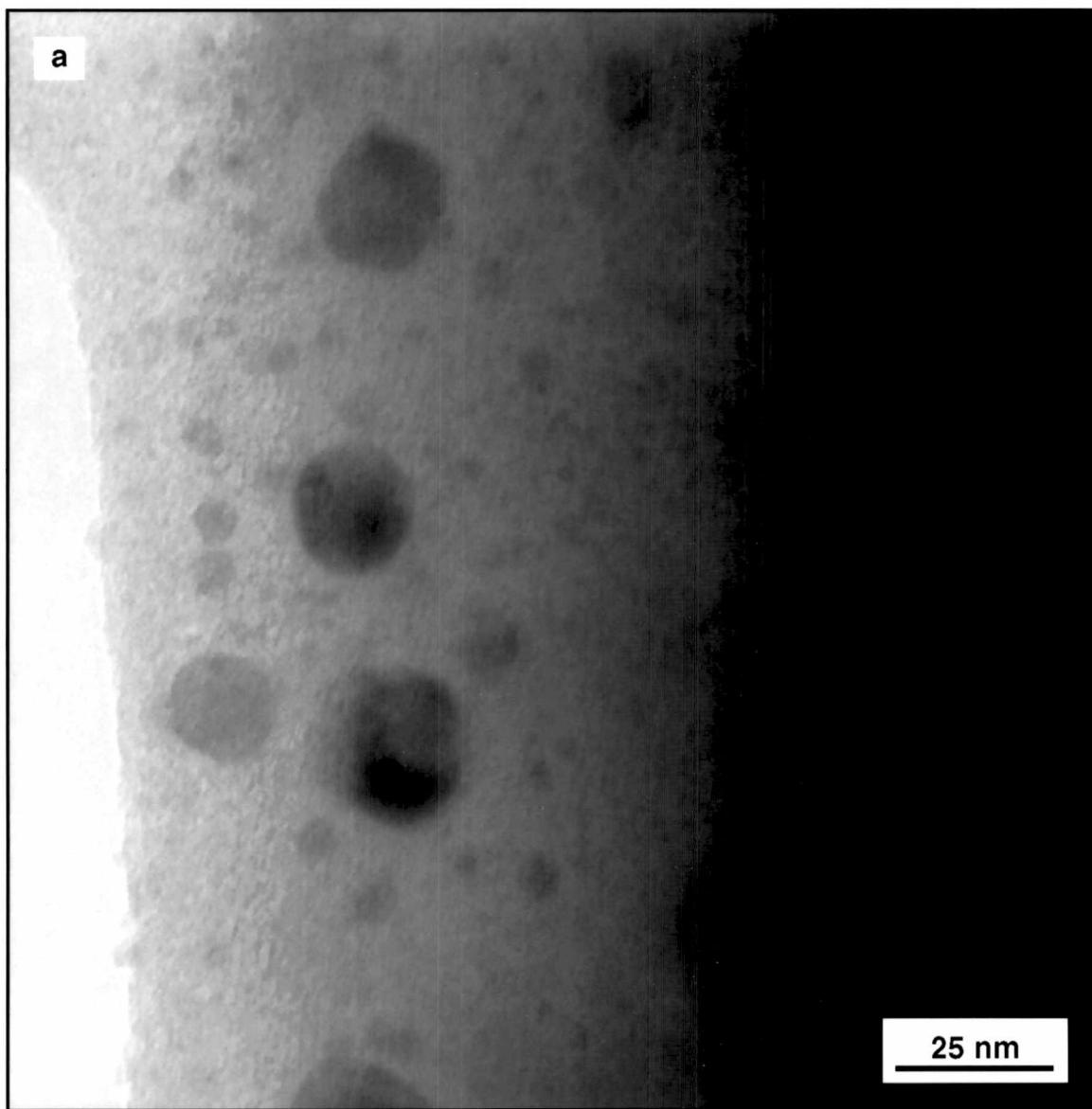


Figure 4.10 (a) and (b) Micrographs of cross-sectioned specimen of α - Al_2O_3 implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ and annealed at 900°C .

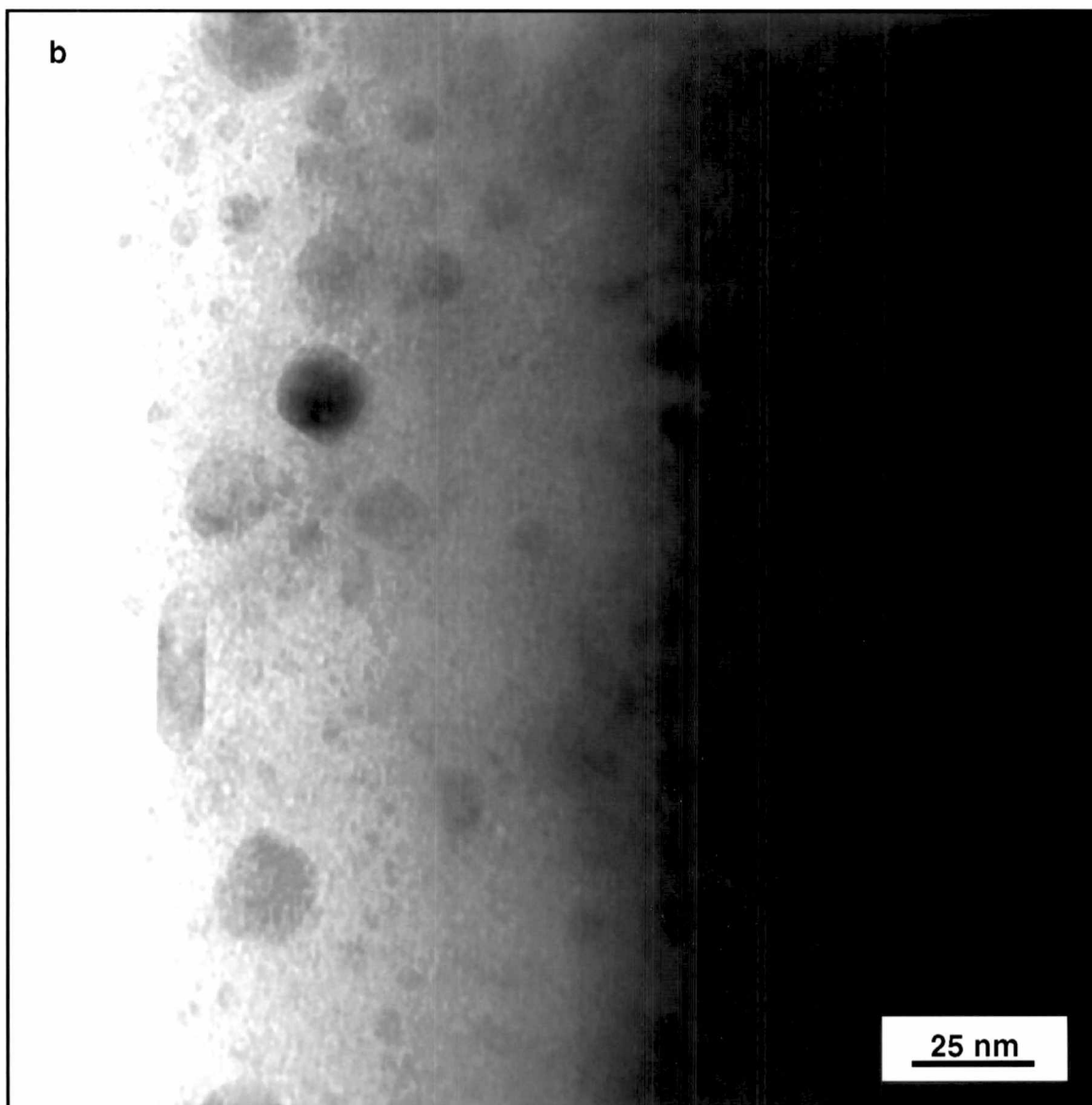


Figure 4.10 continued

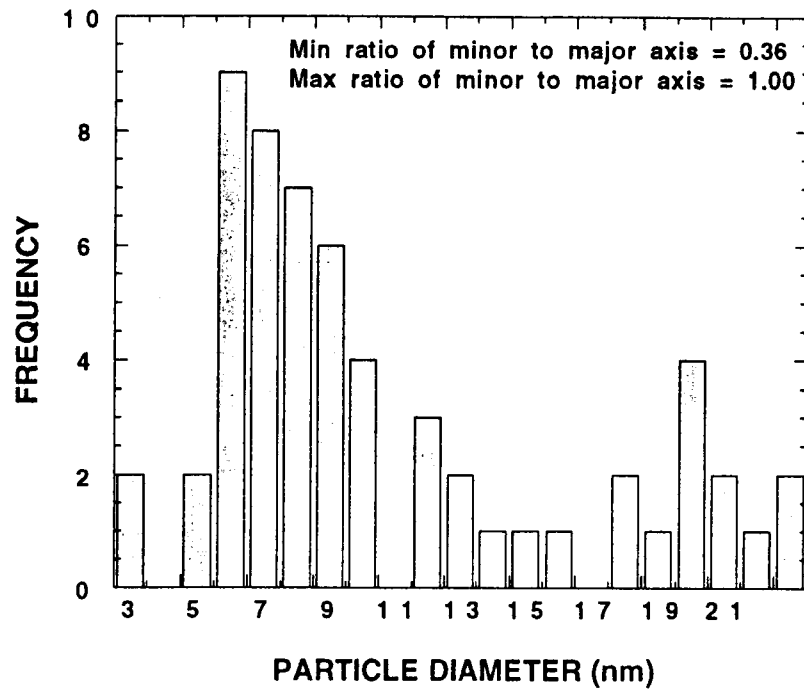


Figure 4.11 Particle distribution measured from several micrographs of cross-sectioned specimen of α - Al_2O_3 implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ and annealed at 900°C .

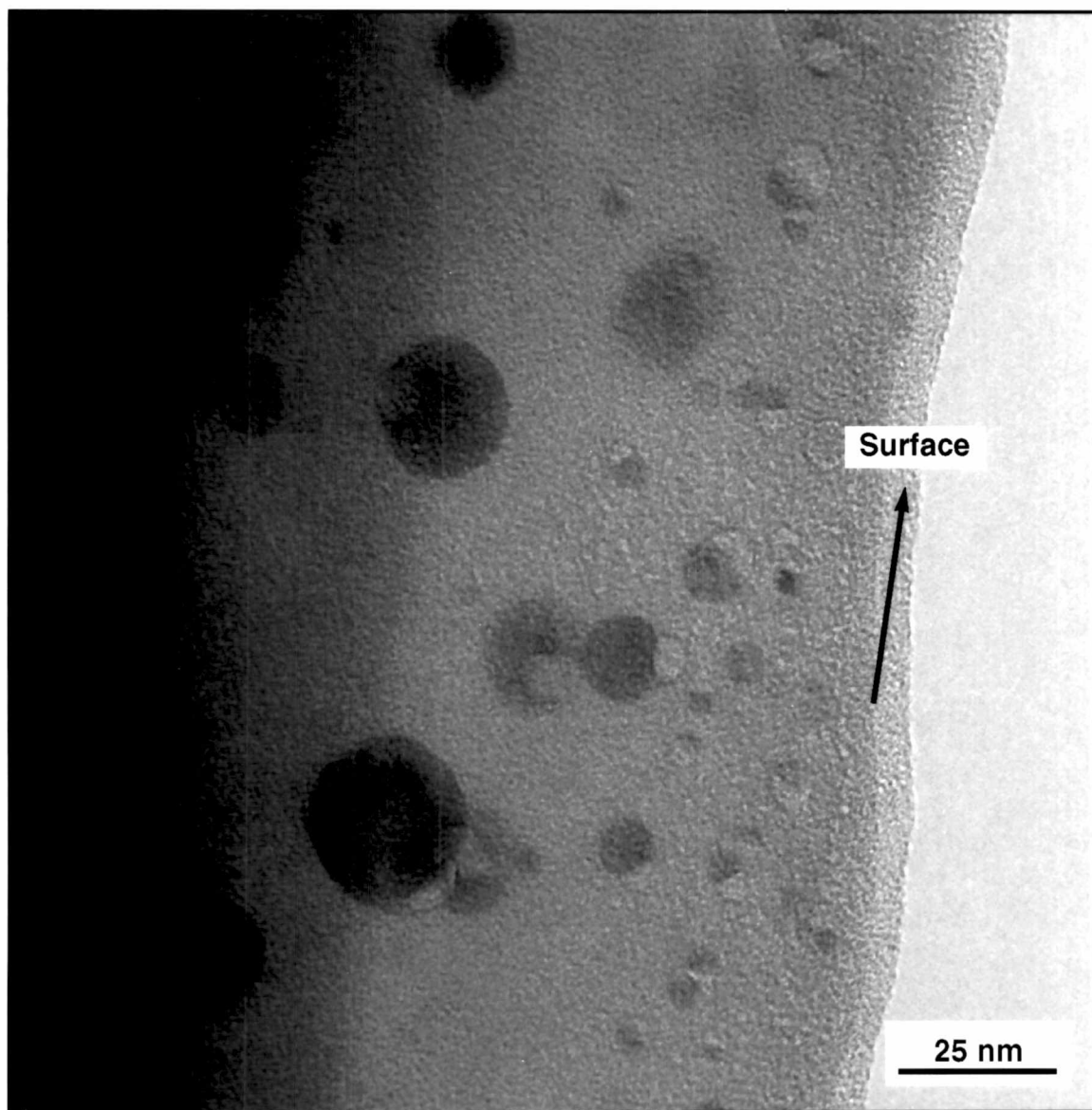


Figure 4.12 Micrograph of cross-sectioned specimen of α - Al_2O_3 implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ and annealed at 1100°C .

are shown in figure 4.13 (a) and (b) respectively. Precipitates ranged in diameter from 3 to 26 nm, with the peak value of 5 nm, while the voids were relatively smaller with the sizes only from 5 to 9 nm in diameter. The minimum ratios of minor axis to major axis for the precipitates and voids are 0.80 and 0.82 respectively, and the maximum ratios of minor axis to major axis for them are 0.96 and 0.95 respectively. The results suggest the trend that round (i.e. spherical) precipitates would be easily formed at high annealing temperature.

Faceted precipitates appeared when the as-implanted sample was annealed at 1400°C in a reducing atmosphere, shown in figure 4.14 (a) and (b). Those faceted precipitates as large as 50 nm in diameter were found to be iron rich by EDS measurements. They were scattered in the range of 25 to 150 nm below the surface. The low density of iron particles is consistent with RBS results indicating that a loss of iron from the implanted zone occurred at the highest annealing temperature.

Figure 4.15 (a) and (b) show micrographs of the cross-sectioned specimen of α -Al₂O₃ implanted with 1×10^{17} Fe/cm². The lattice fringes confirmed that the implanted layer remained crystalline as found in the RBS measurements shown in figure 4.3. However, some lattice fringes are distorted (twisted or tilted) because more damage was introduced into the implanted layer at this implantation fluence. Previous CEMS measurements indicated that about 0.36 of the implanted iron existed as Fe⁰, about 0.37 as Fe²⁺ and about 0.27 as Fe⁴⁺ [16]. Previous micrographs from a back-thinned sample showed the presence of 1 to 3 nm diameter precipitates, which were identified as α -Fe (BCC). However, modifications in progress to the electron microscopy equipment at high temperature materials laboratory precluded the use of convergent beam technique to search for these 1 to 3 nm particles from a cross-sectioned specimen. Since the total volume percentage of α -Fe was only 5%, no BCC iron pattern was observed in selected area diffraction pattern.

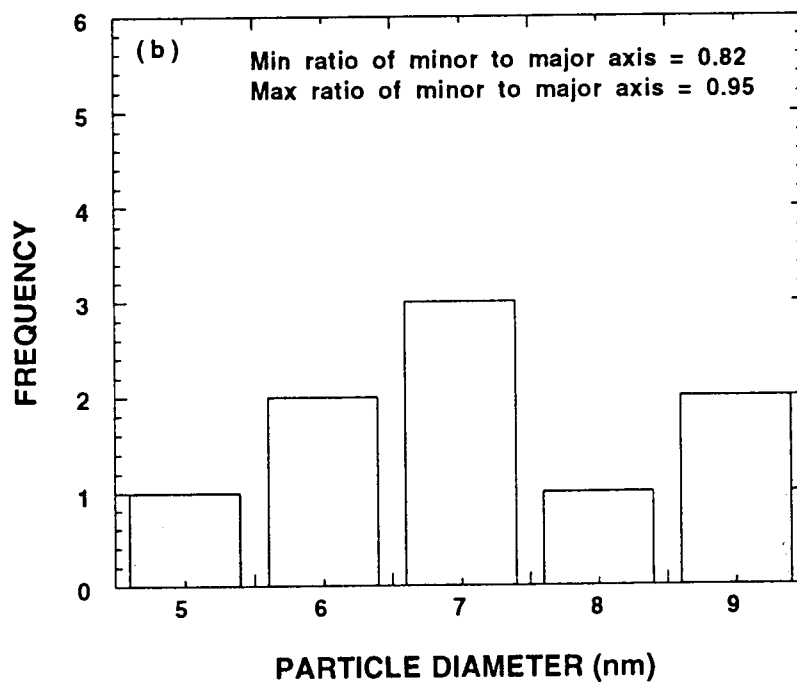
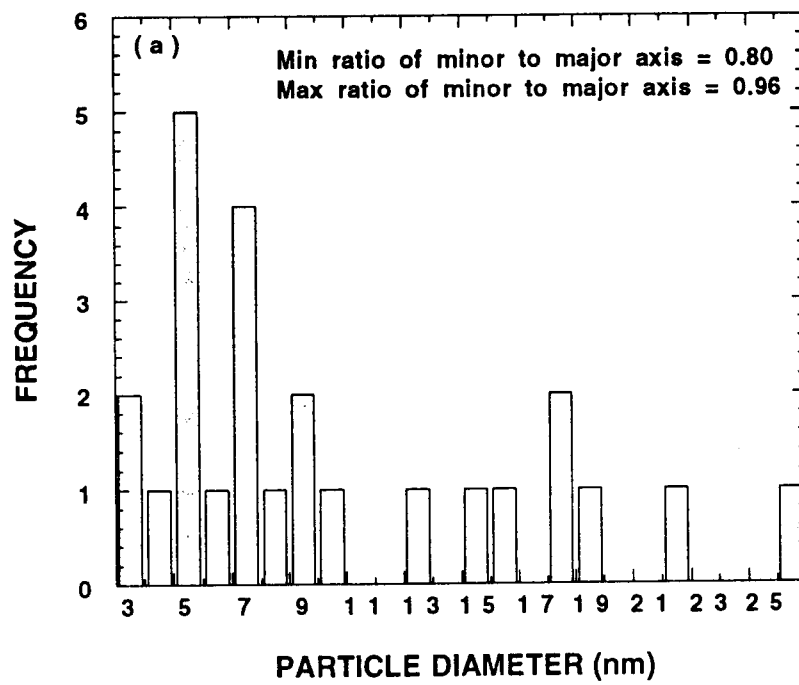


Figure 4.13 (a) Precipitates and (b) voids distributions measured from micrograph 4.12.

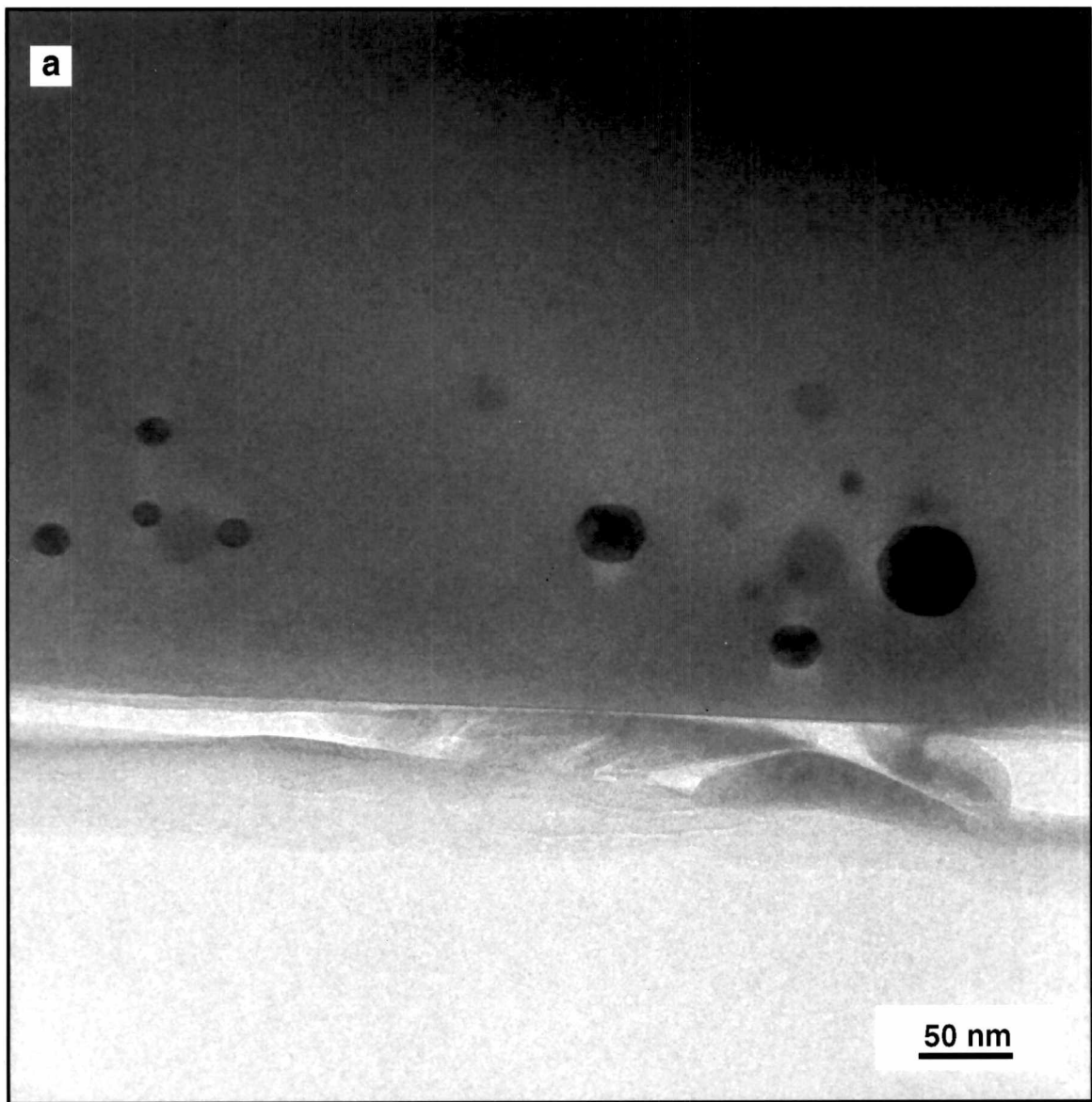


Figure 4.14 Micrograph of cross-sectioned specimen of α - Al_2O_3 implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ and annealed at 1400°C . (a) x30K and (b) x70K

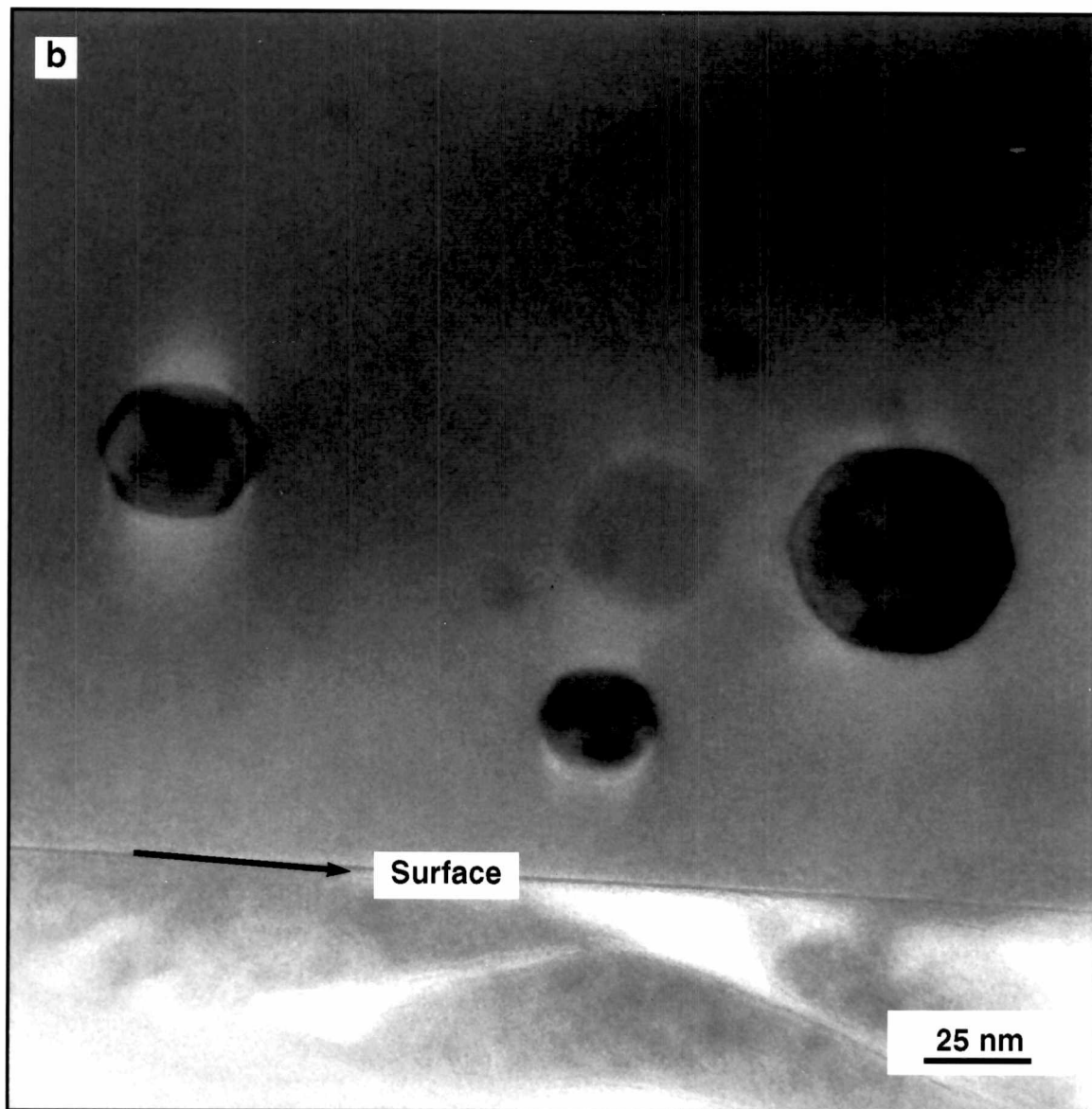


Figure 4.14 continued

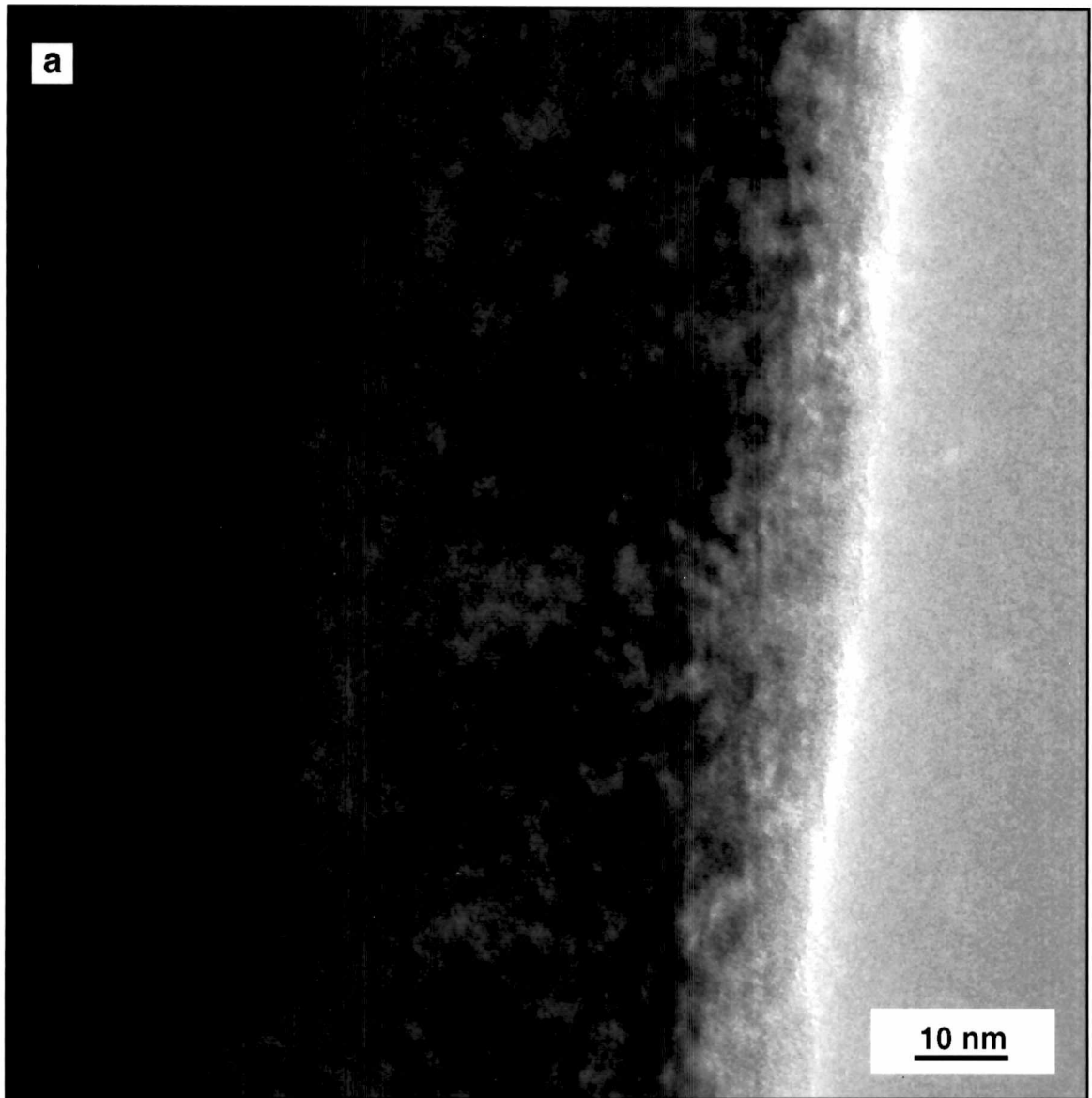


Figure 4.15 Micrograph of cross-sectioned specimen of α -Al₂O₃ implanted with 1×10^{17} Fe/cm². (a) Low magnification and (b) High resolution

