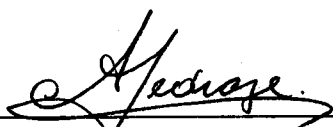


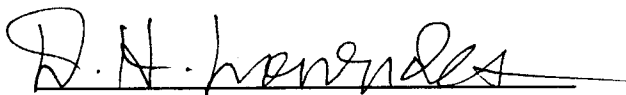
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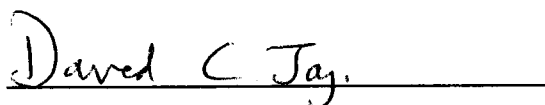
I am submitting herewith a thesis written by Michael Andrew Strauss entitled "Transmission Electron Microscopy Characterization of II-VI Semiconductor Compounds Grown by Pulsed Laser Deposition." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Metallurgical Engineering.



Anthony J. Pedraza, Major Professor

We have read this dissertation
and recommend its acceptance:





Accepted for the Council:



Associate Vice Chancellor and
Dean of The Graduate School

**Transmission Electron Microscopy Characterization of II-VI
Semiconductor Compounds Grown by Pulsed Laser
Deposition**

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Michael Andrew Strauss
December 1996

Dedication

Dedicated to my parents

Acknowledgments

I wish to thank my major professor, Dr. Anthony J. Pedraza, for his guidance and support throughout this thesis work. I also wish to thank Dr. Douglas H. Lowndes for his guidance and Dr. David C. Joy for serving on my thesis committee.

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Abstract

ZnTe and ZnSe films grown on (001) GaAs substrates by pulsed laser deposition (PLD) were characterized by transmission electron microscopy (TEM). The microstructure and electrical properties of the films were determined and correlated with growth parameters such as laser energy density, partial pressure of the background gas, gas flow rate, and substrate cleaning method. Stacking faults, dislocations, and columnar structures were examined by cross-section TEM. The degree of epitaxiality between film and substrate was determined by high resolution TEM analysis of the interfaces.

The film microstructure is a strong function of the gas pressure in the growth chamber during deposition. A background pressure of 50 mtorr or less of N_2 resulted in single crystalline ZnTe films, with stacking faults as the main observable crystalline defect. Growth pressures of 88 or 100 mtorr of N_2 give rise to columnar grains that propagate from an initial layer of heavily faulted single crystal. Evidence of cluster deposition was found in the ZnTe films grown in high pressures of N_2 . A similar columnar microstructure was observed in a ZnSe film grown in 1000 mtorr of a He/ Cl_2 atmosphere, but no clusters were observed. Growth conditions are responsible for film microstructure rather than the degree of lattice mismatch between the film and substrate.

The film-substrate interfaces were semicoherent, with interfacial misfit dislocations spaced so as to accommodate the film-substrate lattice parameter mismatch. The density of stacking faults initiating at the interface was found to be a function of the method used to clean the substrate surface prior to film growth rather than the lattice mismatch. A more effective removal of oxides led to decreased interfacial stacking fault densities.

The electrical properties of ZnTe films were significantly improved by rapid thermal annealing (RTA). Point defect annihilation is the most likely cause of this improvement.

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Chapter 1

Literature Review

1.1 Introduction

The pulsed laser deposition (PLD) process has proven successful in growing thin films of a wide range of materials, from high temperature oxide superconductors to polymers. The growth of highly doped, epitaxial thin film semiconductors for laser diode applications is a new challenge for PLD. The electrical and optical properties of such devices are far more sensitive to microstructural defects and stoichiometric considerations than are most materials previously grown by PLD.

The purpose of this research is to characterize the microstructure of ZnTe and ZnSe thin films grown by PLD as a function of growth conditions and to correlate the film microstructures with electrical properties. Cross-sectional transmission electron microscopy and high-resolution transmission electron microscopy were employed for microstructural and interface studies. A method of improving the electrical properties of these semiconductor films by rapid thermal annealing is described.

1.2 Materials Properties

ZnTe and ZnSe are present in two crystallographic forms: sphalerite, that has the zinc blende structure, and wurtzite. The sphalerite structure, which belongs to the space group $F(4)3m$, number 216, is face centered cubic (FCC) with a motif of one atomic species located at (0,0,0) and the other at (1/4,1/4,1/4). It is equivalent to two interlocked face centered cubic sublattices, one sublattice for each species. The wurtzite structure is equivalent to two interlocked close-packed hexagonal (HCP) sublattices. The sphalerite phase is stable at growth temperatures lower than 500°C while the wurtzite phase is stable at growth

temperatures above 1000°C [1]. The growth temperatures of ZnSe and ZnTe studied in this work are 300°C and 320°C, respectively. X-ray diffraction confirmed that sphalerite is the only phase present in ZnSe or ZnS films grown by pulsed laser deposition (PLD) at similar growth temperatures [1].

The lattice parameter at room temperature for the sphalerite phase of ZnTe is 6.1026 Å and 5.667 Å for ZnSe. The substrate material used in all cases studied here is GaAs, which has the sphalerite crystal structure and a lattice parameter at room temperature of 5.6534 Å. The lattice parameter difference at room temperature between ZnTe and GaAs is 7.9%, while the difference between ZnSe and GaAs is only 0.24%, with both measurements being made relative to GaAs.

ZnTe and ZnSe are wide, direct band gap II-VI semiconductors, the magnitude of the gap at room temperature being 2.26 eV (518 nm) for ZnTe and 2.71 eV (457 nm) for ZnSe [2]. Figure 1.1 is a photoluminescence (PL) emission spectrum measured at 4.2 K of an n-type ZnTe film grown by metalorganic vapor phase epitaxy [3]. Note the strong emission in the frequency range of 500 to 530 nm.

The stacking fault energies of ZnTe and ZnSe are low relative to GaAs and other elemental and compound semiconductors, so stacking faults are easily generated given suitable growth conditions.

Table 1.1 lists some relevant physical properties of ZnTe, ZnSe, and GaAs.

1.3 II-VI Compound Semiconductor Devices

Wide-band-gap II-VI compound semiconductor light emitting diodes (LEDs) and laser diodes (LDs) have long been sought after and have accumulated a long list of potential applications. Originally, it was envisioned that the major role for these devices, which would emit in the blue-green range, would be in color displays and as substitutes for tunable dye lasers [4]. With the advent and rise of optical data storage such as CD-ROMs, blue-green laser diodes have

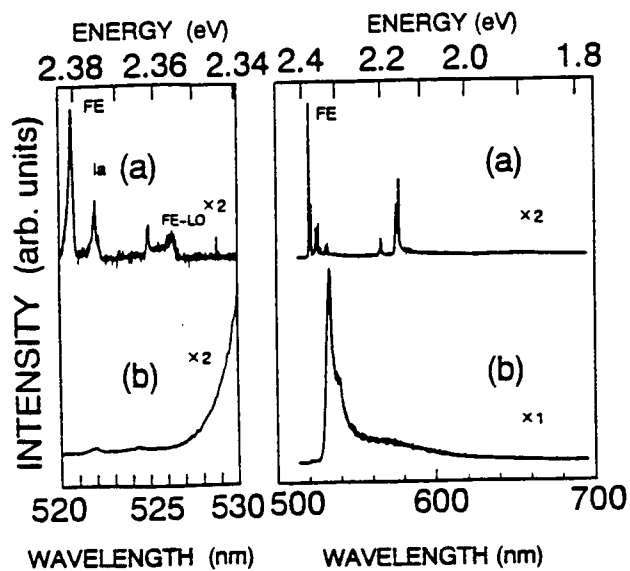


Figure 1.1 Photoluminescence (PL) emission spectra measured at 4.2K of an n-type ZnTe film grown by metalorganic vapor phase epitaxy. a) nominally undoped; b) Al doped.

Source: H. Ogawa, G.S.Irfan, H. Nakayama, M. Nishio, and A.Yoshida, Jpn. J. Appl. Phys. 33, L980 (1994).

Table 1.1 Physical Properties of ZnTe, ZnSe, and GaAs
(References in brackets)

Property	ZnTe	ZnSe	GaAs
Room Temperature Lattice Parameter (Å)	6.1026	5.667	5.6534
Lattice Parameter Mismatch Relative to GaAs	7.9%	0.24%	----
Stacking Fault Energy (mJ/m ²)	16±4 [a]	12.6±0.4 [a]	55±5 [a]
Room Temperature Band Gap (eV)	2.26 [b]	2.71 [b]	1.4257 [b]
Room Temperature Coefficient of Thermal Expansion (× 10 ⁻⁶ K ⁻¹)	8.3 [b]	7.7 [b]	6.86 [b]
Melting Point (°C)	1259 [b]	1520 [b]	1240 [b]

Sources:

[a] S. Takeuchi, K. Suzuki, and K. Maeda, *Phil. Mag. A*, **50**, 171 (1984).

[b] Numerical Data and Functional Relationships in Science and Technology, Group III, Vol. 17b, O. Madelung, ed., New York: Springer-Verlag, 1982.

become even more attractive. Current optical data storage systems use III-V compound semiconductor laser diodes that lase in the red or infrared. A reduction in wavelength by a factor of two (say, from infrared to blue) would increase the data storage density of CD-ROMs fourfold [5]. Figure 1.2 is a plot of band gap versus lattice parameter for elemental and IV-IV, III-V, and II-VI compound semiconductors that shows the wide band gap of II-VI compound semiconductors[6].

In 1967, the lasing of II-VI semiconductors under electron beam pumping was first demonstrated [8]. Electron beam pumping was needed to generate a high density of electrons and holes since it was not possible at that time to achieve the necessary level of doping. In 1990, p-type ZnSe with sufficient dopant levels of nitrogen was grown by molecular beam epitaxy (MBE) so that a ZnSe p-n junction showed blue emission at room temperature [9]. Typically applied voltage and current drawn for these devices were 22 V and 20 mA, respectively, at room temperature, and 13.5 V and 40 mA, respectively, at 77 K. In September of 1991, the first blue-green laser diode was reported by the 3M Company [10]. This device emitted coherent light at 490 nm under pulsed current injection at 77 K; it emitted blue light at room temperature but did not lase. This diode utilized ZnSe thin films grown by MBE, as would other devices to follow. By August of 1993, the continuous-wave (cw) operation of a II-VI laser diode with a wavelength of 523.5 nm at room temperature was demonstrated by a group from Sony [11]. The applied voltage for this device was 17 V. As of the summer of 1996, advancements in these devices have lowered the wavelength for cw operation at room temperature to 500 nm and the threshold voltage to 4.5 V [12]. In pulsed operation, a wavelength of 463 nm has been achieved [13].

A major problem is the lifetime of these devices. The current record is 101.5 hours of cw operation at room temperature [14], obviously far short of commercial requirements, so recent work has focused on the issue of degradation.

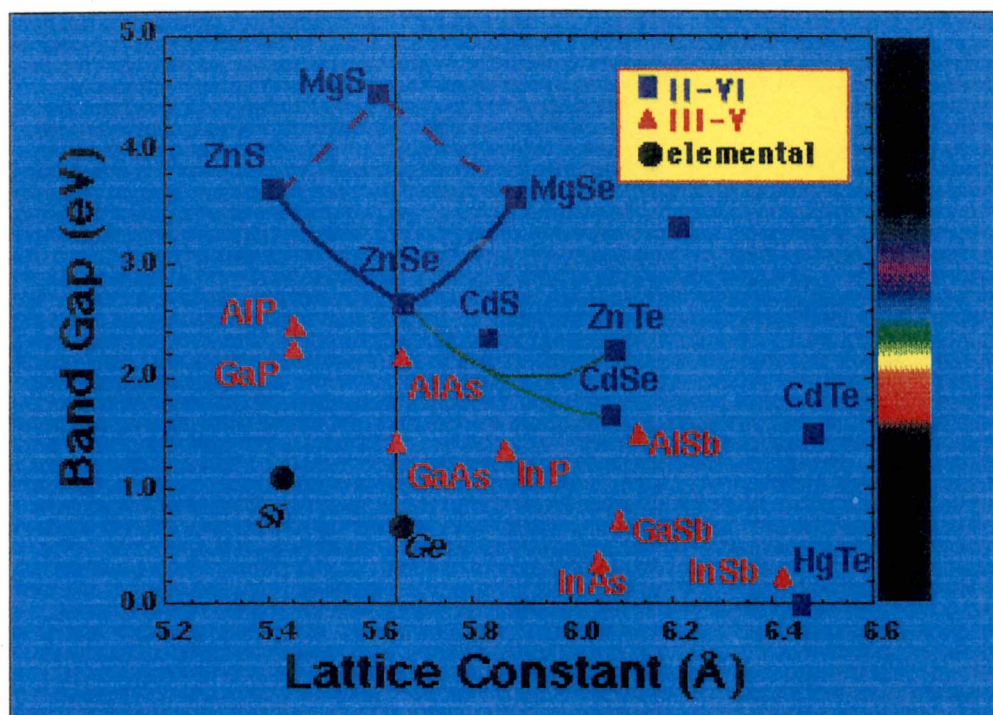


Figure 1.2 Band gap vs. lattice parameter plot of elemental and compound semiconductors.

Source: http://www.nml.org/blue_laser/blue_green_lasers.html

It has been determined that degradation is due to three different kinds of microstructural defects: in-grown stacking faults, dark patches, and $\langle 100 \rangle$ dark line defects (DLDs) [15-17]. Dark patches are areas of small, closely spaced dislocations that originate near in-grown stacking faults during lasing. $\langle 100 \rangle$ DLDs is the name given to the defect structure that causes progressive darkening in $\langle 100 \rangle$ directions during operation of these devices. TEM observations revealed no dislocation networks associated with these $\langle 100 \rangle$ DLDs; it is postulated that the darkening may correspond to areas of point defects aligned along $\langle 100 \rangle$ that would not image well in TEM [17]. All of these defects reduce the efficiency of the lasing by acting as nonradiative recombination centers. Microstructural control is therefore an important issue.

1.4 The Pulsed Laser Deposition Process

In the pulsed laser deposition (PLD) process, high energy laser pulses are directed at a target which has the same stoichiometry as the desired film. The target may be either solid or liquid. The electromagnetic energy of the pulsed photons is converted at the target into thermal energy, resulting in evaporation and ablation of the target material into a supersonic plume. The substrate onto which the film is to be grown is placed in the path of the plume. Each laser pulse, then, produces a new plume from the target and deposits new material on the film surface. PLD was first demonstrated by Smith and Turner in 1965 using a ruby laser [18]. Several materials were deposited, including ZnTe, a material studied in the present work. These experiments demonstrated "the feasibility in many instances of thin film vacuum coating utilizing a laser external to the vacuum chamber as the evaporation power source [18]." PLD remained merely a feasible process rather than a practiced one as far as industry was concerned until the late 1980's when high temperature superconducting oxide thin films were successfully produced by PLD [19].

PLD of epitaxial, doped, compound semiconductors presents some special problems since the microstructural and chemical requirements are more stringent than those of the superconducting films mentioned above. First is the question of how best to dope the film to sufficient levels. One method is to dope the target, as was done with Li-doped II-VI targets [20]. Another is to incorporate the dopant into the film by carrying out the ablation in a reactive gas such as N_2 or Cl_2 . This method has produced p-type ZnTe films with free hole concentrations of 10^{19} - 10^{20} per cm^3 , equal to concentrations of ZnTe grown by any other method [21].

The second problem is how best to tune the kinetic energy and composition of the ablation plume to obtain optimum film growth conditions. Ablating through a gas offers the opportunity to exert some control over these characteristics of the ablation plume. Figure 1.3a shows time-resolved ion probe current measurements of ZnTe ablation performed in N_2 pressures ranging from vacuum (10^{-6} torr) to 100 mtorr for a target to substrate distance of 10 cm [22]. The effect of the ambient pressure is to split the ablation plume into modes having different kinetic energies and velocities. Figure 1.3b shows a deconvolution of the ion probe data performed by the fitting of exponentially-modified-gaussian distributions that allows the amplitude of each mode to be known as a function of N_2 pressure [22]. This deconvolution reveals that the plume splits into three distinct modes in this pressure range. The fastest mode (mode 1) dominates when the ablation is carried out in N_2 pressures ranging from vacuum to 15 mtorr. Absorption and emission spectroscopy indicate that mode 1 consists almost entirely of individual ions and neutral atoms [22]. Constituents of mode 1 travel to the substrate without undergoing collisions with ambient gas molecules. With mode 1 velocities of roughly 10^6 cm/s, individual Zn and Te ions have energies of roughly 34 and 67 eV, respectively. This is enough energy to create point defects in the film lattice [22]. Mode 2 becomes dominant at pressures of about 15 mtorr. Through collisions with the ambient gas molecules, individual atoms in this group have had

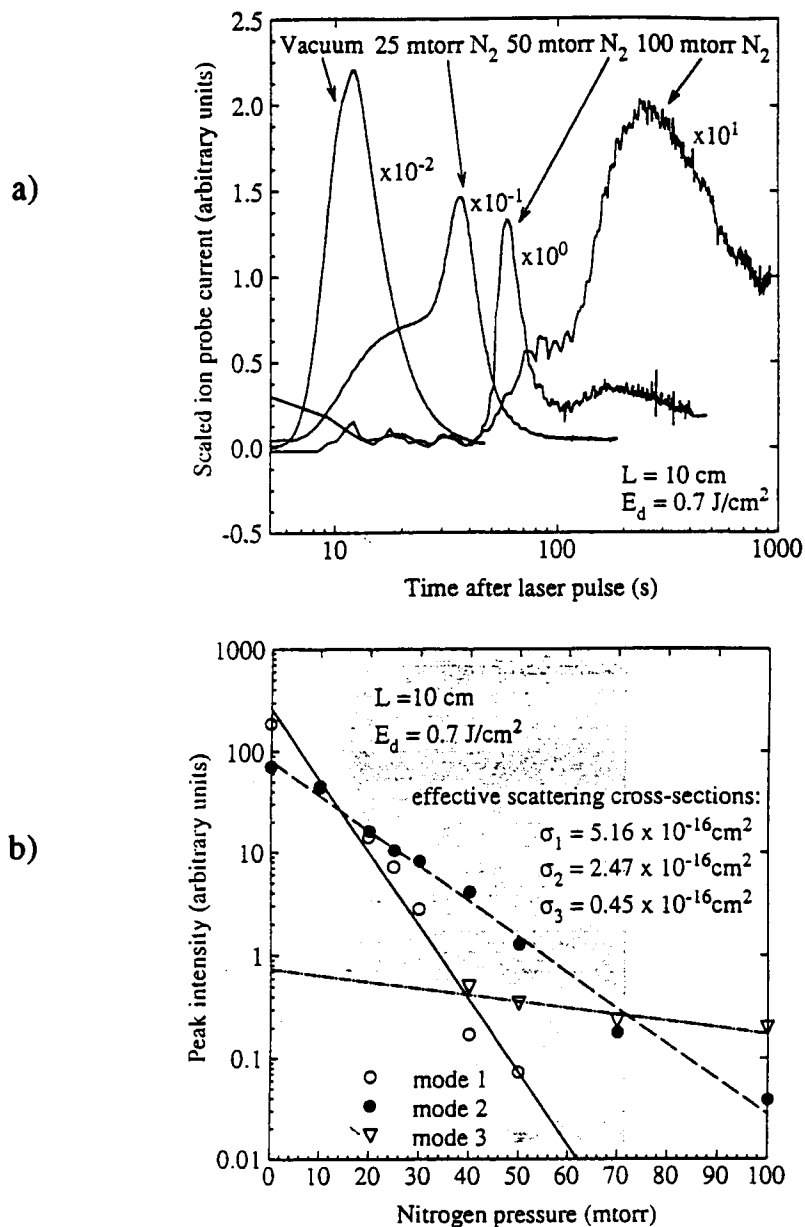


Figure 1.3 The separation of the ablation plume into distinct modes as a function of N_2 pressure. a) time-resolved ion probe current as a function of N_2 pressure; b) mode amplitudes as a function of N_2 pressure. The ablation was performed at 10 cm separation with a laser energy density $E_d=0.7 \text{ J/cm}^2$.

Source: C.M. Rouleau, D.H. Lowndes, M.A. Strauss, S. Cao, A.J. Pedraza, and L.F. Allard, Mater. Res. Soc. Symp. Proc. 397, to be published.

their velocities reduced to 10% of mode 1 velocities; thus, their energies have been reduced to about 1% of mode 1 energies. Mode 3 dominates closer to 100 mtorr N_2 . Individual atoms in this mode have had their energies reduced by further collisions to about 0.1% of mode 1 energies. The energies of individual atoms in mode 3 are of the same order of magnitude as energies found in MBE. As will be shown, the constituents of mode 3 are not all individual atoms but include nanometer-sized clusters of several thousand atoms. Ablating ZnTe through N_2 gas pressures of up to 100 mtorr provides a means to distribute individual atom energies over 3 orders of magnitude and to include both individual atoms and clusters in the plume.

The characteristics of the ablation plume have a significant effect on electrical properties of ZnTe films. Figure 1.4 shows a plot of free hole mobility and free hole concentration versus N_2 pressure for ZnTe films [21]. The peaks in both mobility and concentration occur at the N_2 growth pressure of 50 mtorr where mode 2 dominates. Low mobility and concentration at the N_2 growth pressure of 25 mtorr are most likely the result of a higher density of point defects since the amplitude of the high energy mode 1 has been reduced by a factor of 100 at 50 mtorr relative to 25 mtorr [22]. Low mobility and concentration at the N_2 growth pressure of 100 mtorr will be explained as the result of a change in microstructure from single crystalline to polycrystalline.

1.5 Film Growth Modes

The very early stages of film nucleation and growth greatly determine the microstructural properties of the final film. An understanding of the factors involved in the initial growth of a film can lead to better microstructural control.

The fundamental materials properties that determine the growth mode of a film formed from a vapor on a substrate are the surface free energy of the substrate, the surface free energy of the film, the interfacial free energy between

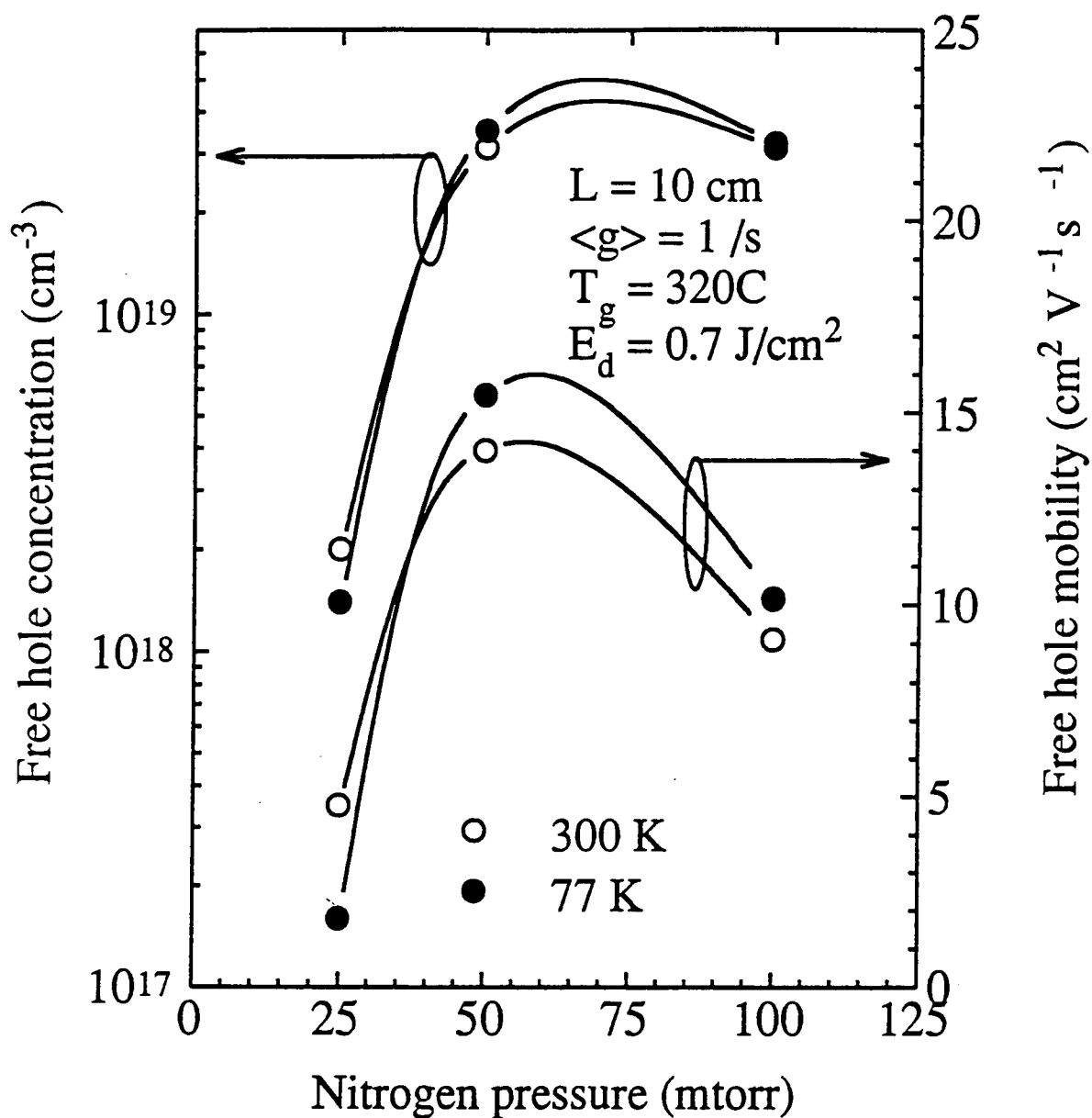


Figure 1.4 Free hole mobility and free hole concentration as a function of N_2 pressure in ZnTe films grown by PLD.

Source: C.M. Rouleau, D.H.Lowndes, J.W. McCamy, J.D. Budai, D.B. Poker, D.B. Geohegan, A.A. Puretky, and S. Zhu, Appl. Phys. Lett. **67**, 2545 (1995).

the film and substrate, the surface mobility of film atoms on the substrate surface, and the lattice mismatch between the film and substrate. The different modes of film growth can be qualitatively explained if it is assumed that the surface mobility is high enough so that the deposited atoms attain positions of minimum free energy. Assume the film is in the shape of a spherical droplet on the substrate surface with a contact angle θ . Figure 1.5 illustrates the situation. The effect of the substrate surface free energy is to minimize free substrate area along the substrate in the direction of arrow 1 by decreasing θ and spreading the film droplet out. The effect of the film surface free energy is to minimize free film area along arrow 2 by increasing θ and decreasing the radius of the film droplet. The effect of the interfacial free energy between film and substrate is to minimize the contact area along arrow 3; this has the same effect as the film surface free energy. θ increases as substrate surface free energy increases and film surface free energy and interfacial free energy decrease. Films grown under these conditions form as discrete, three-dimensional islands. This island mode of film growth is called the Volmer-Weber mode. As substrate surface free energy decreases and film free energy and interfacial free energy increase, θ decreases and the islands are spread out. For film-substrate systems in which $\theta=0$, the initial adatoms spread to cover the substrate uniformly with a layer of one atomic thickness. The film grows in a two-dimensional, layer-by-layer mode called the Frank-van der Merwe mode.

