CHARACTERIZATION OF GaAs/Si INTERFACE STRUCTURE BY X-RAY DIFFRACTION

DE91 004769

E.D. SPECHT*, G.E. ICE*, C.J. PETERS*, C.J. SPARKS*, N. LUCAS†, X.-M. ZHU†, R. MORET†,
AND H. MORKOÇ‡

*Metals and Ceramics Division, Oak Ridge National Lab., Oak Ridge, TN 37831-6118

†Dept. of Physics and Materials Research Lab., University of Illinois, Urbana, IL 68101

‡Coordinated Science Lab. and Materials Research Lab., University of Illinois, Urbana, IL 68101

ABSTRACT

By measuring the intensity profiles along the crystal truncation rods of a Si(001) substrate, we obtain the depth sensitivity necessary for x-ray diffraction measurements of the structure of its interface with a thick GaAs overlayer which is epitaxial to, but not in registry with the substrate. By comparing the diffraction with a model based on a grid of misfit dislocations, we find that the atoms at the interface have a root mean square displacement of 1.09 ± 0.1 Å from this ideal structure, and that the interface has a roughness of 2.9 ± 1 Å. The diffraction indicates an anomalously small strain perpendicular to the interface in the GaAs near the interface.

INTRODUCTION

Lattice misfit in heteroepitaxial films may be accommodated in two ways. For thin films, a small misfit may be accommodated by growing a defect-free film in registry with the substrate and with strain equal to the misfit. As either film thickness or misfit increases, a registered film becomes unstable as defects nucleate.¹ Beyond this thickness, a defect-free film can form only if the misfit dislocations are localized at the interface.

We have chosen GaAs on Si as a model heteroepitaxial system. Due to its technological importance,^{2,3} this system has been the subject of much study. Registered GaAs films have not been grown beyond two layers, so a variety of techniques have been applied to confine misfit dislocations to the GaAs/Si interface, including an initial growth at reduced temperature,^{4,5} use of a strained-layer superlattice buffer,^{6,7} and growth on vicinally cut substrates.^{6,8} As defects extend into the bulk of the film, electron mobility is observed to decrease.⁷

With proper growth techniques, dislocation density is very low far from the interface; about 10^4 cm⁻² at a distance of 2 μm from the interface in one case.⁹ For a thinner film (900 Å), x-ray diffraction was used to profile the strain perpendicular to the interface.¹⁰ These measurements show a linear strain gradient of 0.8% across the thickness of the film. This accounts for some 20% of the 4.1% misfit; the other 90% must be taken up near the interface. High resolution electron microscopy does indeed show an array of dislocations in small areas of the GaAs/Si interface.^{9,11} In order to obtain a quantitative measure of the perfection of the interface and of the degree of confinement of dislocations to the interface, we have developed a new X-ray diffraction technique for measuring the partial registry of the interfacial atoms of an incommensurate film with the substrate.

We have adapted a technique used in the study of fully registered thin films.¹² To obtain sensitivity to the near interface region, we measure the intensity profile along the Si crystal truncation rods (CTR). The integrated intensity is proportional to the square of the modulus of the scattering amplitude

$$F(Q) = \frac{a_0^2}{A} \sum_j f_j(Q) e^{iQ \cdot r_j} \quad \text{MASTER} \quad (1)$$

where $a_0 = 5.431$ Å is the Si lattice constant, A is the area of the interface, and f_j and r_j are the scattering factor and position of each atom. For the (001) interface studied, F is nonzero in the limit of large A only when the reciprocal lattice vector (RLV) $Q = 2\pi(h,k,l)/a_0$ has integral h and

k. Because the Si substrate is virtually free of defects, it contributes to $F(Q)$ only near the Si Bragg peaks. The GaAs film, on the other hand, has a different lattice constant and will not contribute at all to the Si CTR. As we shall see, the material near the interface is in partial registry with the substrate, giving a characteristic contribution to the Si CTR.

EXPERIMENTAL

A Si (001) substrate was degreased and subjected to a metal removal process and a series of oxidation/deoxidation cycles to remove carbon contamination. The last oxide, which was left on the surface, was grown in a 5:3:3 ($H_2O:HCl:H_2O_2$) solution. This volatile oxide was removed by thermal outgassing at $1000^\circ C$ under vacuum just prior to growth. The GaAs layer was then grown at a substrate temperature of $510^\circ C$ and a growth rate of $0.2 \mu m/h$ to a thickness of $900 \text{ \AA}$.

X-ray diffraction measurements were made at beamline X-14 of the National Synchrotron Light Source.¹³ Incident flux was monitored by a N_2 filled ion chamber; we obtained an absolute measure by calibrating the ion chamber with a PIN diode, which was in turn calibrated with a scintillation counter. Typical flux was 10^{11} sec^{-1} ; the wavelength was $\lambda = 1.410 \text{ \AA}$. We eliminated air scatter by mounting the sample in vacuum under a beryllium dome. Data were collected with incident and scattered beams at equal angles to the surface. Resolution was determined by slits before and after the sample.