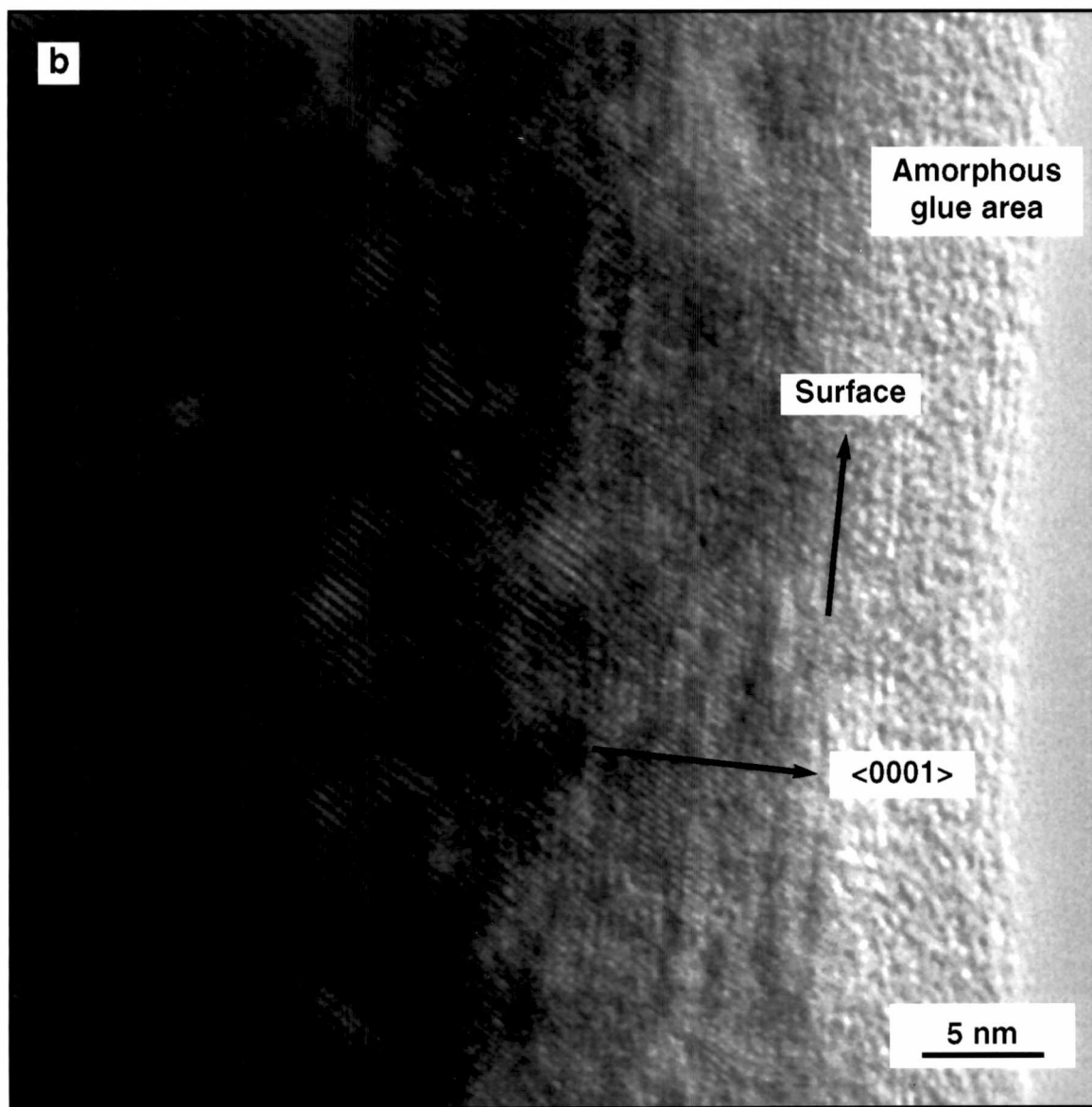


Figure 4.15 continued

Annealing the samples implanted with $1 \times 10^{17} \text{ Fe/cm}^2$ at 900°C resulted in the coalescence of the precipitates shown in figure 4.16 (a) and (b). Note that the dark area on the left side of figure 4.16 (a) was from the diffraction aperture. Each specimen need to be correctly oriented before all the micrographs were taken so that specimen orientation could be identified and parameters such as the extent of the damage and impurities layer could be determined. Figure 4.17 (a) and (b) are energy dispersive spectroscopy (EDS) measurements obtained from region A and B of figure 4.16 respectively. The results indicate that region A is iron-rich, while region B has a spectrum similar to virgin $\alpha\text{-Al}_2\text{O}_3$, which appears to be "end-of-range" damage often reported. The fact that the end-of-range region is more clearly observed after 900°C annealing suggests that some defect agglomeration occurred during annealing. Precipitates of either iron or vacancy rich were identified at a higher magnification as shown in figure 4.18 (a) and (b). Precipitates and vacancies of 3 to 15 nm in length were revealed in the crystalline matrix. The formation of Moiré pattern in electron microscope image indicates that the overlap occurs between two crystals (matrix and precipitate) with almost exactly equal or multiple lattice parameter, and correct double diffraction conditions have been satisfied [57].

Micrographs of a cross-section specimen of $\alpha\text{-Al}_2\text{O}_3$ implanted with $1 \times 10^{17} \text{ Fe/cm}^2$ and annealed at 1100°C are shown in figure 4.19 (a), (b) and (c). A series of elongated precipitates of 40 to 60 nm in length and 40 nm in width were found about 50 nm away from the surface shown in figure 4.19 (c). These elongated appearance of precipitates might result from the overlap of the several individual precipitates. It is believed that coalescence should have taken place at 1100°C annealing. Round precipitates as small as 10 to 20 nm in diameter were also observed between the elongated precipitates and specimen surface. A bimodal particle size distribution from micrograph 4.19 (a) is obtained and shown in figure 4.20. The particles range in size from 17 to 56 nm in diameter with two major distributions, one is peaked at 17 nm, and the other is around 45

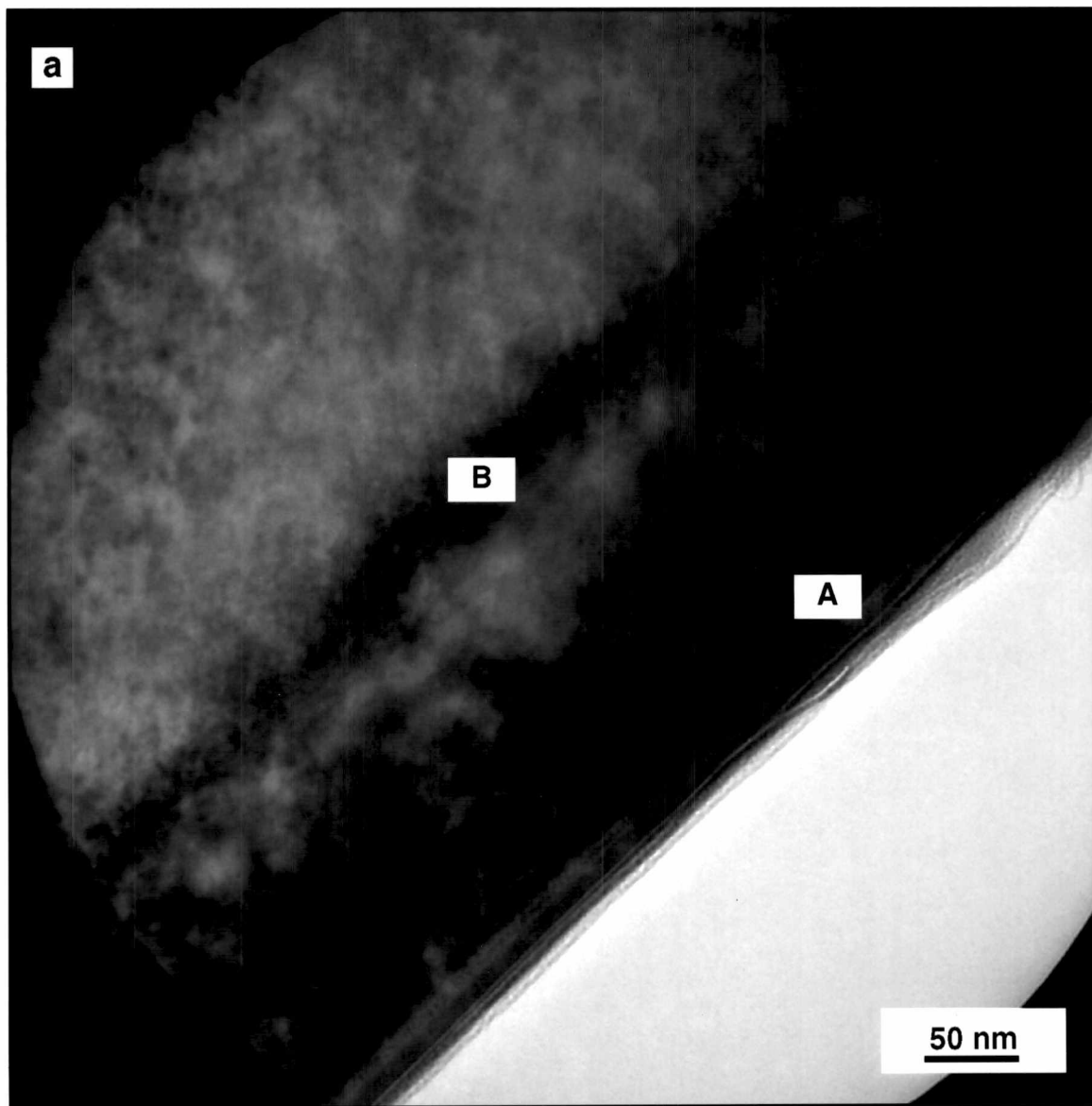


Figure 4.16 Micrograph of cross-sectioned specimen of α -Al₂O₃ implanted with 1×10^{17} Fe/cm² and annealed at 900°C. (a) x30K and (b) x70K

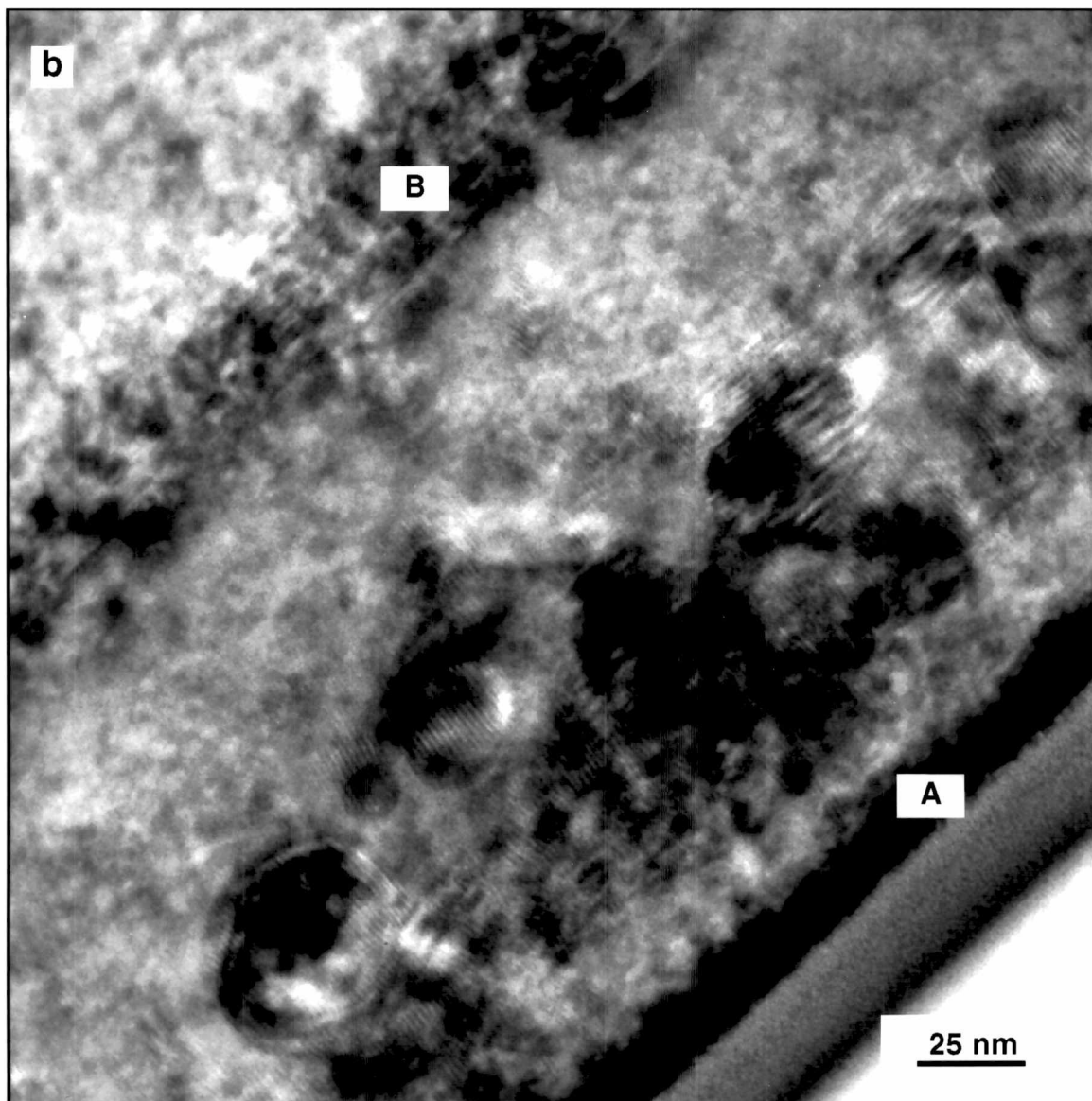


Figure 4.16 continued

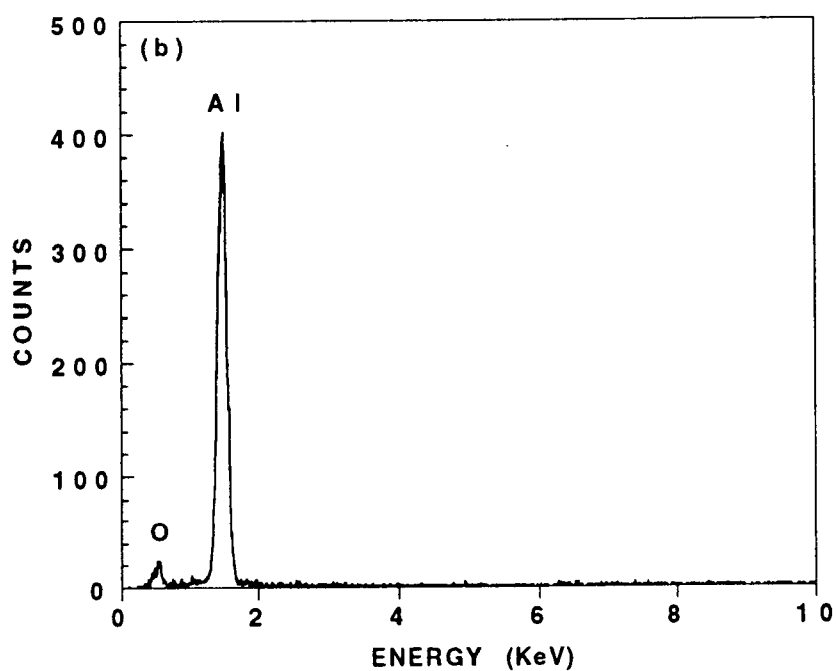
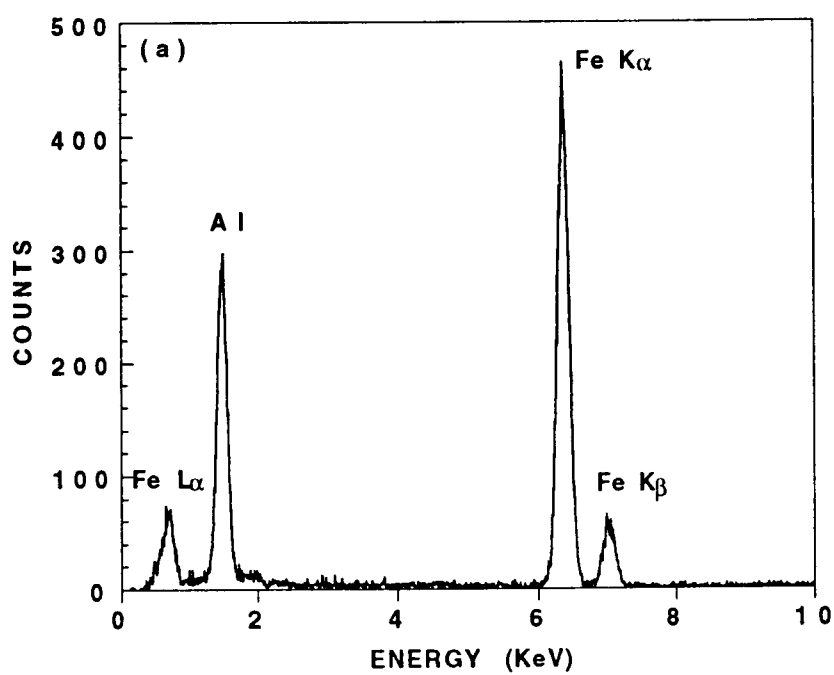


Figure 4.17 EDS of cross-sectioned specimen of α -Al₂O₃ implanted with 1×10^{17} Fe/cm² and annealed at 900°C. (a) region A, and (b) region B

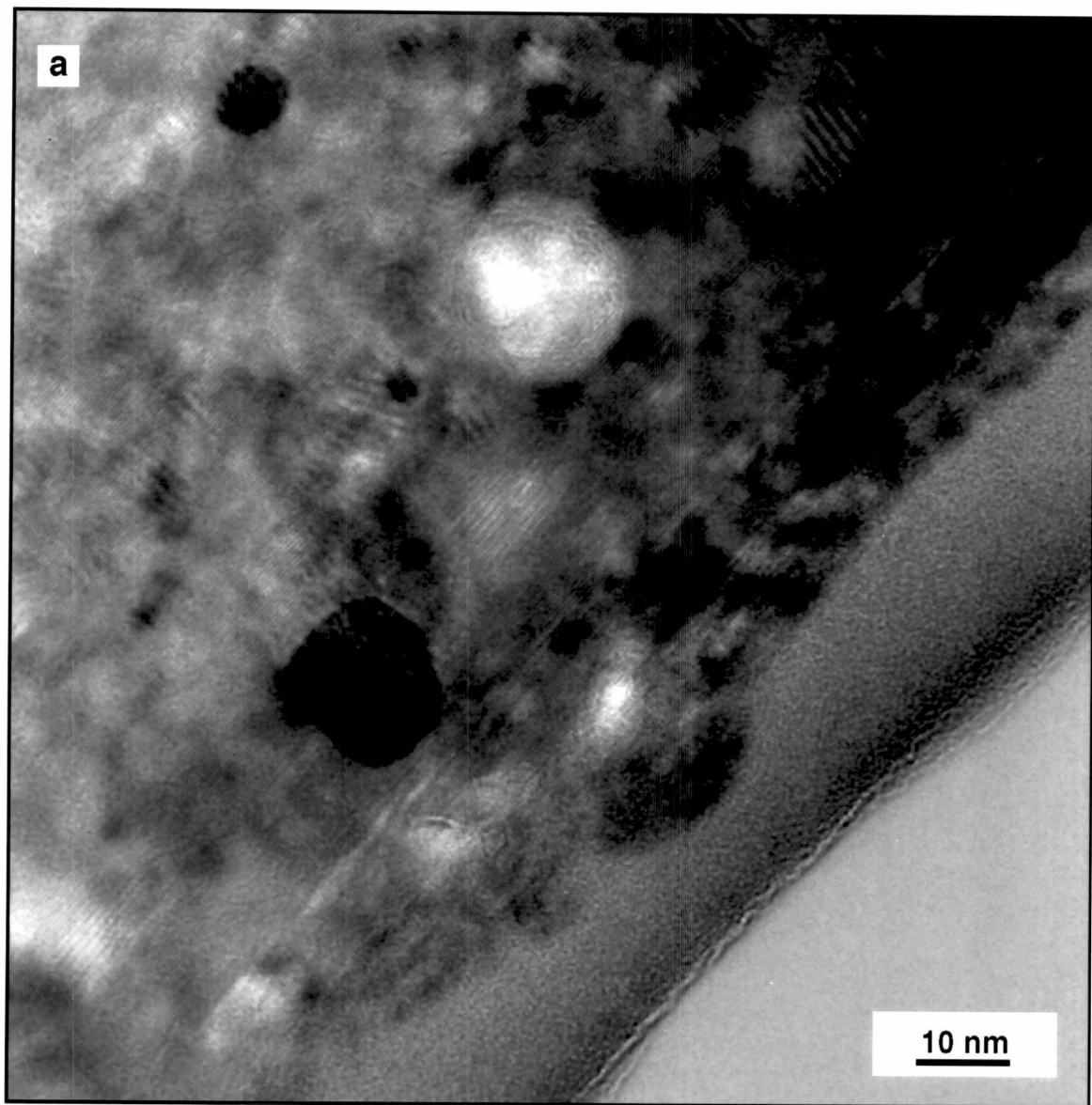


Figure 4.18 Micrograph of cross-sectioned specimen of α - Al_2O_3 implanted with $1 \times 10^{17} \text{ Fe/cm}^2$ and annealed at 900°C . (a) $\times 150\text{K}$, and (b) $\times 300\text{K}$