An additional mode is possible when the film wets the substrate and the film-substrate lattice mismatch is greater than $\sim 2\%$ [23]. The film may strain to take on the lattice parameter of the substrate for the first few monolayers. As some film thickness is reached, the tendency to form monolayers is overridden by the strain required to remain lattice matched to the substrate. The film then relaxes to its bulk lattice parameter and islands are nucleated. Misfit dislocations along the interface and stacking faults are introduced to accommodate the new

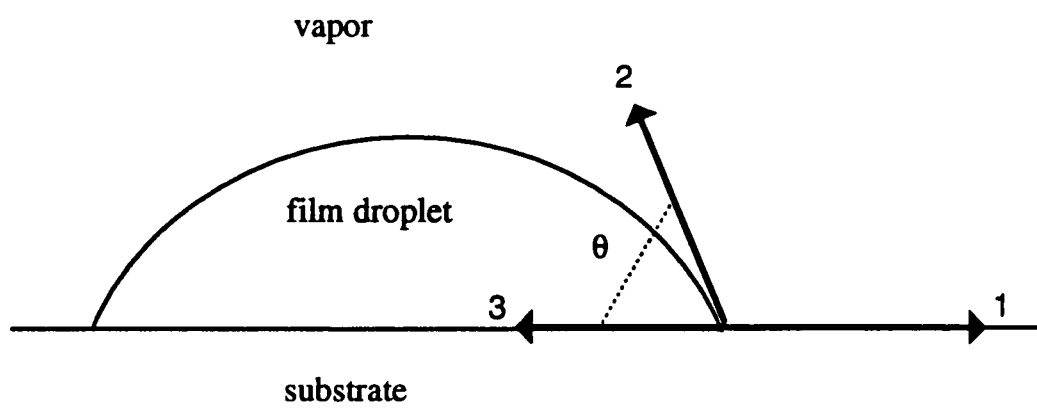


Figure 1.5 The geometry of the free energy model of initial film growth mode.

lattice mismatch. This film growth mode of growing as islands after initiating as layers is called the Stranski-Krastanow mode. Classic SK growth has been observed in the MBE growth of ZnTe on (001) GaAs [24]. A 5 monolayer (ML) thickness of ZnTe is observed by HRTEM as a continuous film with complete substrate coverage, i.e. layer growth. HRTEM lattice images and grazing incidence x-ray diffraction show that the film is strained to match the GaAs substrate lattice. A 30 ML ZnTe layer, though, is in the form of islands on top of the ~5 ML continuous film. Here, the film has relaxed, and stacking faults and interfacial misfit dislocations accommodate the lattice mismatch.

A number of experimentally controlled factors exist that can force a transition between initial film growth modes. In compound films the interface stoichiometry controls the film-substrate interfacial surface free energy. The surface diffusion coefficient of the adatoms on the substrate is another important factor. The discussion above assumed sufficient surface mobility to allow the free energy terms to control the film growth. A decrease in surface mobility can force layer growth where the free energy model would predict islanding, and vice versa. Surface mobility can be affected by the substrate temperature, substrate surface quality, energy of adatoms, and the arrival rate of adatoms at the substrate. Manipulation of any of these factors is able to induce transitions in initial film growth mode.

The effect of the free energy term on the film growth mode is easily observed in the MBE growth of compound semiconductors by adjusting the interfacial stoichiometry. This is achieved through combinations of substrates having different surface terminating planes and exposing them to a flux initially from only one of the sources. For ZnSe grown on GaAs, a Ga terminated substrate surface with an initial exposure of Se results in island growth (as determined by RHEED) while an As terminated surface and initial exposure of Zn gives layer growth [23,25,26]. The As-Zn interface films had fewer defects and

better x-ray rocking curves [26]. The ZnTe/GaAs film mentioned above was grown on an As terminated substrate [24]. XPS analysis of the continuous film indicated As-Zn interface. Controlling which element forms the film/substrate interface in PLD of compound films is not possible as long as a single target is used. Alternate ablating of separate elemental targets would be required to achieve a proper interface stoichiometry.

The quality of the substrate surface is another factor that controls the initial growth mode. Surface contaminants can act as barriers to smooth layer growth. In the case of homoepitaxy, the free energy model predicts layer growth since a deposit wets a substrate of the same material. A study of Si homoepitaxy indicated that island growth was promoted by carbon contamination of the substrate [27]. Layer growth was observed only after the contamination was reduced to very low levels. Surface features such as regular steps on a crystal tilted from a major axis can promote layer growth by providing many nucleation sites [28]. GaAs growth on (100) Si tilted 3.5° towards [011] showed layer growth [28]. After reactive ion etching (RIE) of the substrate, though, islanding occurred due to the irregular substrate surface produced by RIE [28].

In MBE growth of GaAs on (100) Si it was found that above a substrate temperature of 300°C , film growth initiated as islands while below this temperature the film grew as layers [29]. The decreased surface diffusion of the lower temperature substrates prevented the formation of islands that would be predicted by the free energy model. In contrast, a molecular-dynamics simulation of homoepitaxy showed that a low substrate temperature ($T=0\text{K}$) deposition contained voids characteristic of island growth whereas a higher temperature ($T=40\%$ of melting temperature) produced layer growth, as would be predicted by the free energy model [30].

A high arrival rate has the effect of lowering surface diffusion if this rate prevents deposited atoms from moving to stable sites before being buried by the

next layer of atoms. Modifications of MBE that prevent a constant flux of atoms at the substrate have been successful in producing better quality films [26,28]. In migration enhanced epitaxy (MEE), the surface is exposed to only one element source at a time with a short delay in-between, allowing for greater surface migration. ZnSe films grown in this manner had lower defect densities as compared to traditional MBE films [26]. In modulated molecular beam epitaxy (MMBE) one source is pulsed while another source remains open. Growth of GaAs with the As source being pulsed open and closed induced a change to layer growth from MBE island growth on the RIE processed Si substrates mentioned above [28]. The MMBE films also had reduced density of stacking faults near the interface. This was seen as a result of the fact that more time is available for the diffusion of Ga atoms on the surface [28]. PLD has an advantage in that the arrival rate can be controlled simply by adjusting the pulse rate of the laser. In general, the ablation plumes arrive in short time scale windows with relatively large times between pulses. In the present study, each pulse deposits $\sim 0.25 \text{ \AA}$, so there is no chance of the material from one pulse completely burying material from the previous pulse. Thus, conditions are good for more surface diffusion in PLD as compared to traditional MBE.

One important parameter that is easily manipulated in PLD but not at all in MBE is the energy of incoming atoms. As was discussed above, ablating through varying gas pressures in PLD has the effect of varying the distribution of adatom energies as they arrive at the growing film. Adatom energies can be varied from $\sim 0.1 \text{ eV}$ to several tens of eV. As a comparison, MBE energies are thermal ($\sim 0.1 \text{ eV}$) and are essentially fixed. The benefit of an energetic flux was demonstrated in a molecular-dynamics study that investigated the homoepitaxial growth of Ag at various adatom energies. The growth mode changed from islanding below 1 eV to layering above 10 eV [31]. Increased surface mobility of the adatoms and the

breakup of clusters were seen as the cause of the transition [31]. Thus the ability to tailor adatom energies gives PLD an extra advantage over MBE.

1.6 Effect of growth mode on film properties

The overall film microstructure is dependent on the initial growth mode. The island mode can give rise to columnar grains due to shadowing of areas between islands. If surface mobility is low, these shadowed areas between islands never fill and become cavities in the completed film. Columnar grains give poor surface morphology and have a detrimental effect on electrical conductivity as measured parallel to the interface.

1.7 Generation of defects in epitaxial films

A stacking fault is a disruption of the normal ABCABC stacking sequence of the close-packed $\{111\}$ planes of an FCC crystal: ABCBCAB, where the stacking fault comes between the two bold-type letters. A twin is a sequence of stacking faults such that the planes are mirrored across the stacking fault boundaries: ABCBACBABC. Stacking faults and microtwins on $\{111\}$ planes make an angle of 54.7° with (001), the plane containing the GaAs substrate surface.

Stacking faults can be produced when two islands that are faceted on $\{111\}$ planes coalesce [23]. Stacking faults also form at anti-phase boundaries (APB) [32]. APBs occur in compound materials with the sphalerite structure (such as ZnSe and ZnTe) in which there are two interpenetrating FCC lattices. The surface of an island that is faceted on $\{111\}$ planes consists of a $\{111\}$ plane of either all of one atomic species or all of the other. Two types of APBs are possible: type I involves equal numbers of wrong A-A and B-B bonds, and type II involves only A-A or B-B bonds.

Stacking faults are often generated at the interface between a substrate and

an epitaxial film. Controlled experiments in the homoepitaxial growth of Si have revealed that the presence of stacking faults is related to substrate surface roughness [33]. When the epitaxial layer grows around a surface feature that has a height above the surface that is not equal to an integral multiple of the film lattice spacing in the growth direction, a stacking fault may accommodate the difference. Figure 1.6 illustrates how stacking faults may be introduced on a substrate with a rough surface [33]. For example, substrates which had undergone a thorough oxide removal procedure before deposition contained significantly fewer stacking faults than those that had not [33]. Patches of oxide provide nucleation sites for stacking faults. Another study demonstrated that the impurity concentration of the substrate plays an important role in determining stacking fault density [34]. Si substrates containing a higher level of impurities generated a substantially higher stacking fault density as compared to substrates of lower impurity levels. This increase in stacking fault density is seen as a result of the contamination of the substrate surface through diffusion of impurities. The impurity effect was eliminated by either lapping the back side of the substrate or subjecting it to a boron gettering process. Lapping of the back surface provides dislocation sites for the preferential diffusion of impurities away from the front surface. High stacking fault densities are also associated with scratches made on the Si substrate surface or even on the back side of the substrate [33].

Contaminants may also cause stacking faults to form within the growing film. Again in the case of homoepitaxial Si growth, a heavily boron-doped Si source resulted in a large number of in-grown stacking faults throughout the film thickness [34]. This was attributed to exceeding the bulk solubility of boron in Si at the growth temperature of 700°C.

Some factors that might seem to be candidates for stacking fault generation turn out to have no effect. For example, dislocations rising to the substrate surface would appear to be easy nucleation sites for stacking faults. Nearly perfect layers,

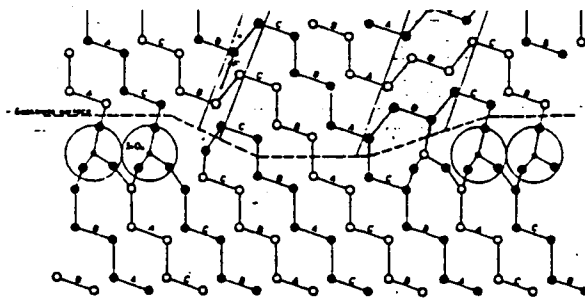


Figure 1.6 The generation of stacking faults on a substrate with a rough surface. A (110) section of an epitaxial Si layer deposited on a Si (111) surface that is partially oxidized. Stacking faults are introduced to accommodate the surface steps. The dotted line represents the film-substrate interface.

Source: R.H. Finch, H.J. Queisser, G. Thomas, and J. Washburn, J. Appl. Phys. 34, 406 (1963).

though, can be grown on heavily faulted substrates [33]. Another factor that conceivably could contribute is substrate-film lattice mismatch. One study demonstrated, though, that ZnS films contained stacking faults regardless of whether they were grown on lattice mismatched GaAs or lattice matched GaP [35].

1.8 Ion Milling Damage

II-VI semiconductors have been shown to be susceptible to ion milling induced damage that may complicate the analysis of TEM images. Milling under certain conditions produces a high density of small (5-10 nm) faulted dislocation loops lying on {111} planes, giving a "black dot" contrast [36]. Milling of CdTe, ZnSe, ZnTe, or ZnS with Ar^+ ions in the energy range of 2-7 keV is capable of producing this damage [36-39]. The dislocation loops are confined to near-surface regions. These dislocation loops are formed by the aggregation of milling induced lattice point defects. Liquid nitrogen cooling of the sample during milling does not eliminate these defects but does lead to more, smaller loops due to the decreased distance of point defect migrations [36]. Another artifact of ion milling is a thin (about 50 Å) layer of ZnO on the surface of ZnSe films [39].

Chapter 2

Experimental Procedure

2.1 Film Growth Procedure

Films were grown by ablating a pressed powder target of stoichiometric ZnTe or ZnSe in a high vacuum (10^{-6} torr) chamber with a pulsed KrF excimer laser. A 0.5 mm thick single crystal, undoped GaAs substrate was placed in the path of the ablated plume at a distance of 10 cm. Hall effect measurements were made of the II-VI films on these insulating substrates to correlate growth parameters and electrical properties. The GaAs substrates were offcut 2° from (001) towards [110] since steps on the substrate surface promote layer-by-layer growth. Each laser pulse deposits about 0.25 Å of the target material on the substrate, depending on the ambient gas pressure. Less target material is deposited on the substrate as the pressure is increased due to scattering of ablated material by the gas atmosphere. The laser pulse rate was approximately 4 Hz so that a film growth rate of approximately 1 Å/s could be maintained. ZnTe films were grown with a substrate temperature of 320°C, while ZnSe films were grown at 300°C. This ZnSe growth temperature gives optimal crystallinity as determined by x-ray diffraction [1]. Growth parameters in this study include laser energy density at the target, composition and pressure of the chamber atmosphere, and gas flow rate during film growth. Films were generally about 500 nm thick; 50 Å thick films were grown for initial film growth mode studies. Atmospheres studied include N_2 and He/Cl_2 since MBE grown ZnSe has been successfully doped as p-type or n-type using atomic nitrogen or chlorine, respectively, generated by an rf source in the growth chamber [9].

Substrate surface preparation provides another growth parameter. Earlier films were grown on substrates manufactured by Sumitomo that required wet chemical processing to produce an oxide-free “clean” surface, while later films

used substrates manufactured by AXT that were “epi-ready” and did not require this surface preparation step. In addition, an *in-situ* hydrogen atom cleaning procedure was implemented for later films. Hydrogen atom cleaning has been shown to produce a smoother surface on GaAs substrates through more uniform oxide desorption [40,41]. Previously, the substrates were only thermally desorbed at 580°C. A reflection high energy electron diffraction (RHEED) system incorporated in the deposition chamber also enabled a check of substrate cleanliness for later samples.

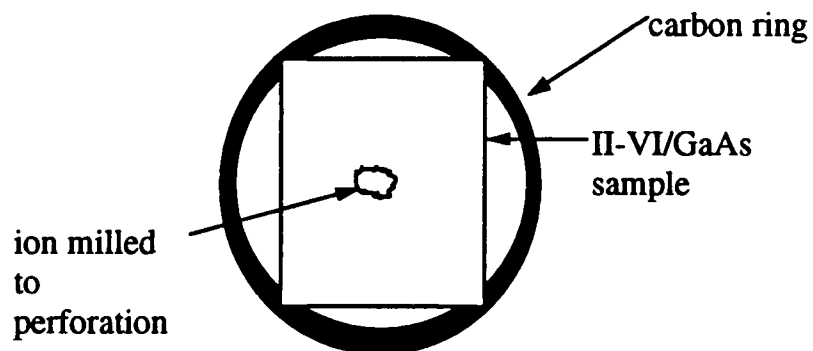
2.2 TEM Sample Preparation

Cross-sectional and planar view of II-VI films deposited on (001) GaAs substrates were thinned to electron transparency for TEM observation. Cross-sectional samples, illustrated in Figure 2.1a, were viewed along $\langle 110 \rangle$ in the plane containing the interface so that defects lying on $\{111\}$ planes could be imaged in cross-section. These samples were used for high-resolution TEM of the interface region and for assessing the overall microstructure of the film. Planar samples, illustrated in Figure 2.1b, were viewed along $\langle 001 \rangle$ normal to the plane containing the interface allowing a full view of defect structures.

2.2.1 Cross-Sectional TEM Sample Preparation

A layer of In was used as a thermal contact between the hot stage and the substrate during PLD. The In was removed from the back side of the GaAs substrate by either grinding it off or by heating the GaAs to above the melting point of In (157°C) and wiping the In with a cotton swab. Two strips of GaAs about 4 or 5 mm long and 75 mils wide were cut along cleavage directions ($\langle 110 \rangle$) with a low speed diamond blade saw. Two equally sized strips of Si were cut as dummy pieces. A sandwich was made of these four strips by facing the II-

a)



3 mm

b)

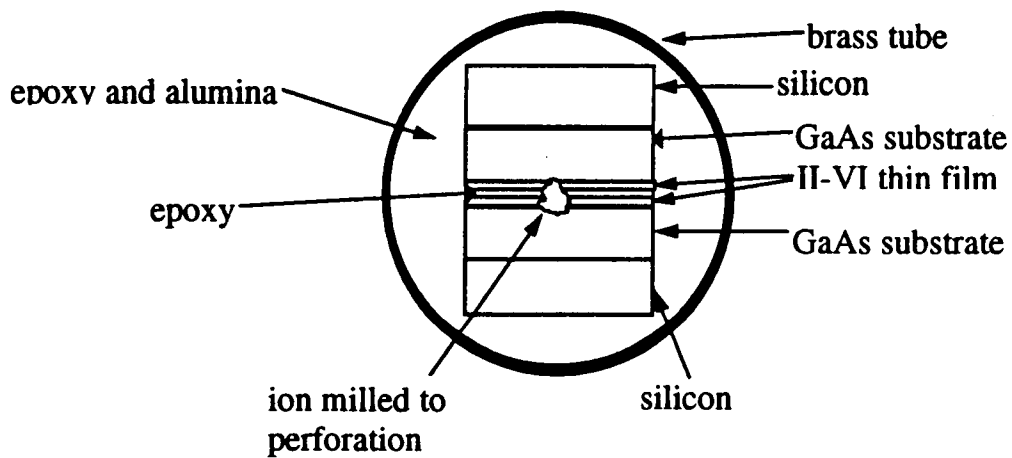


Figure 2.1 TEM samples used in this work. a) planar view; b) cross-sectional view.

VI films towards each other and surrounding the two GaAs back sides with the two dummy Si pieces. M-Bond 610 epoxy bound the layers together. The epoxy was set by heating the sandwich at 90°C for three hours. During this heating, the sandwich was confined in a block of Teflon to prevent slippage of the strips, and the sandwich was squeezed gently with a vise to ensure a thin epoxy layer between each strip. The sides of the sandwich were sanded to remove excess epoxy, and the sandwich was placed into a 3 mm outside diameter brass tube. A mixture of Epo-tek 353ND epoxy and alumina polishing powder holds the sandwich in the tube. 25 mil slices cut from the tube with a low speed diamond saw were then ground and polished to a thickness of 100 microns, with one side being polished to a 1 micron finish. The sample was dimpled on the rough polished side to a thickness of about 20 microns and a 1 micron finish. The dimpling was centered on the interface between the II-VI films. The sample was then ion milled in a Gatan 600 Dual Ion Mill from both the top and bottom sides to perforation using Ar⁺ ions and a liquid nitrogen cooled sample stage. Bulk milling was performed at a gun voltage of 4 kV, a gun current of 0.5 mA per gun, and an angle of 12° relative to the plane of the sample. In the final milling stage, the parameters were reduced to 2.5 kV at 11°.

2.2.2 Planar TEM Sample Preparation

A 3 mm disk was cut with an ultrasonic disk cutter, or a square was cleaved from the original sample. The TEM sample was then ground from the substrate side to a thickness of 100 microns and dimpled to a thickness of 20 microns and a 1 micron finish. Cleaved squares were epoxied to a carbon ring at this point. The sample was ion milled from the substrate side only under the same conditions as were used for preparing cross-sectional samples.

2.3 TEM Procedure

Bright field, 7 beam images were used for cross-sectional samples. Diffraction spots included by the objective aperture were the four {111} spots, the two {002} spots, and the central spot. Most samples were examined with a JEOL 4000-EX operating at 400 kV. The JEOL 4000-EX has a spherical aberration coefficient of 1.0 mm and a chromatic aberration coefficient of 1.7 mm. Some samples were examined with a Hitachi HF-2000 operating at 200 kV. Each is equipped with a CCD camera for digital imaging.

2.4 Rapid Thermal Annealing and Hall Effect Measurements

Rapid thermal annealing (RTA) of a ZnTe film grown in 25 mtorr N_2 was performed in an AG Associates Heatpulse 410. A system of halogen lamps quickly heats the sample at rates of 50-100°C/second and maintains a specified temperature for a specified time. The cooling rate can also be specified. The chamber was purged with Ar for several minutes before each annealing run, during the run, and during the cool down period to eliminate oxidation. A brass film (70% Cu/30% Zn) was placed above, but not touching, the ZnTe film in an attempt to provide a Zn-rich atmosphere in the vicinity of the ZnTe to prevent the loss of Zn during annealing.

Hall effect measurements were made to assess any changes in hole concentration or mobility. Electrical contacts of 75 Å Pd and 450 Å Au were deposited on the ZnTe film at each corner of a square sample, and the contacts and film were annealed in Ar/4% H_2 at 200°C for 1 hour. Hall effect measurements were made at room temperature.

Room temperature photo-luminescence (PL) was performed by Dr. W. Brock Alexander of the Naval Research Laboratory to determine the effect of RTA on the emission spectra.

Chapter 3

Results*

3.1 General Microstructure

3.1.1 Films Grown by MBE

ZnTe/GaAs (001) samples grown by MBE at the University of Florida were examined by cross-sectional TEM to provide comparisons with the PLD samples. Table 3.1 lists the characteristics of the examined films grown by MBE. Both an undoped film seen in Figure 3.1 and a nitrogen doped film seen in Figure 3.2 were single crystal with stacking faults on {111} and threading dislocations off of {111} extending up from the interface and scattered throughout the bulk of the film.

3.1.2 ZnTe films grown by PLD

Cross-sectional TEM indicates a steady degradation of general microstructure of the ZnTe films as the pressure of the ambient atmosphere is increased. Table 3.2 lists growth parameters and microstructural characteristics of the ZnTe films. All of the ZnTe films had a region above the interface, about 200 nm thick, with a high density of stacking faults lying on {111} planes as illustrated in Figure 3.3. ZnTe films grown in N₂ pressures ranging from vacuum to 50 mtorr were single crystalline with stacking faults running up through the bulk of the films as illustrated in Figures 3.4 to 3.7. Threading dislocations such as those observed in MBE films were not observed in PLD films. The density of stacking faults in the bulk of the film increased as the ambient pressure was

* All images in this chapter are <110> cross-sectional TEM images of PLD films on (001) GaAs unless otherwise noted.

Table 3.1 ZnTe/GaAs Films Grown by MBE

Sample	Overall Microstructure
undoped ZnTe	single crystal, stacking faults and threading dislocations concentrated near the interface
nitrogen doped ZnTe	single crystal, higher density of stacking faults and threading dislocations in the bulk of the film than the undoped film

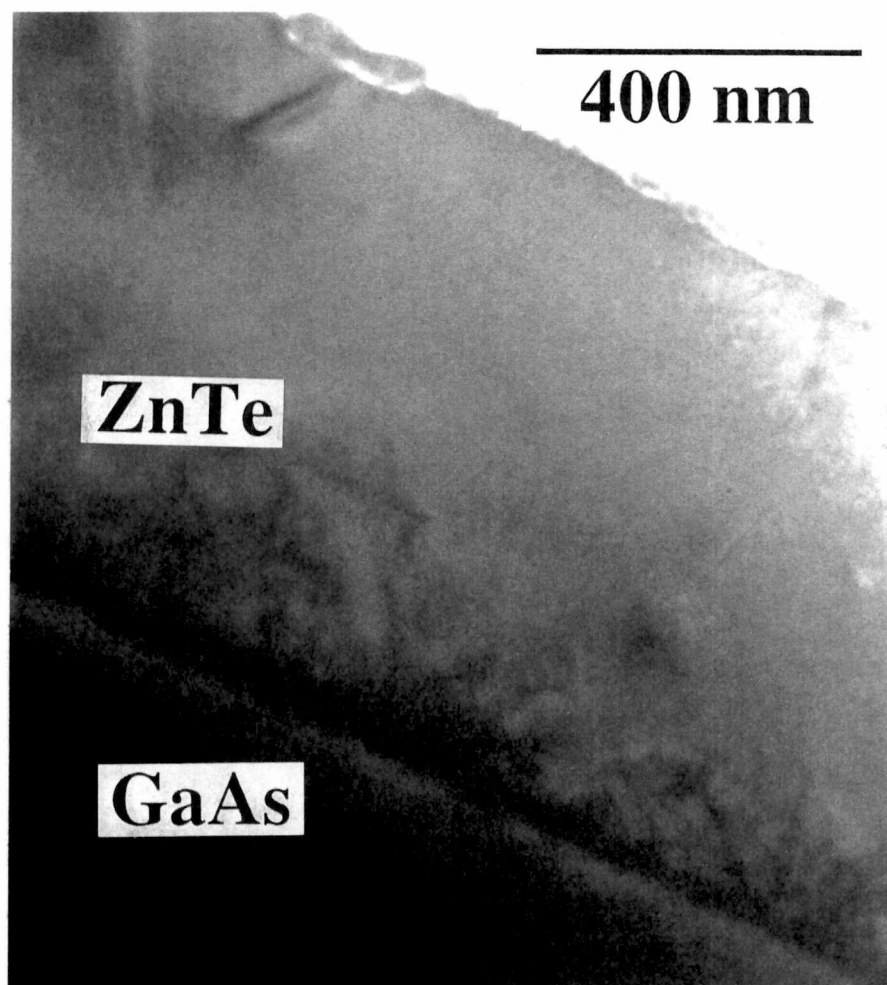


Figure 3.1 Overall microstructure of an undoped ZnTe film grown by MBE.

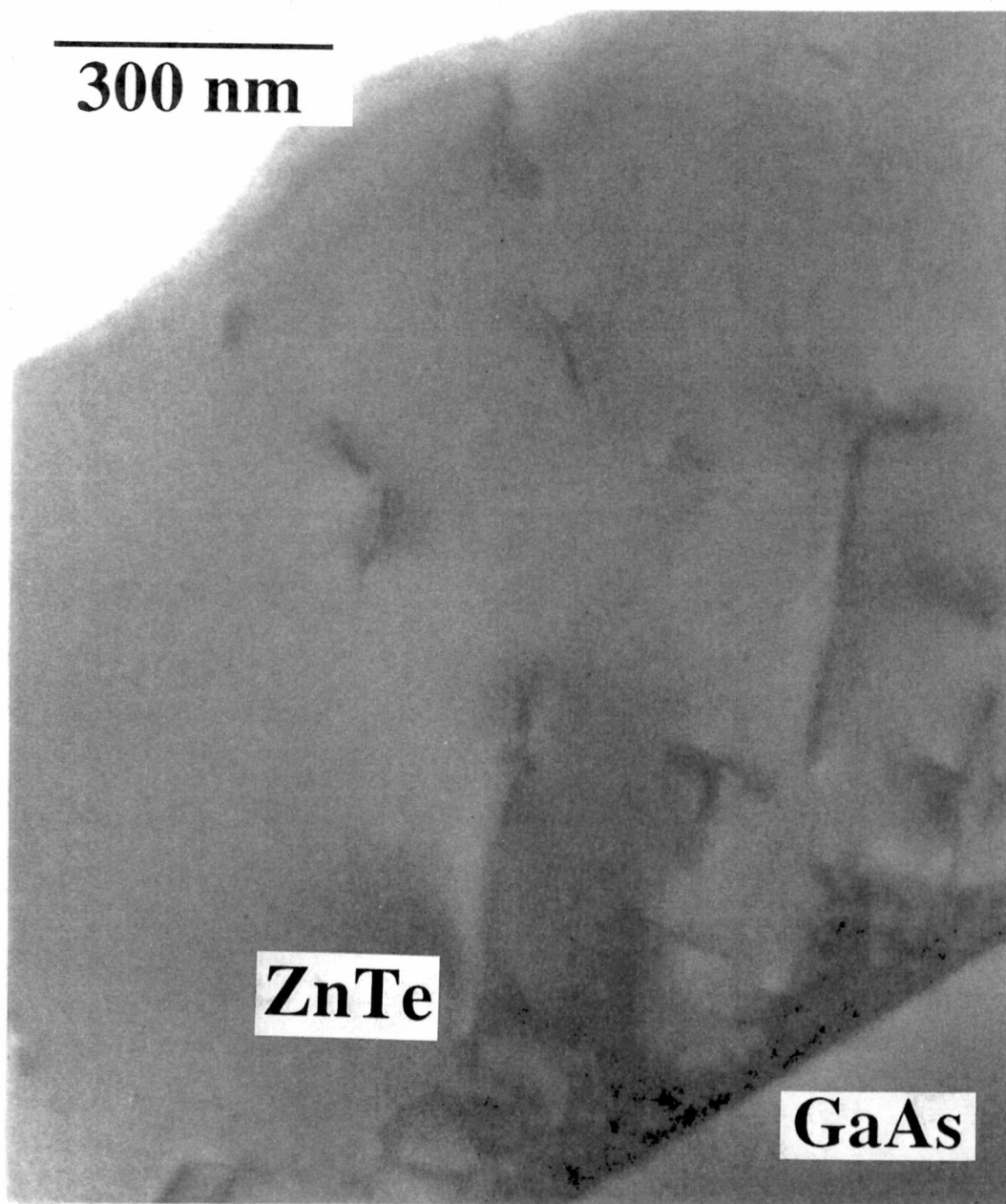


Figure 3.2 Overall microstructure of a nitrogen doped ZnTe film grown by MBE.