At each point along the Si CTR we measure intensity as we rotate the sample, subtracting a smooth background to determine peak intensity. To verify that the features we observe are indeed interface scattering, we reproduced the data from $Q = 2\pi(1,1,.5)/a_0$ to $Q = 2\pi(1,1,1.2)/a_0$ with the slits after the sample replaced by a Ge(111) crystal for higher resolution. We confirmed that the interface scattering forms a sharp rod in reciprocal space, normal to the interface, matching the Si periodicity to within 10^{-4} . Since the bulk of the GaAs film is poorly ordered, with a 0.5° mosaic, this long range order must be at the interface.

Intensities are corrected by a Lorentz factor and for the area of the interface exposed to the beam and normalized to the incident intensity, giving $|F(Q)|^2$ in electron units.¹⁴ We plot the observed intensity along the (11 $\bar{1}$) and (20 $\bar{1}$) Si CTR in Figure 1. A more complete account of the data collection and analysis techniques applied here will be published elsewhere.¹⁴

MODEL

We compare the observed scattering with that produced by a square grid of misfit dislocations at the interface. Well ordered GaAs/Si interfaces have been found¹¹ to develop

Figure 1: Diffracted intensity along Si (11 $\bar{1}$) and (20 $\bar{1}$) CTR, observed (circles) and calculated for a grid of misfit dislocations, with no adjustable parameters. Scattering from Si and GaAs lattice are indicated, as well as the coherent sum.

such a lattice of dislocations with Burger's vectors of $\frac{1}{2}[110]$ and $\frac{1}{2}[\bar{1}\bar{1}0]$. Van der Merwe has calculated¹ the strain at this interface by modeling each crystal with continuum elastic theory. This approximation is valid for dislocation spacing (96 Å) much larger than the lattice parameter (3.84 Å for the primitive cell). The approximation will break down at each dislocation core. The van der Merwe model assumes infinite crystals: this is a good approximation for this system because far from the interface the interfacial strain falls off exponentially with a 15 Å decay length. Because Si has a higher elastic modulus than GaAs, the model, which takes them to be equal, will overestimate the strain in Si and underestimate it in GaAs. We use a Poisson's ratio of 0.30 for both Si and GaAs. The GaAs lattice constant, 4.1% larger than that of Si, is well approximated by $25a_{\text{Si}}/24$.

We illustrate in Figures 2 and 3 two planes of atoms as calculated by the van der Merwe model. The first (001) plane of GaAs atoms, parallel to the interface, is shown in Figure 2. The lattice is dilated near the dislocation lines (solid lines). A (100) plane, perpendicular to the interface, is shown in Figure 3. The Si (filled circles) and GaAs (open circles) atoms are in registry at the interface except near the dislocation at the center of the figure. The GaAs within 12 Å of the interface is compressed in the plane of the interface and dilated out of plane in the region between dislocations, dilated in plane and compressed out of plane near the dislocation lines. Further from the interface this behavior is reversed. The signal we observe along the Si CTR is created by the GaAs atoms between the dislocations and close to the interface, where the atoms are in registry; thus we observe an out of plane dilation.

From Equation (1) we calculate $F(Q)$ using the Ge form factor as an average of As^+ and Ga^- ions.¹⁵ We treat atoms within 100 Å of the interface using the van der Merwe model;¹ Si atoms further from the interface are taken to be at bulk positions, GaAs atoms further from the interface are ignored, as they do not contribute to the Si CTR.

A Si(001) surface may be truncated by a plane of atoms at either $z=0$ or $z=1/4$ in coordinates of the cubic unit cell. Since one surface is simply a rotation of the other, they will occur with equal frequency. In our calculation we average the scattering intensities from these two truncations.

The measured intensity of the Si CTR (circles) is compared to that predicted by the van der Merwe model (lines) in Figure 1. We plot $|F_{\text{Si}}|^2$ and $|F_{\text{GaAs}}|^2$ as well as the total $|F_{\text{Si}} + F_{\text{GaAs}}|^2$. We have included no adjustable parameters. Our observations agree qualitatively

Figure 2: Model atomic positions for the first (001) plane of GaAs atoms, compressed near misfit dislocations (solid lines). The box is a 5.65 Å unit cell.

Figure 3: Model atomic positions for the (100) plane located at the broken line in Fig. 2. Si atoms are filled circles, GaAs open circles. Lines highlight the misfit dislocation.

with the predictions; we will first discuss qualitatively the observed diffraction, then consider how disorder at the interface produces large quantitative differences.

In both calculation and measurement, scattering from GaAs produces a peak on the low l side of each Si Bragg peak; we call this an interface peak. GaAs near the interface and between the dislocations is contracted in the plane of the interface, producing partial registry with the substrate. This leads to a dilation out of plane. The positions of the interface peaks reflect this dilation in a complex way: the calculated interface peaks are found at Si RLV of (1,1,0.935), (2,0,1.845), and (1,1,2.865), corresponding to strains of 2.8%, 4.2%, and 0.6% relative to bulk GaAs, normal to the interface. Interference of differently strained regions of the interface produces various shifts in the interface peaks.