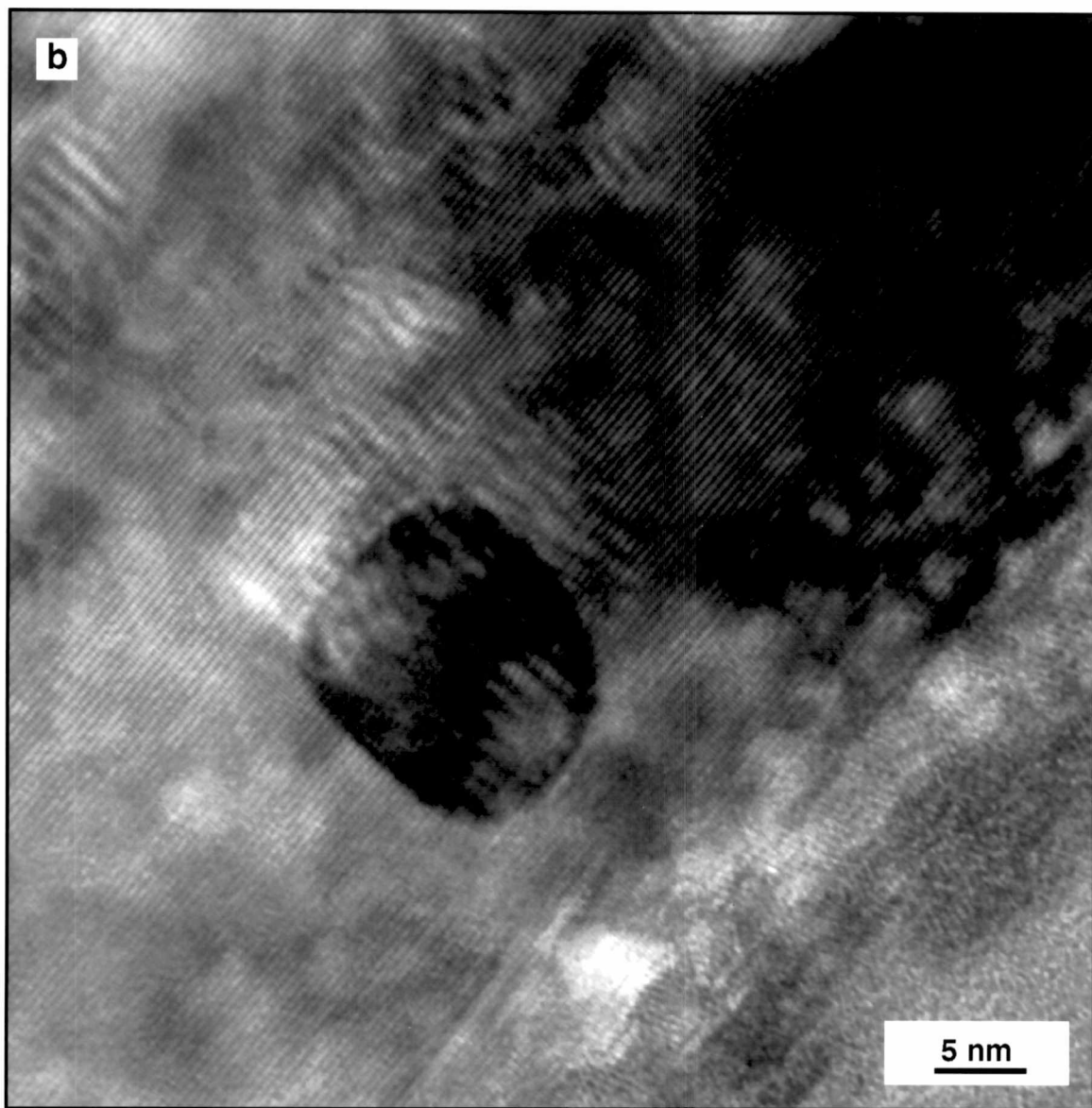


Figure 4.18 continued

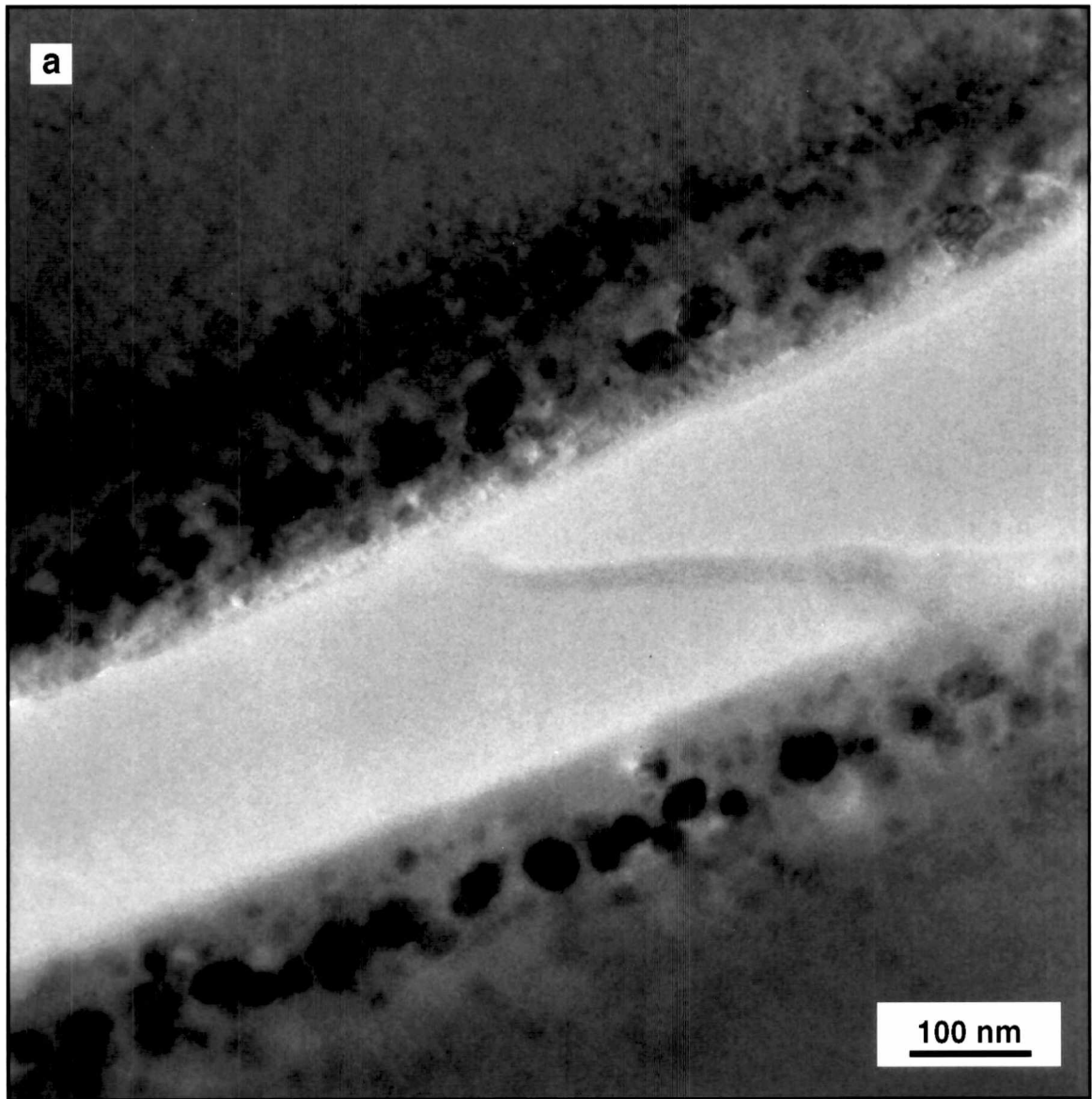


Figure 4.19 Micrograph of cross-sectioned specimen of α -Al₂O₃ implanted with 1×10^{17} Fe/cm² and annealed at 1100°C.
(a) x20K, (b) x30K, and (c) x50K

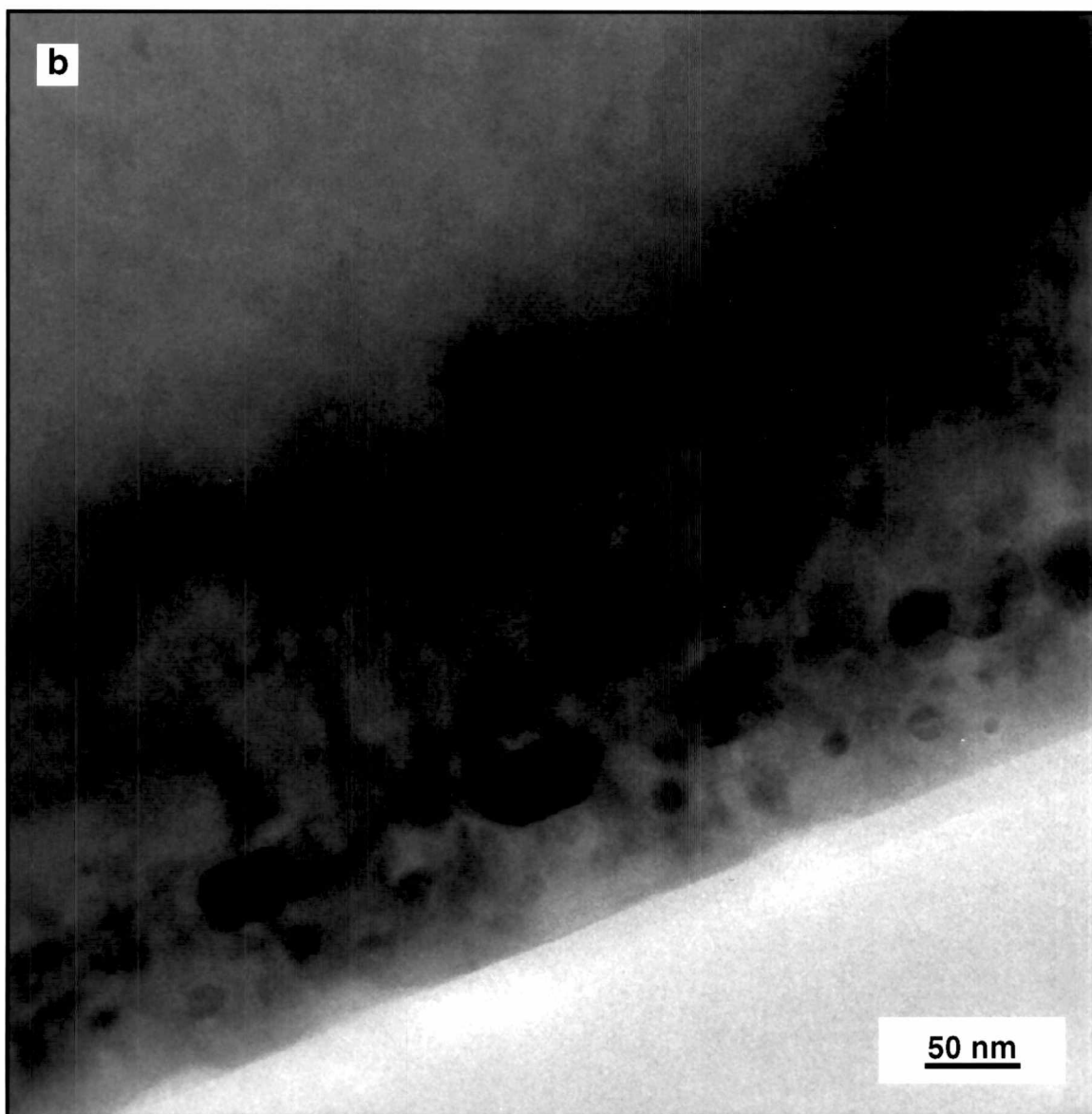


Figure 4.19 continued

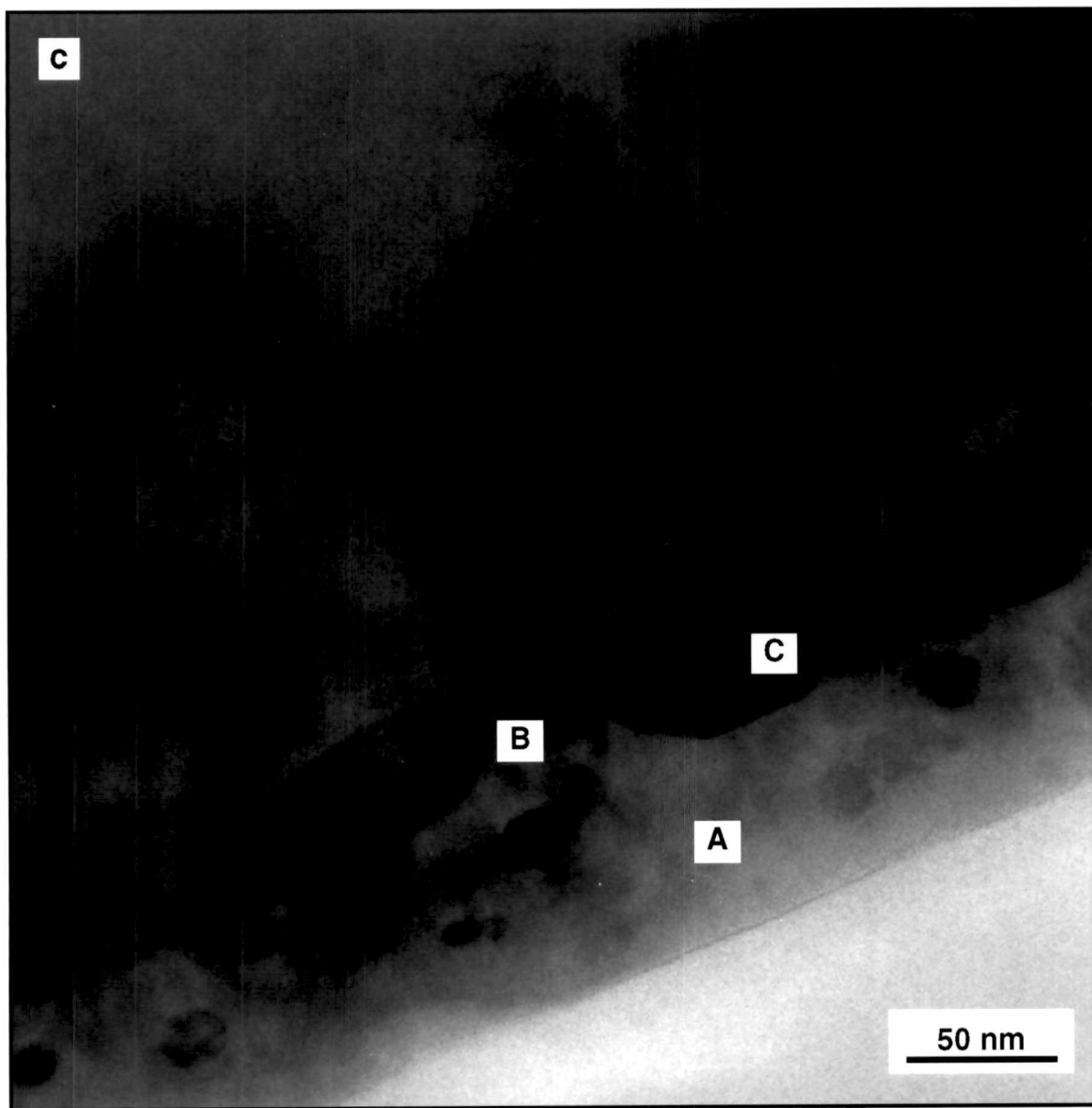


Figure 4.19 continued

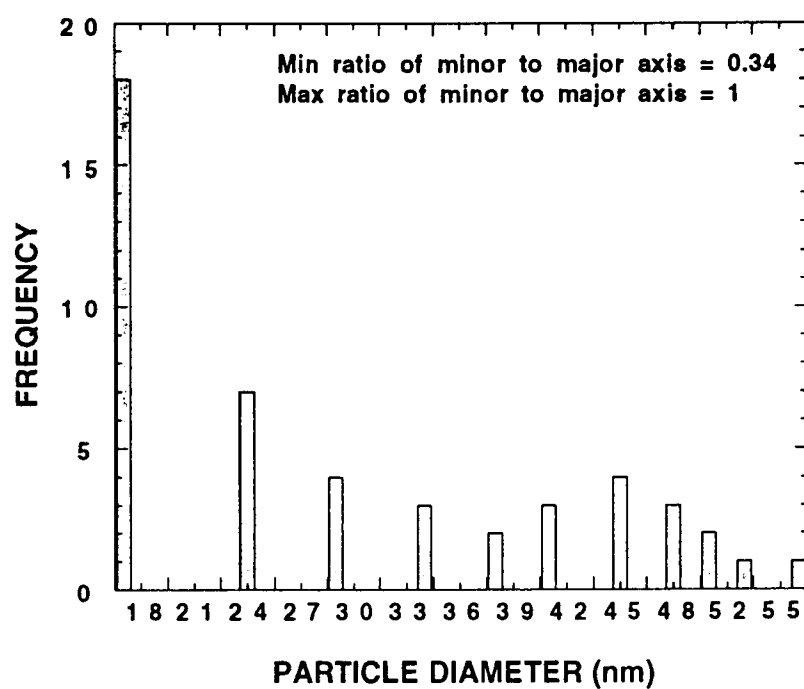


Figure 4.20 Particles distribution measured from micrograph 4.19 (a).

nm diameter. The minimum ratio of minor to major axis is 0.34 indicating the existence of some ellipsoidal particles. EDS measurements made at area A, B, and C on micrograph 4.19 (c) are shown in figure 4.21 (a), (b), and (c). The results indicate that no iron was found in area A, iron precipitates appeared in area B, and more iron precipitates showed in area C.

Figures 4.22 (a), (b), (c), and (d) are the micrographs of the cross-sectioned specimen of sapphire implanted with $2 \times 10^{17} \text{ Fe/cm}^2$. Oriented precipitates were observed in the amorphous Al_2O_3 matrix in figure 4.22 (d). This observation suggests that the particles first precipitate while the matrix was still crystalline. EDS measurements indicated that these precipitates were iron-rich. A series of ultra-fine X-ray probes were scanned from the surface to the end of damage region for the purpose of chemical analysis on the iron-implanted sapphire as shown in figure 4.23 (a) to (e). The results suggest that area A was attributed to the glue between the implanted surfaces; a few iron precipitates appeared in area B at the subsurface region; high density of iron precipitates showed in the peak iron concentration area C; some iron precipitates were found in area D, the tail of the peak iron concentration; and area E indicated the "end-of-range" damage region.

A selected area diffraction pattern from the same area is shown in figure 4.24 (a). Two sets of patterns are resulted from the combination of $\langle 111 \rangle_{\alpha\text{-Fe}}$ and $\langle 310 \rangle_{\text{sapphire}}$ matrix as indexed in figure 4.24 (b) where the large spots represent the diffraction pattern of sapphire, and the small spots represent that of $\alpha\text{-Fe}$. The diffuse $\alpha\text{-Fe}$ pattern was due to the subtle misorientation of the precipitates. These 2 to 3 nm oriented precipitates in figure 4.22 (d) were thus identified as body centered cubic $\alpha\text{-Fe}$ and presented the following orientation relationship with the sapphire matrix: $\langle 111 \rangle_{\alpha\text{-Fe}} \parallel \langle 310 \rangle_{\text{sapphire}}$ and $\{01\bar{1}\}_{\alpha\text{-Fe}} \parallel \{006\}_{\text{sapphire}}$. It appears that the close packed planes $\{01\bar{1}\}_{\alpha\text{-Fe}}$ and $\{006\}_{\text{sapphire}}$ are parallel to each other, but not the close packed directions $\langle 111 \rangle_{\alpha\text{-Fe}}$ and $\langle 210 \rangle_{\text{sapphire}}$. This phenomenon can be explained by the following calculation and

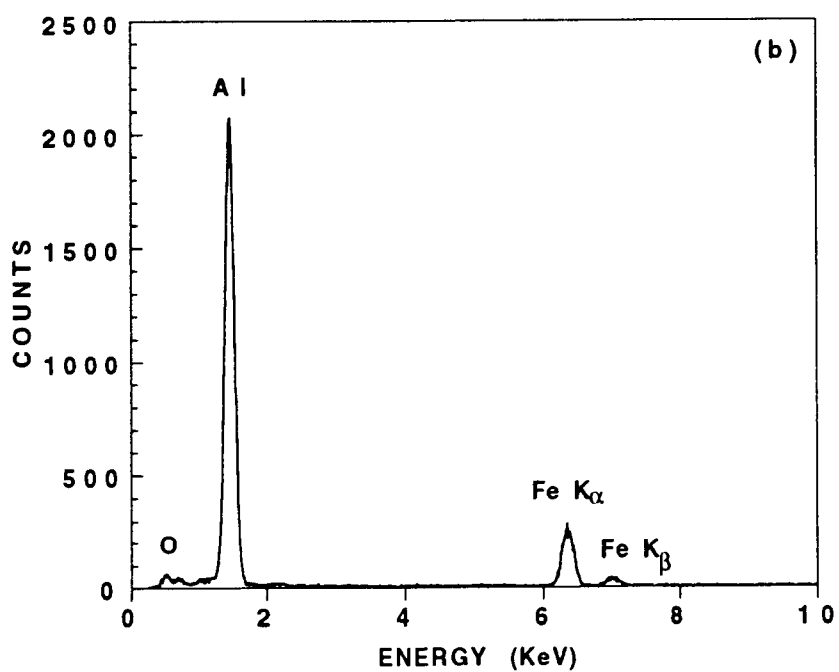
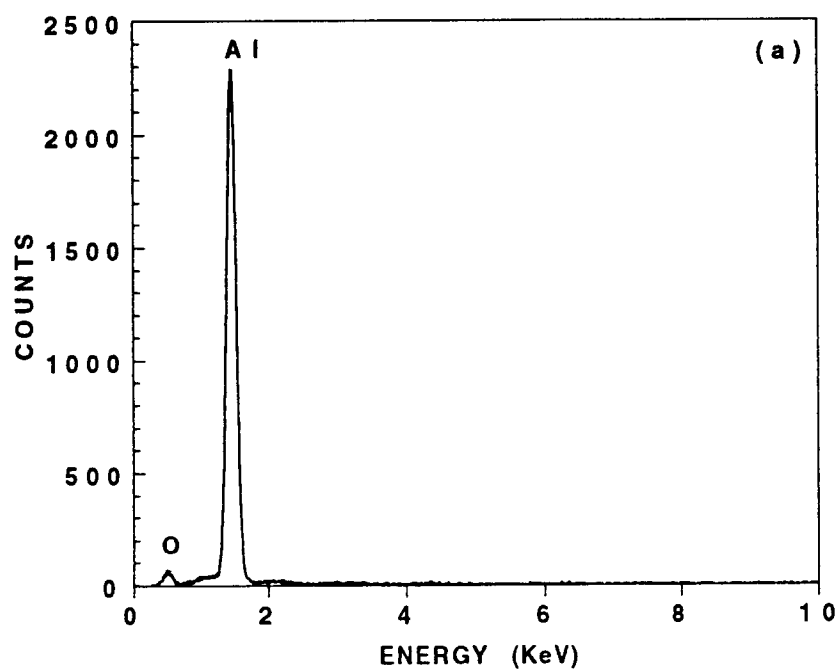


Figure 4.21 EDS of cross-sectioned specimen of α -Al₂O₃ implanted with 1×10^{17} Fe/cm² and annealed at 1100°C. (a) area A, (b) B, and (c) C.

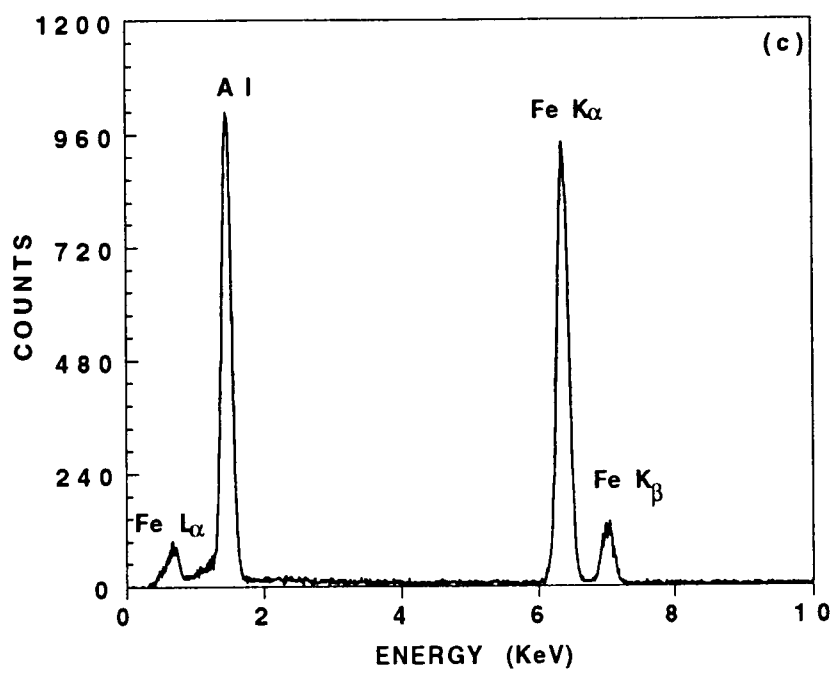


Figure 4.21 continued

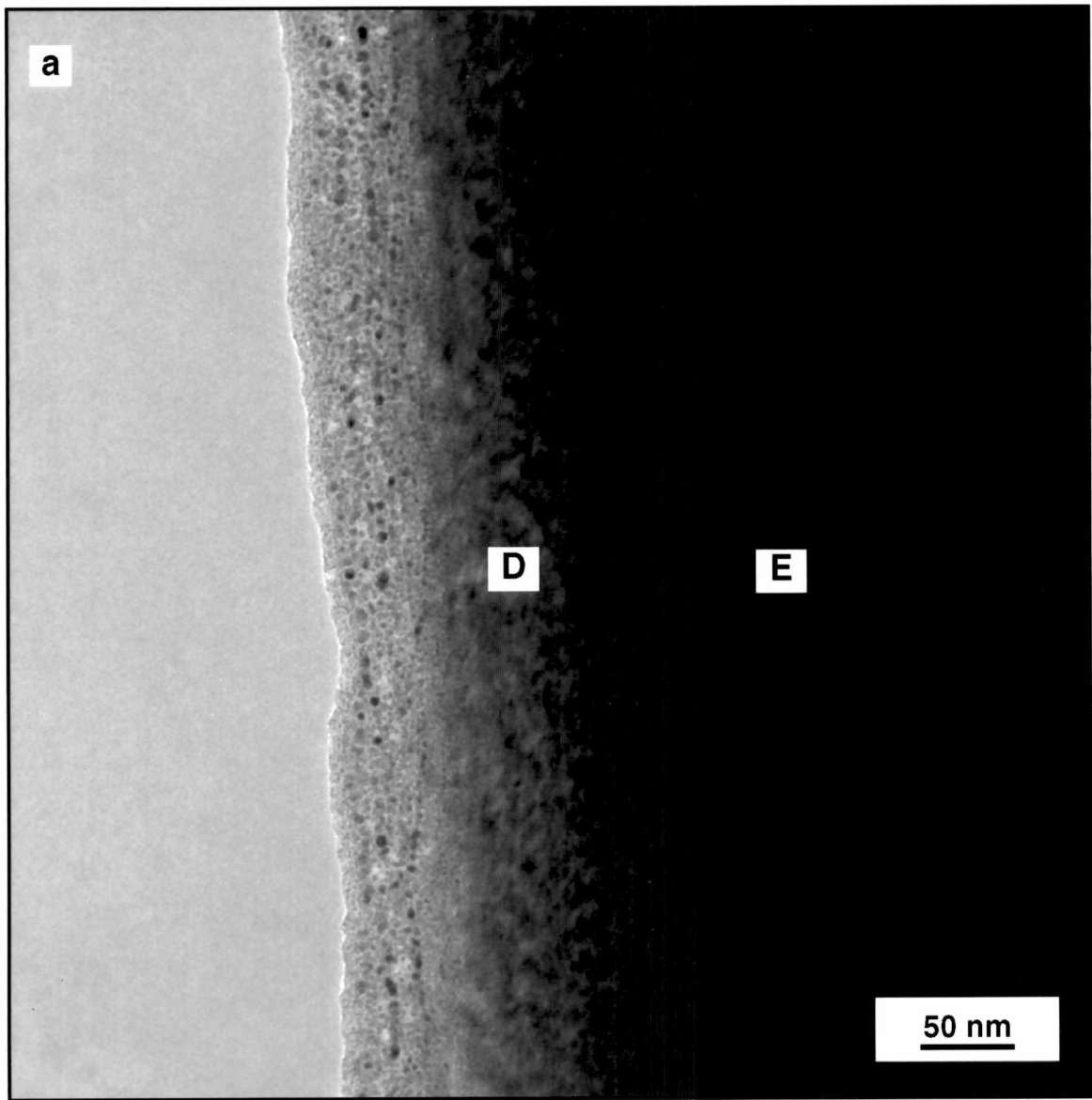


Figure 4.22 Micrograph of cross-sectioned specimen of α -Al₂O₃ implanted with 2×10^{17} Fe/cm². (a) x30K, (b) x200K, (c) x300K, and (d) x500K