Table 3.2 ZnTe/GaAs Films Grown by PLD

Gas Pressure and Flow Rate	Laser Energy Density (J/cm ²)	Substrate Supplier and Cleaning Method	Overall Microstructure
vacuum (10 ⁻⁶ torr)	0.66	B	single crystal, flat upper surface, low stacking fault density
vacuum (10 ⁻⁶ torr)	0.73	C	similar to above film, but with a smoother interface and fewer interfacial stacking faults
25 mtorr N, @ 1 sccm	1.9	A	single crystal, flat upper surface, low stacking fault density
25 mtorr N, @ 4 sccm	0.65	A	similar to above film, but with a higher bulk and interfacial stacking fault density
50 mtorr N, @ 1 sccm	0.65	A	similar to above film, but with a higher bulk stacking fault density
75 mtorr N, @ 20 sccm	0.83	C	single crystal, smoothly varying upper surface, high stacking fault density
88 mtorr N, @ 5 sccm	0.83	C	columnar grains, protrusions and clusters on upper surface
100 mtorr N, @ 10 sccm	1.9	A	irregular columnar grain structure on top of single crystal, many clusters on upper surface, intergranular cavities
100 mtorr N, @ 15sccm	0.65	A	regular , tightly spaced columnar grain structure on top of single crystal, clusters on upper surface, high stacking fault density in grains
100 mtorr N, @ 4 sccm	0.65	A	similar to above film, but with more clusters and intergranular cavities

Notes: Substrate suppliers and cleaning methods are as follows:

A) wet chemical processing and thermal desorption of oxide at 580°C of Sumitomo substrates

B) thermal desorption of oxide at 580°C plus a RHEED check of the surface of AXT substrates

C) hydrogen beam cleaning at 300 °C plus a RHEED check of the surface of AXT substrates

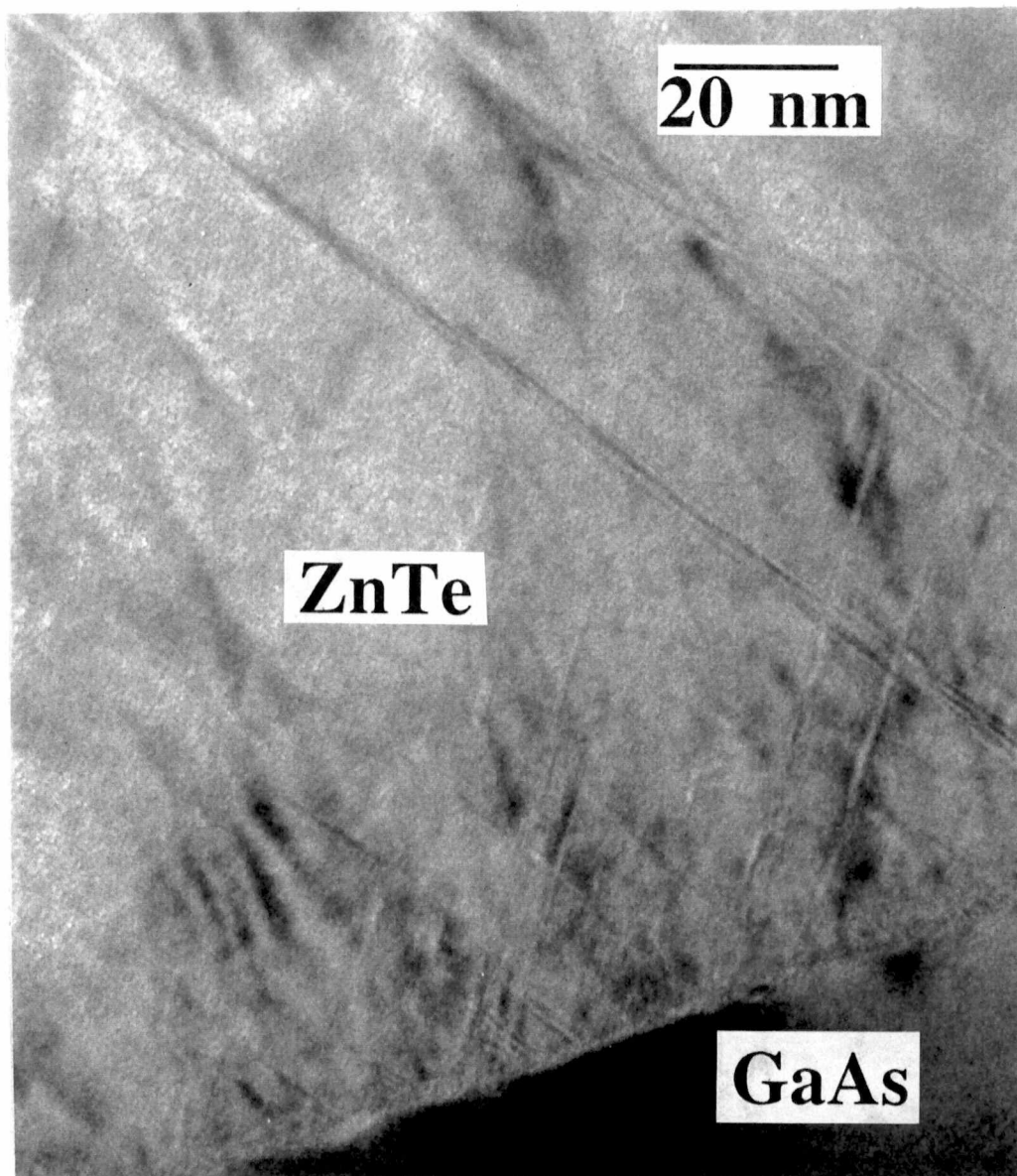


Figure 3.3 Typical region of high stacking fault density near the ZnTe/GaAs interface in a ZnTe film grown by pulsed laser deposition (PLD) in a 25 mtorr N_2 atmosphere using a laser energy density E_d of 1.9 J/cm^2 and a gas flow rate r_g of 1 sccm.

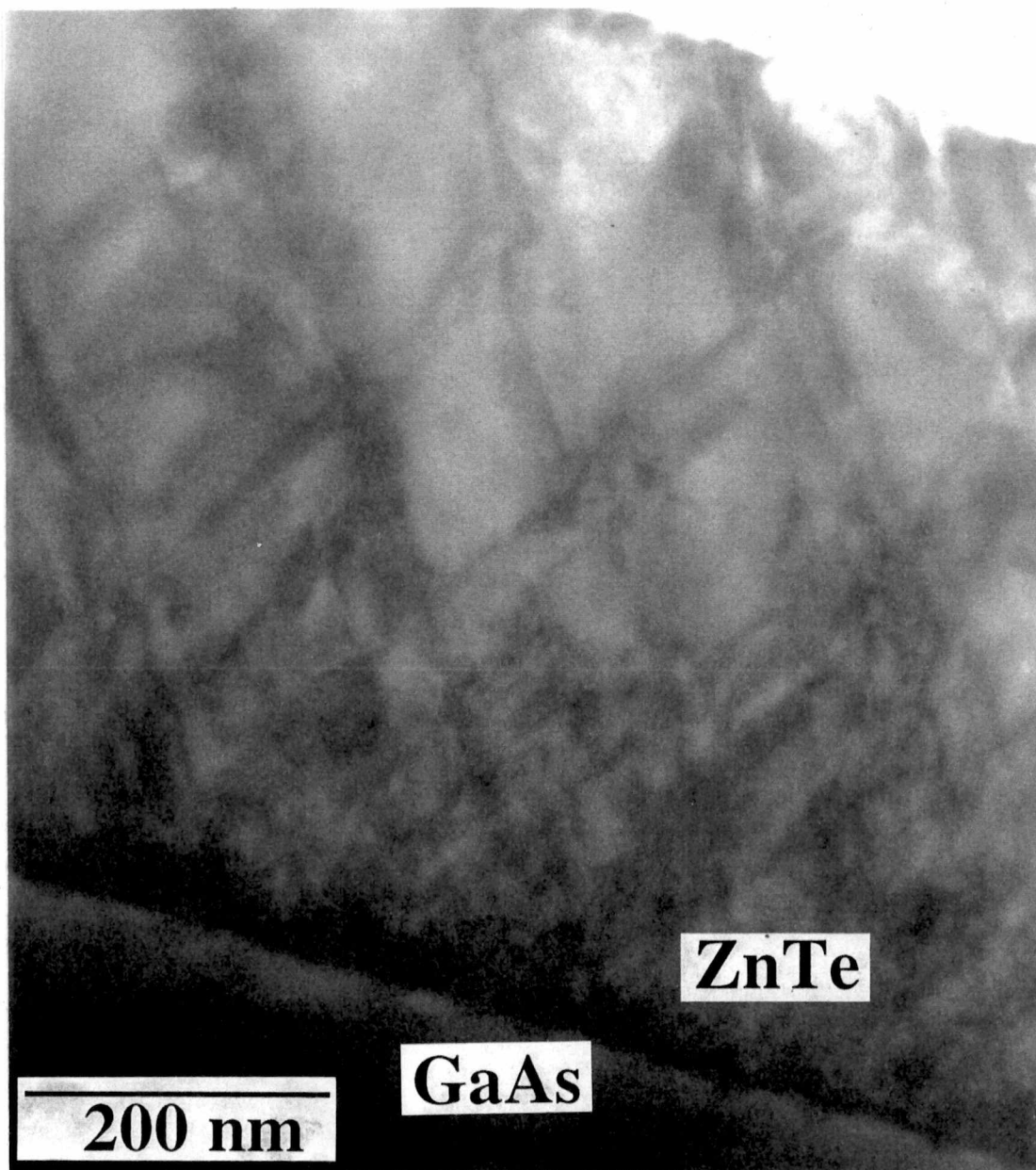


Figure 3.4 Overall microstructure of a ZnTe film grown by PLD in vacuum.
 $E_d=0.66 \text{ J/cm}^2$.



Figure 3.5 Overall microstructure of a ZnTe film grown by PLD in a 25 mtorr N_2 atmosphere. $E_d=1.9 \text{ J/cm}^2$, $r_g=1 \text{ sccm}$.

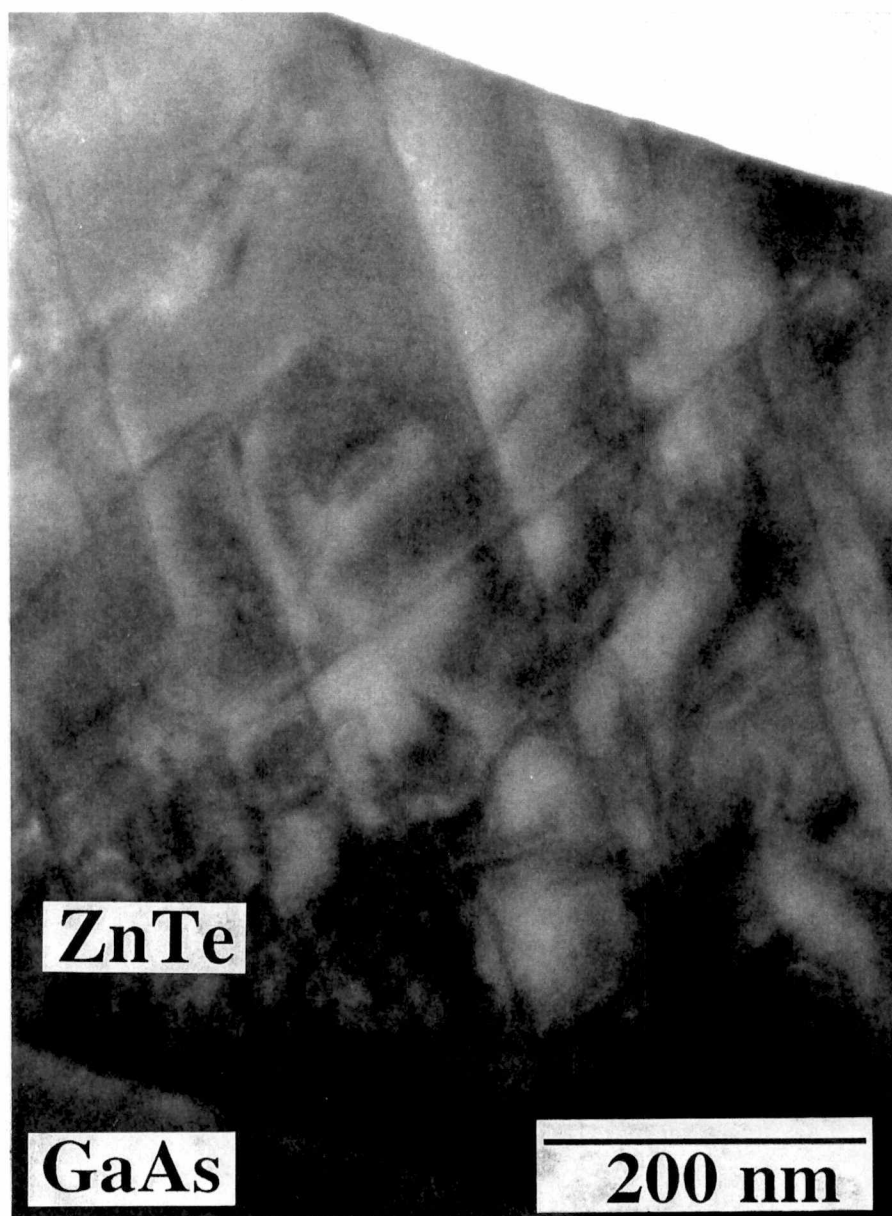


Figure 3.6 Overall microstructure of a ZnTe film grown by PLD in a 25 mtorr N_2 atmosphere. $E_d=0.65 \text{ J/cm}^2$, $r_g=4 \text{ sccm}$.

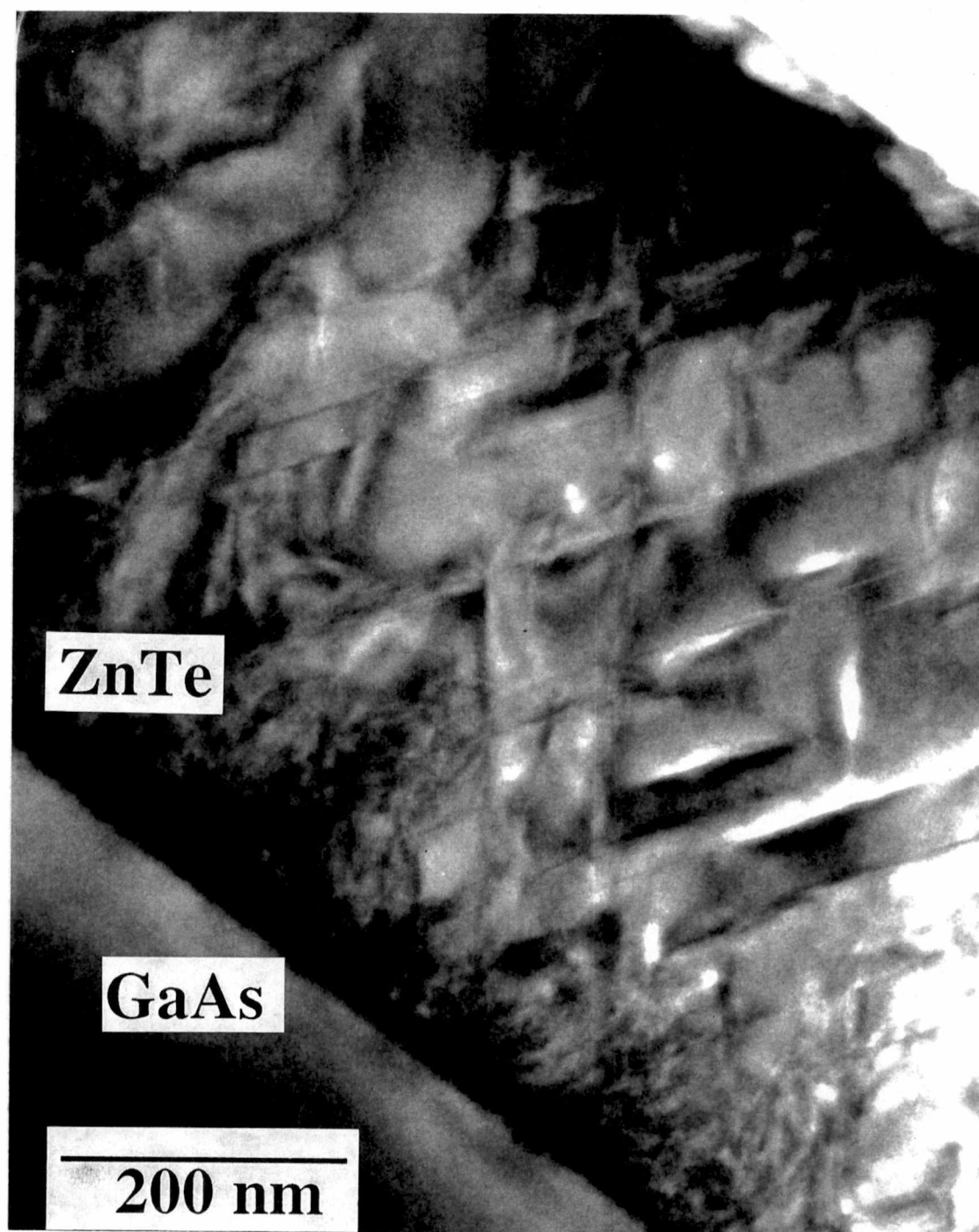


Figure 3.7 Overall microstructure of a ZnTe film grown by PLD in a 50 mtorr N_2 atmosphere. $E_d=0.65 \text{ J/cm}^2$, $r_g=1 \text{ sccm}$.

increased up to 50 mtorr N_2 . The ZnTe films shown in Figures 3.5 and 3.6 offer a comparison of the effect of laser energy density at the target on overall film microstructure since both were grown in 25 mtorr N_2 . The film grown with the higher laser energy density shown in Figure 3.5 has a significantly reduced stacking fault density in the bulk of the film as compared to the film shown in Figure 3.6 that was grown with one-third of this laser energy density. Note that the gas flow rate varied between these two samples, but it can be expected that this is a relatively small effect. The upper surfaces of these films were locally flat to a width of a few unit cells.

Films grown in 75 and 88 mtorr N_2 show a departure from the microstructures of films grown in lower N_2 pressures. The microstructure of the film grown in 75 mtorr N_2 shown in Figure 3.8 shows tightly spaced columnar grains. The upper surface of the film was not flat but gently undulated with an amplitude of about 10 nm as shown in Figure 3.9. No clusters were observed at or on the upper surface of the film. An irregular columnar structure was observed in the ZnTe film grown in 88 mtorr N_2 as shown in Figure 3.10. The upper surface of this film was not well defined and had many crystalline protrusions and clusters attached to or just above the film surface as shown in Figure 3.11. These features came in two shapes: roughly spherical with diameters of about 10 nm and roughly ellipsoidal with major axes of about 15 nm and 7 nm. Figure 3.12 shows a cluster attached to the upper surface that is not epitaxial with the film. Cluster deposition, then, becomes important at growth pressures of approximately 88 mtorr N_2 .

ZnTe films grown in 100 mtorr N_2 exhibited fully developed columnar microstructures and evidence of cluster deposition. The upper surface of each ZnTe film grown in 100 mtorr N_2 was covered by spherical crystalline clusters of diameters ~10-20nm. A film grown with a laser energy density of 1.9 J/cm² and at a gas flow rate of 10 standard cubic centimeters per minute (sccm) of N_2 had irregularly shaped columnar grains separated by cavities, as shown in Figure 3.13.

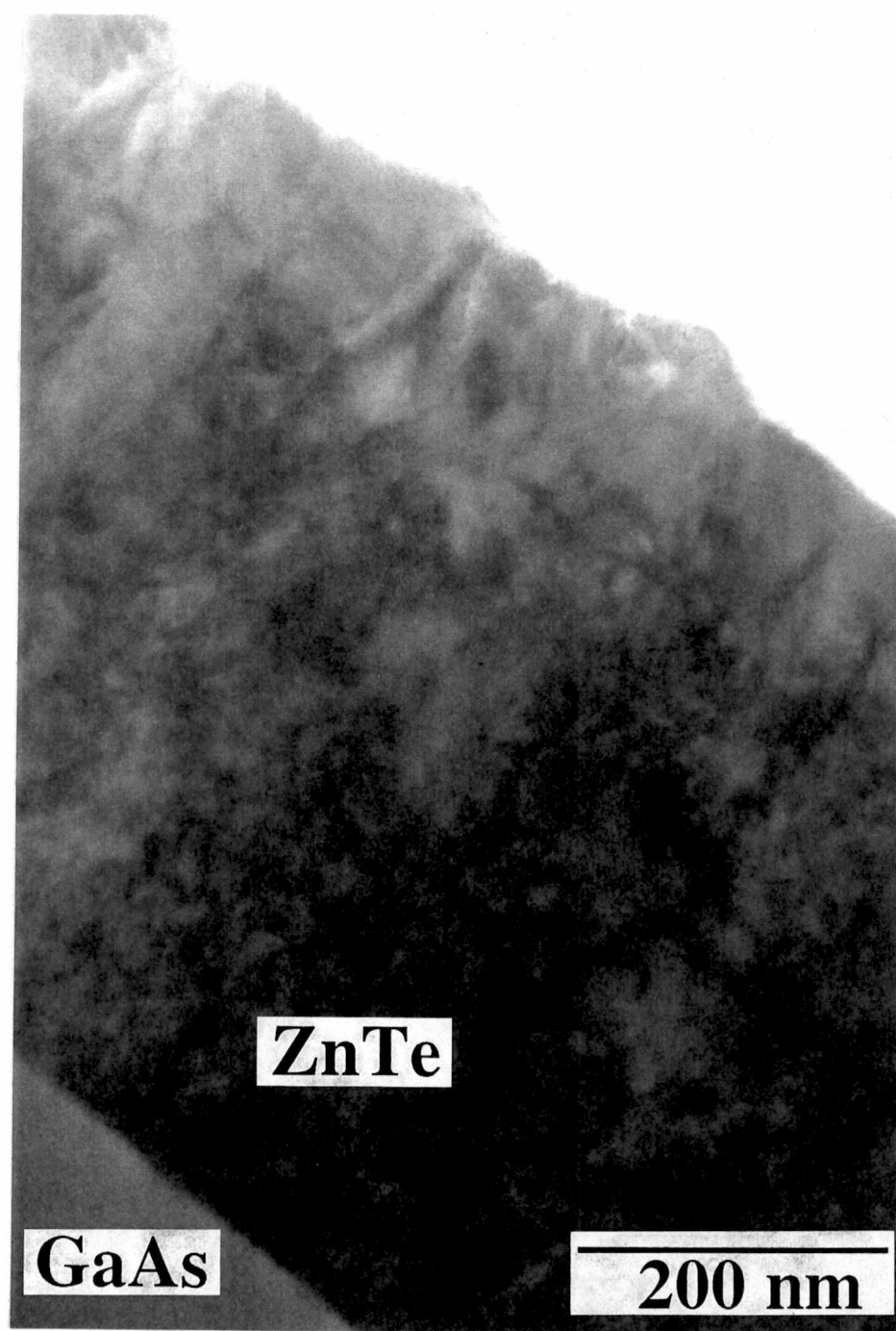


Figure 3.8 Overall microstructure of a ZnTe film grown by PLD in a 75 mtorr N_2 atmosphere. $E_d=0.83 \text{ J/cm}^2$, $r_g=20 \text{ sccm}$.

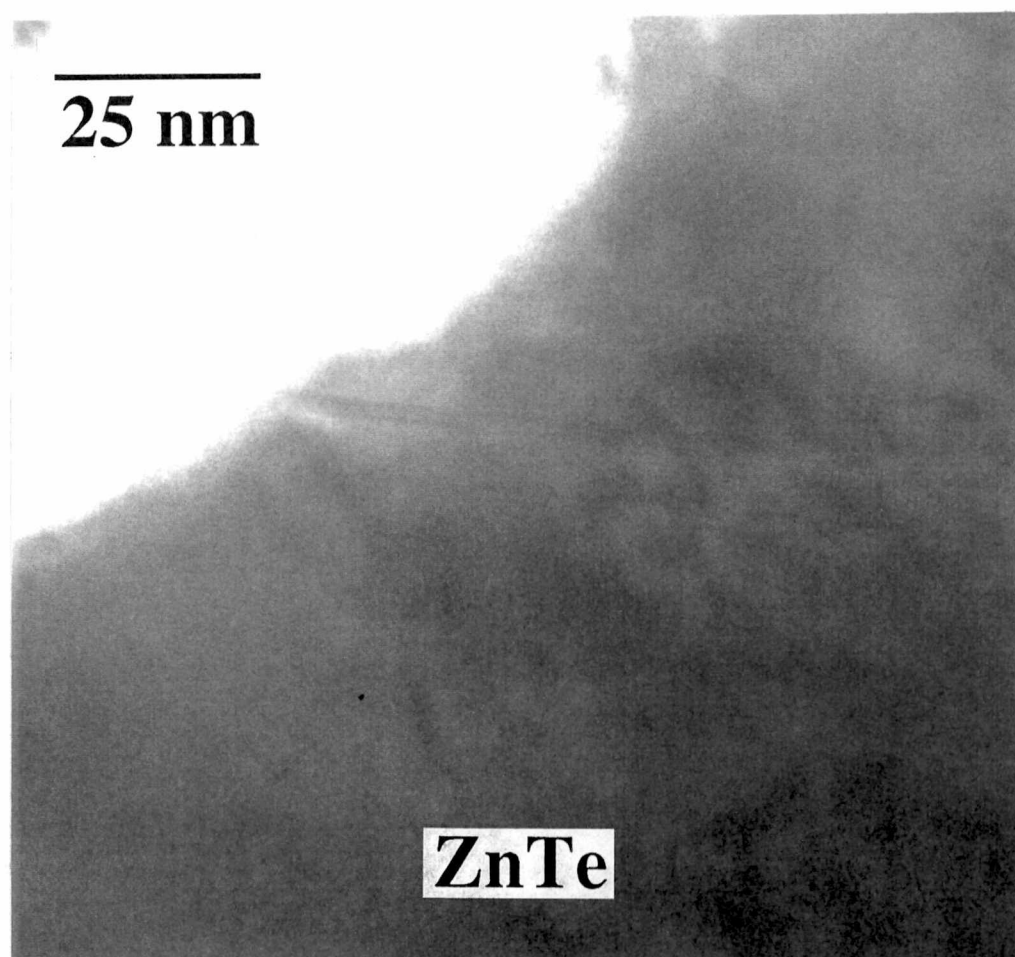


Figure 3.9 Uppermost portion of the ZnTe film shown in Figure 3.8 showing rounded surface.