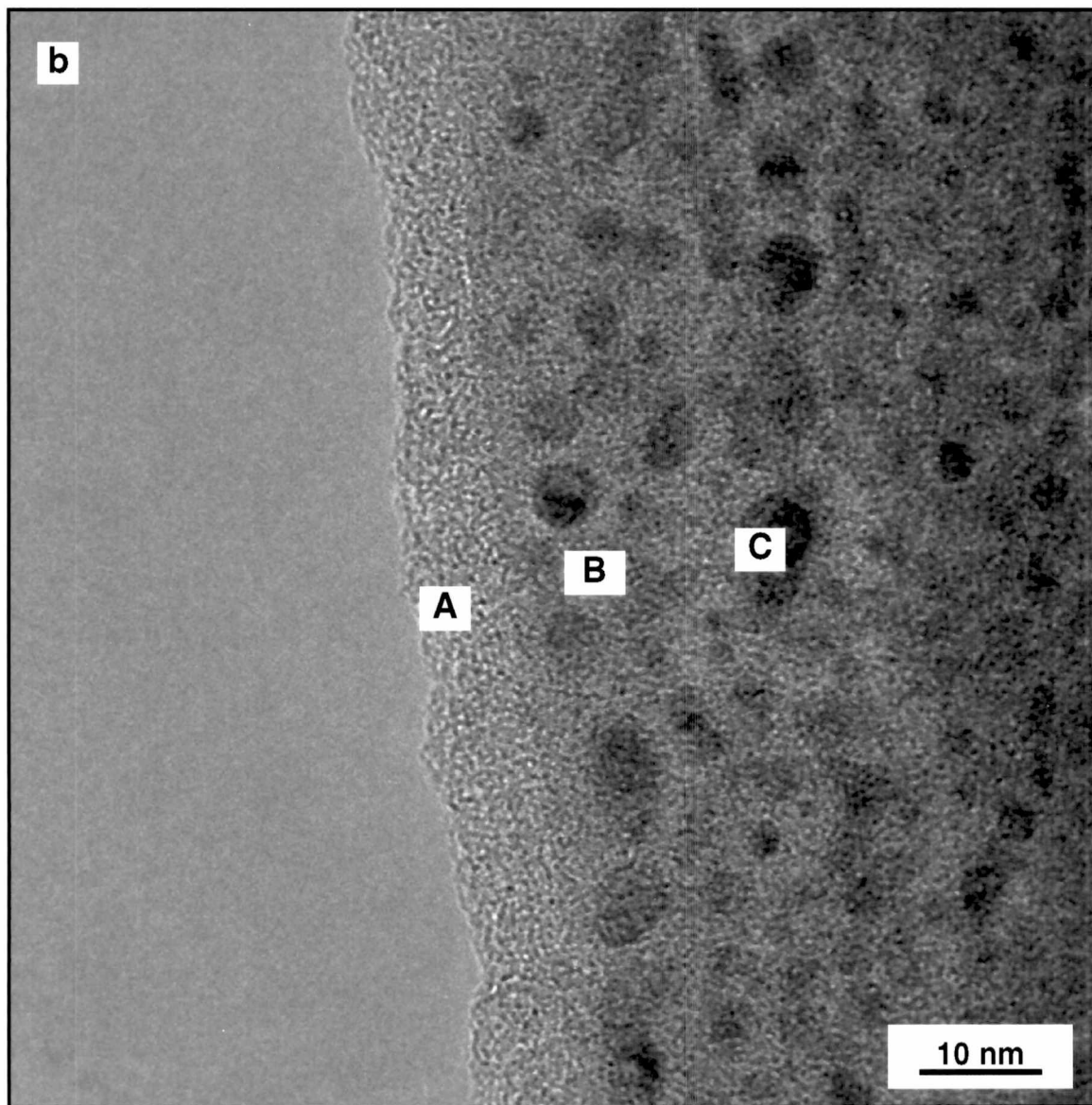


Figure 4.22 continued

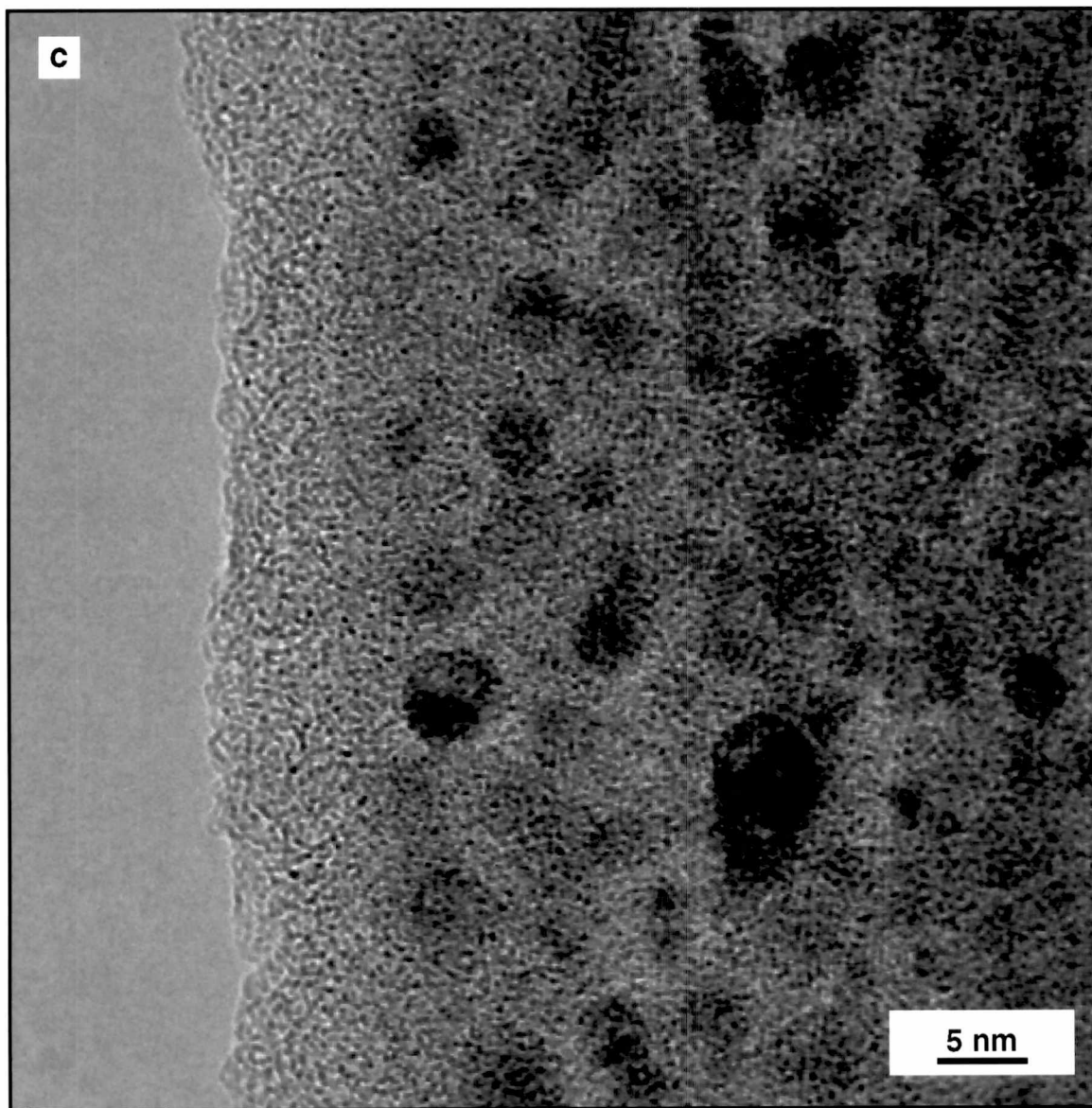


Figure 4.22 continued

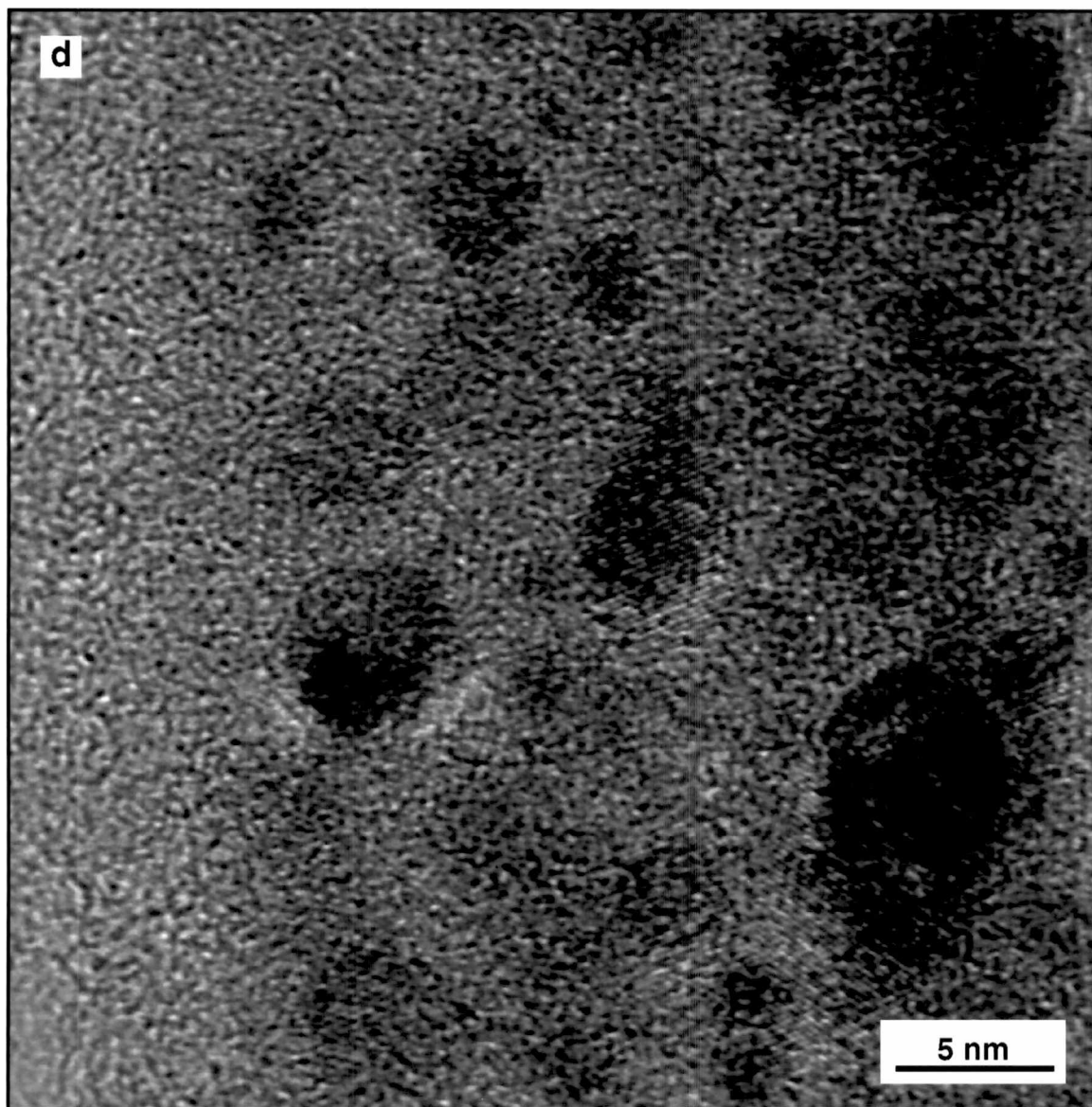


Figure 4.22 continued

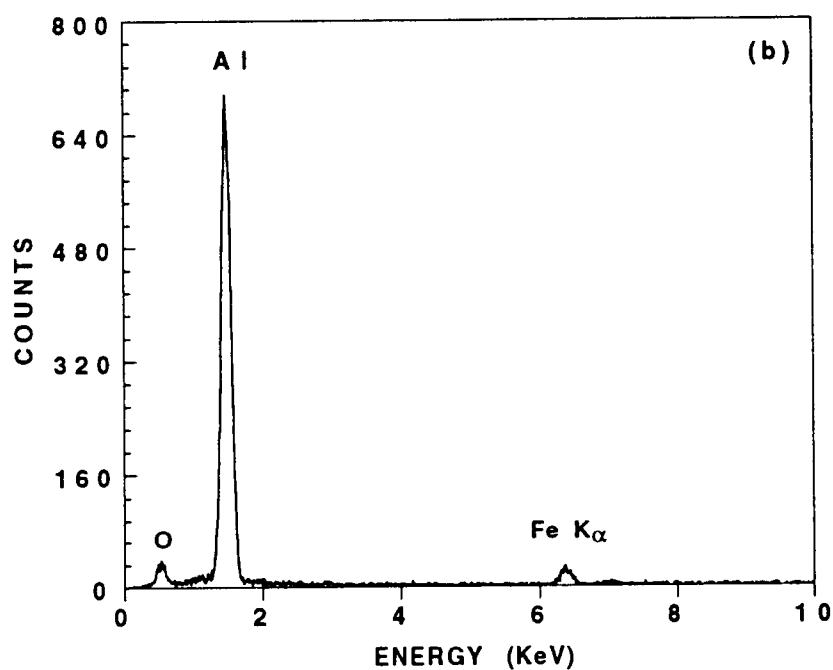
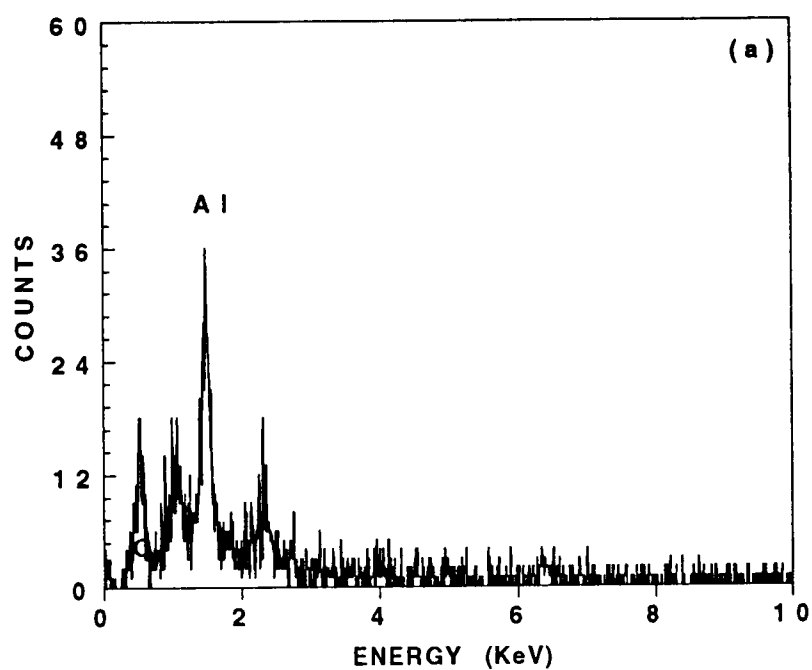


Figure 4.23 EDS of cross-sectioned specimen of α -Al₂O₃ implanted with 2×10^{17} Fe/cm².
at point (a) A, (b) B, (c) C, (d) D, and (e) E.

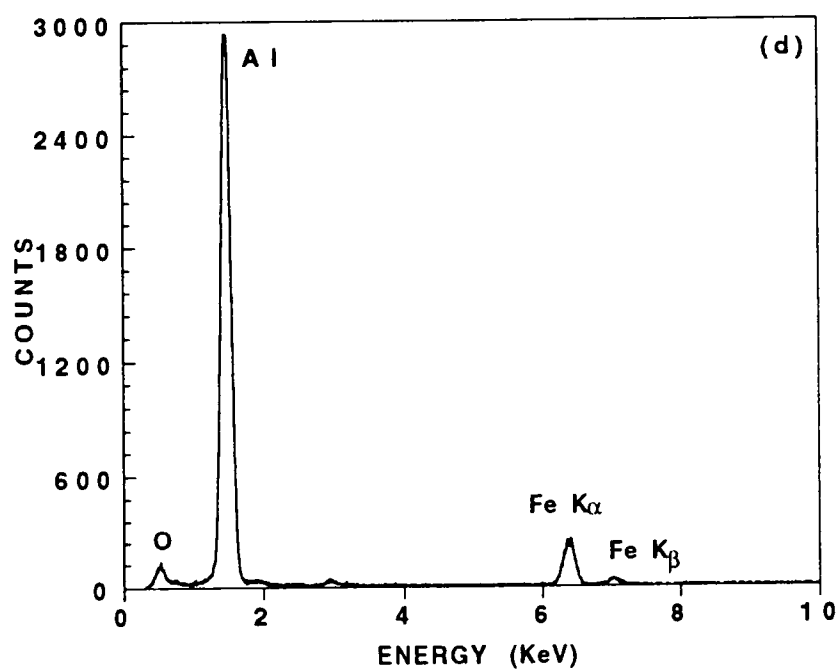
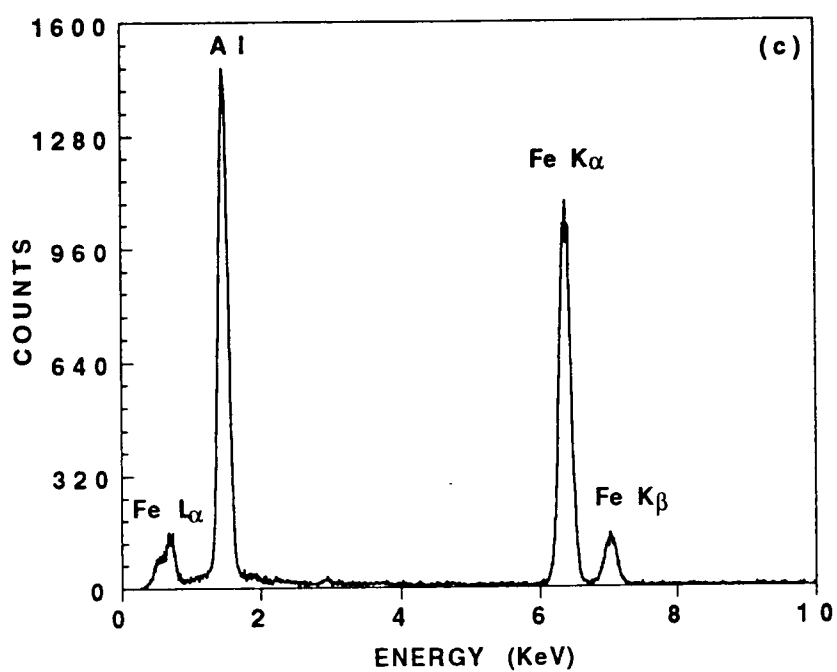


Figure 4.23 continued

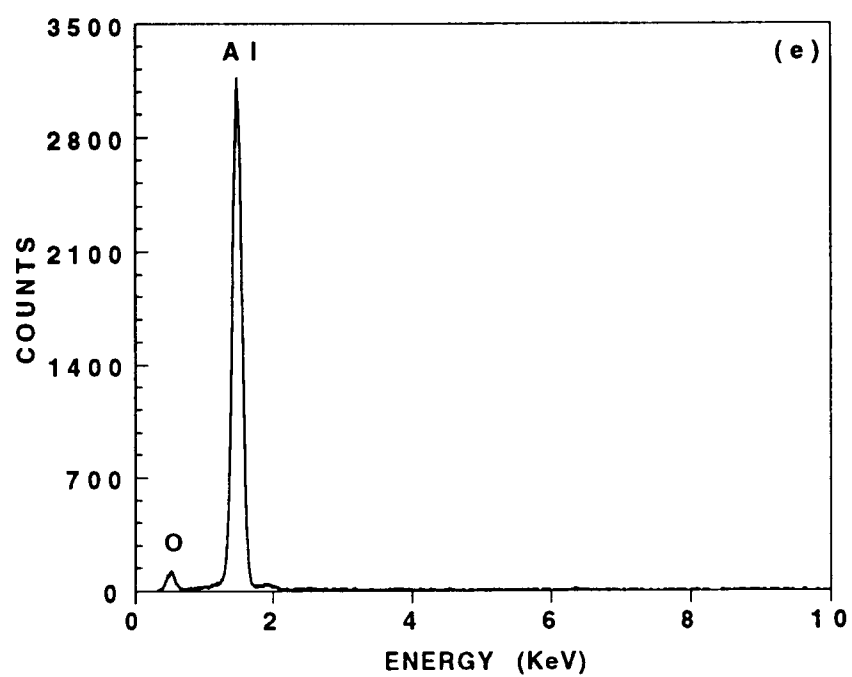


Figure 4.23 continued

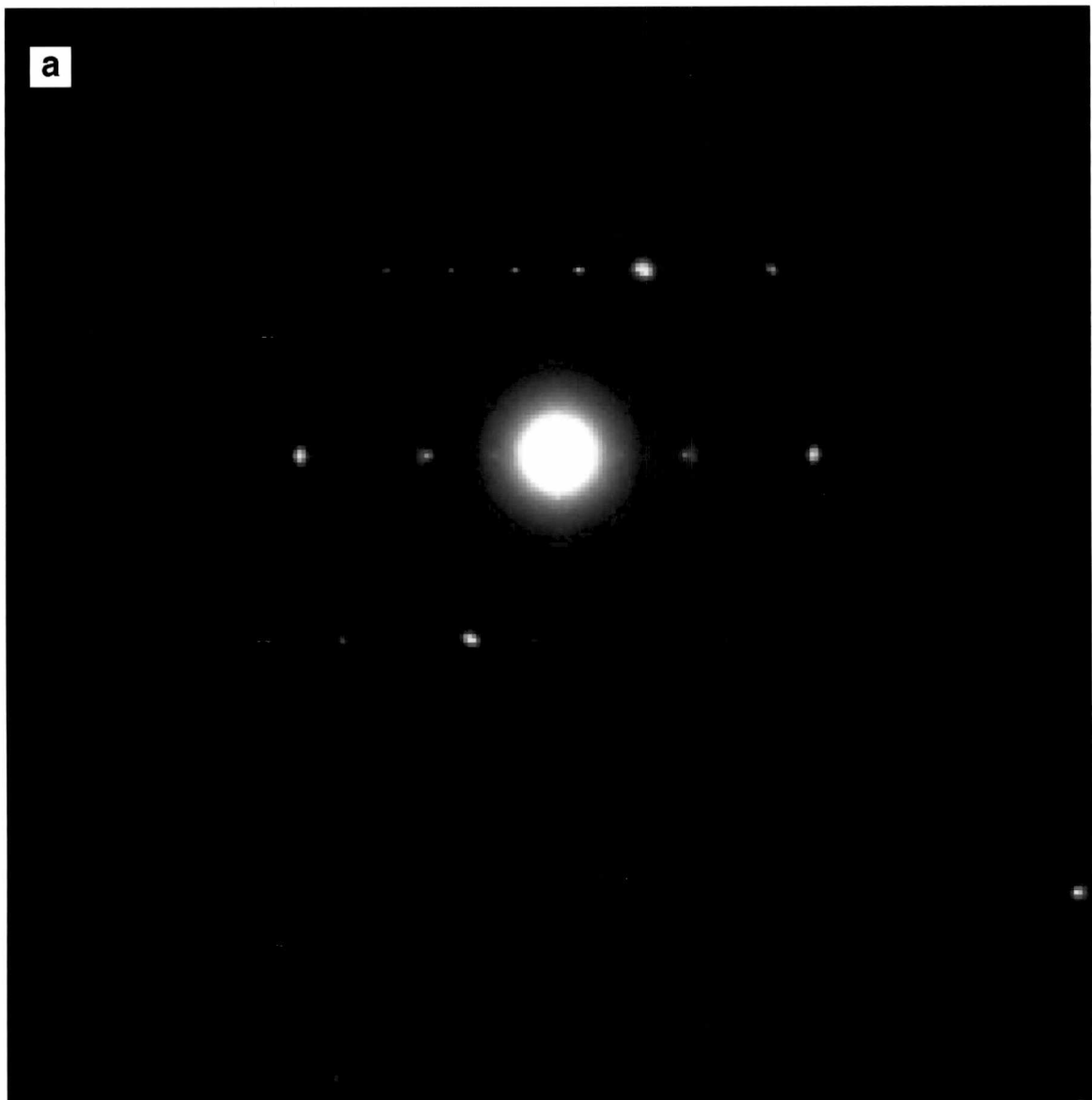


Figure 4.24 SAD patterns of cross-sectioned specimen of α - Al_2O_3 implanted with $2 \times 10^{17} \text{ Fe/cm}^2$. (a) experimental results and (b) calculated data

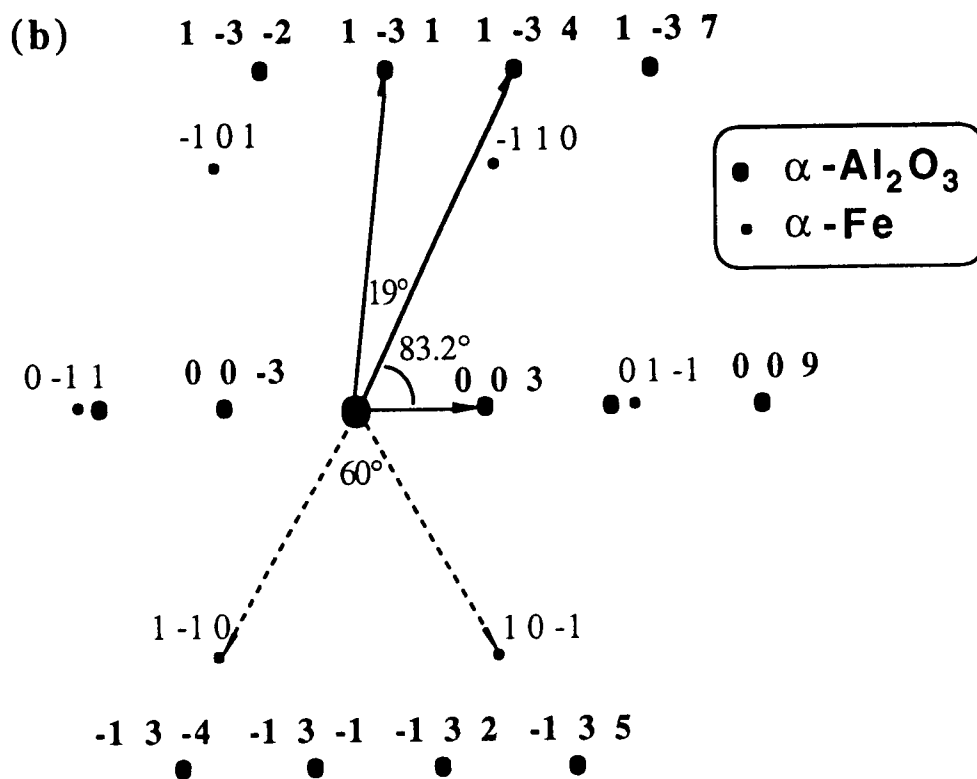


Figure 4.24 continued

schematic illustration shown in figure 4.25.

$$\begin{aligned}\text{Assume: } a_0 (\alpha\text{-Fe}) &= 0.2866 \text{ nm,} \\ a_0 (\alpha\text{-Al}_2\text{O}_3) &= 0.475 \text{ nm}\end{aligned}$$

$$\begin{aligned}\text{By geometry, we have: Fe-Fe spacing} &= 0.2866 \text{ nm along } \langle 001 \rangle \\ &= 0.4053 \text{ nm along } \langle 110 \rangle \\ \text{Al-Al spacing} &= 0.2742 \text{ nm along } \langle \bar{1}\bar{1}0 \rangle \\ &= 0.475 \text{ nm along } \langle 110 \rangle\end{aligned}$$

$$\begin{aligned}\text{Misfit: } \frac{0.2866 - 0.2742}{0.2866} &= 4.3\% \quad \text{along } \langle \bar{1}\bar{1}0 \rangle \text{ sapphire} \\ \frac{0.4053 - 0.475}{0.4053} &= 17\% \quad \text{along } \langle 110 \rangle \text{ sapphire}\end{aligned}$$

Since there is a large misfit along $\langle 110 \rangle$ sapphire for the close packed directions of $\langle 111 \rangle \alpha\text{-Fe}$ and $\langle 210 \rangle$ sapphire to be parallel to each other, it's necessary to have sapphire rotated about 10° from direction $\langle 210 \rangle$ to $\langle 310 \rangle$ in order to release some strains.

Micrographs of samples implanted with $2 \times 10^{17} \text{ Fe/cm}^2$ and annealed at 900°C are shown in figure 4.26 (a), (b), and (c). EDS measurements made at the positions A and B as indicated on figure 4.19 (c) confirmed that the dark area in the band was iron rich, and the light area contained almost no iron. It is very interesting to note that the iron concentrated in a band about 25 nm wide at a depth of 50 nm below the surface. Elliptical $\alpha\text{-Fe}$ precipitates of 10 to 40 nm in length were found on both sides of the band. These precipitates appear to exhibit the tendency of forming parallel bands as well. However, the distribution of iron in the band shown in figure 4.26 (c) was not continuous, and the intermediate regions contained amorphous material. It is speculated that the discontinuity

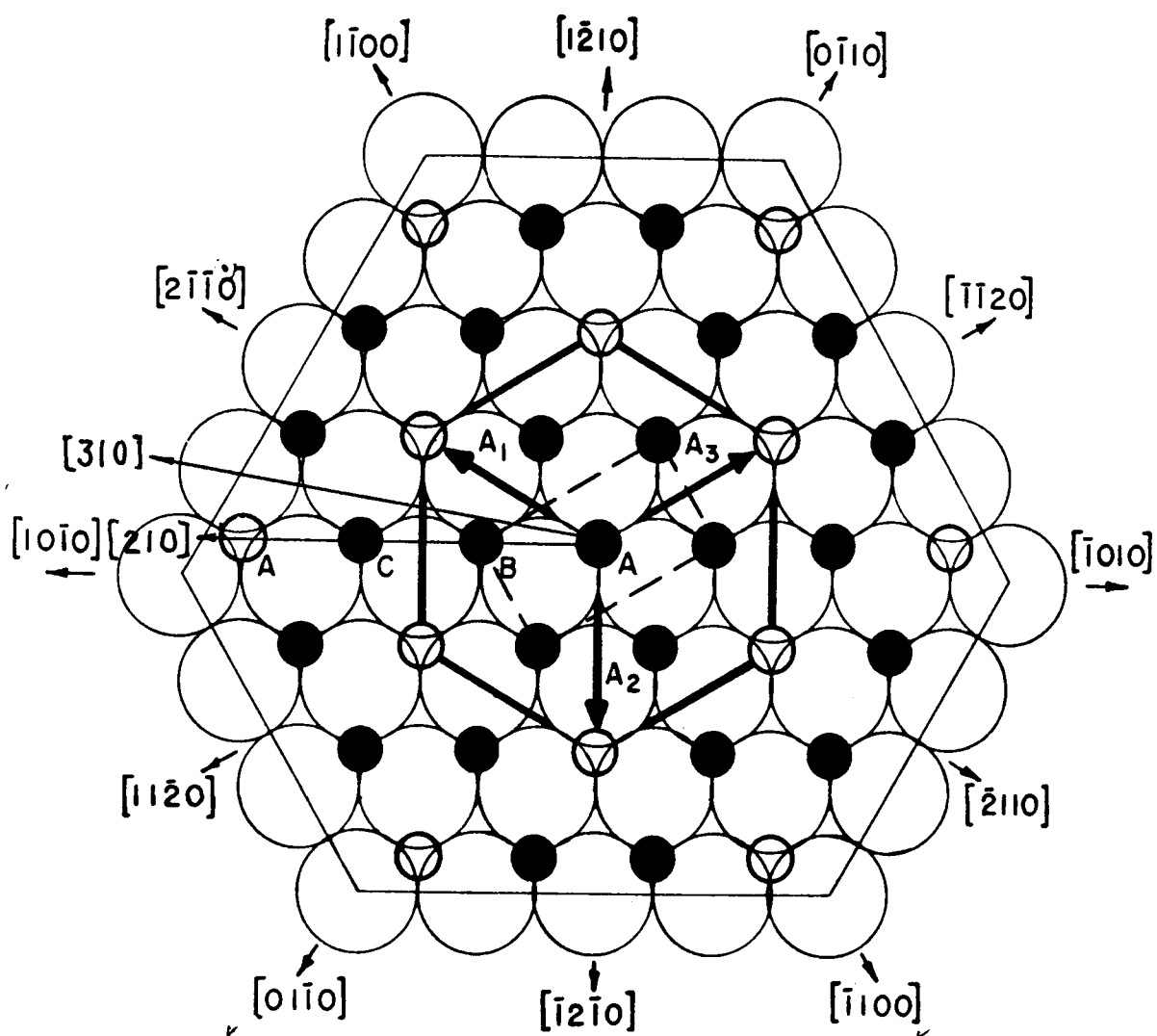


Figure 4.25 Schematic illustration of two closed-packed parallel planes. Basal hexagonal cell of sapphire (solid lines) and $\{110\}$ plane of α -Fe (dashed lines).

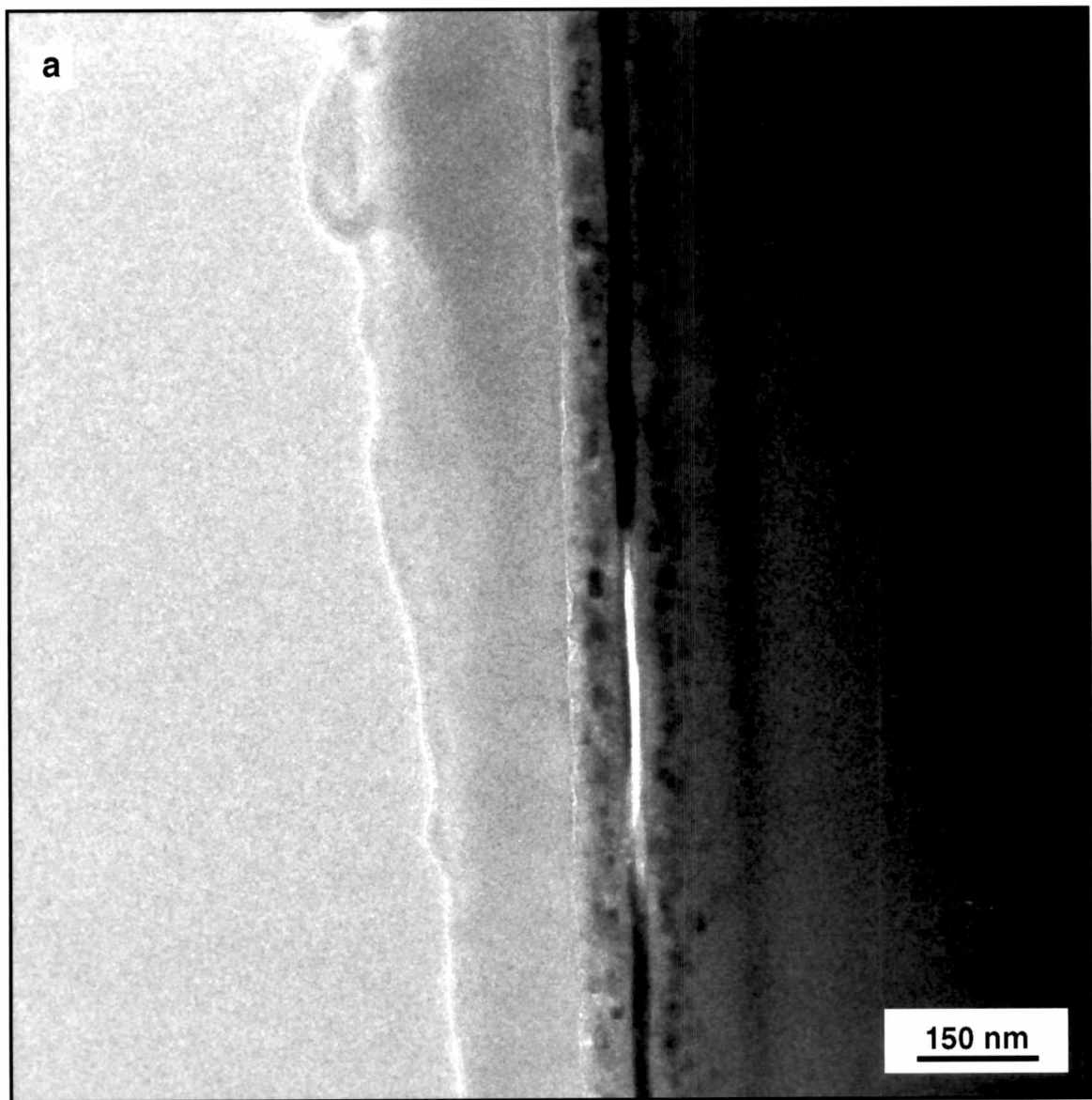


Figure 4.26 Micrograph of cross-sectioned specimen of α -Al₂O₃ implanted with 2×10^{17} Fe/cm² and annealed at 900°C.
(a) x15K, (b) x30K, and (c) x70K

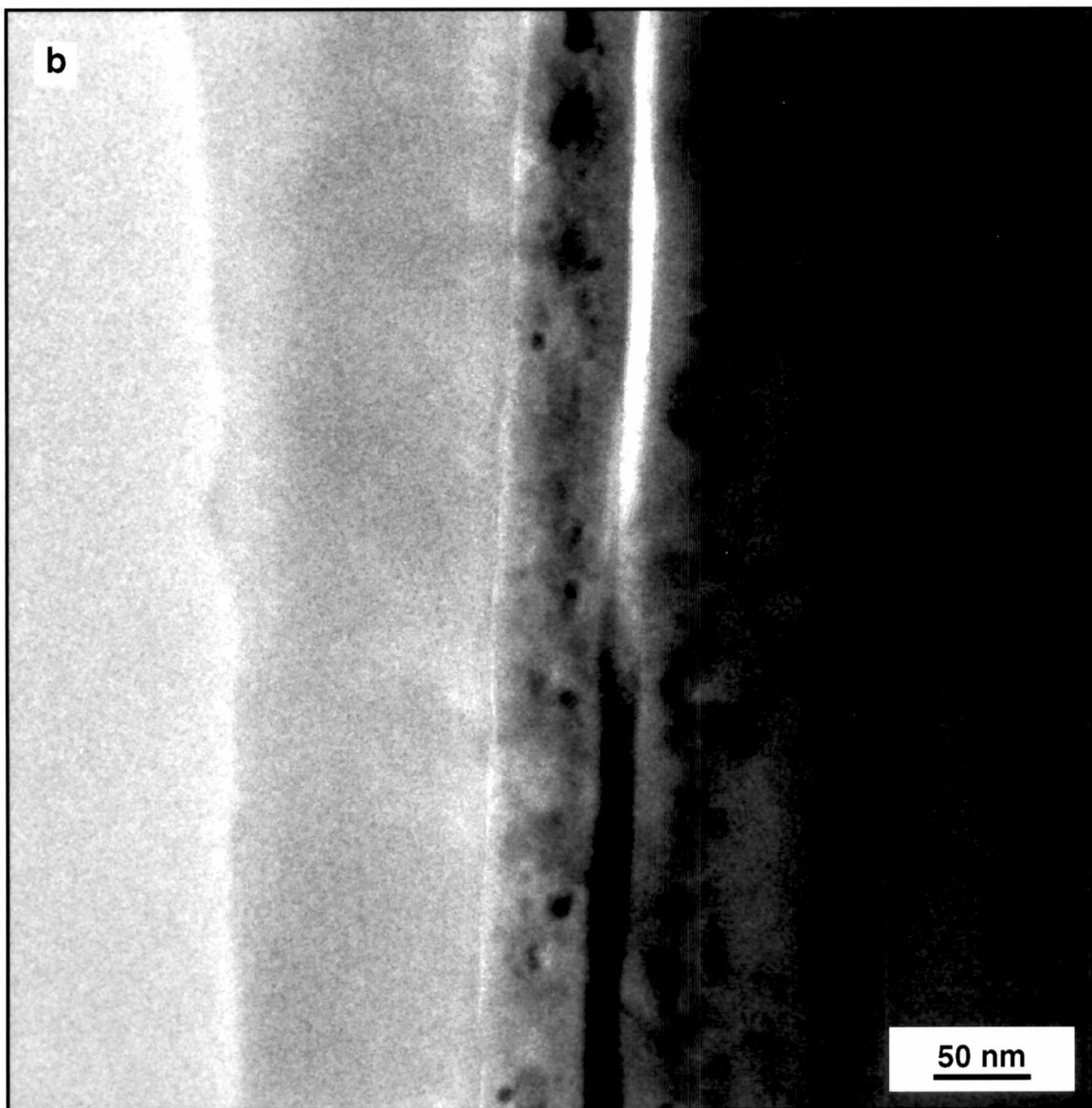


Figure 4.26 continued

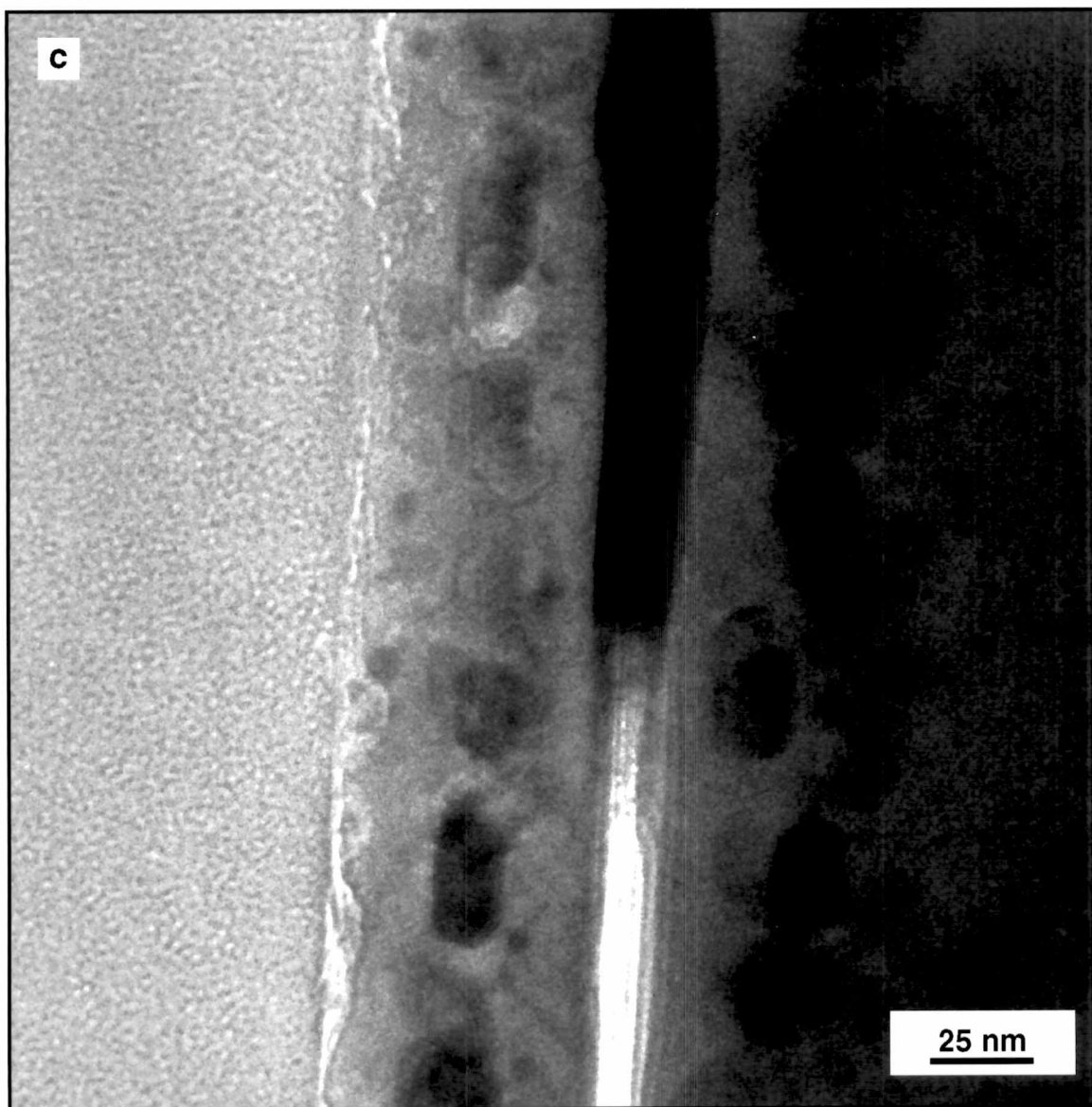


Figure 4.26 continued

of the band resulted from the coalescence of the precipitates and the cavities as well, or was due to stresses generated by the difference in coefficient of thermal expansion.

The discontinuity of the embedded iron was also found in the specimens which were annealed at 1100°C shown in figure 4.27 (a). Moreover, a high resolution micrograph provided lattice fringes showing the recrystallized implanted layer, as seen in figure 4.27 (b). The smallest precipitates found were about 5 nm in diameter and only 2.5 nm away from the surface. This microscopic observation also gave an evidence that iron impurities did diffuse toward the surface region and would finally evaporate from the surface as discussed in the section 4.1. Moiré fringes appeared in the Fe rich precipitates showing the crystalline nature of these precipitates.

The observation that the size of the iron precipitates depends on their position relative to the specimen surface means that the size is determined by the iron-concentration for a given annealing treatment. A single implantation energy was used in this study which gave a Gaussian distribution of iron, peaking at a position of 100 nm from the surface. Multi-energy implantation can produce an approximate constant concentration. Using those micrographs of the annealed samples, one can choose a composition and annealing treatment to obtain a predetermined narrow size distribution in the entire implanted region.

Some further studies are recommended herein to reach a higher level understanding of the microstructure changes produced by ion implantation. Additional researches include the study of the nature of ion milling damage, and the structure of Fe/sapphire interfaces. Convergent beam electron diffraction is needed to study the as-implanted precipitates. EELS measurement is suitable to obtain the chemical effects. Further annealing, in laser or microwave, is desired to try to obtain a continuous metallic layer.

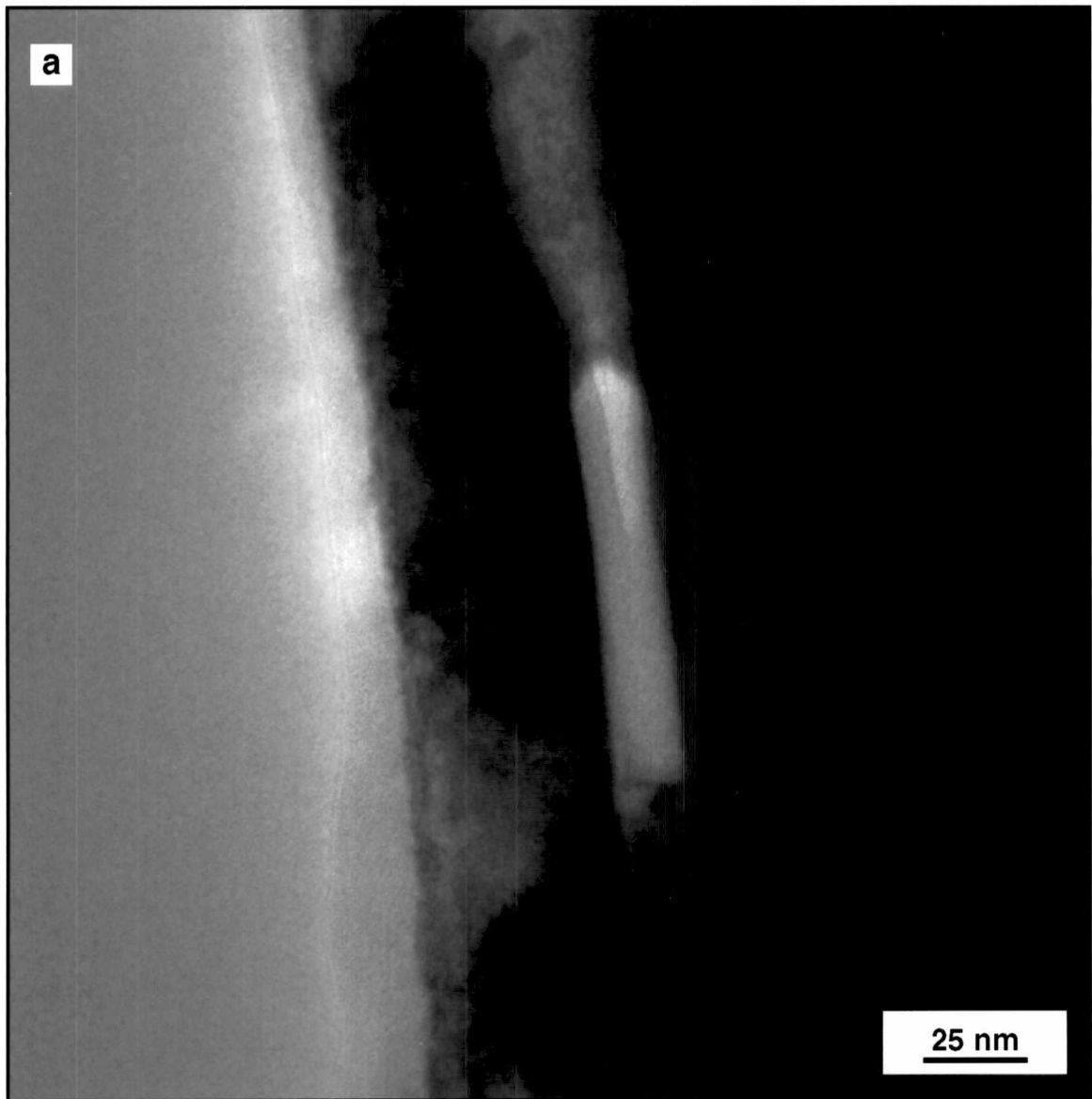


Figure 4.27 Micrograph of cross-sectioned specimen of α - Al_2O_3 implanted with $2 \times 10^{17} \text{ Fe/cm}^2$ and annealed at 1100°C . (a) $\times 70\text{K}$, and (b) $\times 400\text{K}$

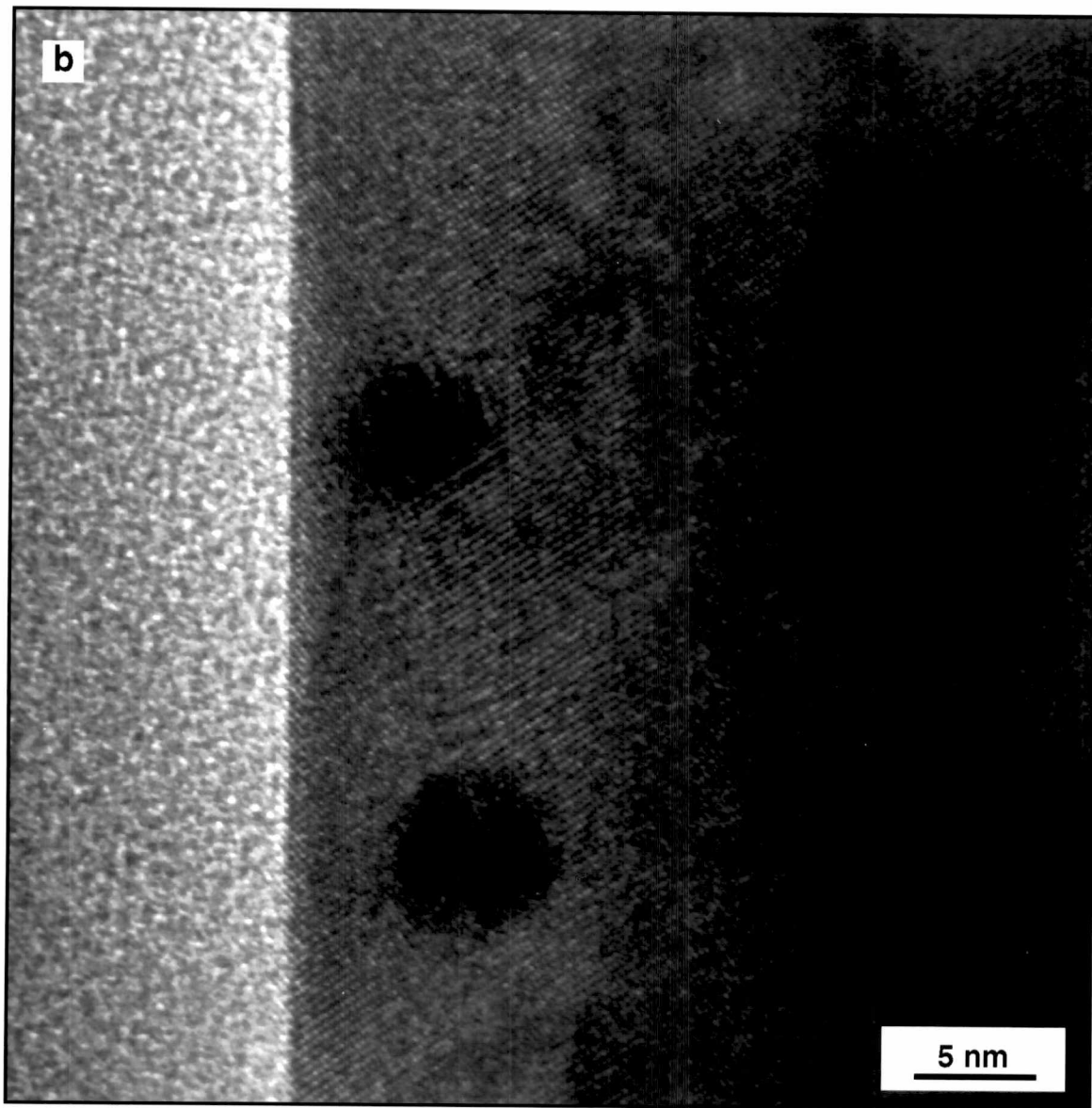


Figure 4.27 continued

4.3 Optical Properties

The optical properties of sapphire are particularly sensitive to the presence of point defect complexes. Defects based on the anion sublattice have been extensively studied and provide a base to analyze the structures produced in this study [19, 39].

Optical absorption measurements of α -Al₂O₃ implanted with 4×10^{16} Fe/cm² and annealed for 1 h in an Ar-4% H₂ atmosphere at selected temperatures, shown in figure 4.28, exhibit a strong absorption band at about 200 nm. This absorption has been identified as being due to F centers (an oxygen vacancy containing two electrons) [19] as illustrated in figure 2.4. The optical density of this band, which is proportional to the concentration of the F centers, decreased as the annealing temperature increased. In the figure, the broad extinction band between 230 to 400 nm is attributed to Mie scattering [29] from the precipitates. It is also noted that the optical density of this broad band increased as the annealing temperature was increased, which is consistent with TEM measurements that the density of iron precipitates increased with increasing annealing temperature due to the coalescence mechanism.

Figure 4.29 shows optical absorption spectra of α -Al₂O₃ implanted with 1×10^{17} Fe/cm² and annealed for 1 h in an Ar-4% H₂ atmosphere at selected temperatures as indicated on the spectra. Again, the absorption band located at about 200 nm is attributed to F centers. The density of this band is inversely proportional to the annealing temperature due to the damage recovery during heat treatment. The broad extinction band from 230 to 440 nm results from Mie scattering from the precipitates. More iron was implanted in this specimen, and more precipitates were expected, therefore, the extinction band became higher and broader.

Optical absorption spectra of α -Al₂O₃ implanted with 2×10^{17} Fe/cm² and annealed for 1 h in an Ar-4% H₂ atmosphere at selected temperatures were shown in figure 4.30. The

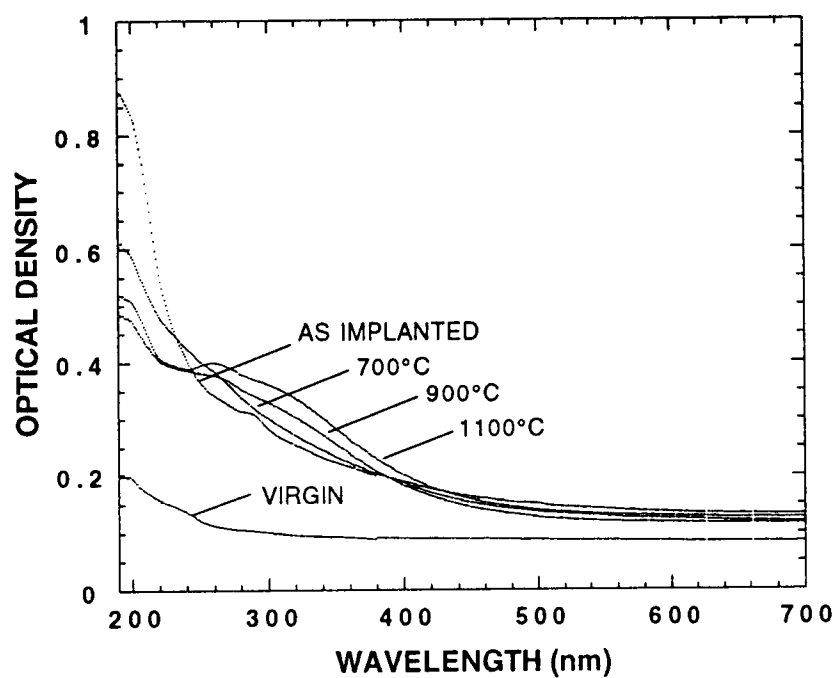


Figure 4.28 Optical absorption spectra of α - Al_2O_3 implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ and annealed for 1 h in an Ar-4% H_2 atmosphere at selected temperatures.