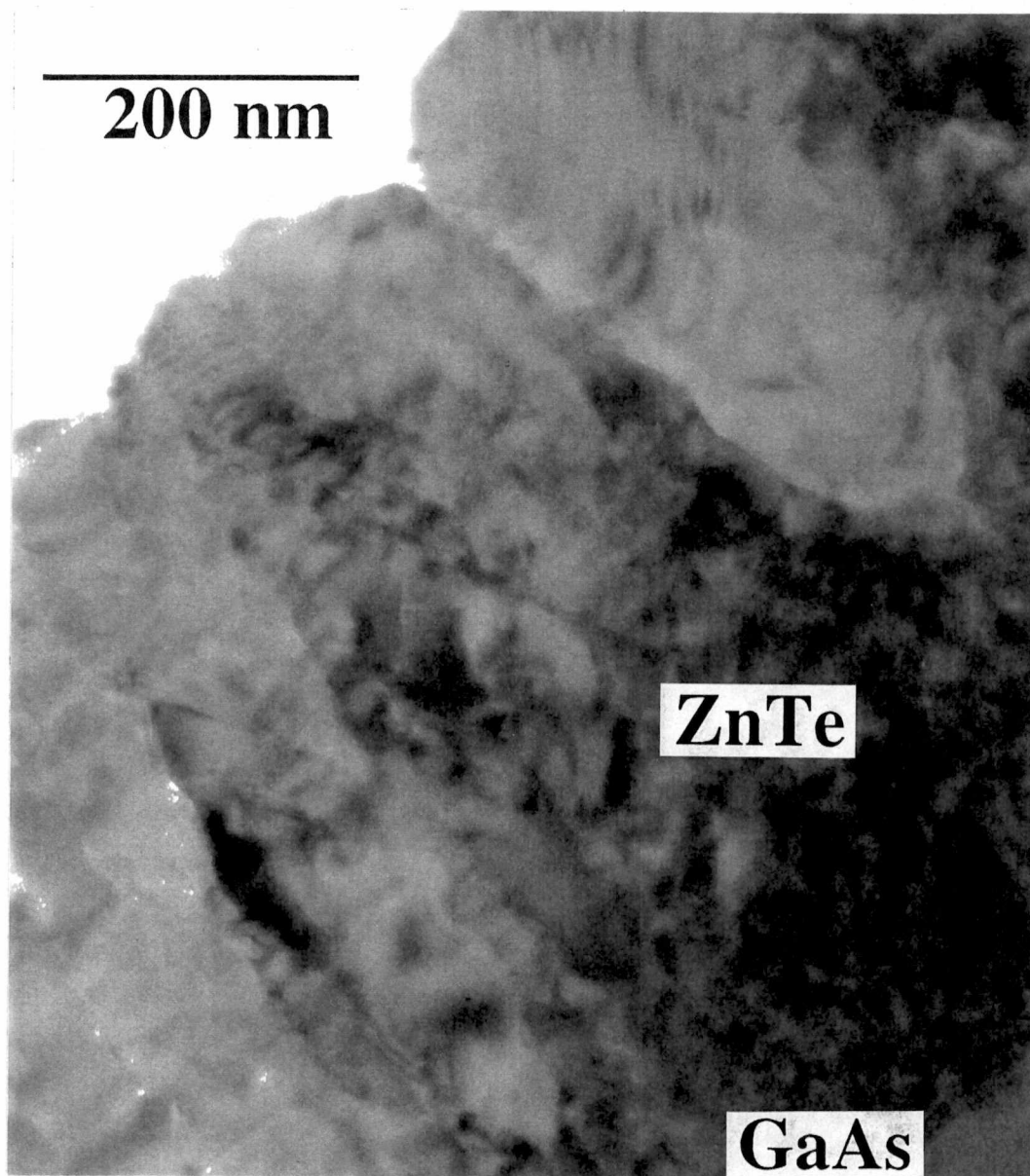


Figure 3.10 Overall microstructure of a ZnTe film grown by PLD in a 88 mtorr N_2 atmosphere. $E_d=0.83 \text{ J/cm}^2$, $r_g=5 \text{ sccm}$.

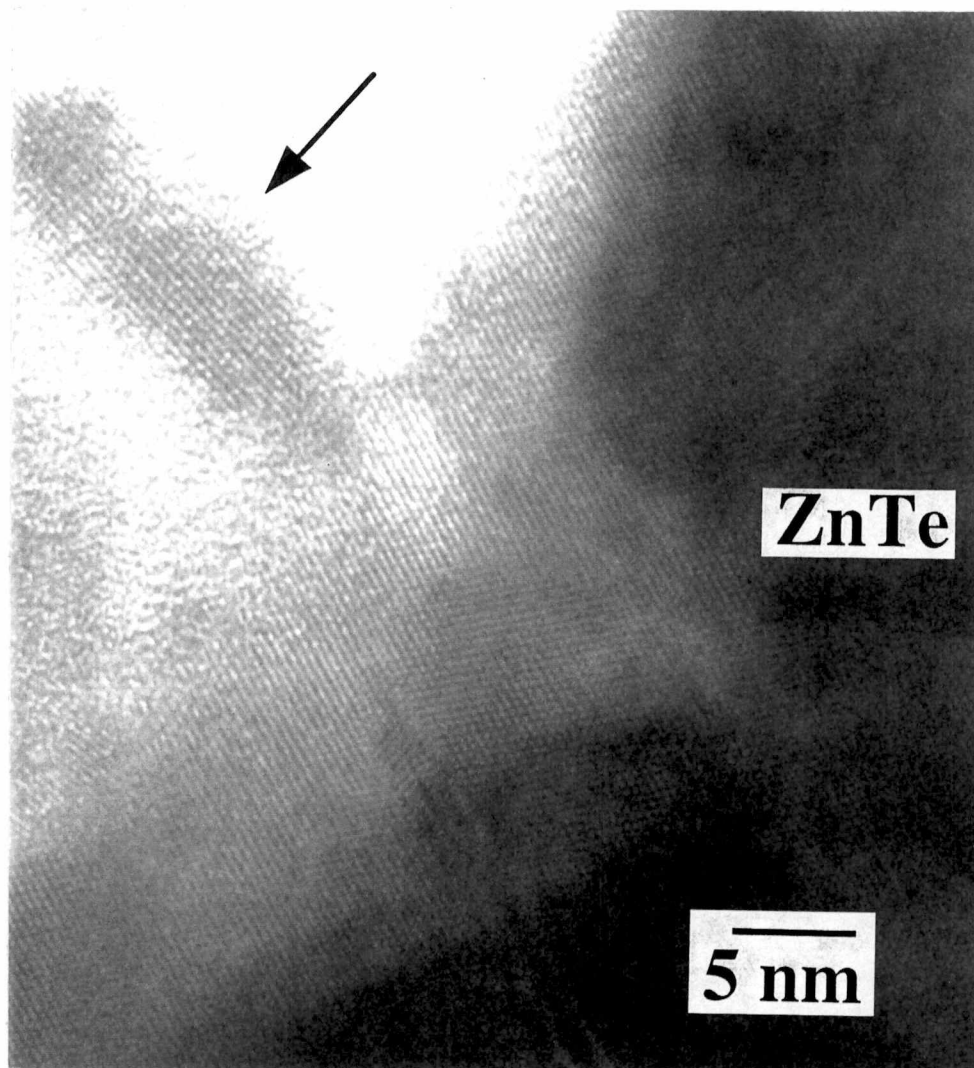


Figure 3.11 Protrusions and clusters (arrow) on the uppermost surface of the ZnTe film shown in Figure 3.10.

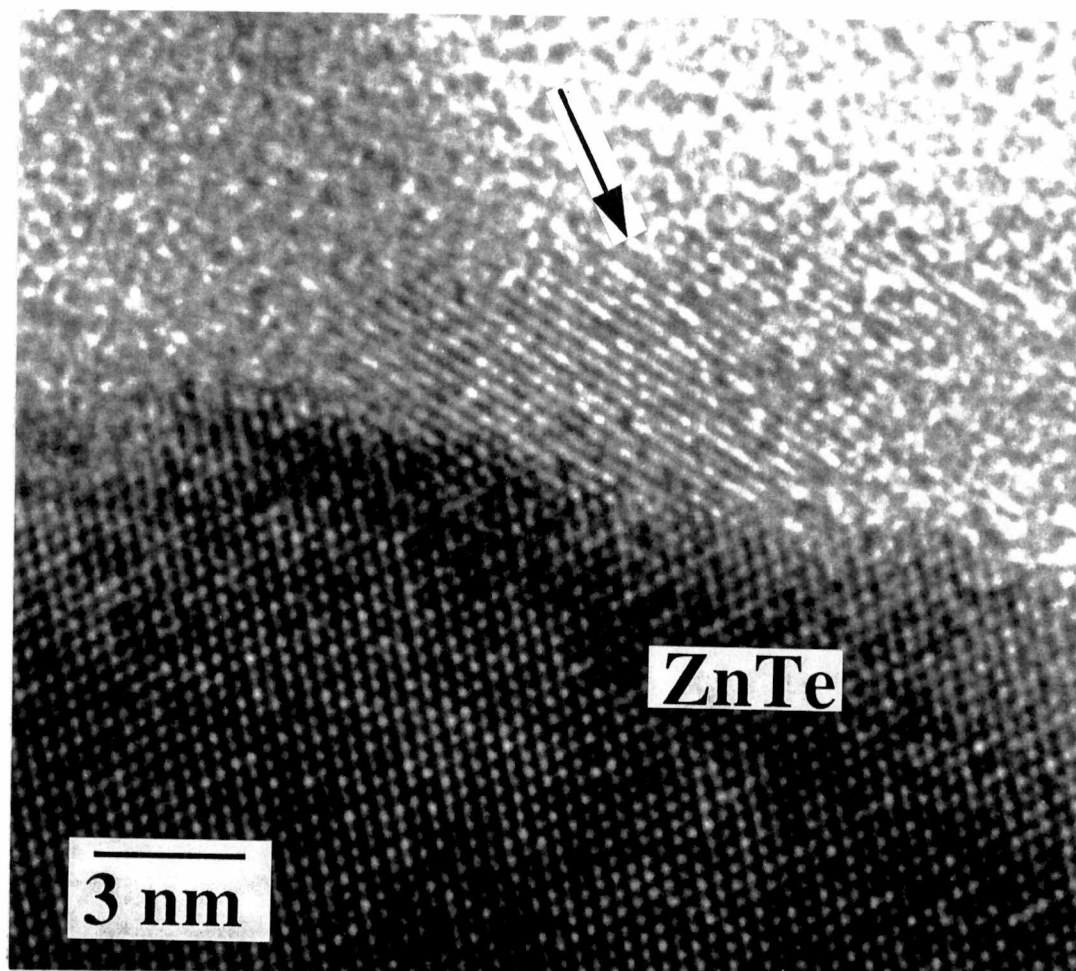


Figure 3.12 A cluster (arrow) attached to the upper surface of the ZnTe film shown in Figure 3.11.

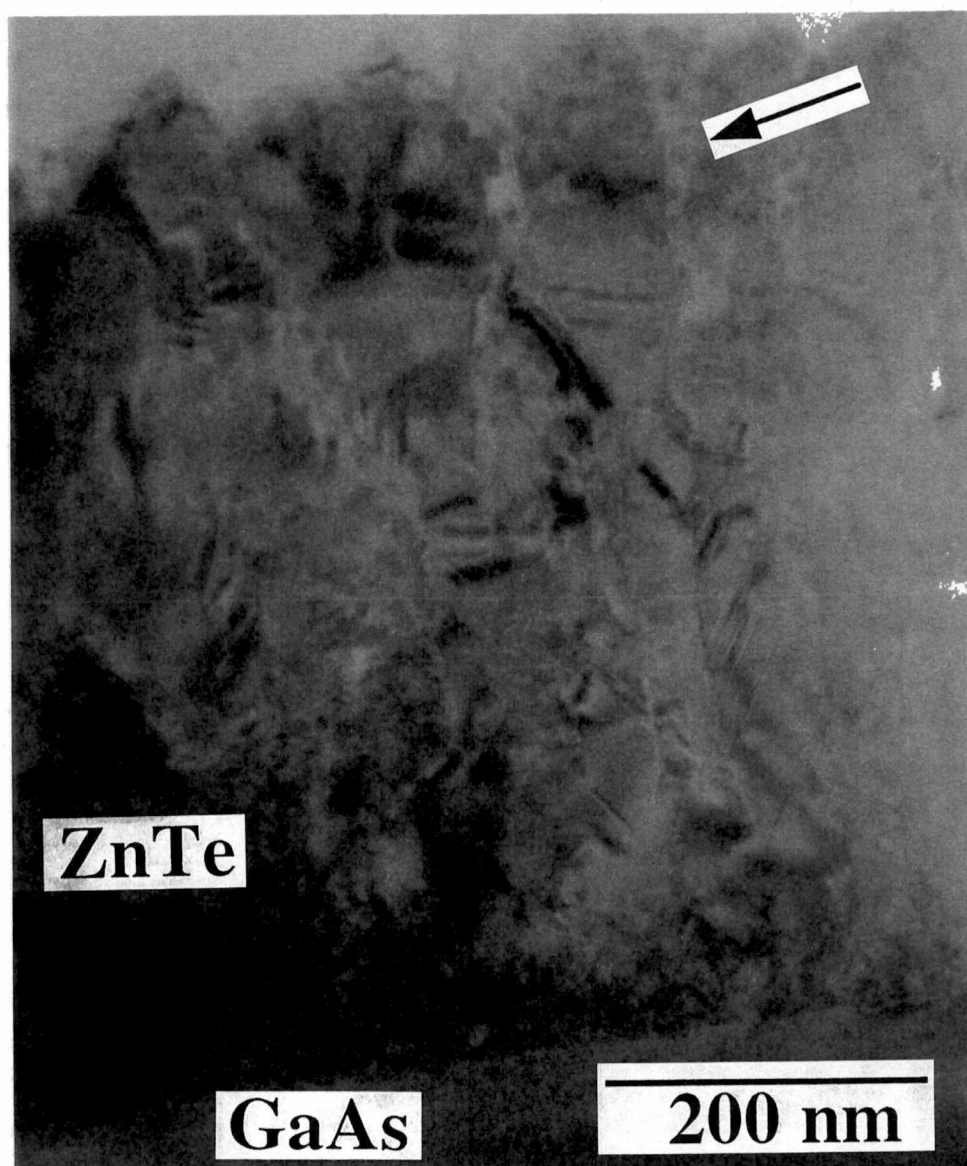


Figure 3.13 Overall microstructure of a ZnTe film grown by PLD in a 100 mtorr N_2 atmosphere. $E_d=1.9 \text{ J/cm}^2$, $r_g=10 \text{ sccm}$. Arrow indicates clusters in intergranular cavities.

Figure 3.14 shows a film grown with a laser energy density of 0.65 J/cm^2 and a gas flow rate of 15 sccm that has quite regularly sized, tightly spaced columnar grains. These grains contained areas of high stacking fault densities; one such area is shown in Figure 3.15. A third film grown in 100 mtorr N_2 is shown in Figure 3.16. This film was grown with a laser energy density of 0.65 J/cm^2 and a N_2 flow rate of 4 sccm. Its microstructure was similar to that of the previous film, confirming the conclusion that the gas flow rate has a smaller effect on film microstructure than laser energy density or growth pressure. Figure 3.17 shows clusters on the upper surface of this film and in cavities between grains. A feature common to all of these ZnTe films grown in 100 mtorr N_2 is that the columnar grains grow on top of a heavily faulted region of single crystal of average thickness of $\sim 100 \text{ nm}$. The interface between this faulted region and the columnar grains is not flat, but has peaks and valleys of amplitude $\sim 50 \text{ nm}$.

3.1.3 ZnSe films grown by PLD

ZnSe films grown in pressures less than 100 mtorr were considerably “cleaner” than their ZnTe counterparts. Table 3.3 lists characteristics of the ZnSe films. ZnSe films grown in vacuum, shown in Figure 3.18, and in 75 mtorr N_2 , shown in Figure 3.19, had a much lower density of stacking faults near the ZnSe/GaAs interface as well as throughout the film. Figure 3.20 is an [001] planar TEM view of this film showing stacking faults of various lengths and threading dislocations. The ZnSe film deposited in 75 mtorr N_2 is a single crystal, as opposed to the columnar grain structure of the ZnTe film grown in the same atmosphere. The microstructure of a ZnSe film grown in 1000 mtorr (see Table 3.3 for complete atmosphere information) was similar to that of the ZnTe films ablated in 100 mtorr N_2 mentioned above, as shown in Figure 3.21a. Narrow columnar grains $\sim 50 \text{ nm}$ in diameter had grown on a heavily faulted region that varied in height between $\sim 130\text{--}250 \text{ nm}$. The $\langle 110 \rangle$ electron diffraction pattern in

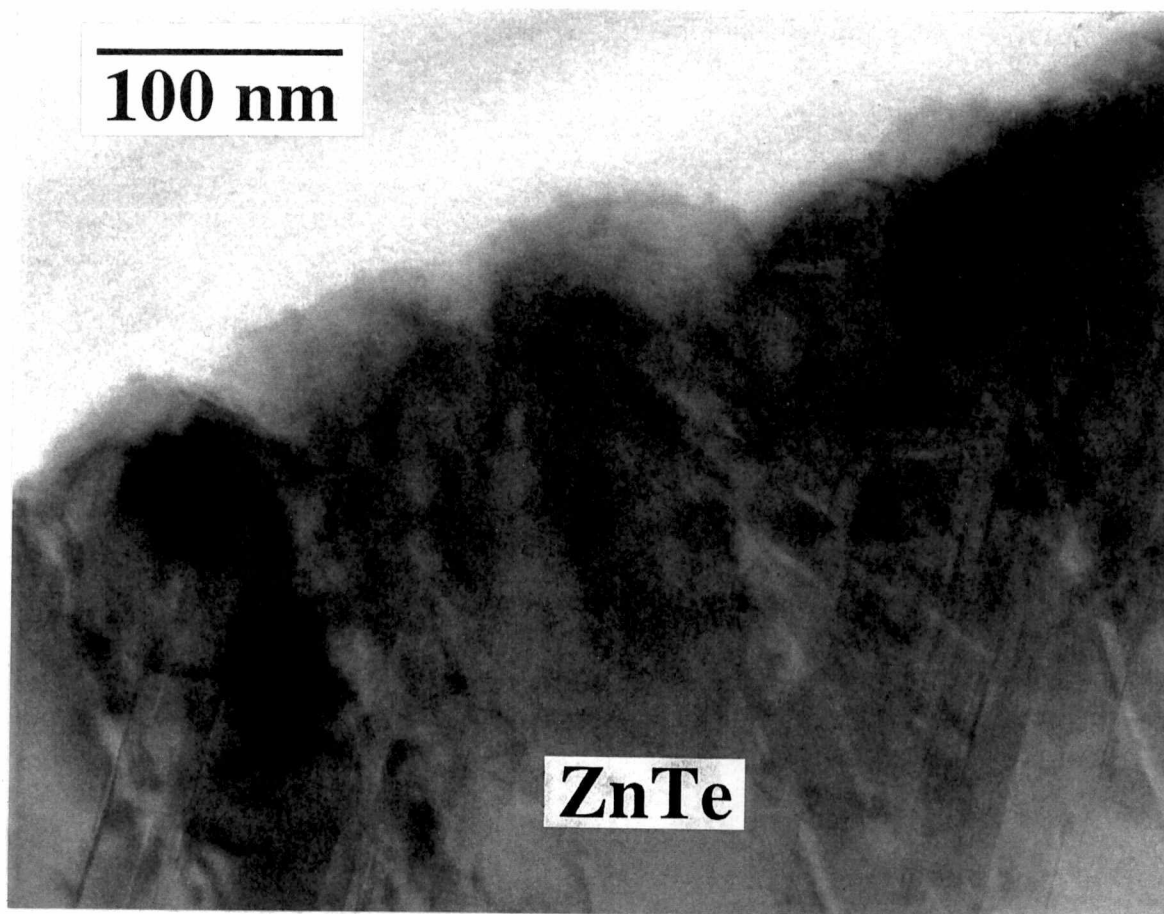


Figure 3.14 Uppermost portion of a ZnTe film grown by PLD in a 100 mtorr N_2 atmosphere. $E_d=0.65 \text{ J/cm}^2$, $r_g=15 \text{ sccm}$.



Figure 3.15 Complex of stacking faults in the bulk of the ZnTe film shown in Figure 3.14.

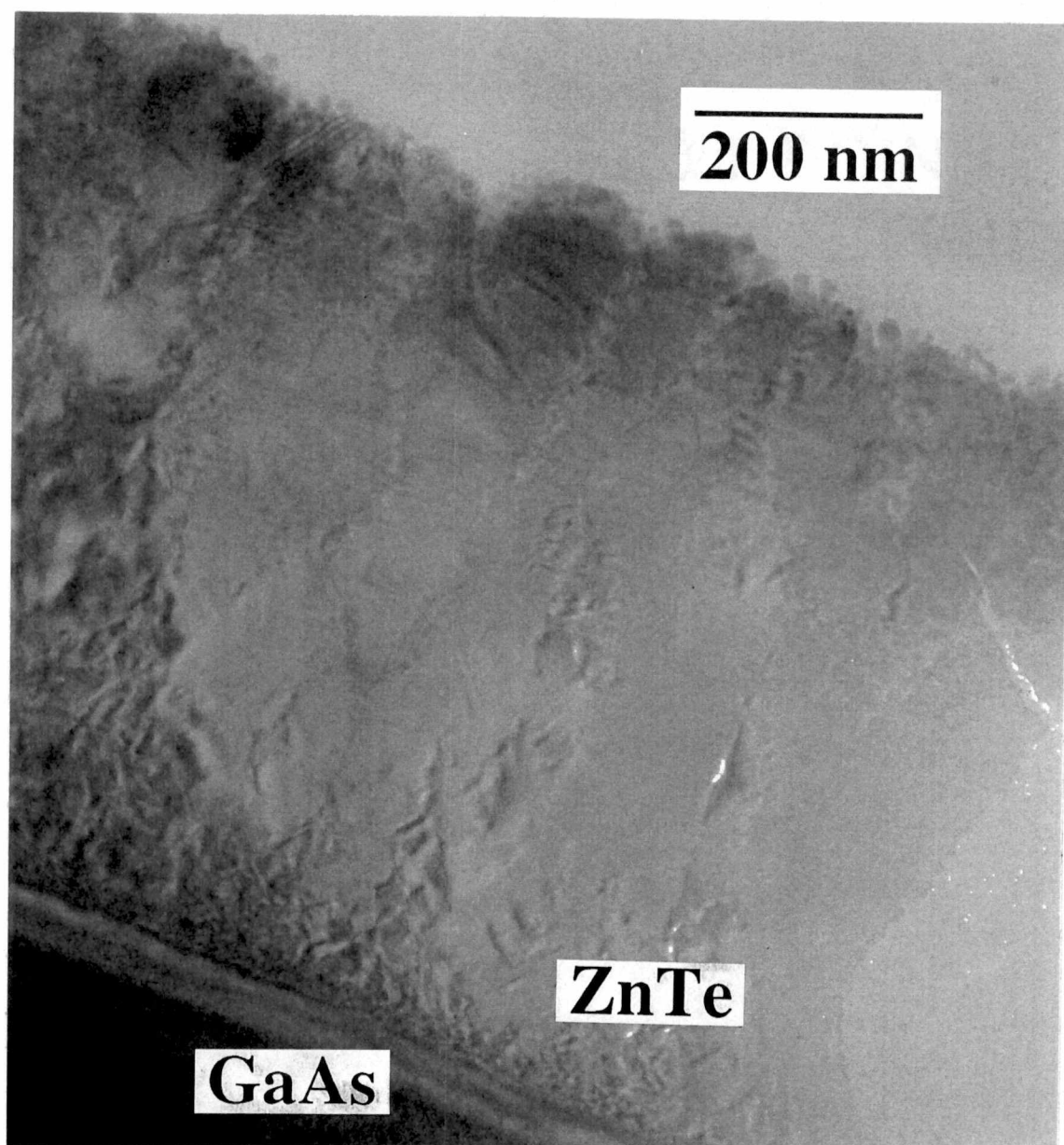


Figure 3.16 Overall microstructure of a ZnTe film grown by PLD in a 100 mtorr N_2 atmosphere. $E_d=0.65 \text{ J/cm}^2$, $r_g=4 \text{ sccm}$.

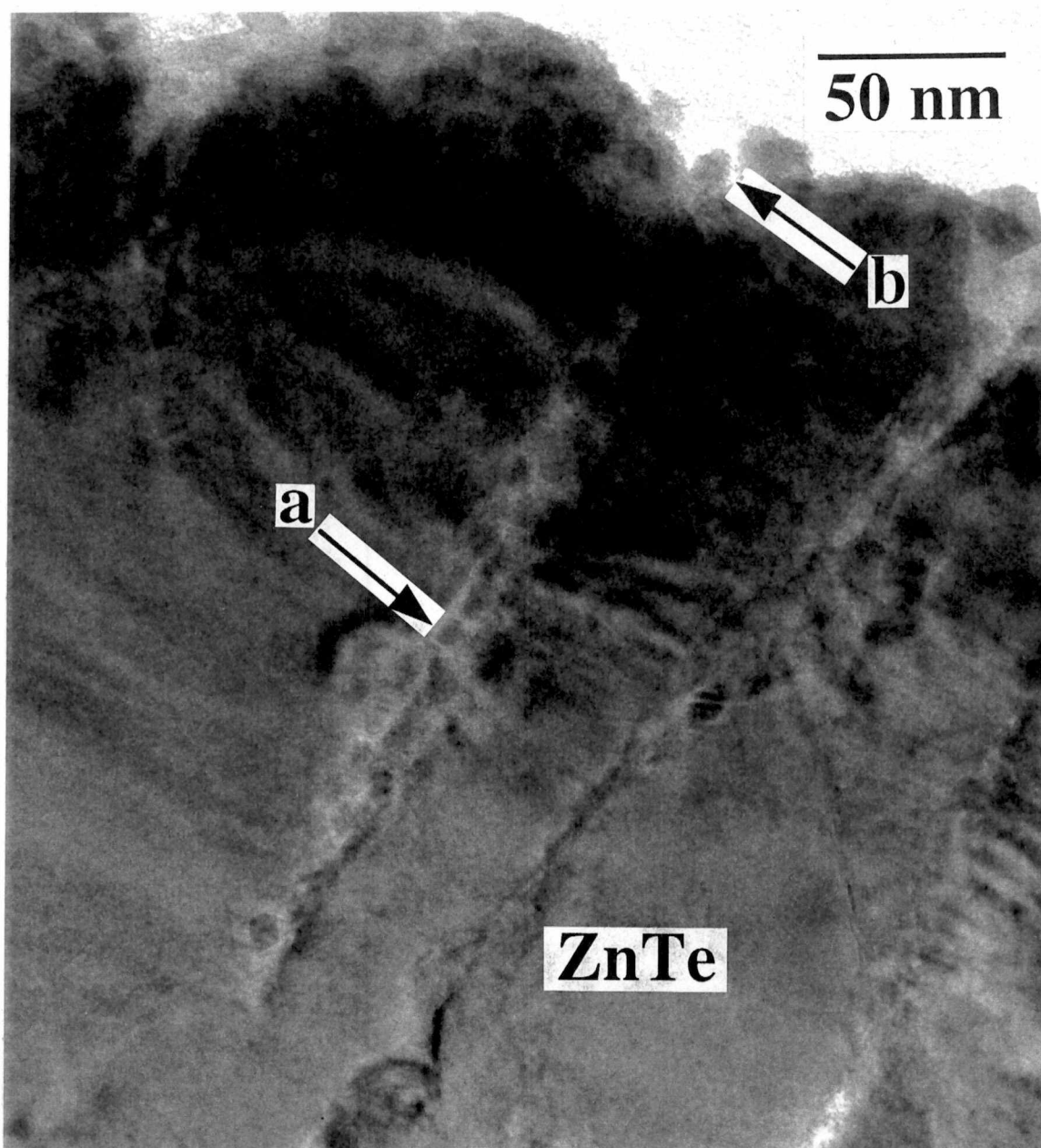


Figure 3.17 Clusters (a) in intergranular cavities and (b) on the uppermost surface of the ZnTe film shown in Figure 3.16.