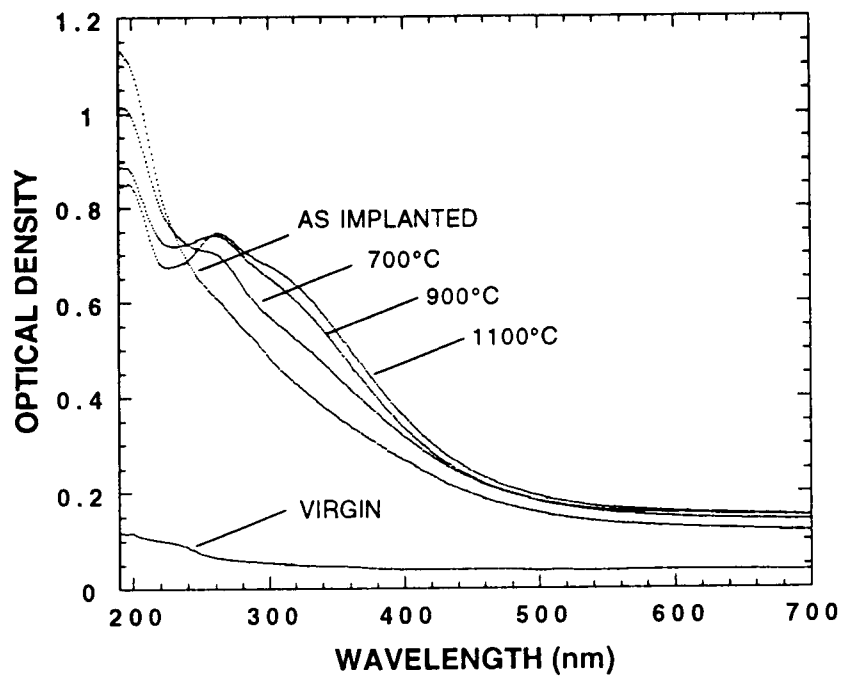


Figure 4.29 Optical absorption spectra of α - Al_2O_3 implanted with $1 \times 10^{17} \text{ Fe/cm}^2$ and annealed for 1 h in an Ar-4% H_2 atmosphere at selected temperatures.

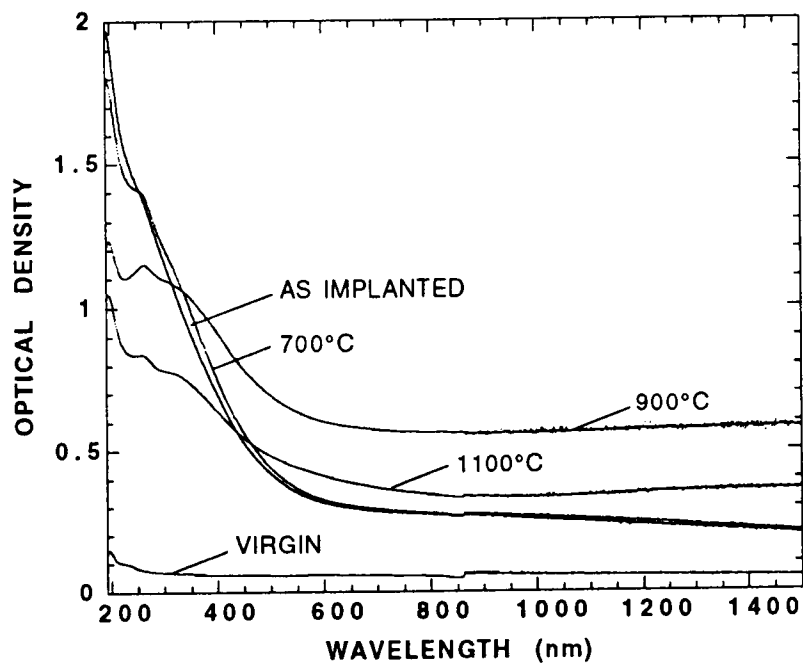
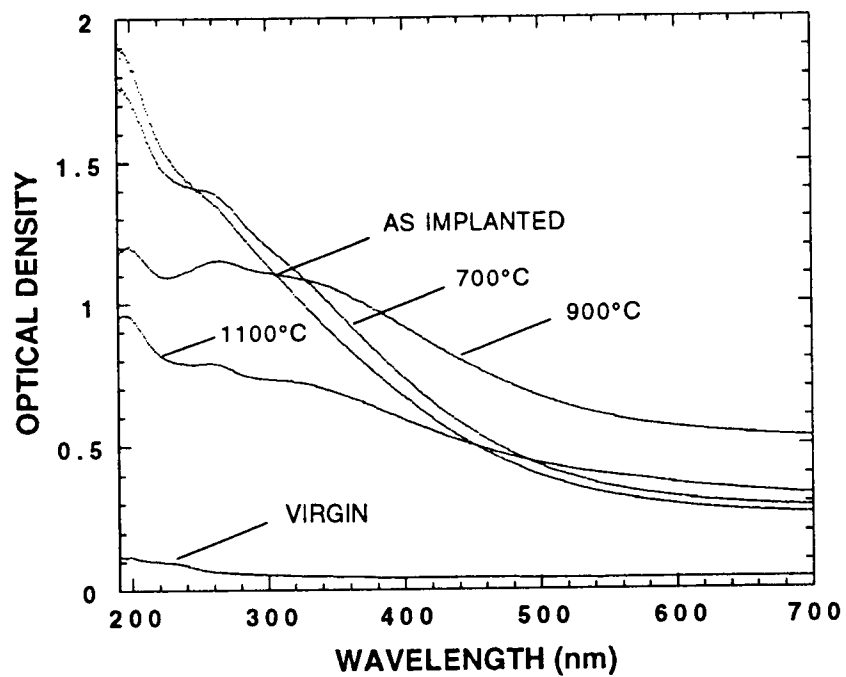


Figure 4.30 Optical absorption spectra of α - Al_2O_3 implanted with $2 \times 10^{17} \text{ Fe/cm}^2$ and annealed for 1 h in an Ar-4% H_2 atmosphere at selected temperatures.

relationship between the optical density of F centers (200 nm absorption band) and annealing temperature is consistent with the other implantation fluences. The extinction band at the peak of 260 nm of 700°C annealing specimen was attributed to Mie scattering from small precipitates. The optical density of this band is dramatically decreased since most precipitates gradually diffused toward the surface during annealing at 1100°C, consistent with RBS and TEM observations for this specimen as discussed before. The abnormal optical density observed with 900°C annealing, i.e. the enhanced extinction between 900 and 1500 nm, is probably caused by the presence of α -Fe and the intermediate phase γ -Al₂O₃.

Figure 4.31 shows optical absorption spectra of virgin α -Al₂O₃ and α -Al₂O₃ implanted with 4×10^{16} Fe/cm², 1×10^{17} Fe/cm², and 2×10^{17} Fe/cm² at 160 keV. As the implantation fluence was increased, the optical density increased since more ions were introduced and more damage was generated during implantation.

A luminescence technique, which is more sensitive than the optical absorption method, was employed to identify both F and F⁺ centers (an oxygen vacancy containing one electron). Luminescence spectra for sapphire implanted with 4×10^{16} Fe/cm² were measured by excitation with 230, 245, 255 nm light respectively as shown in figure 4.32. Excitation at 230 and 245 nm produced luminescence from both the F⁺ and the F centers because these two wavelengths overlap both absorption bands. The absorption peak at 330 nm has been attributed to F⁺ centers, and the one at 420 nm to F centers. As expected, luminescence only from F⁺ center absorption was observed when the specimen was excited with 255 nm light since the only absorption band was from F⁺ centers at this wavelength.

Figure 4.33 illustrates the luminescence spectra obtained by excitation with 230 and 245 nm light for sapphire implanted with 4×10^{16} Fe/cm², which produced luminescence from both the F⁺ and the F centers since these wavelengths overlap both absorption bands. Annealing at 1100°C diminished the defect concentration and therefore the luminescence

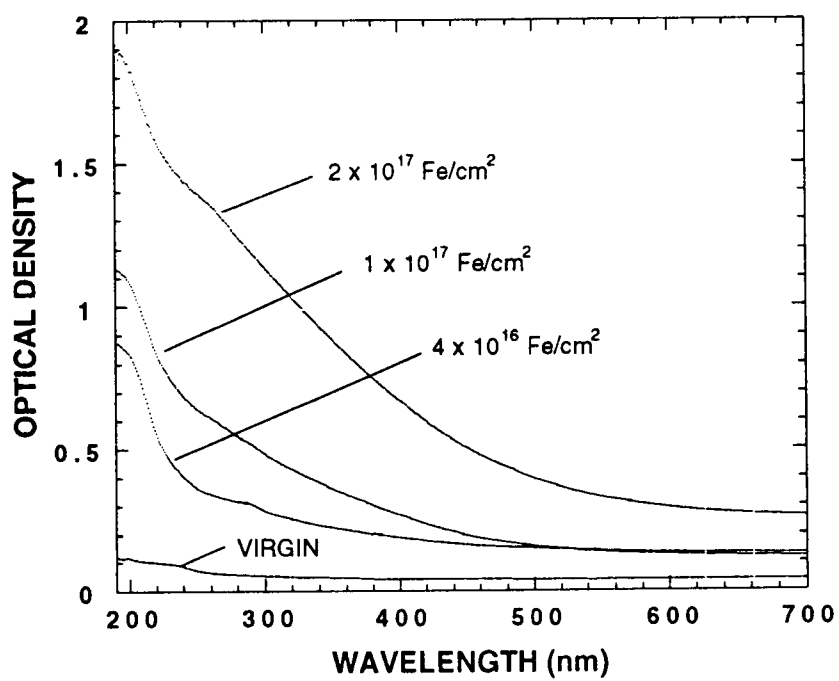


Figure 4.31 Optical absorption spectra of α - Al_2O_3 implanted with $4 \times 10^{16} \text{ Fe/cm}^2$, $1 \times 10^{17} \text{ Fe/cm}^2$, and $2 \times 10^{17} \text{ Fe/cm}^2$ at 160 keV.

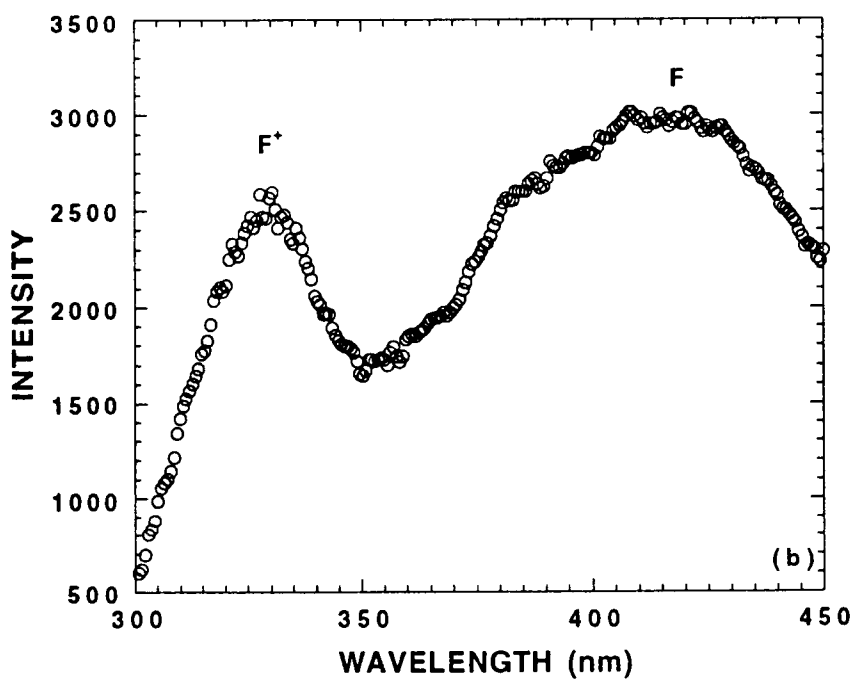
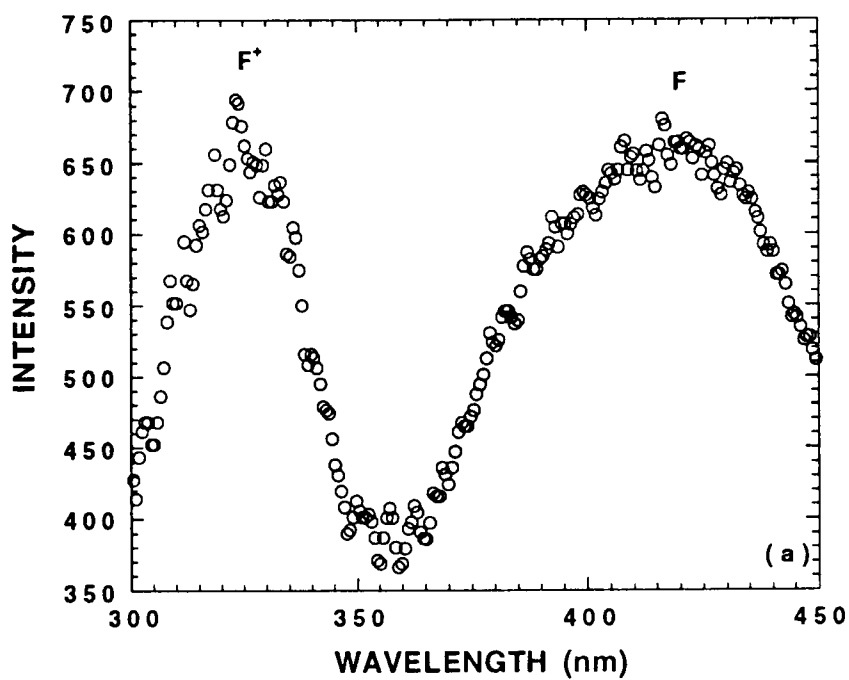


Figure 4.32 Luminescence spectra of $\alpha\text{-Al}_2\text{O}_3$ implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ by excitation with light at wavelength (a) 230 (b) 245 (c) 255 nm, and (d) as indicated.

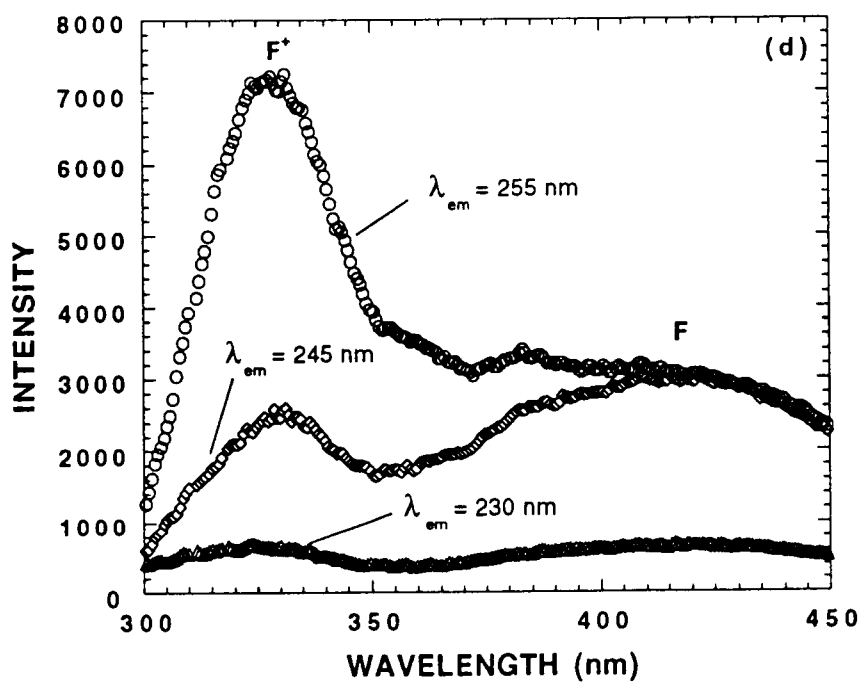
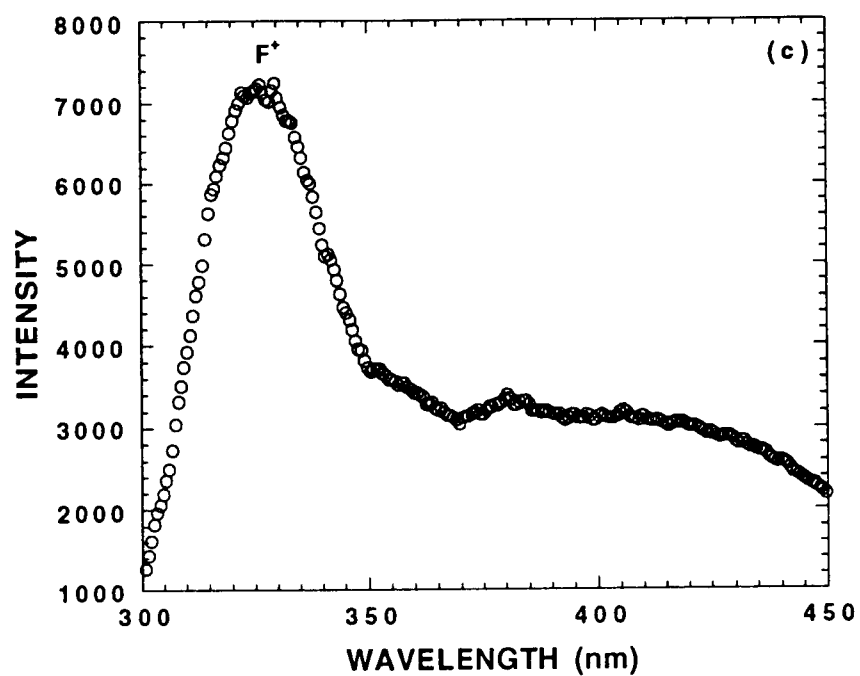


Figure 4.32 Continued

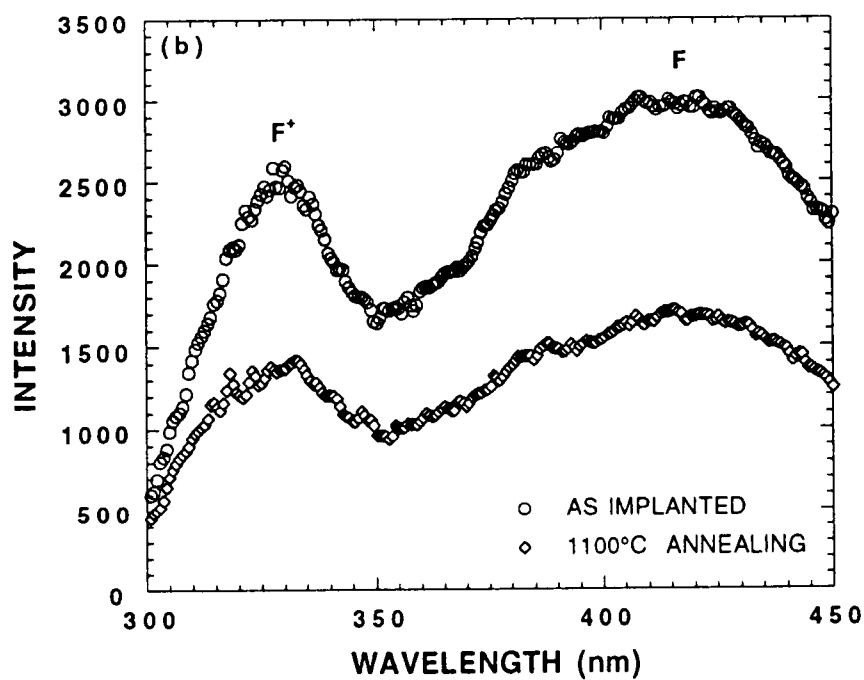
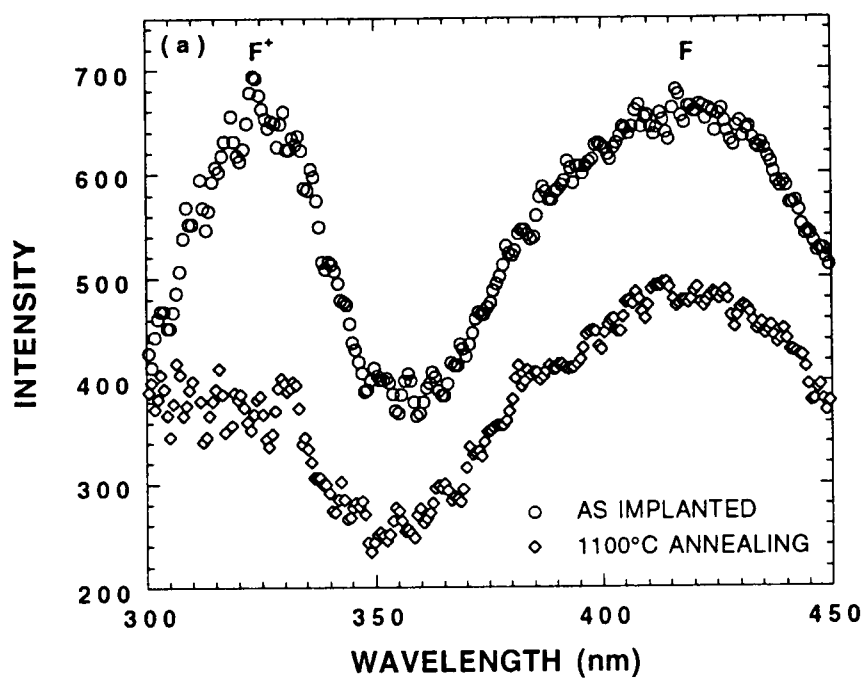


Figure 4.33 Luminescence spectra of α - Al_2O_3 implanted with $4 \times 10^{16} \text{ Fe/cm}^2$ and annealed at 1100°C by excitation with light at (a) 230, and (b) 245 nm.

intensity (lower curve) for both excitations.

These optical data reinforce the conclusions reached in the Mössbauer study, i.e., many of the implanted iron ions are associated with oxygen vacancies. The annealing results are also consistent with the proposition that the iron-oxygen vacancy migrates as a unit to form the metallic colloids and voids.

4.4 Electrical Properties

The electrical property measurements were conducted to determine if previously reported improvements in conductivity of Nb-implanted sapphire occurred in iron-implanted samples. Experimental conditions were chosen to replicate that study. As described in Chapter III, in the electrical property characterizations of this study, the current was recorded with time. A typical plot of the recorded data is presented in figure 4.34. It is evident in this figure that as the time elapsed during the 1000 minute measurement, the current data concentrated around a certain value. This value was first calculated as the average current value from all the data points collected during the 1000 minutes by the computer, and then the resistivity was determined from the average current, the applied voltage and the configuration of the specimen. The specimen for figure 4.34 was sapphire implanted with 2×10^{17} Fe/cm². The average current of this specimen was 6.62×10^{-12} (A) with a standard deviation of 3.51×10^{-13} (A).

The results of the four tests run in this investigation are listed in table 4.2. The effects of ion-implantation are evident from the results of the first two specimens, i. e., the virgin sapphire and the sapphire implanted with 2×10^{17} Fe/cm². As shown in this table, the virgin sapphire at the applied voltage of 1000 (V) has a current of 1.06×10^{-11} (A), while the ion-implanted sapphire at 100 (V) has 6.62×10^{-12} (A). Assuming that the current and voltage have a linear relationship, as given by the Ohm's law, the ion-implanted sapphire at

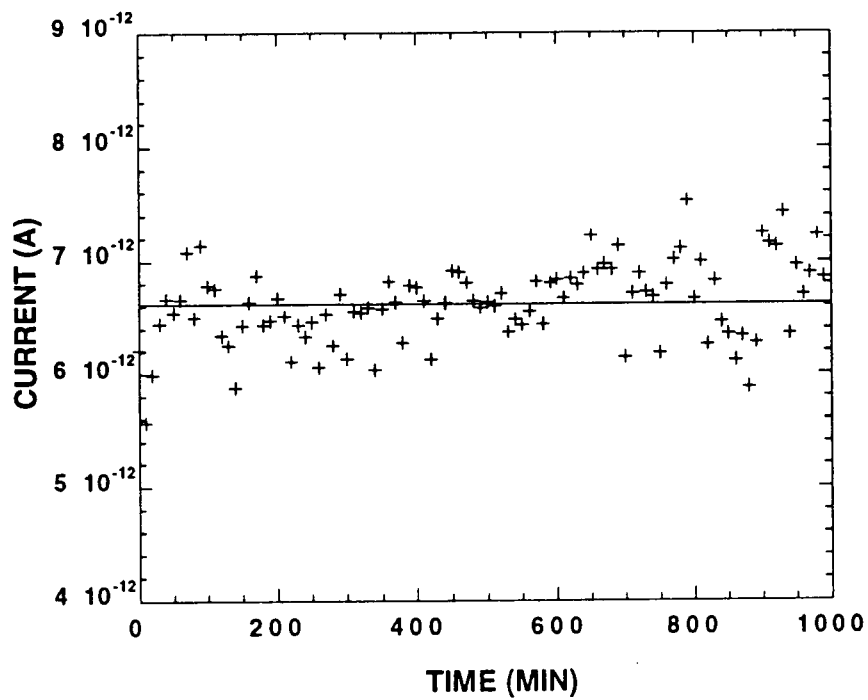


Figure 4.34 Currents measured in 1000 minutes during for sapphire implanted with 2×10^{17} Fe/cm² at 160 keV.

Table 4.2 Results of measured electrical properties and calculated resistivity for virgin and iron implanted sapphire materials

Specimen	Virgin sapphire	2E17 Fe/cm ² implantation	2E17 Fe/cm ² implantation and 1000° C anneal	2E17 Fe/cm ² implantation and 1000° C anneal @ Low RH
Filename	SHE11N.dat	REN3.dat	2E17.dat	2E17LRH.dat
Voltage (Volt)	1000	100	100	100
Average Current (Ampere)	1.06E-11	6.62E-12	6.52E-12	6.49E-15
Standard Deviation of Current	2.75E-13	3.51E-13	4.60E-13	1.84E-13
Bulk Resistance (Ω)	9.43E13	1.51E13	1.53E13	1.54E16
Length (cm)	2.54	0.5	0.5	0.5
Width (cm)	0.5	0.25	0.25	0.25
Resistivity of Sapphire (Ωcm)	4.64E12	4.64E12	4.64E12	-----
Resistivity of implanted layer (Ωcm)	-----	8.12E8	8.83E8	-----

1000 (V) should have a current value of 6.62×10^{-11} (A), a current slightly greater than that of the sapphire under the same testing conditions. Therefore, the implanted sapphire has a higher conductivity than the virgin material. The equivalence and the reliability of the current data from these two specimens are confirmed by their small and comparable standard deviations, 2.75×10^{-13} for the virgin sapphire and 3.51×10^{-13} for the implanted material, respectively.

It should be pointed out that the above discussion is based on the analysis of the electrical current carried by the bulk material before and after ion-implantation. If any improvement in electrical conductivity of the sapphire can be achieved through ion-implantation, a comparison between the resistivity of the virgin sapphire and the implanted surface or near surface layer of the sapphire should more obviously reveal such an improvement than the current. This was compared in table 4.2. The calculations of the resistivity values of the virgin sapphire and the implanted surface layer of the sapphire have been described in Chapter III. The results in table 4.2 show that the virgin sapphire and the ion-implanted layer have a resistivity value of 4.64×10^{12} and 8.12×10^8 ($\Omega \cdot \text{cm}$), respectively. It seems that the ion-implantation has caused a decrease of resistivity of approximately 10^3 to 10^4 ($\Omega \cdot \text{cm}$) in the implanted surface layer. This decrease is significant. However, because the implanted surface layer is very thin, approximately 200 nm, this change in electrical property may not be obvious when the material is examined through a parameter such as the current in a bulk specimen.

The results from the specimen implanted with 2×10^{17} Fe/cm² followed by annealing at 1000°C for 1 hour in an Ar-4%H₂ mixture atmosphere are also presented in table 4.2. It has a current value of 6.52×10^{-12} (A) at 100 (V) applied voltage with a standard deviation of 4.60×10^{-13} . The resistivity of its implanted layer is 8.83×10^8 ($\Omega \cdot \text{cm}$). All these values are very close to those of its corresponding specimen without annealing. This trend indicates that the annealing at 1000°C for 1 hour conducted in this investigation did not

affect the electrical property.