Table 3.3 ZnSe/GaAs films grown by PLD

Gas Pressure and Flow Rate	Laser Energy Density (J/cm ²)	Substrate Supplier and Cleaning Method	Overall Microstructure
vacuum (10 ⁻⁶ torr)	1.9	A	single crystal, flat upper surface, low stacking fault density
75 mtorr N ₂ @ 4 sccm	1.9	B	similar to above film, but with a lower stacking fault density
<u>buffer layer:</u> 1000 mtorr He @ 15 sccm <u>doped layer:</u> 133 mtorr of 98%He/2%Cl ₂ @ 2 sccm plus 867 mtorr He @ 13 sccm	1.9	A	tightly spaced columnar grains on top of single crystal, no clusters observed

Notes: Substrate manufacturers and cleaning methods are as follows:

A) wet chemical processing and thermal desorption of oxide at 580°C of Sumitomo substrates

B) thermal desorption of oxide at 580°C plus a RHEED check of the surface of AXT substrates

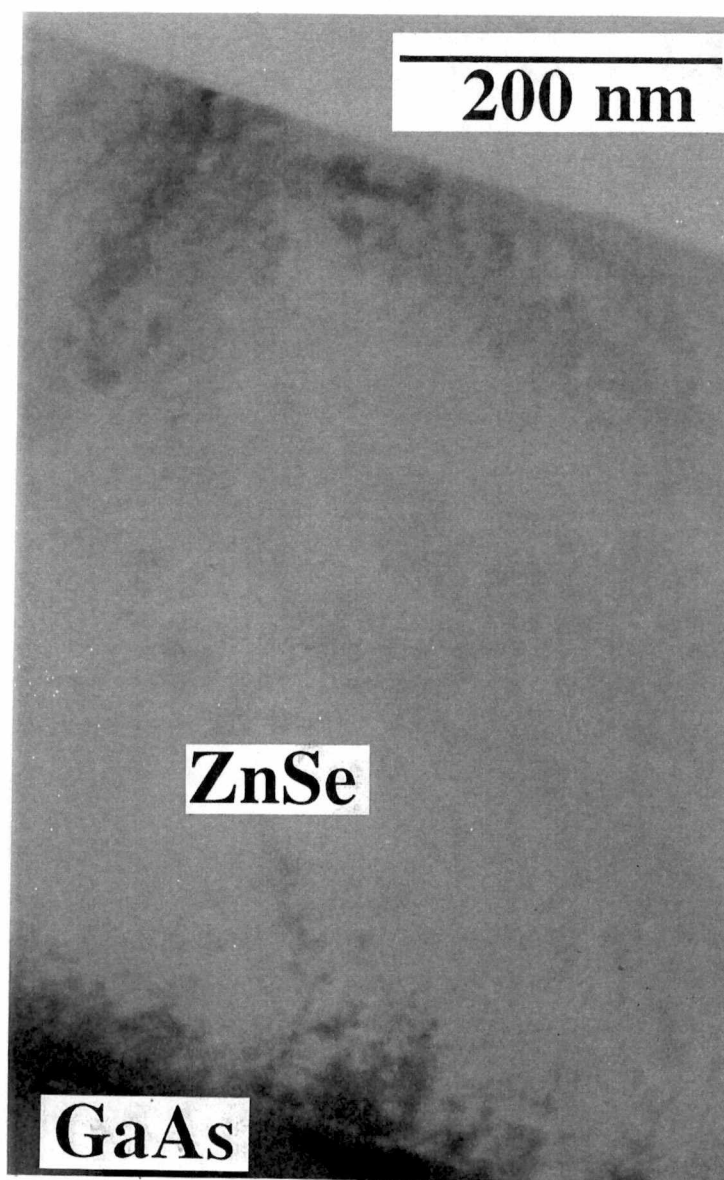


Figure 3.18 Overall microstructure of a ZnSe film grown by PLD in vacuum.
 $E_d=1.9\text{J}/\text{cm}^2$.

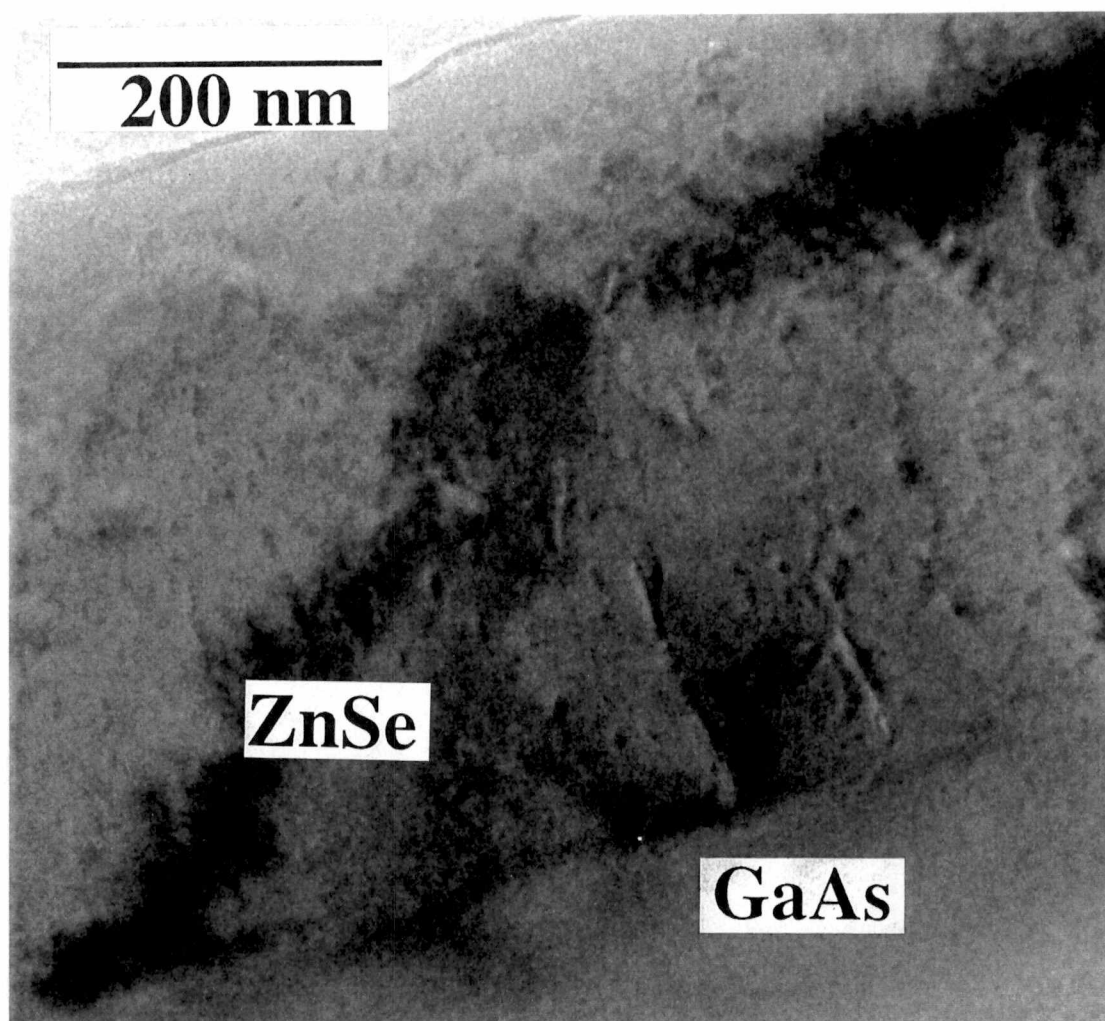


Figure 3.19 Overall microstructure of a ZnSe film grown by PLD in a 75 mtorr N_2 atmosphere. $E_d=1.9J/cm^2$, $r_g=4$ sccm.

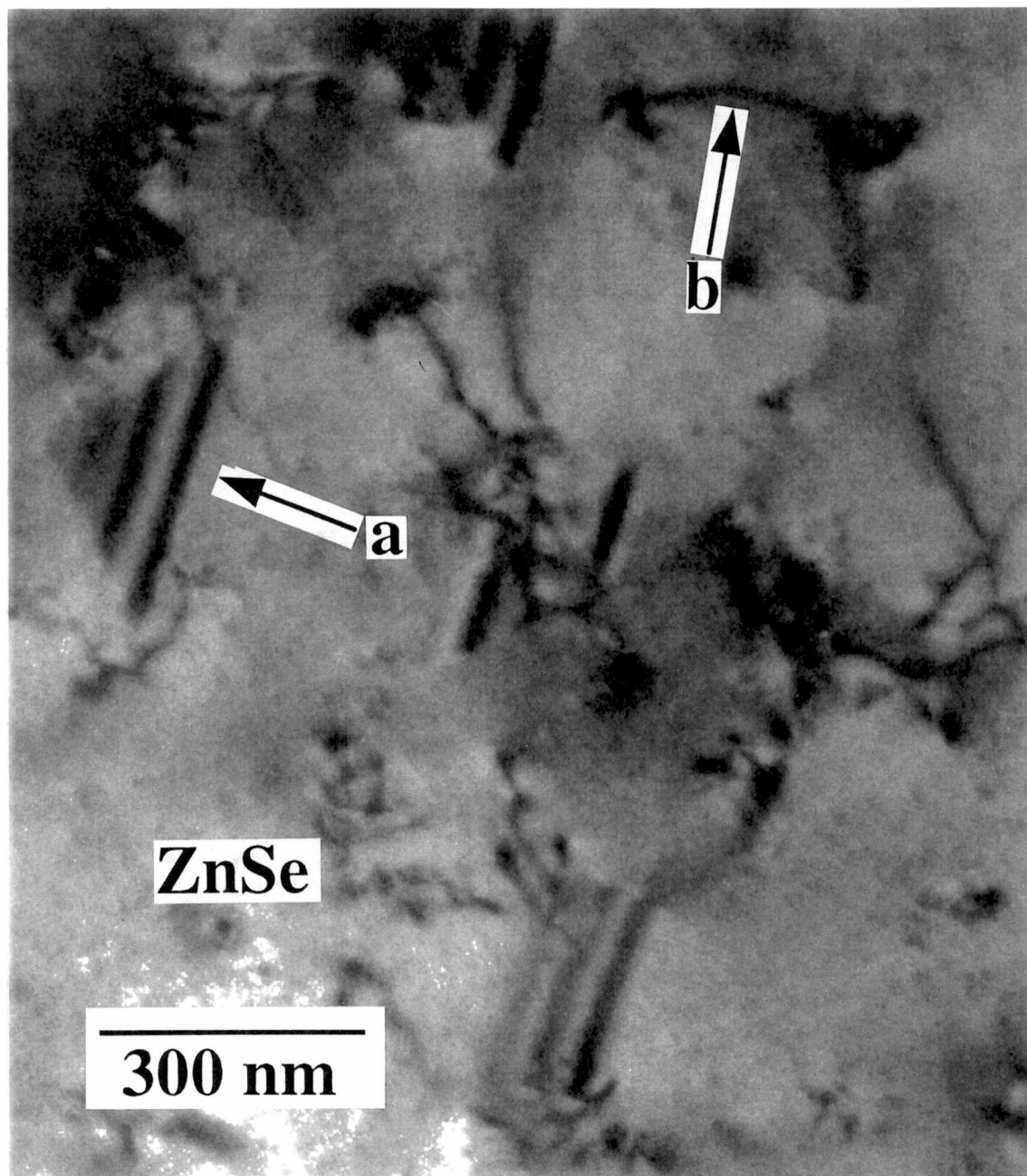
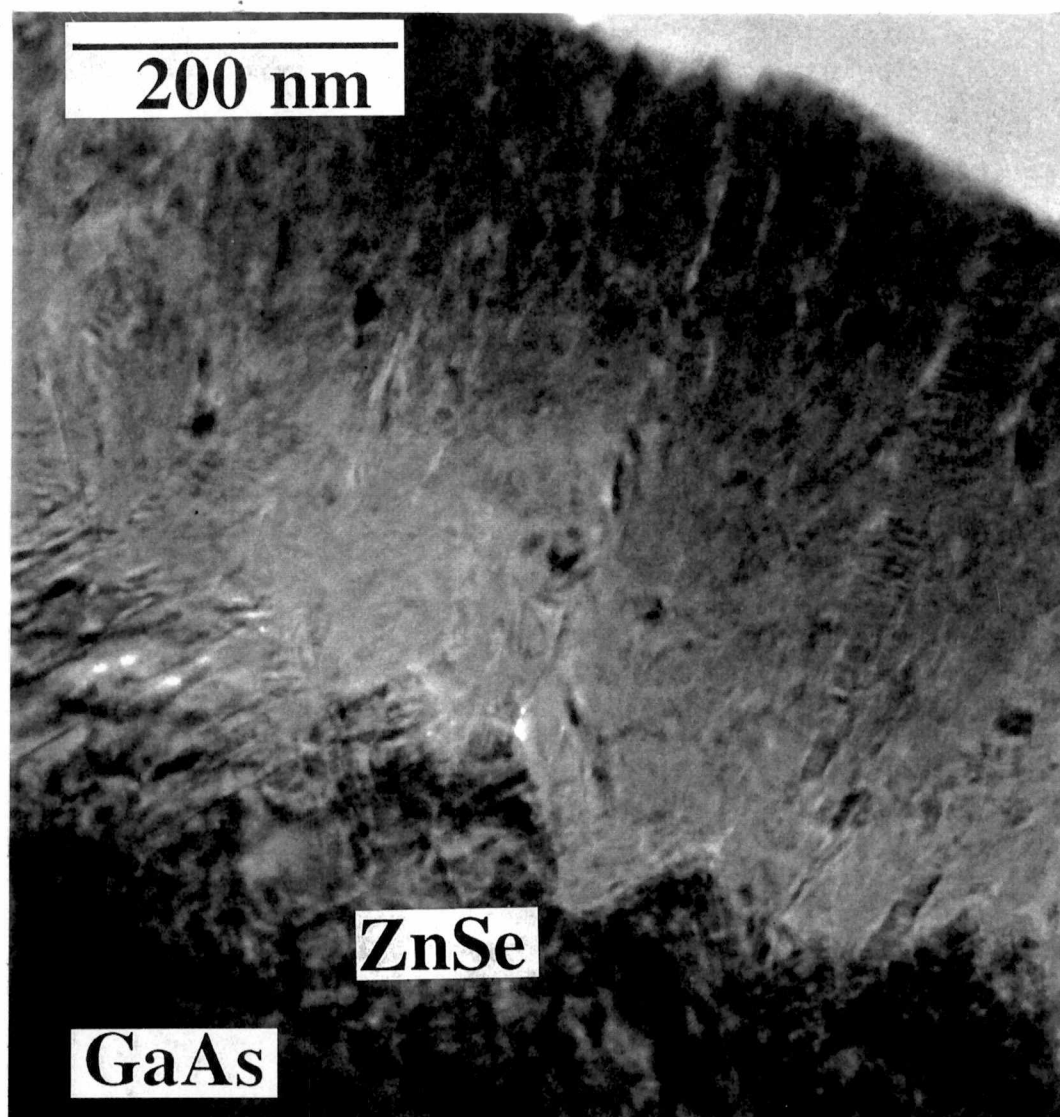


Figure 3.20 [001] planar view of the ZnSe film shown in Figure 3.19 showing (a) stacking faults, and (b) line dislocations.

a)



b)



c)



Figure 3.21 Microstructure of a ZnSe film grown by PLD in a 1000 mtorr He/Cl₂ atmosphere. $E_d=1.9\text{J}/\text{cm}^2$, $r_g=15$ sccm. a) overall microstructure b) $\langle 110 \rangle$ electron diffraction pattern of the entire film thickness c) $\langle 110 \rangle$ electron diffraction pattern of the columnar grain region only.

Figure 3.21b includes the columnar grains and single crystal region of the film. The [110] electron diffraction pattern in Figure 3.21c is of the columnar grains only and demonstrates the scattered grain orientations about the [110] axis. Figures 3.22a and 3.22b show this region in more detail. An interesting observation is that clusters are not observed in this ZnSe film deposited in a high pressure atmosphere of He and Cl₂ as they are in the ZnTe films deposited in 100 mtorr N₂.

3.1.4 Ion Milling Damage

Several features were observed in the MBE and PLD films that are most likely attributable to Ar⁺ ion milling induced damage. The “black dot” contrast observed by others in ion milled II-VI compounds was also observed here [36-39]. An example is given in Figure 3.23 of this contrast in a nitrogen doped ZnTe film grown by MBE. An amorphous layer ~70 Å thick was observed bordering the II-VI films where an exposed edge had been ion milled as shown in Figure 3.24. It was found that a similar amorphous layer produced during ion milling was a ZnO layer [39]. Also, small circular areas of Moire fringes of diameters ~50-80 Å were observed in ZnSe and ZnTe films. Figure 3.25 shows these fringes superimposed on a lattice image of a nitrogen doped ZnTe film grown by MBE along with a Fast Fourier Transform (FFT) of one of these circular fringe patterns. It shows the <110> diffraction pattern of ZnTe plus extra spots closer to the center spot due to the Moire fringes. These fringes are likely artifacts produced by ion milling.

3.2 Interface

High resolution TEM images of the II-VI/GaAs interface region show a semicoherent, completely epitaxial relationship. The II-VI film <001> axis was, in every case, exactly aligned with the GaAs <001> axis, agreeing with the “cube-

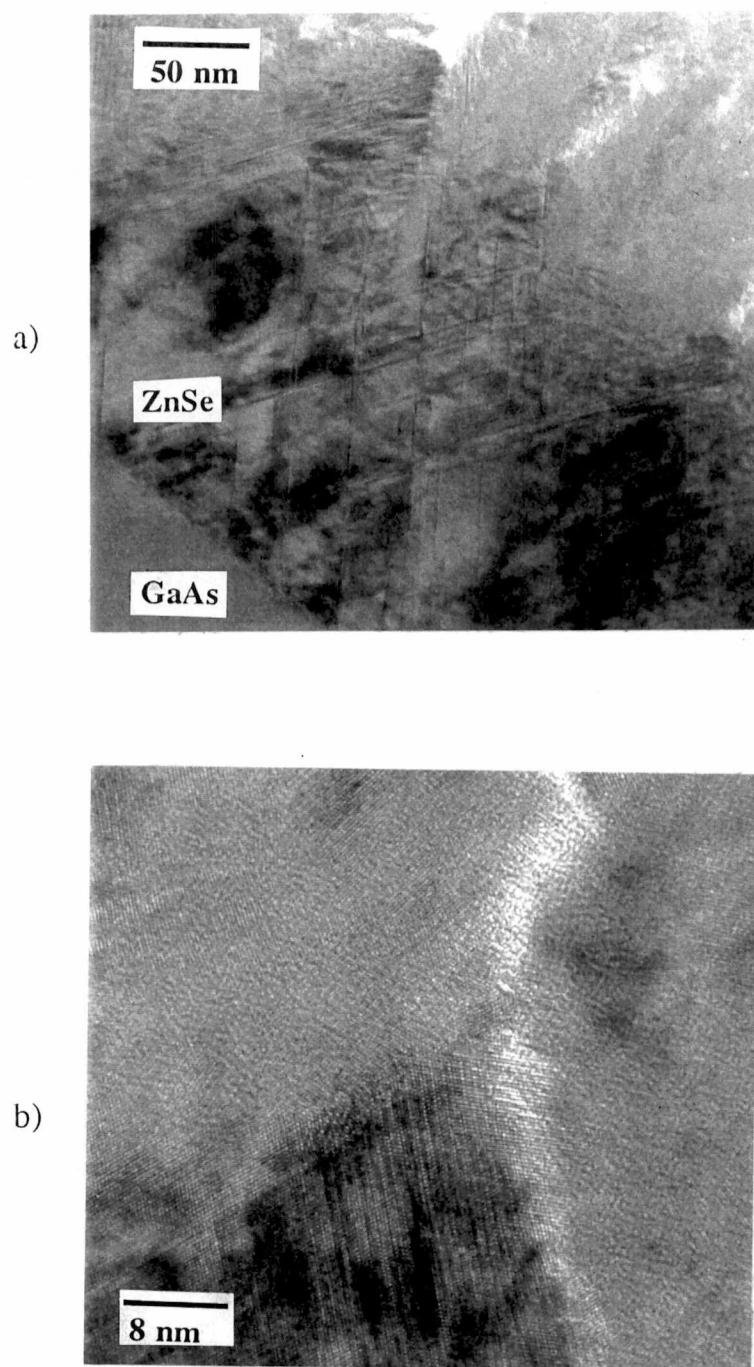


Figure 3.22 Single crystal-to-columnar grain transition region of the ZnSe film shown in Figure 3.21. a) overall view b) high resolution TEM image.

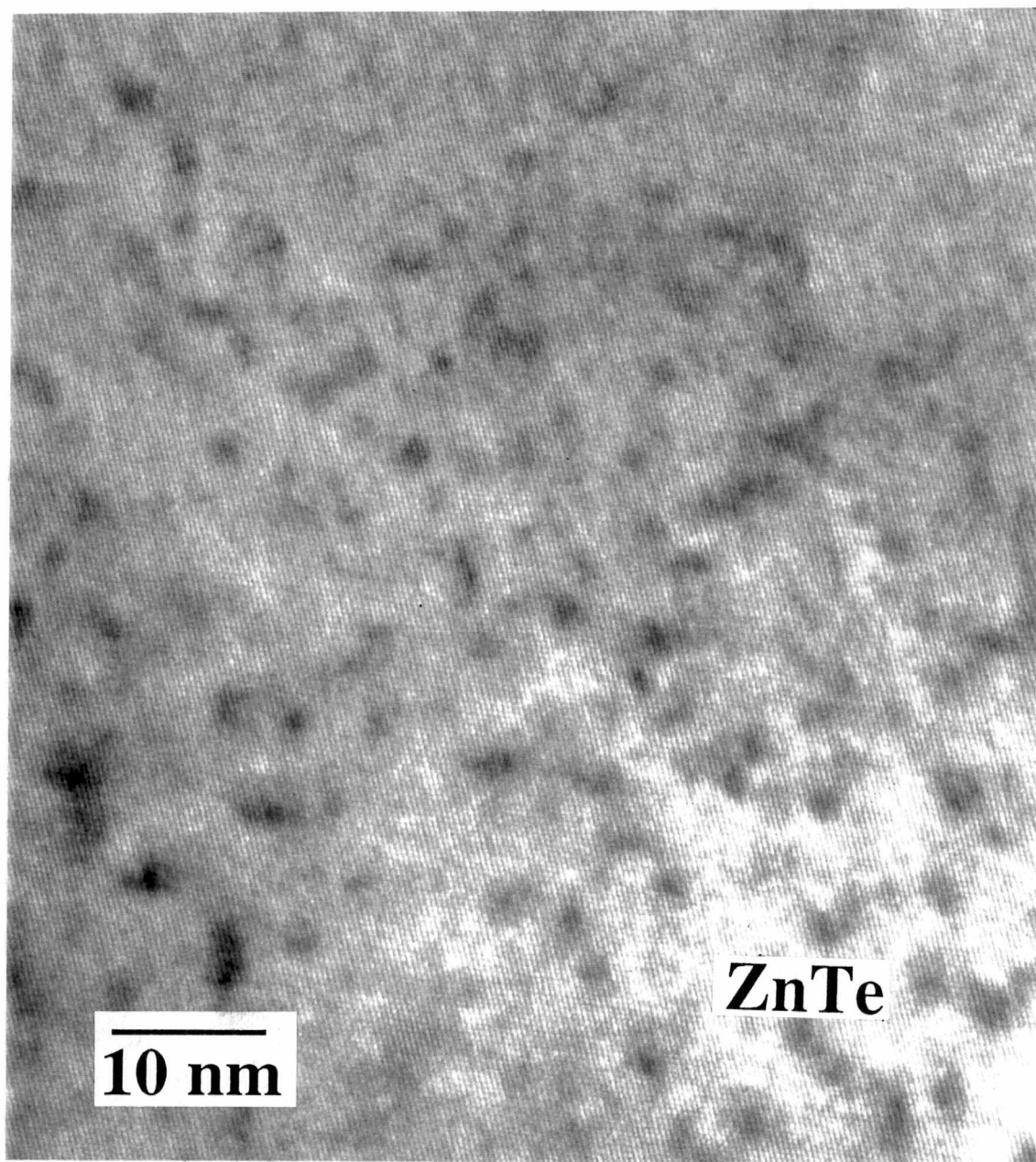


Figure 3.23 “Black dot” contrast due to ion milling in the nitrogen doped ZnTe film grown by MBE shown in Figure 3.2.

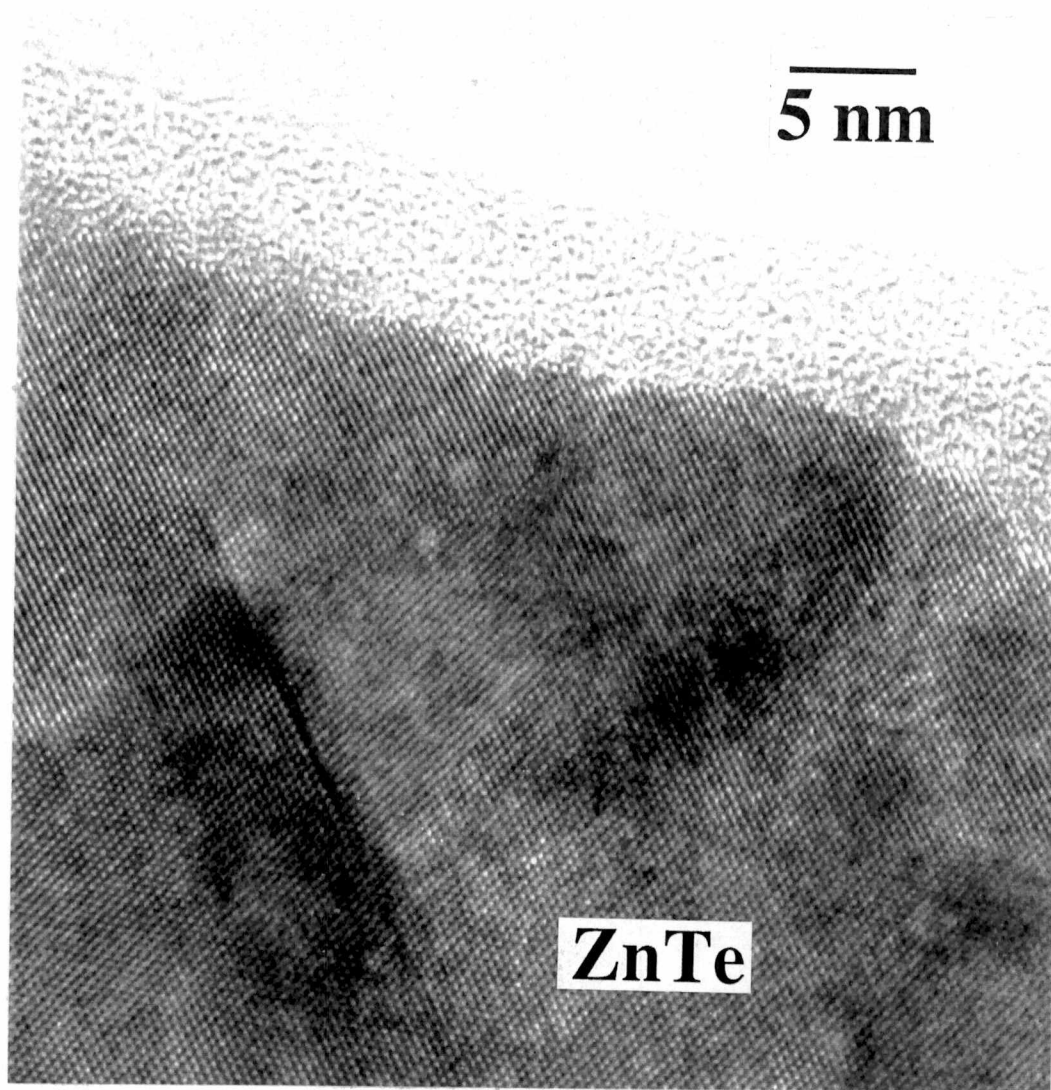


Figure 3.24 Amorphous layer at an ion milled edge of the ZnTe film shown in Figure 3.8.