The three specimens discussed above, i. e., the virgin sapphire, the sapphire implanted with 2×10^{17} Fe/cm², and the sapphire implanted with 2×10^{17} Fe/cm² followed by annealing at 1000°C for 1 hour in an Ar-4%H₂ mixture atmosphere, were all measured at a normal relative humidity of 67%. The improvement of electrical conductivity has been found through ion-implantation, but no further increase was observed for post implant annealing. To study the effect of relative humidity on the electrical conductivity, the results obtained at zero relative humidity from the sapphire implanted with 2×10^{17} Fe/cm² followed by annealing at 1000°C for 1 hour in an Ar-4%H₂ mixture atmosphere are listed in table 4.2. Compared to its average current value of 6.52×10^{-12} (A) measured at the normal relative humidity, the specimen has an average electrical current of 6.49×10^{-15} (A) at zero relative humidity. The decrease of average current from 6.52×10^{-12} (A) to 6.49×10^{-15} (A) at the two different relative humidities at 100 (V) means that the bulk resistance of the specimen is increased for approximately 10^4 times. It is evident that the conductivity of the ion-implanted sapphire is greatly affected by relative humidity of the test atmosphere.

In this study of ion-implantation, it was hoped that the implanted metallic precipitates could contribute to the increase in conductivity of insulating materials. In discussing the mechanisms for the improvement of electrical conductivity of composite materials, it has been suggested by Tallan [58] that the tunneling effect might take place when the implanted metallic precipitates or the second phase particles were aggregated at distances of several tenths of nanometer from each other. In this investigation, the microstructural analysis has shown that the distances between the metallic precipitates were approximately several nanometers in the as-implanted sample, about 10 times greater than those at which the tunneling effect might take place. In the post-implantation-annealed specimen, a discontinuous metallic band was found beneath the surface with some metallic precipitates scattered nearby at distances of several nanometers from each other, which were also too

great distances for the expected tunneling effect to occur.

However, the results from the measurements at normal relative humidity have shown an increase of conductivity in the ion-implanted specimens. Combine the results from the four specimens examined, it seems that both the implantation and the humidity have participated in increasing the electrical conductivity of the material. At zero relative humidity, the distances among the implanted metallic precipitates are too large for the expected tunneling effect to take place, but at the relative humidity of 67%, such effect seems to have occurred that decreased the resistivity of the ion-implanted surface layer and increased the average electrical current.

It is well known that water molecules are dipoles which can become conductive if combined with some impurities. There are certain materials in our environment that have an excellent potential to be dissolved in water as impurities, one of which is carbon dioxide in the air. When carbon dioxide is dissolved in water from the air, the water becomes a weak electrolyte. If some of these electrolyte ions diffuse into the near surface region of an ion-implanted specimen subjected to electrical voltage, they are aligned in the direction of the electrical field between the implanted metallic precipitates. This obviously provides weak electrical conducting "bridges" between implanted metallic precipitates, and thus, increases the conductivity of the material.

Previous report of increased conductivity induced by ion implantation were not confirmed by this study. An apparent increase was noted for tests conducted in normal laboratory humidity, but not in low moisture condition. This is attributed to the possible tunneling effect generated by water molecules.

To further improve electrical conductivity of the material, heating the specimen in an oriented magnetic field, such as a microwave field, might be a good attempt to make a continuous metallic band in such materials. On the other hand, since only the DC technique was employed to measure the electrical resistance in this study, the electrical properties

under AC conditions can be investigated to explore any possible new features and applications in future studies.

4.5 Mechanical Properties

4.5.1 Measurements

The mechanical-properties microprobe (MPM) measurements of hardness and modulus were performed on all the as-implanted and post-implant annealed samples. The relationships among hardness, elastic modulus, implantation fluence, indentation depth, and annealing temperature are developed from the experimental recording and discussed as follows:

To study the effects of implantation on the hardness of sapphire, the hardness of the virgin material must first be determined. The results of the hardness and elastic modulus measurements from the virgin material are presented in table 4.3. Table 4.3 contains the results obtained from two samples at three nominal indentation depths of about 25, 50, and 110 nm respectively. It is found that the hardness measured at three different indentation depths shows higher and more scattered values in the shallow indentation measurements compared to those of the deep indentation measurements. For sample S2E17.vir, the average hardness values at the indentation depths of 24.89 and 50.86 nm are 47.22 and 52.43 GPa with the standard deviation values of 2.9 and 11.7 respectively, while at 109.82 nm it has an average hardness of 33.38 GPa with a standard deviation of 1.20. For sample S4E16.vir, the average hardness values at the indentation depths of 24.22 and 46.03 nm are 51.46 and 61.24 GPa with the standard deviation values of 3 and 1.7 respectively, while at 114.16 nm it has an average hardness of 29.42 GPa with a standard deviation of 0.37. This trend of higher hardness at shallow indentation measurements on the surface may be related to the so called “pop-in” phenomenon. It has been explained by Oliver et al.

Table 4.3 The average hardness and modulus values measured at three different contact depths
for two unimplanted c-axis sapphire samples

Sample I.D.	Contact Depth (nm)	Average Modulus E (GPa)	Standard Deviation of E (GPa)	Contact Depth (nm)	Average H (GPa)	Standard Deviation of H (GPa)
4E16.vir	24.22	546.97	27.52	24.22	51.46	3.01
	46.03	512.90	10.78	46.03	61.24	1.71
	114.16	479.67	9.28	114.16	29.42	0.37
2E17.vir	24.89	528.66	30.69	24.89	47.22	2.91
	49.98	500.89	20.23	50.86	52.43	11.71
	109.82	475.83	9.73	109.82	33.38	1.20

[59, 60] that the pop-in behavior might be associated with the presence of defects or even defect nucleation. Since the virgin material was measured to compare with the ion-implanted sapphire, only the values from deep indentation measurements are considered as the bulk hardness value beyond the pop-in point, and the average values of the two samples at deep indentation depths were employed for discussion, i.e. hardness value is assumed as 31.4 GPa, and modulus value as 477.74 GPa. For a convenient discussion, the virgin material is plotted at a fictitious fluence of 2×10^{16} Fe ions/cm² together with the implanted sample results in the following figures for the purpose of comparison.

Figure 4.35 (a) shows the changes of the hardness values with the implantation fluences measured at three different nominal indentation depths, i. e., 26, 56, and 110 nm respectively. The error bars represent standard deviations of ten indentation measurements at each implantation fluence and indent depth. In the shallow indentation measurements, hardness increases initially with the ion fluence. This is attributed to the production of an enhanced defect-induced strain by both alloy strengthening (second phase precipitates) and radiation damage hardening (defect strengthening) when the damaged layer remains essentially crystalline. However, as the implantation fluence is increased to 2×10^{17} Fe ions/cm², the crystalline to amorphous transition occurs and the hardness is decreased markedly.

In deep indentation depth measurements, the substrate can affect the measurement results because the obtained hardness represents the combined composite properties of the implanted layer and the substrate region. Therefore, the variation of hardness as a function of implantation fluence is not as obvious for the deep indentations as the shallow indentation measurements.

The effect of indentation depth on the hardness of the material with different implantation fluences is also obvious in figure 4.35 (a). For those alloy or damage strengthened specimens obtained with low implantation fluences, the combined hardness

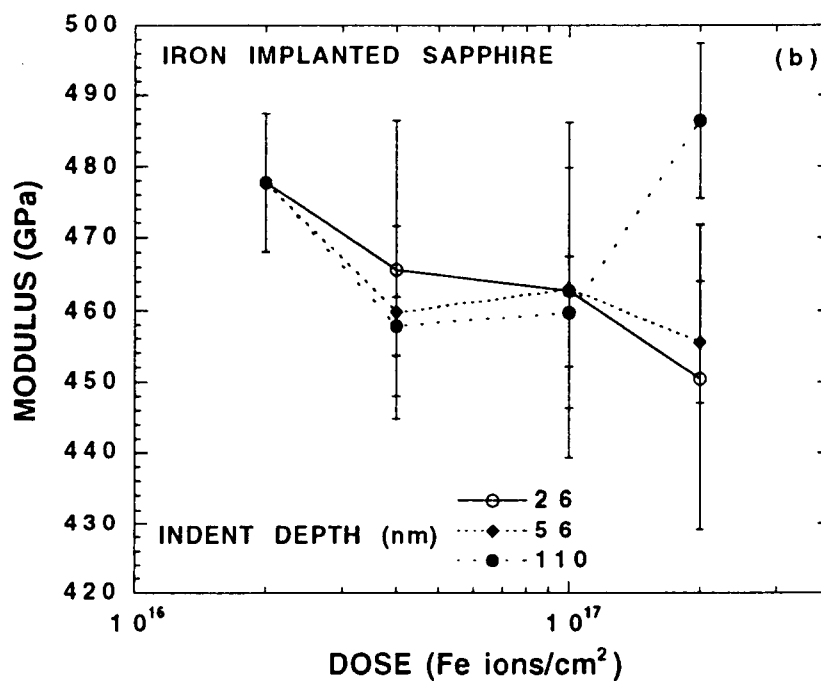
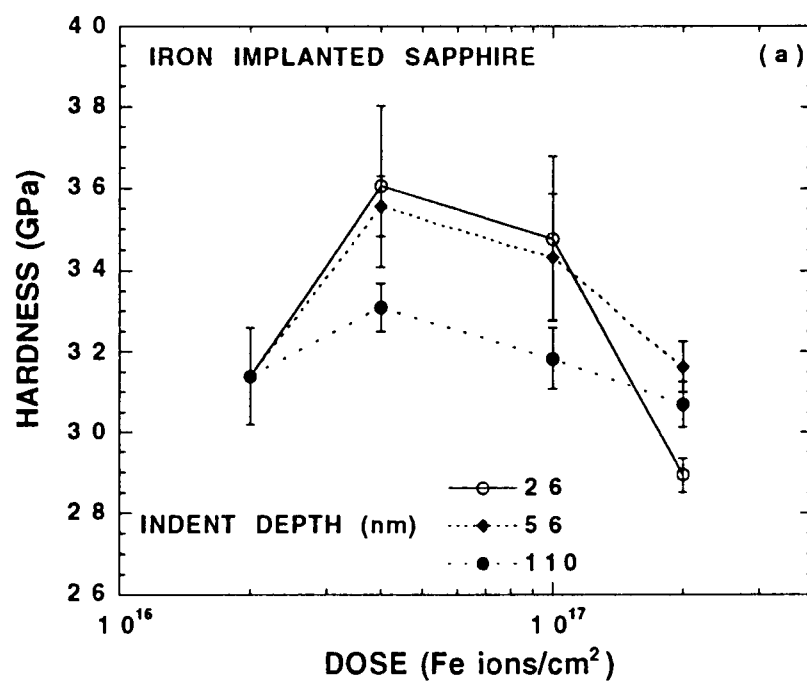


Figure 4.35 (a) Hardness and (b) Modulus determined by MPM analysis of sapphire implanted with fluences spanning the crystalline-to-amorphous transition.

values are decreased as the indent depth is increased; while for the high fluence implantation sample which has an amorphous implanted layer, the hardness value increased with the indent depth. In addition, the error bars at the higher implantation fluences are significantly reduced since the amorphous phase is relatively homogeneous compared to the damaged or precipitates aggregated crystalline phases.

Figure 4.35 (b) shows the elastic modulus results for the same set of specimens as shown in figure 4.35 (a). Generally, the modulus values are decreased as the implantation fluences are increased. This is because more defects were generated at higher fluences so that the modulus or the resistance to elastic deformation is decreased.

Hardness and modulus results from the shallowest indentation measurements, i. e., 26 nm indentation depth, were considered as the most appropriate data to characterize the mechanical properties of the implanted layer since the results were the least affected by the substrate properties even if the plastic zone effect was considered. For this reason, the hardness and modulus data for 26 nm indentation contact depth measurements are presented in figure 4.36. It is clear that the hardness values are increased at lower fluences because of the second phase and radiation damage strengthening effects, and then decreased at higher fluences because of amorphization. On the other hand, the modulus values drop gradually as the fluences are increased since the order of the structure is disturbed with the increasing implantation fluences, and therefore the elastic deformation becomes easier and easier as more damage is introduced.

Figure 4.37 (a) and (b) show effects of annealing in a reducing atmosphere on the mechanical properties of the implanted specimens. Again, hardness and modulus data measured from 26 nm indentation contact depth are used for analysis.

For the specimen with an implantation fluence of 4×10^{16} Fe ions/cm², as the annealing temperature changes from room temperature to 700°C, the hardness and modulus values are increased because of the partial recovery of the radiation damage. However, as the

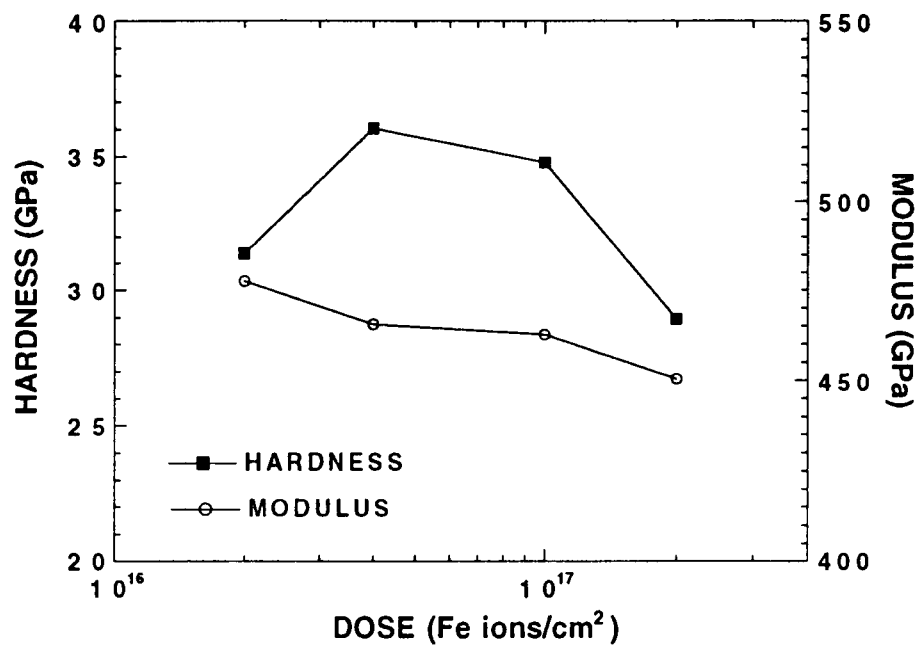


Figure 4.36 Hardness and elastic modulus of sapphire as a function of iron implantation fluence for the shallow indent contact depth (26 nm).

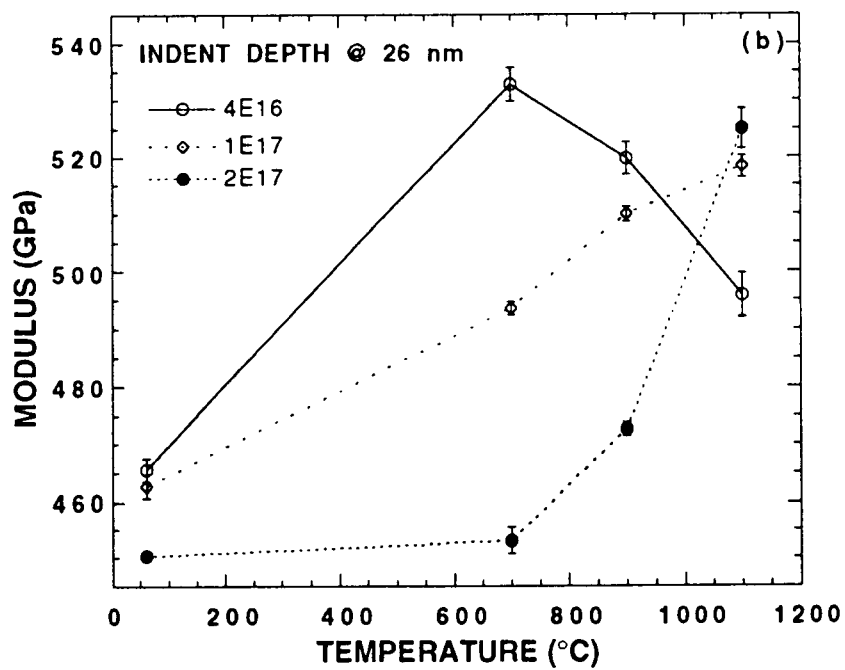
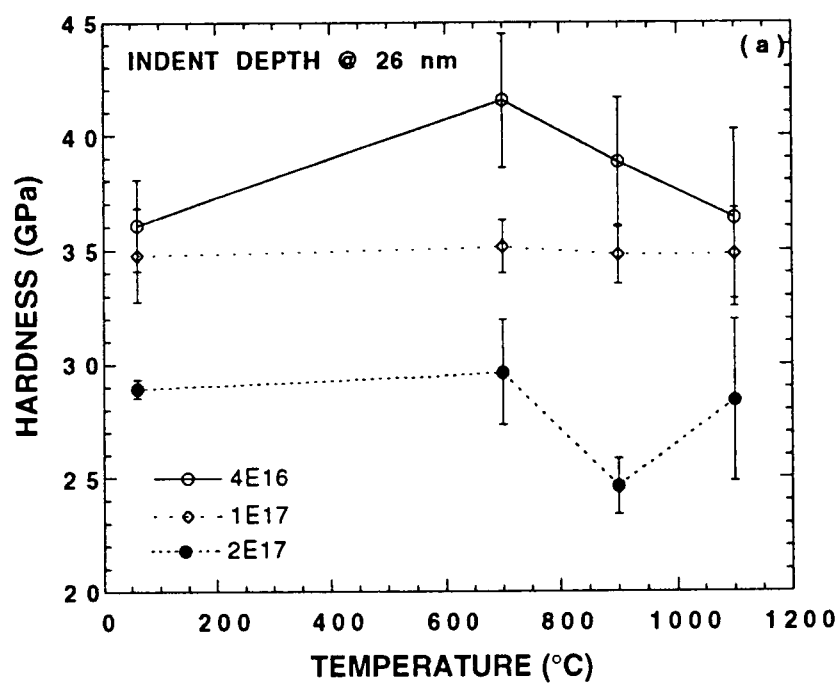


Figure 4.37 (a) Hardness and (b) Modulus of sapphire as a function of annealing temperature at different implantation fluences.

annealing temperature is further increased to 900 and 1100°C, the hardness and elastic modulus values decrease from the maximum values because of the coarsening of the precipitates. It seems that for low fluence implantation, thermal annealing can reduce strain, and therefore increase the hardness and modulus values at low annealing temperatures. However, at high annealing temperatures, precipitates coarsening effects become dominant so that both hardness and elastic modulus values decrease.

In figure 4.37 (a), the curve from the specimen with an implantation fluence of 2×10^{17} Fe ions/cm² shows a slight increase in hardness at low annealing temperature, and then a rapid decrease followed by an increase as the annealing temperature increases above 900°C. This is because at the high fluence of 2×10^{17} Fe ions/cm², the material is in an unstable state due to its high energy. Thermal annealing can provide the additional amount of energy needed for amorphous-recrystalline-transition. Therefore, as the annealing temperature rises over 700°C, this transition becomes more and more completed and finally recrystallization occurs. Different phases form in the process of recrystallization greatly affect the mechanical properties of the material. It is believed that the decrease in hardness as the annealing temperature rises from 700°C to 900°C is caused by the appearance of γ -Al₂O₃, while the followed increase in hardness is attributed to the formation of α -Al₂O₃ as the annealing temperature increases. Overall, the mechanical properties changes are determined by the microstructures alteration such as the introduction of the defects, precipitates coarsening, or recrystallization of the amorphous. At low annealing temperatures, the defects and coarsening are important, while at high annealing temperatures, recrystallization becomes the main factor for influencing the mechanical properties. The effects of these factors on elastic and plastic mechanical properties are not the same. As shown in figure 4.37 (b), at an implantation fluence of 1×10^{17} Fe ions/cm², the elastic modulus always increases with annealing temperature.

It is also evident in figure 4.37 (a) and (b) that at low annealing temperatures, both

hardness and elastic modulus decrease with the increase in implantation fluence. This is because high fluence implantation can introduce more defects and damage than low fluence implantation, and eventually an amorphous layer can form on the surface of the implanted material so that both hardness and modulus values become lower than those in the low fluence implantation cases.

4.5.2 Data Reduction

As was discussed in the literature review, three empirical models were available to compute the film or resultant hardness values under different assumptions. Table 4.4 gives the calculated film hardness values on all the as-implanted and post-implant annealed specimens by using Jonsson's model. A Berkovich indenter was employed in this investigation, while the model was developed on the geometry of Vicker indenter. Fortunately, it is reasonable to assume that the ratio of the indentation diagonal to the contact depth and the shape of the plastically strained film is the same for both Berkovich and Vicker indenters. In addition, we have obtained the film thickness as 300 nm from the previous RBS and AEM observations. By applying all the assumption, the film hardness values were calculated decreasing from 40, 33 to 29 GPa, as the implantation fluence was increased from 4×10^{16} , 1×10^{17} to 2×10^{17} Fe ions/cm² respectively.

The law of mixtures approach was also tried during this investigation. By assuming that the film hardness of 2×10^{17} Fe ions/cm² implanted sapphire is about 29 GPa, the resultant hardness is calculated and compared to the measured composite hardness as shown in table 4.5. It is not clear at present why the calculated hardness values are about several GPa lower than the measured one. This may be attributed to the errors caused by the estimated deforming volumes of the substrate and layer, and approximated value of ISE index number.

Figure 4.38 (a) shows the hardness and modulus data versus contact depth for sapphire

Table 4.4 Calculated film hardness values by Jonsson model

B. Jonsson & S. Hogmark, Thin Solid Films, 114(1984) 257-269 The geometrical model for generating film hardness values							
$H_f = H_s + (H_c - H_s) / (2ct/D - c^*c \cdot (t/D)^2)$ where H_f is the film hardness H_c is composite hardness H_s is substrate hardness D is penetration depth or contact depth t is film thickness for soft film $c=0.1403$, hard and brittle film $c=0.0728$							
t(nm)	300						
Fluence (Fe/cm ²)	Annealing Temp. (°C)	D (nm)	H _c (GPa)	H _s (GPa)	c	H _f (GPa)	
4 x 10 ¹⁶	as-implanted	112.88	33.1	29.42	0.0728	40	
	700	110.60	34.21	29.42	0.0728	43	
	900	113.64	30.82	29.42	0.1403	32	
	1100	114.37	29.4	29.42	0.1403	29	
1 x 10 ¹⁷	as-implanted	112.86	31.83	31.40	0.0728	33	
	700	111.36	31.52	31.40	0.0728	32	
	900	112.34	29.33	31.40	0.1403	28	
	1100	108.22	33.15	31.40	0.1403	34	
2 x 10 ¹⁷	as-implanted	110.98	30.71	33.38	0.1403	29	
	700	112.55	28.88	33.38	0.1403	26	
	900	116.52	25.74	33.38	0.1403	20	
	1100	110.86	30.43	33.38	0.1403	29	

Table 4.5 Calculated effective hardness values by Burnett model

An empirical model for the hardness behavior of a composite specimen with a soft layer/hard substrate

Law of mixtures approach: $H_{eff}=(H_sV_s+H_fV_f)/(V_s+V_f)$

where

H_{eff} is the resultant hardness

H_s and H_f are the substrate and surface-layer hardness

V_s and V_f are the deforming volumes of the substrate and layer

$H_s=cd^{m-2}$

$H_f=c'd'^{m'-2}$

where

d is the indentation diagonal of a hardness impression made by a Berkovich indenter

m is ISE index (if $m=2$, no ISE), and c is a constant

To emphasize the substrate hardness:

$H_sV_s=[cd^{m-2}]V_s^2/(V_s+V_f)$

$V_s=\pi h^2(R-h/3)=\pi^*(d/2-t)^2*[d/2-(d/2-t)/3]$

$V_f=V-V_s=1/12\pi d^3-V_s$

$H_{eff}=(c*d^{m-2}*V_s^2/(V_s+V_f)+c'*V_f)/(V_s+V_f)$

$t(\mu m)$	0.3	m	1.88							
Fluence (Fe/cm ²)	Annealing Temp (°)	D (nm)	d (μm)	H _c (GPa)	H _s (GPa)	H _f (GPa)	c	V _s	V _f	H _{eff} (GPa)
2 x10 ¹⁷	as-implanted	110.98	0.78	30.71	33.38	29	32	0.0088	0.11	27
	700	112.55	0.79	28.88	33.38	26	32	0.0100	0.30	25
	900	116.52	0.82	25.74	33.38	20	33	0.0136	0.32	19
	1100	110.86	0.78	30.43	33.38	29	32	0.0087	0.29	28

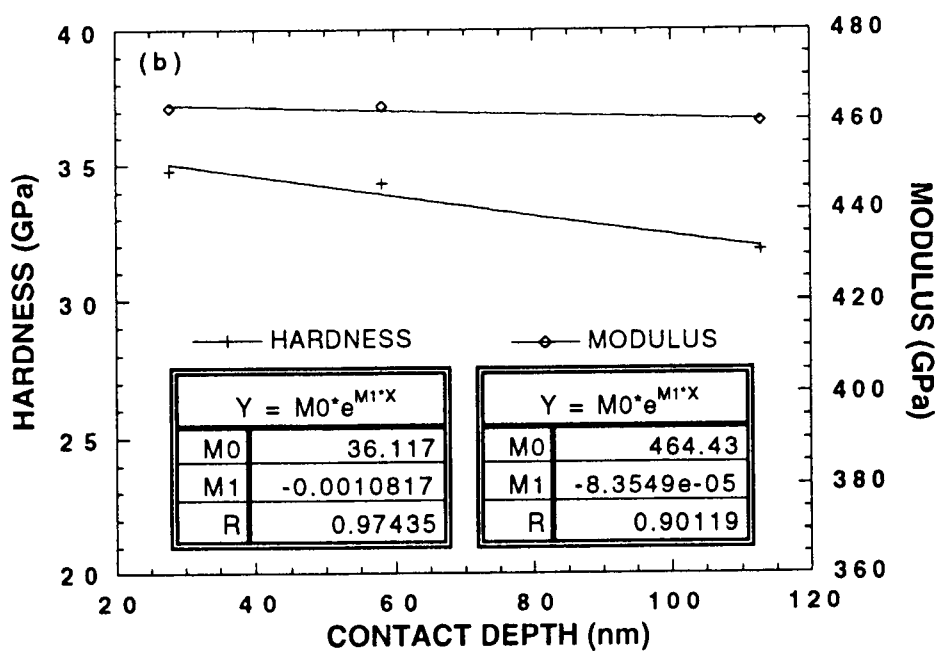
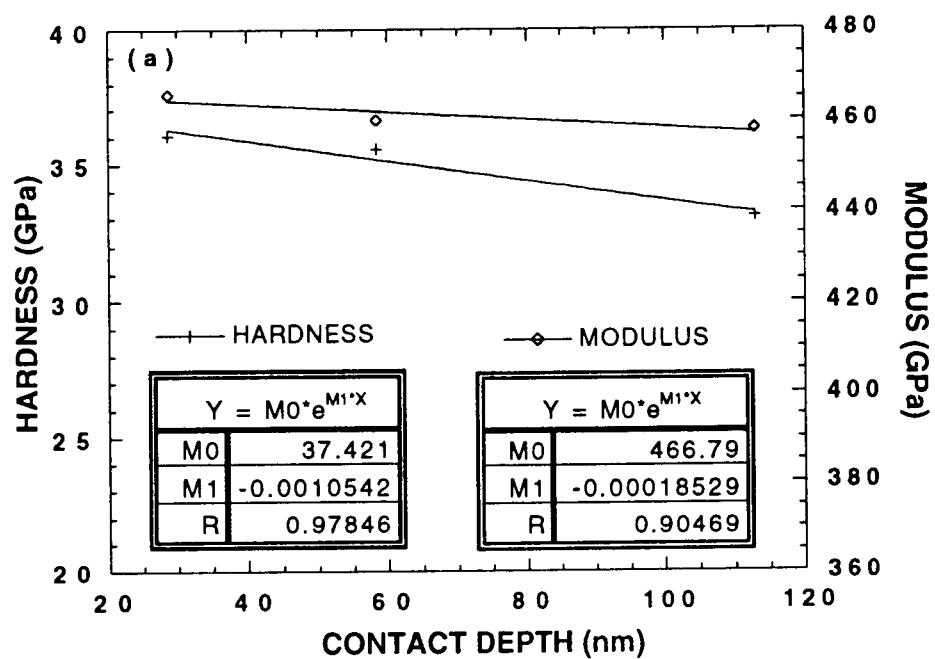


Figure 4.38 Hardness and modulus values as a function of contact depth for sapphire implanted with (a) 4×10^{16} , (b) 1×10^{17} , and (c) 2×10^{17} Fe ions/cm².