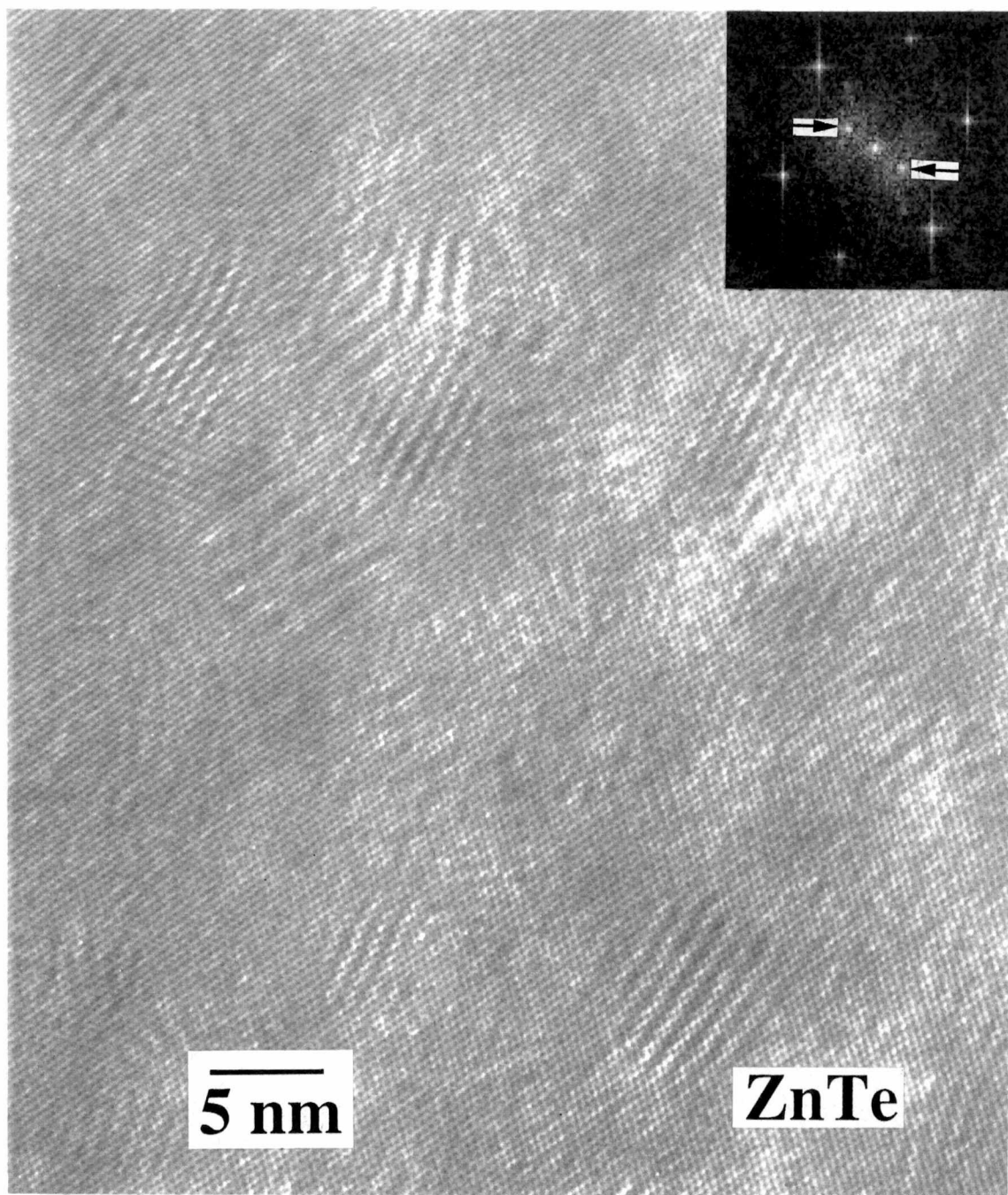


Figure 3.25 Circular areas of Moire fringes in a lattice image of the nitrogen doped ZnTe film grown by MBE shown in Figure 3.2. Inset is a Fast Fourier Transform (FFT) of an area that includes one of the circular areas. Arrows indicate diffraction spots due to Moire fringes; other spots are due to ZnTe.

on-cube" epitaxial relationship as determined by high resolution x-ray diffraction. The electron diffraction pattern of a ZnTe/GaAs interface region shown in Figure 3.26 shows the two sets of spots (ZnTe and GaAs) with equal orientations about $\langle 110 \rangle$. Misfit strain, then, is relieved not by the tilting of atomic planes but by misfit dislocations that run in the plane of the interface. Bright spots spaced nearly regularly at a distance of 5 nm were observed along the smoother ZnTe/GaAs interfaces in HRTEM images as illustrated in Figure 3.27. The 5 nm spacing is equal to the repeat distance of the lattice misfit in $\langle 110 \rangle$ (12 ZnTe planes to 13 GaAs planes), so these bright spots correspond to lattice strains due to bending of planes around misfit dislocations that run along $\langle 110 \rangle$. The strains are seen to extend no more than 1 nm around the dislocation. Misfit dislocations were also observed directly by HRTEM wherever an extra GaAs plane terminated at the interface. Figure 3.28 demonstrates the direct observation of interfacial misfit dislocations along a ZnTe/GaAs interface. Figure 3.29 shows the absence of misfit dislocations along a portion of a ZnSe/GaAs interface. The repeat distance for the ZnSe/GaAs lattice mismatch is 400 GaAs $\langle 110 \rangle$ planes.

The interface perfection is strongly determined by the substrate cleaning method. Figure 3.30 show a structurally high quality interface in a ZnTe/GaAs film grown by MBE in which the substrate underwent the hydrogen cleaning method as described in section 2.1. The interface is narrow and flat, the interfacial stacking fault density is low, and areas between misfit dislocations are free of strain. The interface of a ZnTe/GaAs film grown by PLD in an atmosphere of 100 mtorr N_2 in which the substrate received a wet chemical cleaning and thermal desorption of oxides at 580 °C is illustrated in Figure 3.31. The interface wanders across an area ~5 nm wide and has initiated many stacking faults. A ZnTe/GaAs interface in which the substrate did not receive a wet chemical cleaning but did have a RHEED check of the surface quality before growth initiation is shown in Figure 3.32. The substrate in this case was an "epi-ready" substrate supplied by

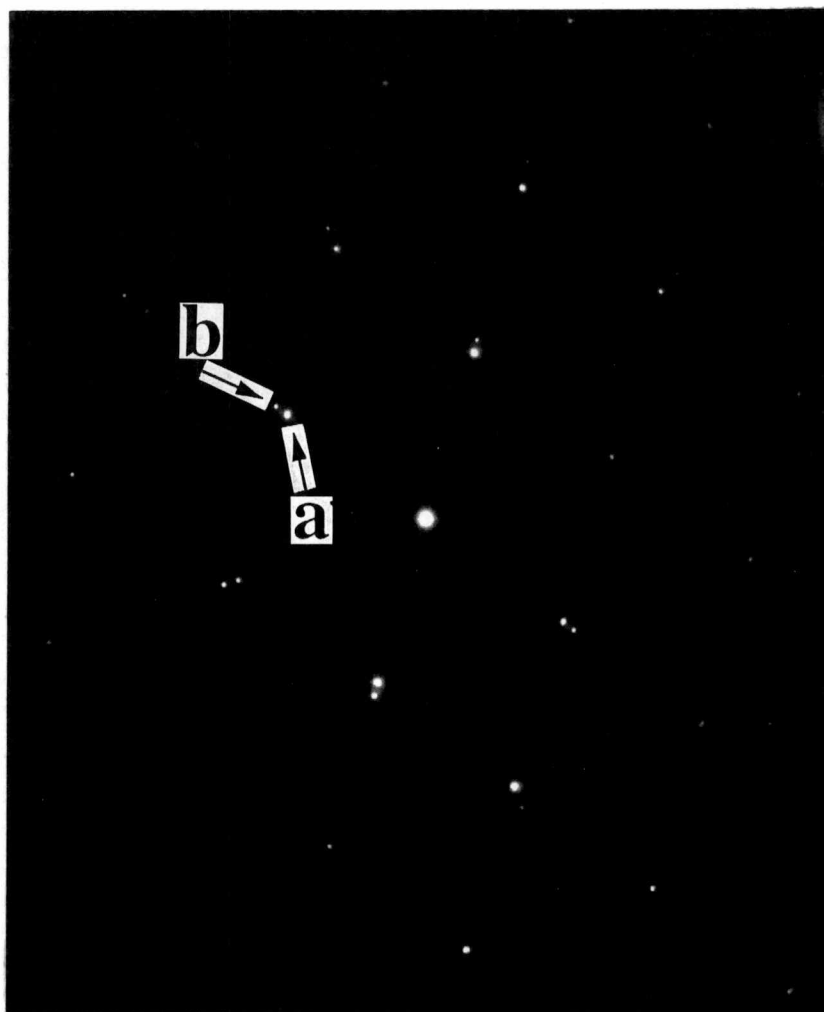


Figure 3.26 $\langle 110 \rangle$ electron diffraction pattern of a ZnTe/GaAs interface showing the epitaxial orientation relationship. Inner sets of spots (a) belong to ZnTe and outer set of spots (b) belong to GaAs.

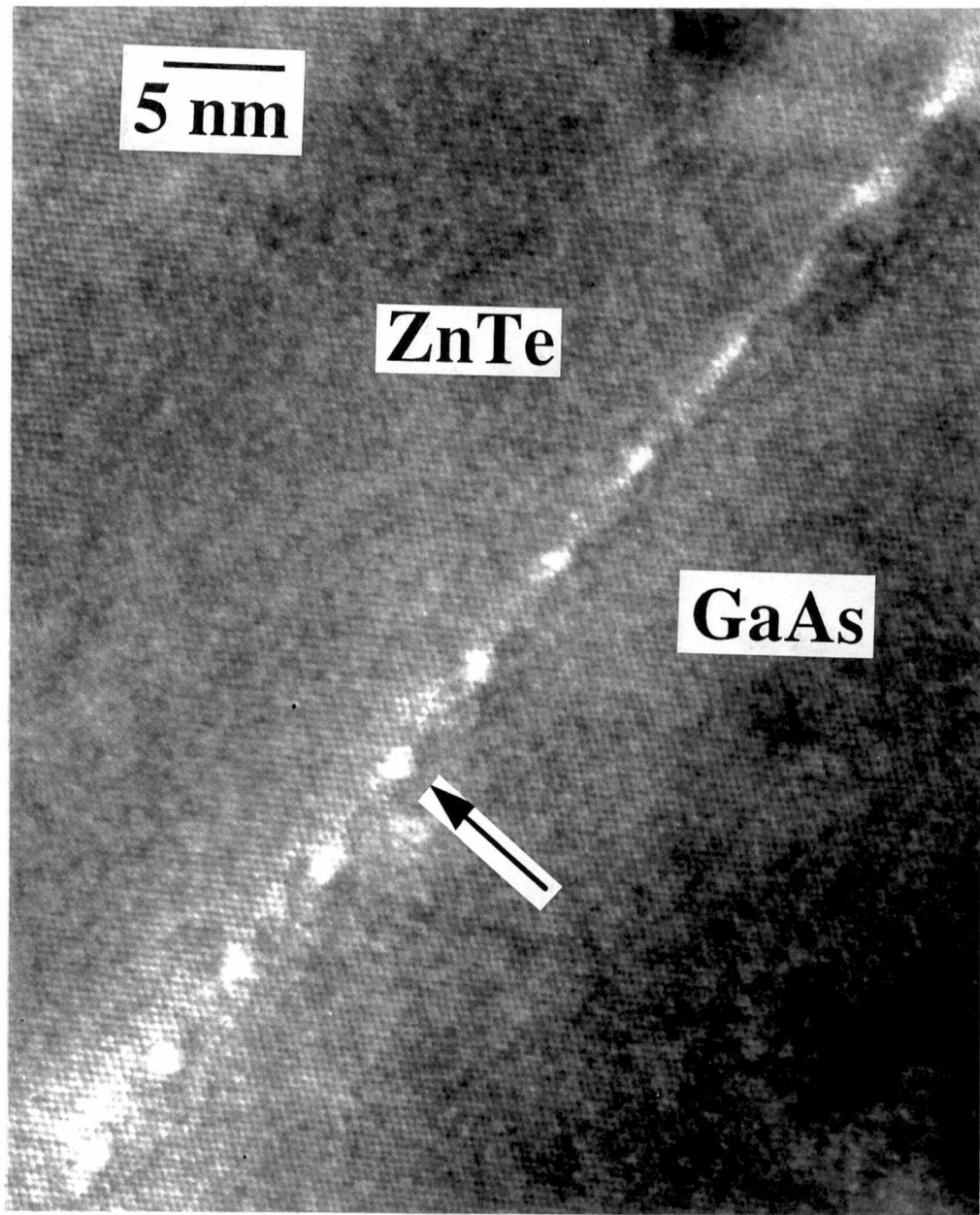


Figure 3.27 Strain fields around misfit dislocations in the nitrogen doped ZnTe film grown by MBE shown in Figure 3.2. Arrow indicates the effect of the strain field around one misfit dislocation.



Figure 3.28 Misfit dislocations (arrows) along the interface of the undoped ZnTe/GaAs film grown by MBE shown in Figure 3.1.

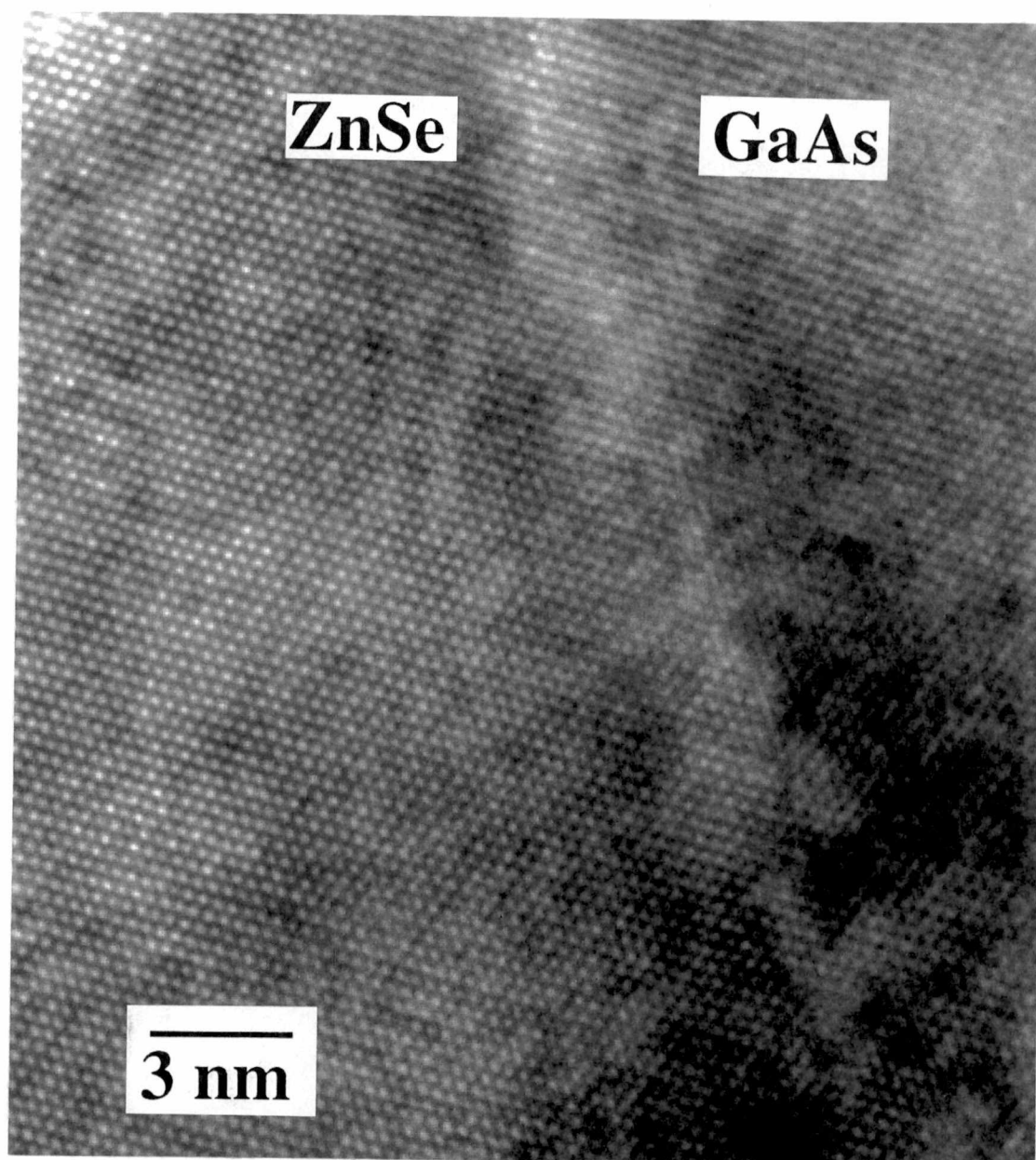


Figure 3.29 The ZnSe/GaAs interface of the film shown in Figure 3.19.

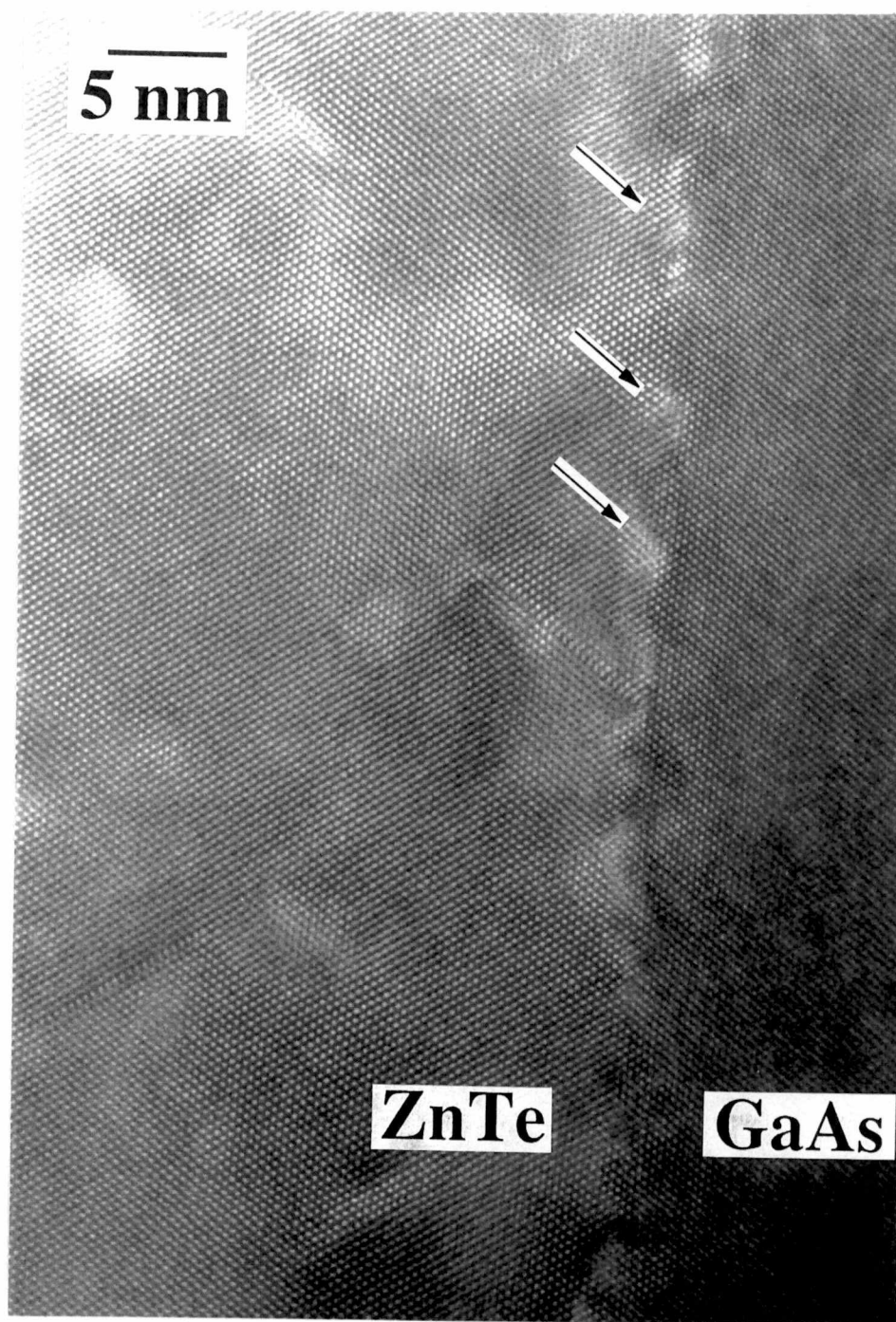


Figure 3.30 The interface of the undoped ZnTe/GaAs film grown by MBE shown in Figure 3.1. Arrows indicate three successive misfit dislocations.

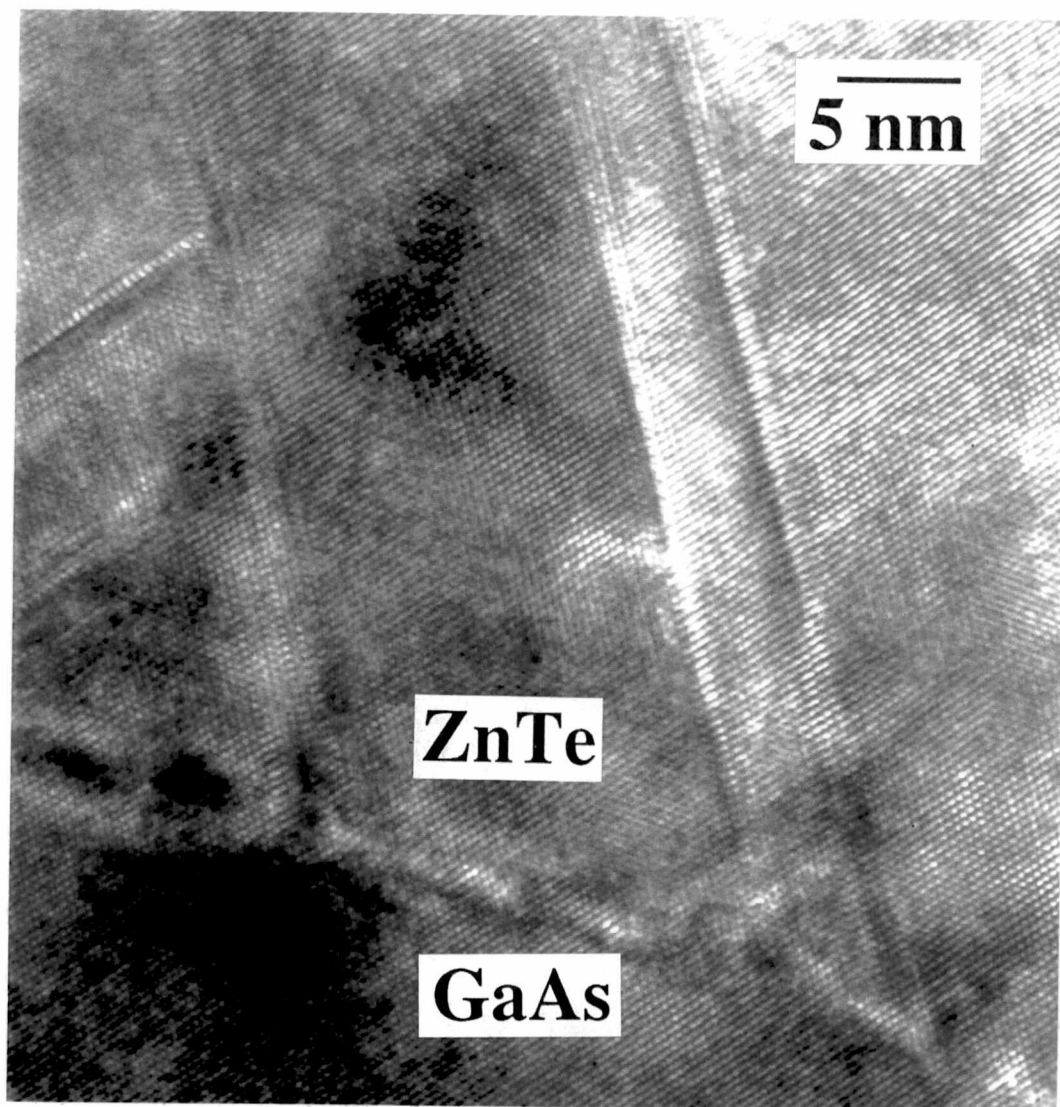


Figure 3.31 The interface of the ZnTe film shown in Figure 3.16.

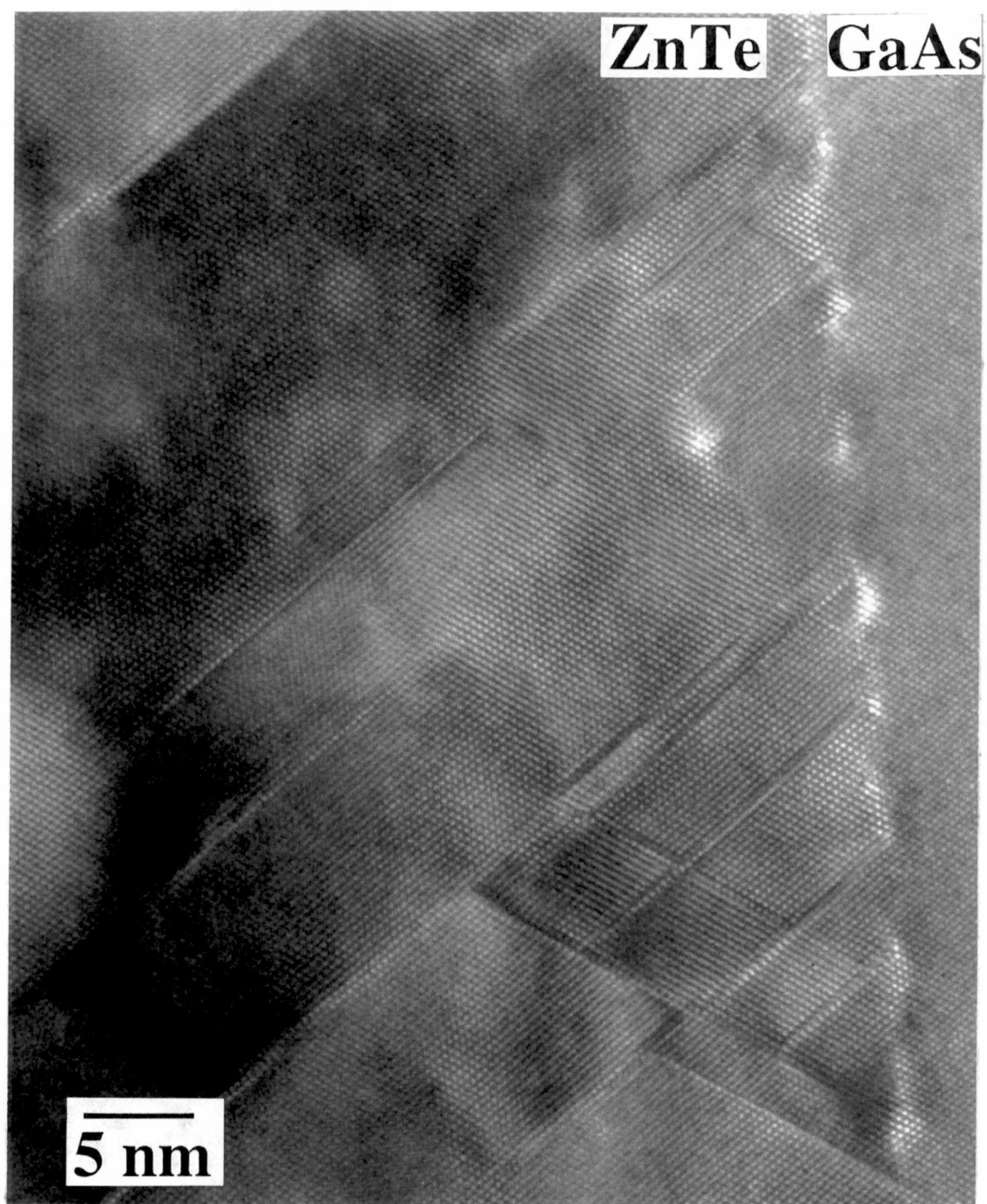


Figure 3.32 The interface of the ZnTe film shown in Figure 3.4.

AXT, while the substrate in the previous case was supplied by Sumitomo and not "epi-ready". This sample was grown in vacuum. The interface is much narrower and flatter than in the previous film, although a high density of interfacial stacking faults are still generated. These defects are typically 10-50 nm in length. The strain fields around misfit dislocations are separated by areas of unstrained interface. A clear reduction in interfacial stacking fault density is obtained by subjecting the substrate to hydrogen cleaning, as is evidenced in Figure 3.33. This ZnTe film was also grown in vacuum. High structural quality interfaces can be obtained when the film growth is performed in high pressures as well as in vacuum, as the ZnTe film grown in 88 mtorr N_2 shows in Figure 3.34. Again, this substrate surface was prepared using the hydrogen cleaning method. The conclusion is that proper cleaning of the substrate surface leads to flatter interfaces, more concentrated strain fields, and low interfacial stacking fault density.

The presence of stacking faults that initiate at the interface is unrelated to the lattice mismatch between the film and substrate in these films. Both ZnTe and ZnSe films contained interfacial stacking faults. Misfit dislocations, which arise due to the lattice mismatch, do not necessarily generate stacking faults; moreover, stacking faults are not necessarily associated with misfit dislocations. A typical interfacial stacking fault is shown in Figure 3.35. This fault has initiated between two misfit dislocations. Figure 3.36 shows this stacking fault and the interface at a higher magnification. The changing in the stacking sequence is evident by the shift in lattice fringes across the stacking fault.

3.3 Film Growth Modes

50 Å (15-20 monolayers) ZnTe films were examined by HRTEM in an attempt to determine the initial growth modes as a function of N_2 pressures. For these experiments hydrogen cleaned AXT GaAs substrates were used.

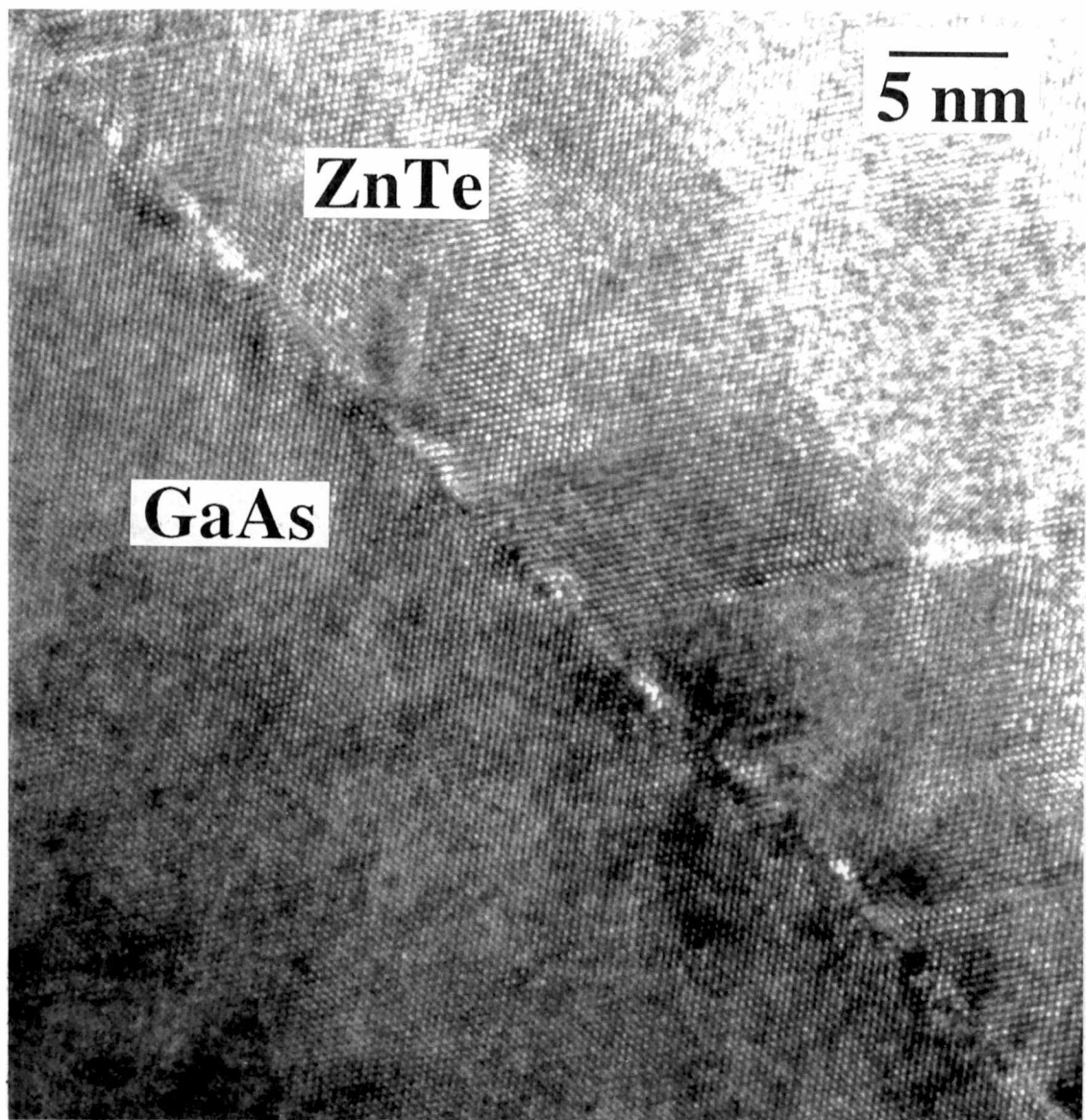


Figure 3.33 The interface of a ZnTe film grown by PLD in vacuum. $E_d = 0.73$ J/cm².

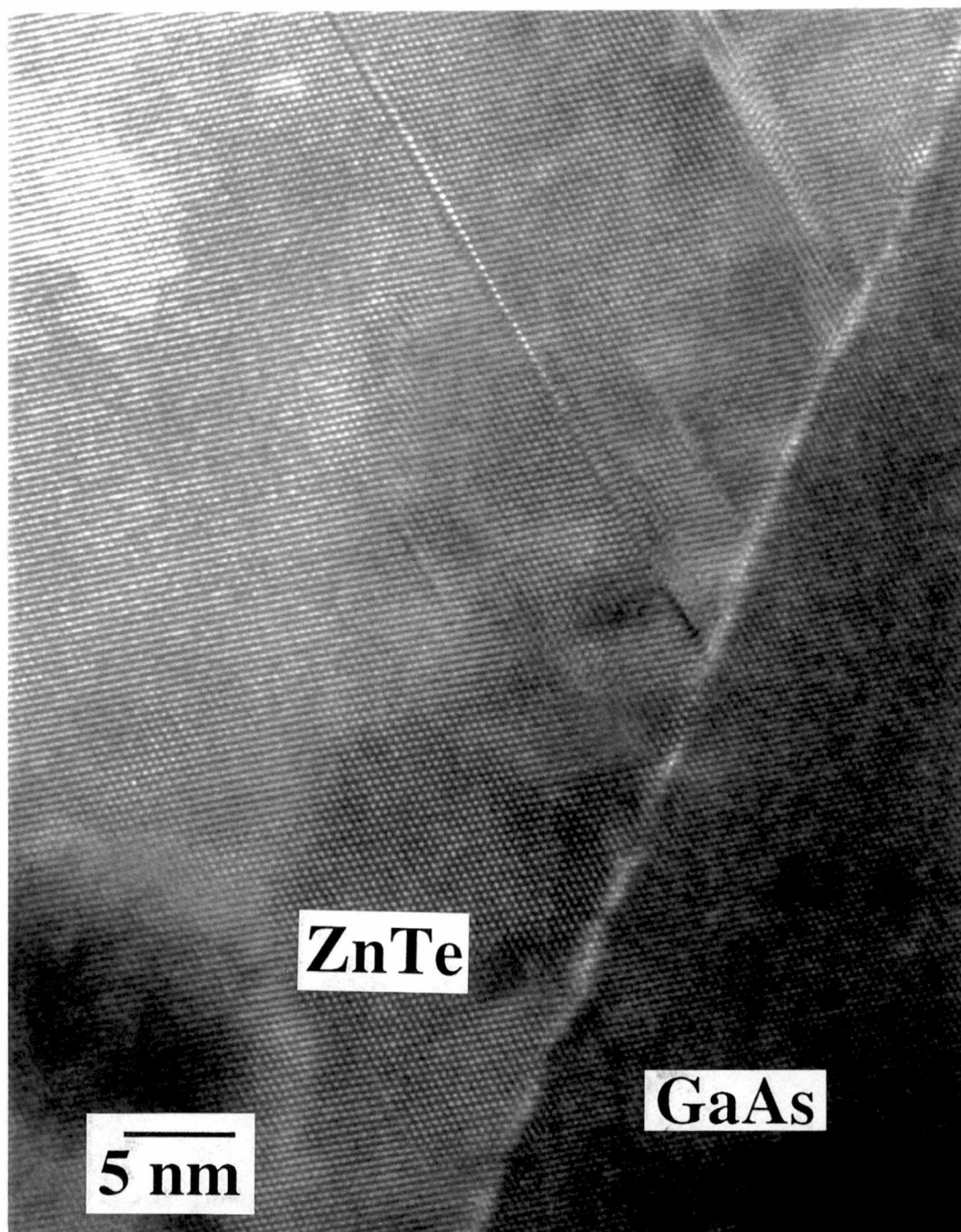


Figure 3.34 The interface of the ZnTe film shown in Figure 3.10.

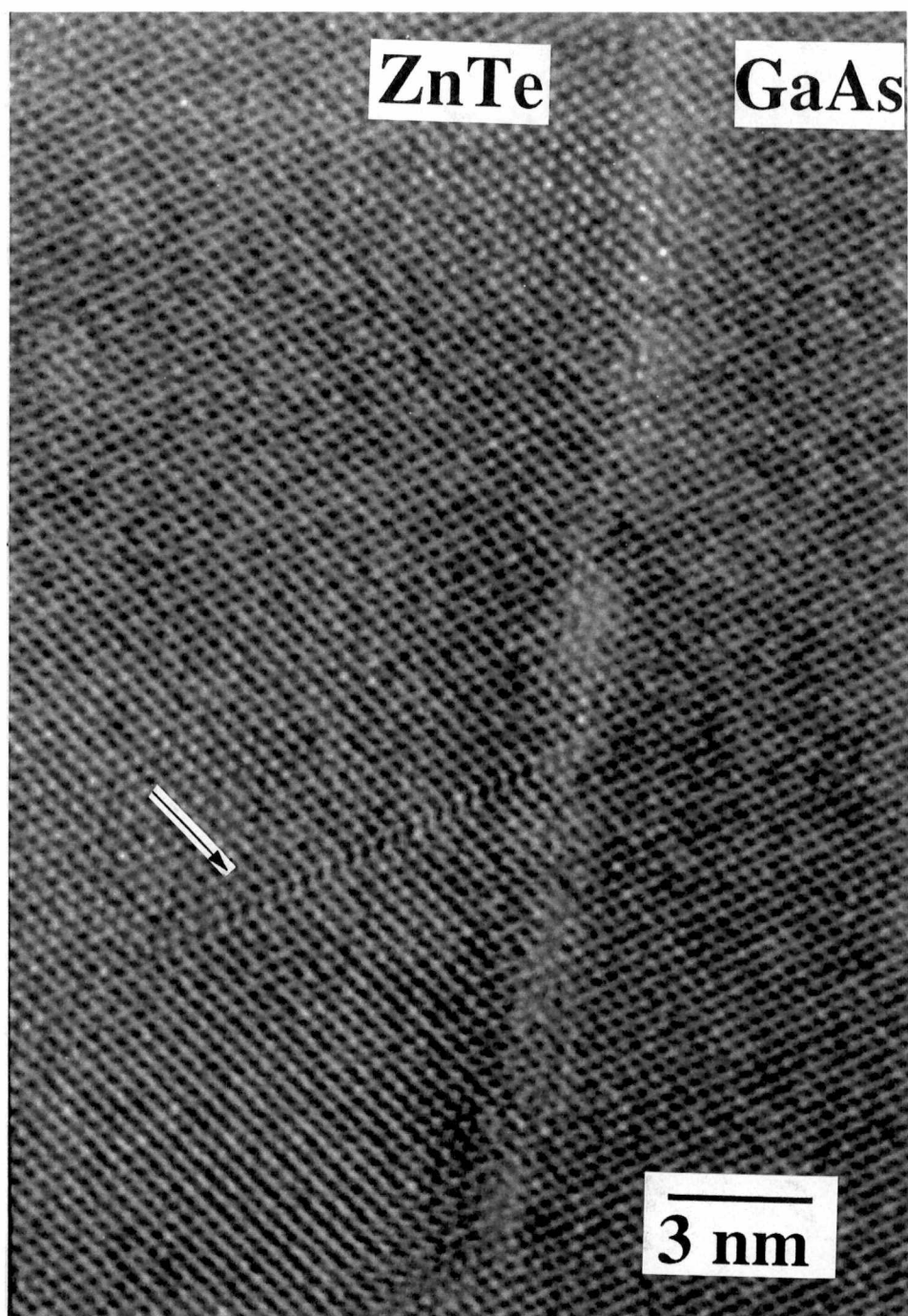


Figure 3.35 Interfacial stacking fault (arrow) in the ZnTe film shown in Figure 3.8.

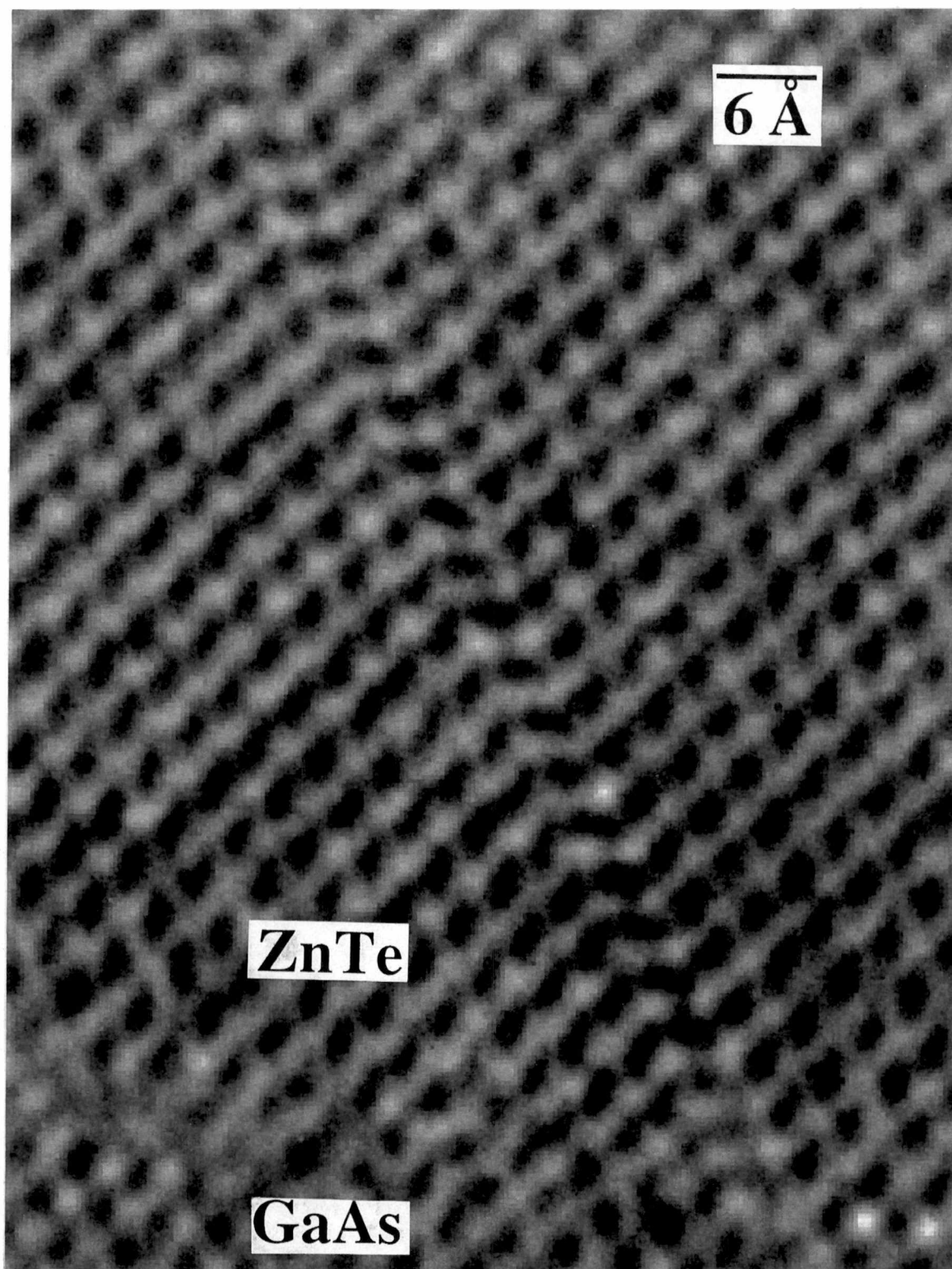


Figure 3.36 High magnification view of the stacking fault shown in Figure 3.35.

The film grown in vacuum showed some evidence of island growth. Substrate coverage was complete but not uniform. Areas ~10-15 nm in diameter with high densities of stacking faults were positioned along the surface at intervals of ~5-10 nm, separated by areas of lower stacking fault densities as shown in Figure 3.37. The highly faulted islands are not faceted along {111} planes but are irregularly rounded. Lattice images and Fourier transforms of a substrate-film area show that the film is epitaxial with the substrate as shown in Figure 3.38. The fact that all the stacking faults make the correct angle, about 54° , with the substrate confirms the epitaxial relationship is the same as in thicker films.

The ZnTe film grown in 100 mtorr N_2 had attained complete, uniform epitaxial substrate coverage. Since the film was so uniform in thickness, it appears that the growth mode is layer-by-layer Frank-van der Merwe. The ZnTe epilayer's lattice parameter is close to the bulk ZnTe lattice parameter, indicating that the film is not strained to match the substrate lattice; stacking faults and misfit dislocations along the interface are responsible for the lattice mismatch accommodation. The fact that islands are not present *and* that the film is relaxed to its bulk lattice parameter rules out the Stranski-Krastanow mode of film growth.

Single crystalline, smoothly rounded clusters ~10 nm in diameter along the film and ~5 nm in diameter perpendicular to the film were attached to the surface of the 100 mtorr film at intervals of ~10 nm as shown in Figure 3.39. Figure 3.40 shows a typical cluster. Unlike the islands seen in the film grown in vacuum, these clusters are free of stacking faults. The cluster lattice fringes appear to be in square pattern; if the cluster material is cubic, then the cluster view may be $\langle 100 \rangle$. Lattice fringe measurements indicate that if the cluster material is cubic and if the direction of viewing is $\langle 100 \rangle$, then the cluster material lattice parameter is ~2.5% greater than the ZnTe film lattice parameter. There are a number of indications that these clusters are produced by PLD and are not merely some foreign object unrelated to the film deposition. All clusters observed along the film surface are

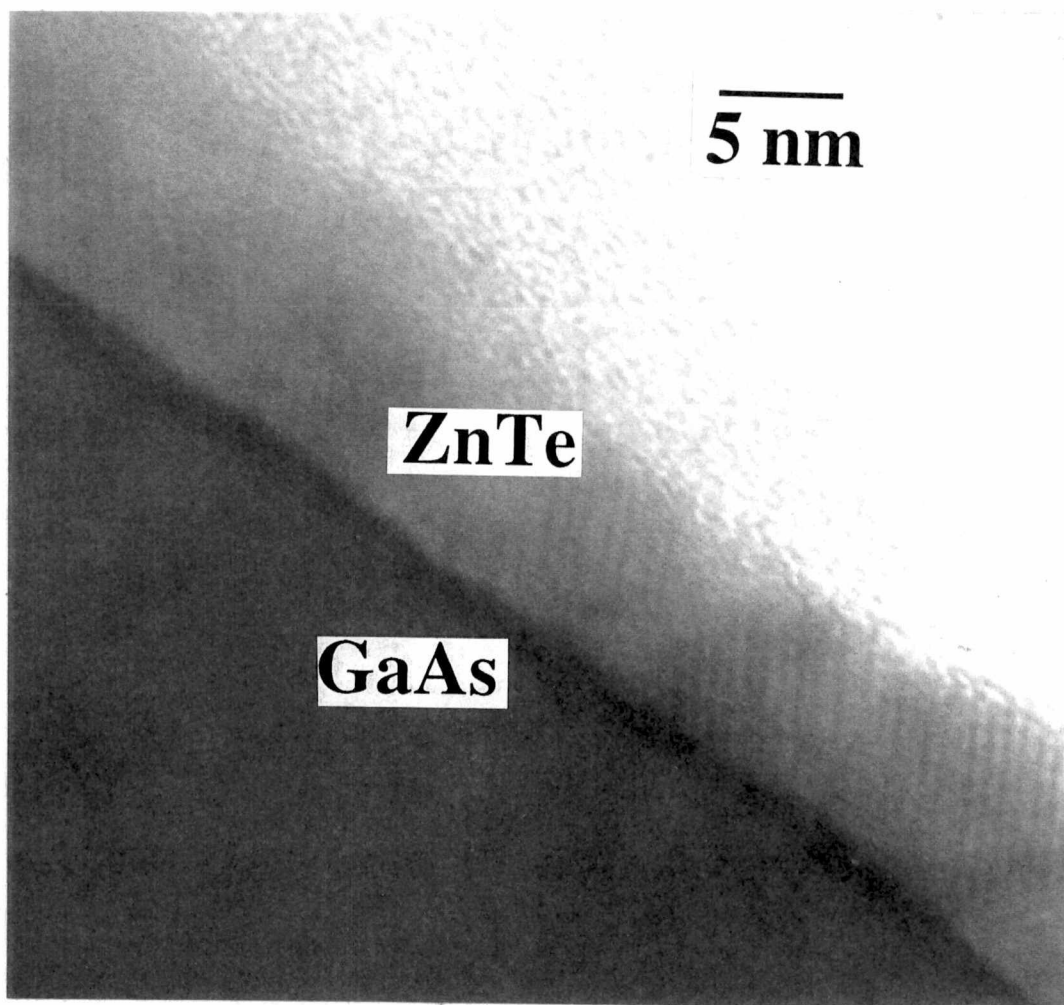


Figure 3.37 Thin ZnTe film grown in vacuum, showing stacking faults in epitaxial islands.

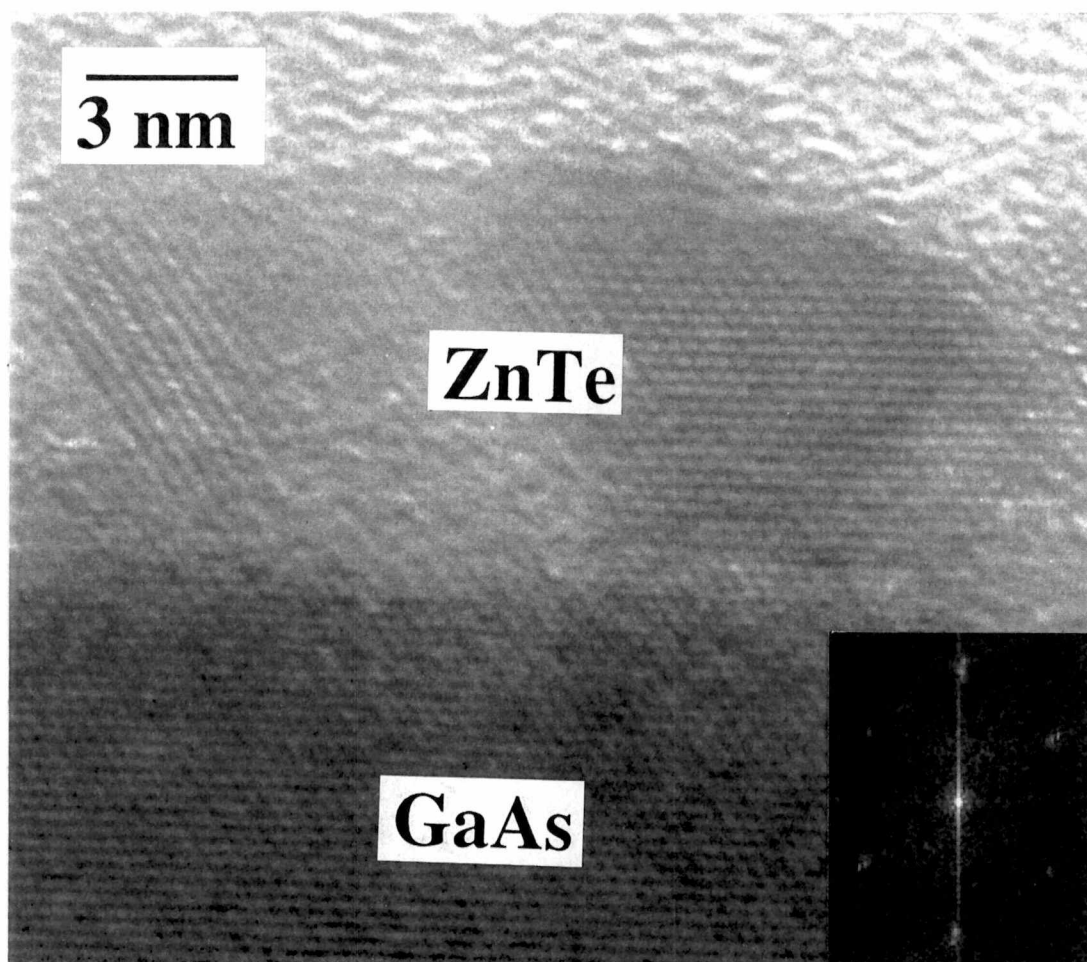


Figure 3.38 High resolution TEM image of epitaxial ZnTe islands of the film shown in Figure 3.37. Inset is FFT of a region containing the island and the substrate, showing the epitaxial orientation relationship of ZnTe and GaAs (compare to Figure 3.26).