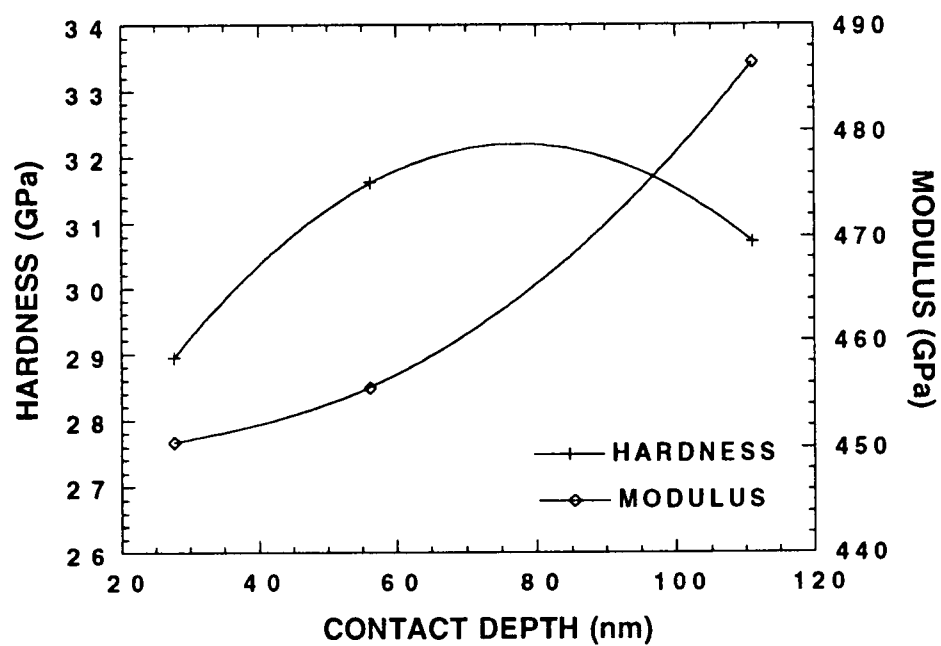


Figure 4.38 Continued

implanted with 4×10^{16} Fe ions/cm². The film hardness and modulus values are obtained as 37.42 and 466.79 GPa respectively, by extrapolating the curve to zero contact depth using exponential curve fit technique. The same approach was applied to sapphire implanted with 1×10^{17} Fe ions/cm² as shown in figure 4.38 (b) and the resulted film hardness and modulus values are 36.12 and 464.43 GPa respectively.

Since the plot of hardness and modulus data versus contact depth for sapphire implanted with 2×10^{17} Fe ions/cm² doesn't give a linear correlation as those shown in low fluences implanted samples, smooth curve fit was attempted and plotted in figure 4.38 (c). The extrapolated film hardness and modulus values are 27.5 and 450 GPa respectively.

Nonlinear least square analysis discussed in chapter II was also adopted in this work. A sample calculation of H_f and C values for sapphire implanted with 4×10^{16} Fe ions/cm² is given by table 4.6, where H_s assumed as 29.4 GPa. Hardness and modulus for as-implanted sapphire as a function of contact depth are shown in figure 4.39. The solid line is the result of nonlinear least-square analysis using the equation $H_m = H_s + (H_f - H_s) \exp(-CH_c^2)$ for the hardness data and the dashed line is the result of nonlinear least-square analysis using the equation $E_m = E_s + (E_f - E_s) \exp(-CH_c^2)$ for the modulus data.

A summary of film hardness and modulus values for all the as-implanted samples obtained on the curve fitting technique, nonlinear least square analysis and together with the calculated film hardness from Jonsson's model is listed in table 4.7. The results from the empirical model and curve fitting techniques show a fairly good agreement for all three as-implanted sapphire specimens.

As was discussed in Chapter III, both Voigt and Reuss's models were attempted to obtain the elastic modulus values for this nanocomposite material. The upper and lower bounds on the elastic moduli were calculated using equation 2.21 and 2.22 as the limiting cases:

Table 4.6 Nonlinear least square analysis for sapphire implanted with 4×10^{16} Fe ions/cm².

Input Data: Measured hardness vs. Contact depth									
Output Data: Film hardness and Constant C									
$H_m = H_s + (H_f - H_s) \exp(-C h_c^2)$									
$H_m - H_s = (H_f - H_s) \exp(-C h_c^2)$									
$\ln(H_m - H_s) = \ln(H_f - H_s) - C h_c^2$									
where									
H_m is the measured hardness									
H_s is the substrate hardness and set as 29.4 GPa from the bulk sapphire hardness measurement									
H_f is the film hardness									
C is a constant									
h_c is the contact depth									
let									
$y_i = H_m$		$x_i = h_c$		$b = \ln(H_f - H_s)$		$a = -C$			
$LY_i = \ln(H_s - y_i)$		$LX_i = x_i^2$							
then									
$LY_i = b + a LX_i$									
i	xi		LXi		LYi=ln(yi-Hs)		LXi2		LXiLYi
1	28.69		823.12		36.06		6.78E+05		1.56E+03
2	58.37		3407.06		35.56		1.16E+07		6.19E+03
3	112.88		12741.89		33.1		1.62E+08		1.67E+04
			16972.07		5.02		1.75E+08		2.44E+04
m	3								
a	-5.07E-05				C (nm ⁻²)		5.07E-05		
b	1.96				Hf (GPa)		36.51		

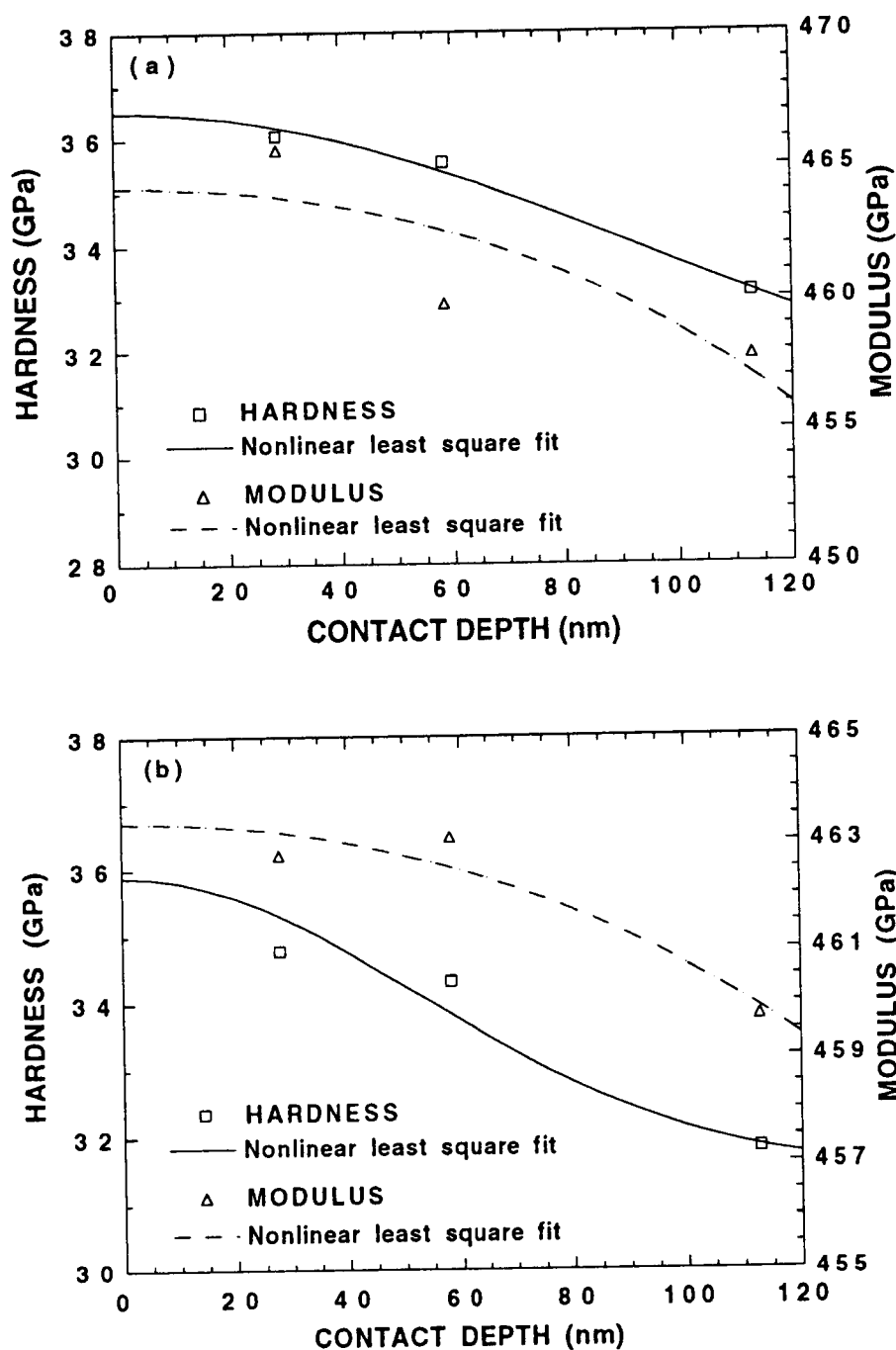


Figure 4.39 Hardness and modulus values as a function of contact depth for sapphire implanted with (a) 4×10^{16} , (b) 1×10^{17} , and (c) 2×10^{17} Fe ions/cm². The solid and dashed lines are the result of nonlinear least-squares analysis for the hardness and modulus data respectively.

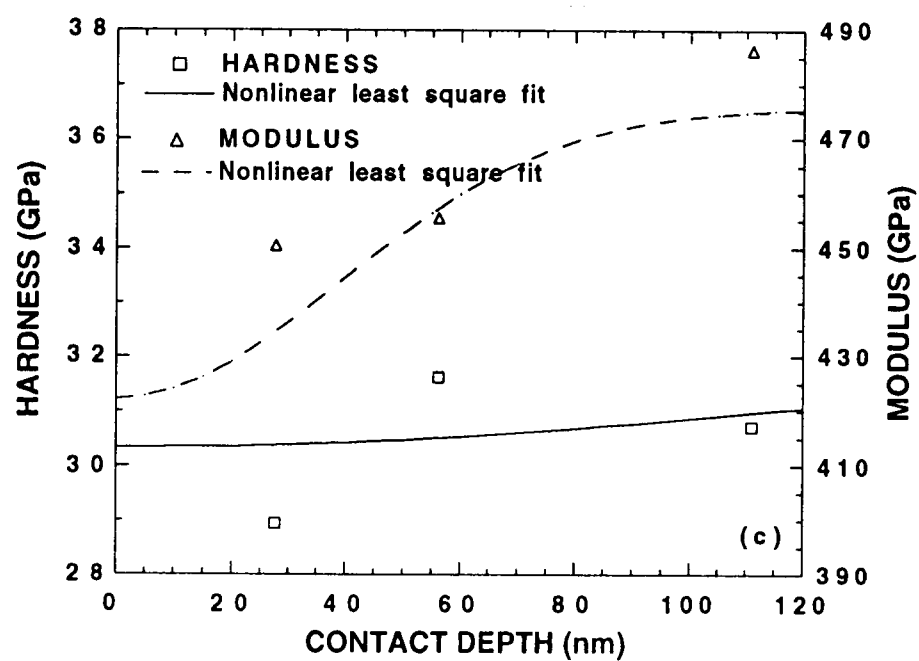


Figure 4.39 Continued

Table 4.7 Summary of film hardness and modulus value by both empirical model and curve fitting technique

Substrate Material		Sapphire	
Implantation Fluence (Fe ions/cm ²)	4 x 10 ¹⁶	1 x 10 ¹⁷	2 x 10 ¹⁷
Substrate Hardness (GPa)	29.4	31.40	33.38
Film Hardness (GPa)			
exponential curve fit	37.42	36.12	27.5
smooth curve fit			
nonlinear least square analysis	36.51	35.89	30.33
Jonsson model	40	33	29
Substrate Modulus (GPa)	475.8	475.8	475.8
Film Modulus (GPa)			
exponential curve fit	466.79	464.43	
smooth curve fit			450
nonlinear least square analysis	464.22	463.39	422.24

Assume: $E_2 = 206.6$ GPa for α -Fe
 $E_1 = 475$ GPa for α -Al₂O₃ (measured)
 $V_2 = 5\%$ (1×10^{17} Fe/cm²)

We have

$$E_U = 0.05 \times 207 + 0.95 \times 475 = 461.6 \text{ (GPa)}$$

and

$$\frac{1}{E_L} = \frac{0.05}{207} - \frac{0.95}{475} = 0.00224$$

$$E_L = 446 \text{ (GPa)}$$

The calculation based on two-phase system model showed that elastic modulus ranged from 446 to 462 GPa. It is consistent with the data obtained from other methods such as exponential curve fit, which gives the film modulus of 466.79 GPa, and nonlinear least square analysis, which gives the film modulus of 466.79 GPa. This is the first time to our knowledge that such measurements have been reported for nanometer size dispersions.

In closing, some further work is suggested on the mechanical property study. Multi-energy implantation is recommended to give more uniform surface layer so that more accurate values can be obtained. The measurements of some other properties such as fracture toughness, flexure strength, wear resistance are needed to obtain a sound data base for the study of the mechanical property alteration on such ion implanted insulating material.

CHAPTER V

SUMMARY AND CONCLUSIONS

In this investigation, Fe implanted α -Al₂O₃ nanocomposites were produced using different implantation fluences and annealing temperatures. Microstructure and property characterizations have been conducted using a series of available experimental techniques. The following conclusions can be drawn from the experimental results presented and discussed in chapter IV:

1. Rutherford backscattering observations:

- Implantation of 160 keV ⁵⁶Fe in single crystal α -Al₂O₃ can produce a crystalline but damaged microstructure with fluences as high as 1×10^{17} Fe/cm² at room temperature.
- Implantation of 160 keV ⁵⁶Fe in α -Al₂O₃ at fluences greater than 1×10^{17} Fe/cm² can create an amorphous region extending to 300 nm deep from the surface with a peak at about 150 nm, while the embedded iron extends to a maximum depth of about 200 nm with a Gaussian distribution centered around 100 nm.
- Thermal annealing at the temperatures above 900°C can restore the crystallinity in the damaged near surface region. At this critical temperature, the channeling effect can be observed, which results from either the diffusion of some iron from interstitial to substitutional sites or the formation of oriented iron precipitates.
- Reduction of yield in the channeling spectra of the iron and a shift of the iron peak to higher energy indicate that, with increasing annealing temperature, the implanted iron diffuses to the surface and then becomes lost by evaporation.

2. Microstructure observations:

- Implantation of 160 keV ^{56}Fe in single crystal $\alpha\text{-Al}_2\text{O}_3$ can produce an amorphous microstructure at a threshold fluence of $2 \times 10^{17} \text{ Fe/cm}^2$ at room temperature.
- At the threshold fluence, most implanted iron particles are present as metallic $\alpha\text{-Fe}$ precipitates as small as 2 to 3 nm in size. The orientation relationships between these metallic $\alpha\text{-Fe}$ precipitates and the sapphire matrix are identified as: $\langle 111 \rangle_{\alpha\text{-Fe}} \parallel \langle 310 \rangle_{\text{sapphire}}$ and $\{01\bar{1}\}_{\alpha\text{-Fe}} \parallel \{006\}_{\text{sapphire}}$.
- Annealing the as-implanted specimens in an Ar-4% H_2 atmosphere leads to the aggregation of metallic colloids, the coarsening of the precipitates, and finally the formation of a discontinuous band.
- Implantation of 160 keV ^{56}Fe in single crystal $\alpha\text{-Al}_2\text{O}_3$ at fluences below $1 \times 10^{17} \text{ Fe/cm}^2$ can create a crystalline but damaged subsurface layer approximately 300 nm deep with the embedded iron extending to about 200 nm below the surface. This observation matches the result from the Rutherford backscattering analysis.
- Lattice fringes in the implanted sapphire layer, which provides strong evidence of crystalline nature for low fluence implantation, have been observed using high resolution transmission electron microscopy.
- Annealing within the temperatures range of 900° to 1400°C in an Ar-4% H_2 atmosphere can restore crystallinity to the damaged near-surface region, can aggregate and coarsen the metallic colloids in shapes of either sphere or elongated, and also can form some faceted precipitates.

3. Optical property observations:

- The predominant defects are F centers (an oxygen vacancy containing two electrons) giving an absorption peak of 200 nm.
- The concentration of F centers, shown as optical density of this band, decreases as

the annealing temperature is increased.

- F⁺ centers (an oxygen vacancy containing one electron) have been identified by the presence of an absorption peak of 330 nm, observed in luminescence spectra acquired using several specific wavelengths of light to excite the sapphire.

4. Electrical property observations:

- The electrical conductivity of sapphire was improved by iron-implantation, but not by post implant annealing in a normal relative humidity environment. It is speculated that water molecules might provide weak electrically conducting “bridges” between the implanted metallic precipitates to make the channeling effect possible.
- At extremely low relative humidity, the resistivity of sapphire is increased dramatically regardless the implantation effect.

5. Mechanical property observations:

- The average hardness and elastic modulus values of virgin sapphire were determined as 31.4 and 477.7 GPa receptively.
- Implantation fluence effect: The hardness values are increased at lower fluences because of the second phase and radiation damage strengthening effects and then decreased at higher fluences because of amorphization in the shallow indentation measurements; While for deep indentation, the measured hardness represents the combined composite properties of the implanted layer and the substrate region.
- The modulus values drop gradually as the fluences are increased since the order of the structure is disturbed with the increasing implantation fluences.
- Annealing effect: The hardness and modulus values are increased at low temperature annealing because of the partial recovery of the radiation damage, and

then decreasing at the annealing temperature of 900°C because of the coarsening of the precipitates for low fluence implantation; while for high fluence implantation, the defects and coarsening are the main factor for determining the mechanical properties at low annealing temperatures, and recrystallization becomes dominant at high annealing temperatures.

- The implanted layer has the hardness values around 37 to 40 GPa for sapphire implanted with 4×10^{16} Fe ions/cm², 33 to 36 GPa for 1×10^{17} Fe ions/cm², and 28 to 30 GPa for 2×10^{17} Fe ions/cm² obtained from empirical model and curve fitting techniques.
- The modulus values of the implanted layer were found as 465, 464, and 440 GPa for sapphire implanted with 4×10^{16} , 1×10^{17} , 2×10^{17} Fe ions/cm² respectively using curve fitting techniques.

LIST OF REFERENCES

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- [1] J. S. Williams and J. M. Poate, *Ion Implantation and Beam Processing*, J. S. Williams and J. M. Poate eds., Academic Press, New York, 1984
- [2] J. W. Mayer, L. Eriksson and J. A. Davies, eds., *Ion Implantation in Semiconductors*, Academic Press, New York, 1970
- [3] B. L. Crowder, ed., *Ion Implantation in Semiconductors and Other Materials*, Plenum Press, New York, 1973
- [4] J. Gyulai, T. Lohner and E. Pasztor, eds., *Proceedings of the International Conference on Ion Beam Modification of Materials*, Gordon and Breach, New York, 1980, *Radiation Effect* 47-49 (1983)
- [5] R. E. Benensen, E. N. Kaufmann, G. L. Miller and W. W. Scholz, eds., *Proceedings of the 2nd International Conference on Ion Beam Modification of Materials*, North-Holland, Amsterdam, 1981, *Nucl. Instr. Methods* 182/183 (1981)
- [6] B. Biasse, G. Destefanis and J. P. Gaillard, eds., *Proceedings of the 3rd International Conference on Ion Beam Modification of Materials*, North-Holland, Amsterdam, 1981, *Nucl. Instr. Methods* 209/210 (1984)
- [7] B. M. Ullrich, ed., *Proceedings of the 4th International Conference on Ion Beam Modification of Materials*, North-Holland, Amsterdam, 1985, *Nucl. Instr. Methods* B7/8 (1985)
- [8] S. U. Campisano, G. Foti, P. Mazzoldi and E. Rimini, eds., *Proceedings of the 5th International Conference on Ion Beam Modification of Materials*, North-Holland, Amsterdam, 1987, *Nucl. Instr. Methods* B19/20 (1987)
- [9] S. Namba, N. Itoh and M. Iwaki, eds., *Proceedings of the 56th International Conference on Ion Beam Modification of Materials*, North-Holland, Amsterdam, 1989, *Nucl. Instr. Methods* B39 (1989)

- [10] G. K. Hubler, O. W. Holland, C. R. Clayton and C. W. White, eds., *Ion Implantation and Ion Beam Processing of Materials*, North-Holland, Amsterdam, 1984
- [11] G. Dearnley, *Nucl. Instrum. Methods Phys. Res. Sect. B* 7/8 (1985) 158
- [12] McHargue, C. J., *Structure-Property Relationships in Surface Modified Ceramics*, C. J. McHargue, R. Kossowsky, and W. O. Hofer, eds., Kluwer Academic publishers, dordrecht, (1989) 253.
- [13] C. W. White, C. J. McHargue, P. S. Sklad, L. A. Boatner, and G. C. Farlow, *Mater. Sci. Rep.* Vol.4, No.2,3, July 1989, 41-146
- [14] H. Naramoto, C. W. White, J. M. Williams, C. J. McHargue, O. W. Holland, M. M. Abraham, and B. R. Appleton, *J. Appl. phys.* 54, 683 (1983)
- [15] M. Ohkubo, T. Hioki, and J. Kawamoto, *J. Appl. Phys.* 60, 1325(1986)
- [16] C. J. McHargue, P. S. Sklad, C. W. White, G. C. Farlow, A. Perez and G. Marest, *J. Mater. Res.*, vol. 6, No. 10, Oct 1991, 2145
- [17] C. J. McHargue, P. S. Sklad, C. W. White, J. C. McCallum, A. Perez and G. Marest, *J. Mater. Res.*, vol. 6, No. 10, Oct 1991, 2160
- [18] L. Romana, P. Thevenard, S. Ramos, B. Canut and L. Gea, M. Brunel, L. L. Horton, C. J. McHargue, *Surface and Coatings Technology*, 51, 410 (1992)
- [19] B. D. Evans and M. Stapelbroek, *Phys. Rev.* B18 (1978) 7089
- [20] J. S. Williams and J. R. Bird, *Ion Beam for Materials Analysis*, J. R. Bird and J. S. Williams, eds., Academic Press Australia, 1989, 3-45
- [21] P. Mazzoldi and G. Arnold, eds., *Ion beam Modification of Insulators*, Elsevier, Amsterdam, 1(1987)

- [22] W. K. Chu, J. W. Mayer, and M. A. Nicolet, Backscattering Spectrometry, Academic Press, New York, 1978
- [23] G. Foti, J. W. Mayer, and E. Rimini, Ion beam Handbook for Material Analysis, J. W. Mayer, and E. Rimini, eds., Academic Press, INC., 1977
- [24] W. A. Sibley, *Nucl. Instr. Methods B* 1 (1984) 419; B32 (1988)
- [25] G. P. Pells and A. Y. Stathopoulos, *Radiation Effects* 74(1983) 181
- [26] Engineering Materials Handbook, Ceramics and Glasses, Vol 4, ASM International
- [27] M. L. Kronberg, *Acta Met.*, 5, 508, (1957)
- [28] W. E. Lee and K. P. D. Lagerlof, *J. of Electron Microscopy Technique* 2: 247-258 (1985)
- [29] F. Agullo-Lopez, C. R. A. Catlow, and P. D. Townsend, Point Defects in Materials, Academic Press, New York, 1988
- [30] W. C. Oliver and G. M. Pharr, *J. Mater. Res.*, Vol. 7, No. 6, June 1992, pp 1564
- [31] G. Simmons and H. Wang, Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook, 2nd ed., the M. I. T. Press, Cambridge, MA, 1971
- [32] J. Narayan, and Y. Chen, *J. appl. Phys.*, 51 (1980), 1242
- [33] Moty, C., Defects in Solids, A. V. Chadwick and M. Terenzi, Plenum, New York (1986) 377
- [34] G. J. Pogatschnik, Y. Chen and B. D. Evans, *IEEE Trans. Nucl. Sci.* NS-34 (1987) 1709
- [35] K. H. Lee and J. H. Crawford, Jr., *Phys. Rev. B* 15 (1977) 4065

- [36] S. Y. La, R. H. Bartram and R. T. Cox, *J. Phys. Chem. Solids* 34(1973) 1079
- [37] E. Sonder and W. A. Sibgley, *Point Defects in Solids*, vol. 1, eds. J. H. Crawford, Jr. and L. M. Slifkin, Plenum, New York, 1972, p. 208
- [38] K. H. Lee and J. H. Crawford, Jr., *Phys. Rev. B* 19 (1979) 3217
- [39] Y. Chen and M. M. Abraham, *Nucl. Instr. Methods in Phys. Res.* B59/60 (1991) 1163-1166
- [40] C. J. McHargue, *Nucl. Instr. Methods. B* 19/20 (1987) 797
- [41] C. J. McHargue, in: *Ion beam Modification of Insulators*, eds. P. Mazzoldi and G. W. Arnold (Elsevier, Amsterdam, 1987), p. 223
- [42] W. C. Oliver and C. J. McHargue, *Proceeding of the Conference on Ion Implantation and Plasma Assisted Processes for Industrial Applications*, Atlanta, Georgia, May 1988, 157-161, Published by ASM Internation
- [43] B. Jonsson and S. Hogmark, *Thin Solid Films*, 114 (1984) 257-269
- [44] P. M. Sargent, *PhD thesis*, University of Cambridge (1979)
- [45] P. J. Burnett and T. F. Page, *J. Mater. Sci.* 19 (1984) 845-860
- [46] I. J. McColm, *Ceramic Hardness*, 1990, Plenum Press, New York
- [47] A. K. Bhattacharya and W. D. Nix, *Int. J. Solids Structures* 24 (1988) 1287
- [48] W. C. Oliver, J. C. McCallum, B. C. Chakoumakos, and L. A. Boatner, *Radiation Effects and Defects in Solids*, Vol. 132, 1994, pp 131-141
- [49] W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, A Wiley-Interscience Pulication, John Wiley & Sons (1975) 774

- [50] W. C. Oliver and C. J. McHargue, *Thin Solid Films*, 153 (1989) 185
- [51] Hitachi Instrument News, 19th ed., 1990
- [52] P. S. Sklad, *Mat. Res. Soc. Symp. Proc.* Vol. 115, p. 39
- [53] P. P. Tsai, *INDA Fundamental Conference.*, 1993
- [54] J. W. S. Hearle, *J. of the Textile Institute*, T117-T198, 1953
- [55] ASTM Test Method E104, *ASTM Standards*, American society for Testing and Materials, Philadelphia
- [56] C. R. A. Catlow, R. James, W. C. Mackrodt, and R. F. Stewart, *Phys. Rev.*, B 25, 1006 (1982)
- [57] J. W. Edington, *Practical Electron Microscopy in Materials Science*, Van Nostrand Reinhold, New York, 1976
- [58] N. M. Tallan, *Electrical conductivity in Ceramics and Glass*, Part B, in *Ceramics and Glass: Science and Technology*, ed. J. B. Wachtman, Jr. 1974, Marcel Dekker, Inc. New York
- [59] W. C. Oliver, C. J. McHargue, G. C. Farlow, and C. W. White, in *Defect Properties and Processing of High-Techonology Nonmetallic Materials*, edited by J. H. Crawford, Jr., Y. Chen, and W. A. Sibley (*Mater. Res. Soc. Symp. Proc.* 24, Pittsburgh, PA, 1984), pp 515-52
- [60] T. F. Page, W. C. Oliver, and C. J. McHargue, *J. Mater. Res.*, Vol. 7, No. 2, Feb. 1992

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