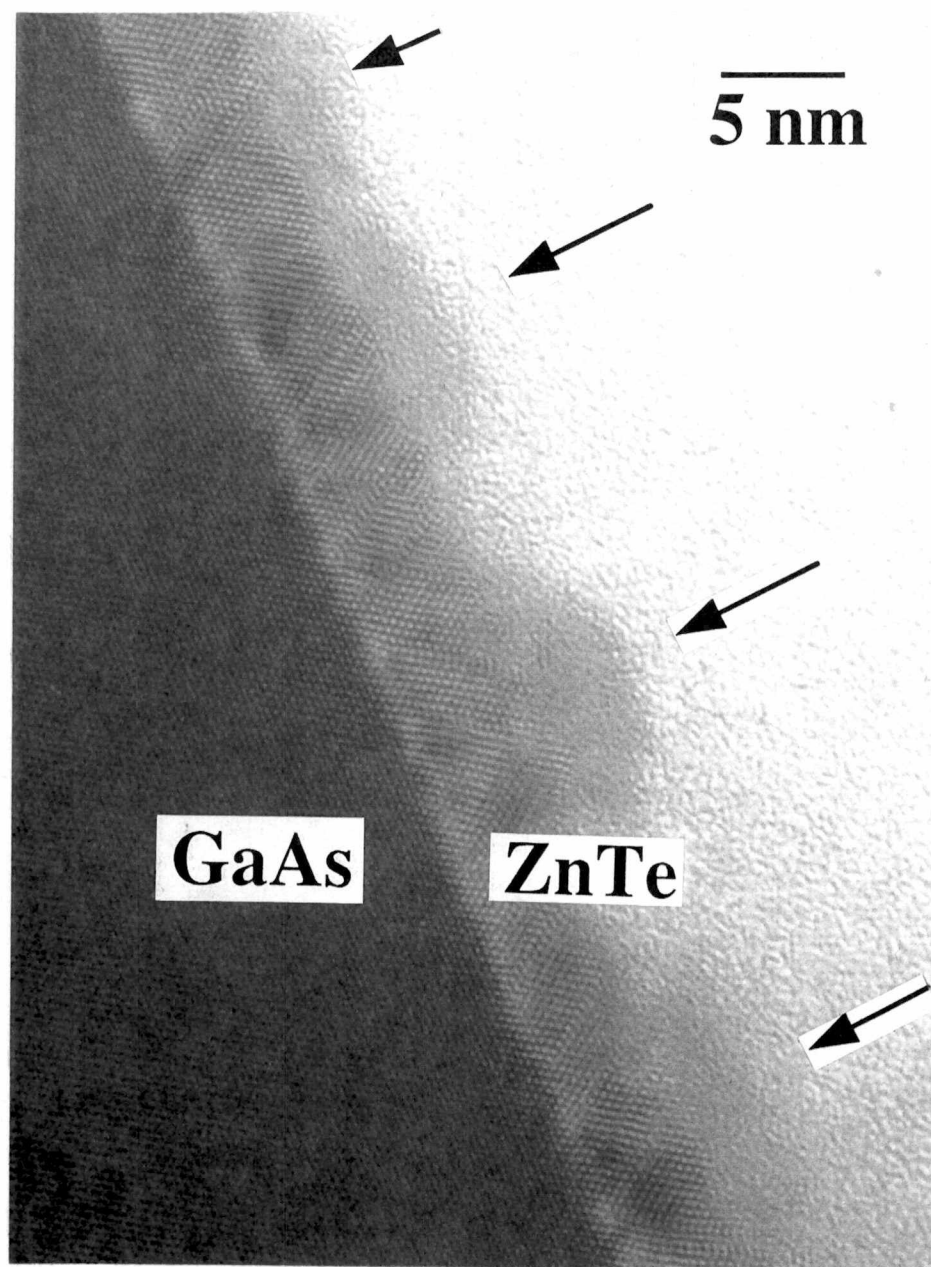


Figure 3.39 Thin ZnTe film grown in 100 mtorr N_2 , showing uniform film layer and attached clusters (arrows).

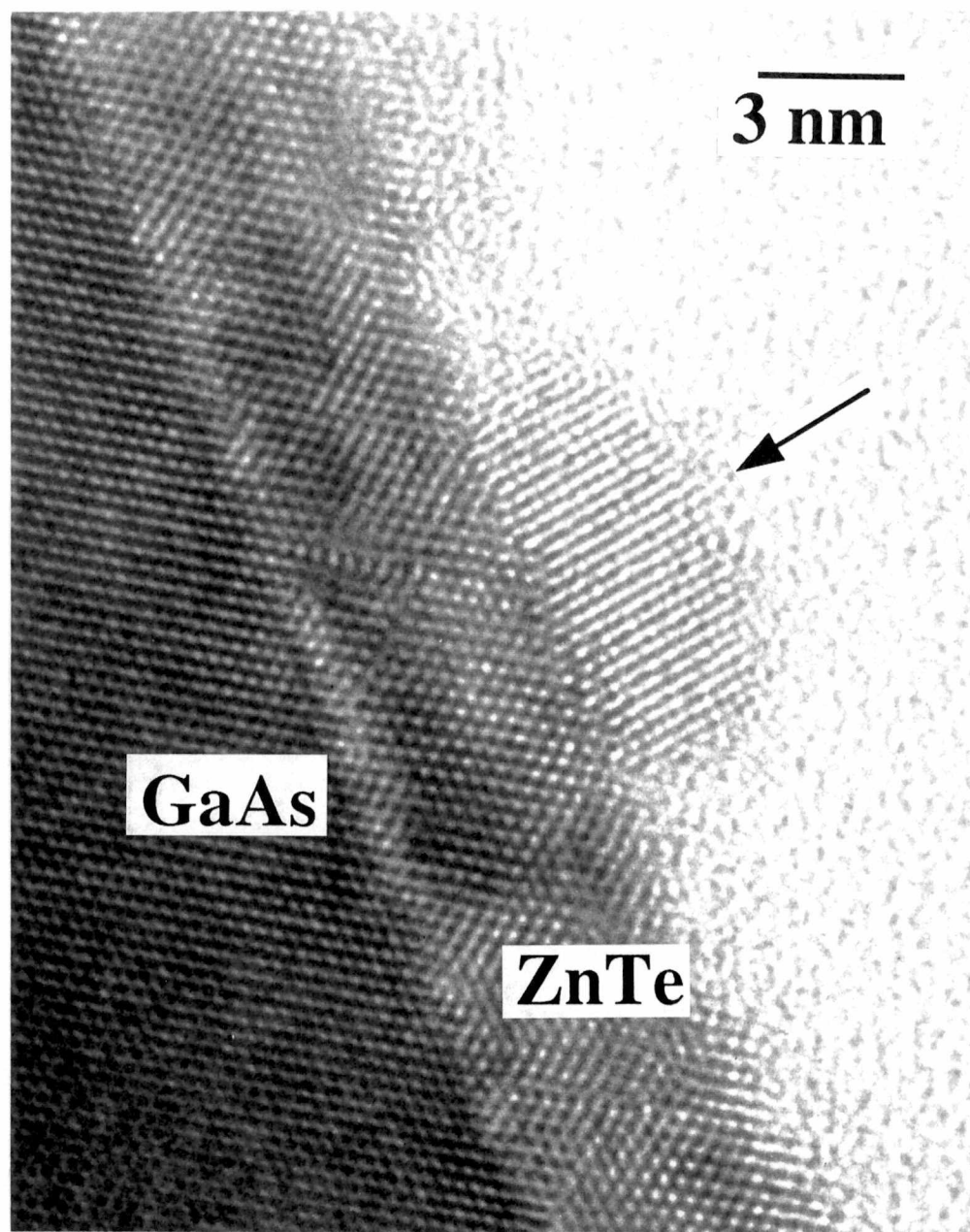


Figure 3.40 High resolution TEM image of the film shown in Figure 3.39. Arrow indicates a cluster attached to the film surface.

quite uniform in size and shape with rounded, smooth surfaces. They are also bound directly to the film along the entire bottom surface of the cluster.

3.4 Rapid Thermal Annealing, Hall effect, and PL

RTA produced a consistent increase in hole mobility and concentration in a 25 mtorr N_2 ZnTe film as the annealing time-temperature parameters increased. Results are given in Table 3.4. With no annealing treatment the film is not conductive as measured by a four point probe. Neither is it conductive when annealed at 550°C for 30 seconds. 650°C and 30 seconds gives a measurable Hall effect voltage. The mobility is 40 cm^2/Vs and the concentration is 1.6×10^{18} per cm^3 . A different 25 mtorr N_2 ZnTe film that did not undergo an RTA treatment had values of 5 cm^2/Vs and 2×10^{18} per cm^3 , respectively. Thus this annealing treatment dramatically increased the hole mobility. While hole mobilities remained roughly constant for the rest of the annealings, the hole concentrations increased with increased time and temperature up to a maximum of 1.3×10^{20} per cm^3 for 850°C and 30 seconds.

Room temperature photo-luminescence (PL) measurements did not reveal much of a difference among any of the annealing treatments, though. Figure 3.41 shows a typical spectrum. All of the PL spectra consisted of low intensity peaks in the 500-600 nm range and a broad hump between 800 and 1000 nm of much higher intensity. Since all other ZnTe PL spectra found in the literature were done at cryogenic temperatures as shown in Figure 1.1, it is not possible to compare the room temperature spectra to a ZnTe "standard".

Table 3.4 Hall effect results of RTA ZnTe film grown in 25 mtorr N₂.

Annealing Temperature (°C)	Annealing Time (seconds)	Brass	Free Hole Mobility (cm ² /Vs)	Free Hole Concentration (per cm ³)
not annealed	----	----	INSULATOR	----
550	30	yes	INSULATOR	----
650	30	yes	40	1.6×10 ¹⁸
750	30	no	35	1.2×10 ¹⁸
750	30	yes	40	3.0×10 ¹⁹
750	120	yes	45	5.3×10 ¹⁹
850	30	no	40	2.2×10 ¹⁹
850	30	yes	40	1.3×10 ²⁰

Note: "Yes" in the column labeled "Brass" indicates that a brass piece was placed over the ZnTe film during annealing.

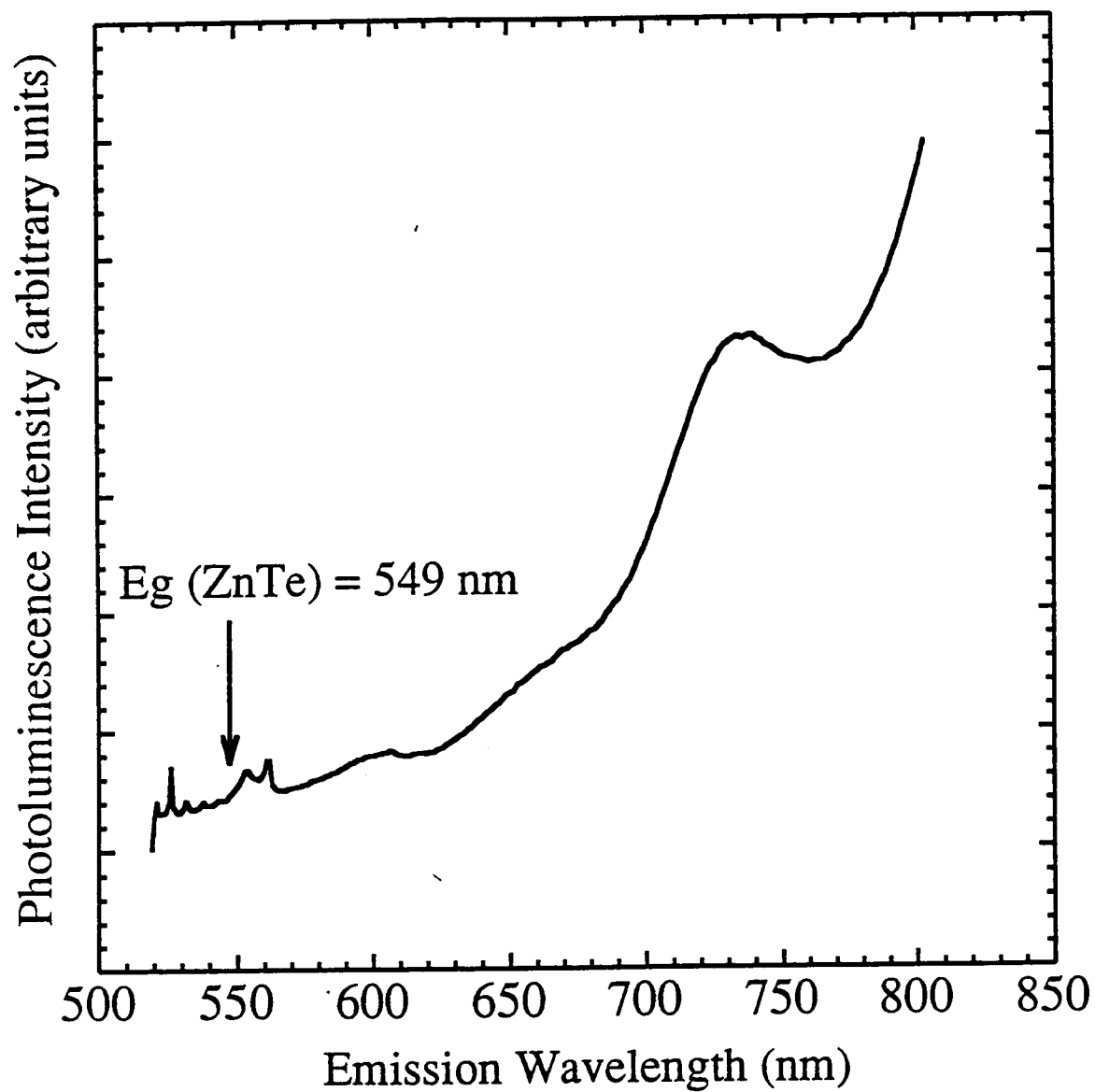


Figure 3.41 Room temperature PL emission spectrum of the ZnTe film annealed with brass at 750°C for 30 seconds. Arrow indicates ZnTe band gap.

Chapter 4

Discussion

4.1 Origin of stacking faults

Possibilities for the origin of stacking faults in these films are film-substrate lattice mismatch, island coalescence, and contaminants on the substrate surface or within the bulk of the film.

Stacking faults are not necessarily a consequence of the lattice mismatch. Stacking faults may relieve stress produced in a film grown on a greatly lattice mismatched substrate. In the present films, though, regularly spaced misfit dislocations take up much of the lattice mismatch, allowing the film to relax to its bulk lattice spacing within a few monolayers. Our TEM observations indicate that ZnTe/GaAs films grown by MBE have a greatly reduced stacking fault density as compared to ZnTe/GaAs films grown by PLD (compare Figures 3.30-3.34), that is, stacking faults are mostly related to the growth process. In addition, stacking faults are present in the ZnSe/GaAs system, where the lattice mismatch is only 0.24%, for all pressures, and the stacking fault density in the ZnSe/GaAs film grown in 1000 mtorr He/Cl₂ (Figure 3.21) rivals that of any ZnTe/GaAs film, where the lattice mismatch is 7.9%. Thus the growth conditions are responsible for stacking fault formation rather than the degree of lattice mismatch.

The hypothesis that stacking faults near the interface are the result of island coalescence does not apply to these films. Stacking faults may form at the boundary between two faceted islands that meet on {111} planes. This method of stacking fault formation in the present films is ruled out for the following reasons: i) the islands of the 50 Å ZnTe film grown in vacuum are not faceted, but rounded (Figure 3.34); ii) they already contain many stacking faults at very early stages of growth; iii) the 50 Å ZnTe film grown in 100 mtorr N₂, which exhibits layer growth, has many stacking faults rising up from the interface (Figure 3.36).

All of the experimental evidence indicates that it is the presence of contaminants on the substrate surface and within the growing film that is responsible for the stacking fault formation. A contaminant is defined here as any species that is neither Zn nor Te that would interrupt the regular lattice spacing of ZnTe. Residual oxides on the GaAs surface qualify as contaminants. Hydrogen cleaning of GaAs substrates has been shown to remove more surface oxide than a simple thermal desorption process[40,41]. It has been observed that ZnTe films grown on hydrogen cleaned substrates contain fewer stacking faults originated from the interface than ZnTe films grown on substrates that underwent the high temperature thermal desorption (Table 3.2). For instance, compare Figures 3.32 (high temperature thermal desorption) and 3.33(hydrogen cleaning). Another source of stacking faults near the interface may be Ga that has diffused into the near interface layers of the film, as evidenced by Auger Electron Spectroscopy (AES) [42]. AES also detected In in ZnTe films [42]. This In presumably is from the In used to bond the GaAs substrate to the heater face. It is most likely incorporated into the film due to sputtering by the ablation plume of excess In surrounding the substrate.

The source of stacking faults within the bulk of the film appears to be related to nitrogen incorporation into the film lattice. As the sequence of micrographs from Figure 3.4 to 3.7, stacking fault density in the bulk of ZnTe films increased with increasing nitrogen pressure in the range of vacuum to 50 mtorr. There is an similar increase in free hole concentration for ZnTe films grown in this N_2 pressure range, indicating increased nitrogen incorporation. X-ray diffraction shows a decrease in ZnTe lattice parameter of 0.4% in films grown in high N_2 pressure relative to films grown in vacuum [21]. This is seen as a result of placing nitrogen in substitutional sites in the ZnTe lattice. The strain associated with these substitutional sites may force the creation of a stacking fault. Since nitrogen has a lower solubility in ZnSe than in ZnTe, this nitrogen incorporation

effect will be smaller in ZnSe films as is evidenced by the relatively clean ZnSe film grown in 75 mtorr N_2 (Figure 3.19). The increased stacking fault density at high pressures may also be caused by the decrease in surface mobility due to the formation of clusters in the gas atmosphere. Contaminants in the target that are ablated along with Zn and Te may also lead to stacking fault formation in the bulk of the film.

4.2 Relationship between growth parameters, microstructure, and electrical and optical properties

Ambient pressure was found to be the most influential parameter affecting the overall microstructure and resultant electrical properties. ZnTe films were single crystal below growth pressures of 88 mtorr N_2 and polycrystals with columnar grains above. ZnSe films were single crystal up to growth pressures of 75 mtorr N_2 ; a ZnSe film grown in 1000 mtorr He/ Cl_2 had a similar microstructure as the ZnTe films deposited in high N_2 pressures. Thus it is evident that, as in the case of stacking fault formation mentioned above, the overall microstructure of ZnTe and ZnSe films is independent of the degree of film-substrate lattice mismatch and entirely dependent on the growth conditions.

One feature of the high pressure films is that the columnar grains do not extend all the way down to the interface but ride on a layer of heavily faulted single crystal. This behavior was observed in all growths in pressures at or above 100 mtorr. The columnar grains, then, do not initiate right at the beginning of growth but only after ~100-200 nm of single crystalline growth. In fact, as shown in Figure 3.39, films grown under a N_2 partial pressure of 100 mtorr start growing in a layer by layer mode. One possible explanation for the single crystal to polycrystal transition in these films grown in high pressure atmospheres is that the accumulation of damage may promote instabilities in the film that favor growth in one direction.

Clusters were observed in ZnTe films grown in pressures of 88 mtorr N_2 and greater but not in a ZnSe film grown in 1000 mtorr of 98%He/2% Cl_2 . The presence of clusters in the ZnTe films grown at high pressures indicates that clusters may be forming in the ablation plume due to increased collisions between ablated atoms and ions with themselves and with atoms in the atmosphere. The absence of clusters in the ZnSe film grown at a high pressure of He/ Cl_2 indicates that not only is this collisional process involved in cluster creation, but also a chemical one that involves reactions between the target atoms and atmospheric atoms. This chemical process would facilitate cluster formation if the ablation were carried out in a reactive atmosphere such as N_2 . Ablating through a He/ Cl_2 atmosphere eliminates the possibility of this chemical reaction with the atmospheric atoms. Note that the Cl_2 partial pressure amounted to only 2 mtorr in the ZnSe film growth, well below the pressure of 88 mtorr at which clusters formed in ZnTe ablated in N_2 . The lack of a sufficient pressure of reactive gas may be the cause of the absence of clusters in the ZnSe film. Another cause may be the differing atomic masses between He and N_2 . The effectiveness of He in cluster formation due to the collisional process will be less as compared to N_2 ; this may also explain the absence of clusters in the ZnSe film. Direct comparison of cluster formation in the two atmospheres thus is complicated by the differences in both physical and chemical effects. Experiments in which the atmospheric pressure and reactivity variables are studied separately will better answer the question of cluster formation in the ablation plume.

Rapid thermal annealing dramatically improved the electrical properties of a ZnTe film grown in 25 mtorr N_2 (Table 3.4). The annealing of an insulating ZnTe film produced a conductive film with free hole mobilities and concentrations superior to those of an unannealed, conductive ZnTe film grown in the same atmosphere. Free hole concentrations increased with increasing annealing time and temperature while free hole mobilities remained constant regardless of the

annealing procedure in all conducting films. The reason for the improved electrical properties of annealed films may be due to the annihilation of point defects at various sinks such as dislocation loops or stacking fault terminating dislocations. The room temperature PL spectra do not reflect any differences, though, in emission spectra among the annealed samples. PL measurements carried out at cryogenic temperatures may be required to fully understand the effect of RTA on emission spectra.

There is a strong effect of the growth pressure of N_2 on the electrical properties of ZnTe films. Both free hole mobilities and concentrations in ZnTe films peak near growth pressures of 50 mtorr N_2 , with mobility showing a sharp decrease at 25 mtorr and 100 mtorr pressures. Concentration is within an order of magnitude for films grown in both 50 and 100 mtorr, but decreases for 25 mtorr growth pressure. The dropoff in mobility at 100 mtorr is explained as a result of the polycrystalline, columnar microstructure of these films. Low mobility at 25 mtorr is most likely due to a large number of point defects caused by the high kinetic energy of the ablation plume. Pressures around 50 mtorr are high enough to slow down the incoming atoms and ions so as to reduce film damage, and low enough to avoid changing over to polycrystalline growth. RTA results indicate that it is possible to achieve great improvements in electrical properties by reducing the point defect density. Thus with this RTA processing it is possible to use lower N_2 growth pressures to benefit from the decreased stacking fault density without sacrificing electrical properties.

4.3 Relationship between growth parameters and film growth mode

By examining thin films of ZnTe at the initial stages of growth, it was found that changing the ambient pressure can force a change in growth mode. Films grown in vacuum initiated as heavily faulted islands, whereas films grown in 100 mtorr N_2 initiated as layers. Since no clusters were observed on vacuum

films, it can be assumed that growth is due to individual ions and neutral atoms. ZnTe films grown in 100 mtorr N_2 , on the other hand, grow by the accumulation of individuals as well as clusters. High pressure layer growth is probably due to a decrease in adatom energy of individual atoms caused by collisions with the ambient atmosphere and cluster growth. These clusters presumably form in the ablation plume. Cluster growth would strongly decrease the tendency to form islands since a cluster sitting on the film surface represents a huge arrival rate of adatoms with no kinetic energy. Embedded clusters are not seen in thicker, high pressure films, so they must either break up or dissolve into the growing film. Either way, the kinetic energy of individual atoms taken from the cluster will be small, so these atoms will experience little surface migration. An application of the findings concerning the initial growth mode to the microstructures of the thick ZnTe films studied is complicated by the different substrate surface cleaning methods among the films. Among the thick ZnTe films studied for overall microstructure, only the films grown in 75 and 88 mtorr N_2 had the hydrogen cleaning (Table 3.2), as did the thin ZnTe films studied for growth mode.

4.5 Ion Milling Damage

The artifacts attributed to Ar^+ ion milling observed in ZnSe and ZnTe films do not affect the interpretation of TEM images. The dislocation loops that are responsible for the "black dot" contrast are shorter than the stacking faults originating at the interface or those in the bulk of the film, so they have no effect on the conclusions drawn from HRTEM images. Both the amorphous layer seen on ion-milled edges of the film and the circular areas of Moire fringes are negligible artifacts.

Chapter 5

Conclusions

The goal of this work was to determine the relationship between film growth parameters and the resultant microstructural and electrical properties of ZnSe and ZnTe thin films grown by the pulsed laser deposition (PLD) process. Conventional and high-resolution transmission electron microscopy (TEM) were used to determine overall film microstructure, defect identification and concentration, and interfacial quality as a function of growth parameters. Rapid thermal annealing (RTA) and Hall effect measurements were used to study the effect of defects generated during growth on the electrical properties of ZnTe films.

The conclusions of this work are as follows:

1. Single crystal, epitaxial ZnSe and ZnTe films can be grown on (001) GaAs substrates by PLD given the proper growth conditions.
2. Cross-sectional TEM samples of these films can be prepared free of significant processing-induced damage that could affect high-resolution TEM images.
3. The overall film microstructure is dependent on growth parameters, with ambient gas pressure being the most important growth variable. ZnTe films are single crystal when grown in N_2 pressures below 75 mtorr and polycrystals when grown in N_2 pressures above 75 mtorr. ZnSe films show a similar pressure dependent microstructural transition. The stacking fault density in the bulk of ZnTe films increased with increasing N_2 pressure. The polycrystalline films of both ZnTe and ZnSe begin growth as a heavily faulted single crystal, and

misoriented columnar grains initiate after a thickness of ~100-200 nm has been reached, perhaps due to a high defect concentration because of the decreased kinetic energy of the ablation plume. As similar microstructures are observed in both ZnTe and ZnSe films, it is concluded at this stage that the degree of film-substrate lattice mismatch has no effect on overall film microstructure.

4. Clusters form in the ablation plume when ZnTe is deposited in N_2 pressures of 88 mtorr and above. ZnSe ablated through 1000 mtorr of He/ Cl_2 , though, does not result in cluster formation. The mechanism of cluster formation appears to have a physical as well as a chemical component. The absence of observable clusters in ZnTe films grown in low N_2 pressures indicates that clusters form due to increased collisions in the ablation plume. The absence of clusters in the ZnSe film grown in 1000 mtorr of He/ Cl_2 hints that a reactive gas helps cluster formation.

5. The film-substrate interface is semi-coherent and has a completely epitaxial orientation relationship. Regularly spaced misfit dislocations along the interface account for lattice mismatch, allowing the films to attain their bulk lattice parameters. Hydrogen beam cleaning of the GaAs substrates results in smoother interfaces that originate fewer stacking faults as compared to substrates that did not receive the hydrogen beam cleaning.

6. Stacking faults are generated at the interface due to the presence of contaminants on the substrate surface and in the bulk of the film due to increasing nitrogen incorporation for films grown in N_2 . The presence of stacking faults in both ZnTe and ZnSe films eliminates lattice mismatch as a cause of stacking fault generation.

7. The initial film growth mode can be altered by varying the film growth

pressure. The initial growth mode of ZnTe films grown in vacuum on hydrogen cleaned GaAs substrates is in the form of islands. The initial growth mode of ZnTe films grown in 100 mtorr N_2 on hydrogen cleaned GaAs substrates is in the form of layers due to cluster deposition and the decreased energy of incoming individual atoms and ions.

8. Microstructural defects directly influence electrical properties. ZnTe films grown in low pressures are single crystal but have a high density of point defects created by damage from the high energy ablation plume that greatly impedes free hole mobility and concentration. Free hole mobility and concentration are also adversely affected by the polycrystalline structure of ZnTe films grown in 100 mtorr N_2 . The maximums in these electrical properties occur around growth pressures of 50 mtorr N_2 since the film is a single crystal with a reduced point defect density due to decreased ablation plume energy. RTA can eliminate the harmful effect of point defects on electrical properties, allowing high mobility and concentration of carriers to be achieved at a lower growth pressure.

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