The width of the interface peaks reflect the thickness over which the film remains in registry with the substrate. The van der Merwe model predicts that strain falls off exponentially with a 15 Å decay length, giving interface peak widths near 0.12 Si reciprocal lattice units FWHM.

While the model predicts equal and opposite strain in the Si and GaAs lattices, the effect on the Si CTR from the two lattices is very different. The scattering from the Si is similar to that of a truncated crystal near the Bragg peaks. Scattering is reduced by a factor of 2 between Bragg peaks, characteristic of a diffuse boundary. While GaAs atoms are strained into partial registry with the Si lattice, producing the interface peaks, the Si atoms near the interface are strained partially out of registry with the substrate, spreading out the otherwise sharp truncation of the Si lattice over several atomic layers.

Comparing the observed scattering to this model, we see a large difference in intensity and a less obvious shift in peak position. The lowest order peaks are close to the calculated intensities, but the higher order peaks are far weaker (Figure 1), characteristic of atomic

displacements from lattice sites. Assuming a Debye-Waller factor of $e^{\frac{-6\pi^2 u^2 \sin^2 \theta}{\lambda^2}}$, we can account for the loss in intensity using root mean square (rms) displacements $u_{\text{GaAs}} = 1.09 \pm 0.1$ Å and $u_{\text{Si}} = 0.96 \pm 0.1$ Å, over 6 times the bulk values.¹⁵

The intensity is still weaker between Bragg peaks, characteristic of interface roughness. Applying a model developed by Robinson,^{14,16} we fit our data by assuming an interface profile varying as $\exp(-z/r)$, obtaining $r = 2.0 \pm 1$ Å.

A third correction is needed to match calculated and observed peak positions: we shift the scattering from the GaAs near the interface by an amount corresponding to a $1.5 \pm 0.2\%$ contraction normal to the interface. We plot in Figure 4 our final model with these four adjustable parameters: Debye-Waller factors for Si and GaAs, interface roughness, and strain. We discuss the corrections below.

Figure 4: Diffracted intensity along Si (111) and (201) CTR (circles) and calculated with adjustable parameters as noted in the text. Intensity for Si and GaAs lattices are indicated, as well as their coherent sum.

DISCUSSION

While we are able to identify an average structure, the interface is highly disordered. The random rms displacement of atoms from the calculated structure is near 1 Å, greater than the 0.80 Å periodic rms displacement from bulk lattice positions calculated for atoms in the layers bordering the interface. This is consistent with the observation¹¹ that inclined dislocations and stacking faults occur at GaAs/Si interfaces with frequency at least as great as that of the edge dislocations included in our model.

The 1.5% observed contraction perpendicular to the interface, relative to the model, suggests that the GaAs near the interface has very little strain perpendicular to the interface. The van der Merwe model predicts that between dislocations the Si and GaAs are in registry at their interface. In the plane of the interface Si will be expanded by 2.05%, GaAs contracted by the same amount. The Poisson response¹⁷ produces a 1.8% out of plane contraction in the Si at the interface; the GaAs is expanded by the same amount. Subtracting the 1.5% shift between this model and our observations leaves an out of plane expansion of just $0.3 \pm 0.2\%$ for the GaAs. We now consider three ways in which this apparent lack of response by the GaAs to the Si may arise from the disorder at the interface.

At one extreme, we consider the possibility that the interface peaks arise from GaAs which is under no strain at all. The scattering is proportional to $|F_{\text{Si}} + F_{\text{GaAs}}|^2$; if small domains of unstrained GaAs at the interface fell in coherence with the Si substrate, the small size of the GaAs domains would broaden F_{GaAs} in reciprocal space to overlap the Si CTR, and we would observe scattering due to the term $F_{\text{Si}}F_{\text{GaAs}}$. For an infinite GaAs crystal, coherence requires strain, as unstrained Si and GaAs lattices will fall out of coherence after ~25 lattice spacings. A GaAs domain smaller than ~25 lattice spacings may be coherent with a Si lattice without strain. We know of no mechanism, however, to place a domain of GaAs in coherence with the Si lattice without straining it as described by the van der Merwe model.

Alternatively, the shift in the interface peaks may be accounted for if we suppose that the GaAs film is strained into partial registry with the Si substrate, as predicted by the van der Merwe model, but the Poisson response does not occur: no out of plane expansion accompanies the in plane contraction. We might expect a reduced Poisson response from the disordered GaAs near the interface--a liquid exhibits no Poisson response at all. However we expect the GaAs near the interface, although defective, to exhibit crystalline structure locally, giving it a Poisson response close to that of the bulk.

At the other extreme, the strain fields may be precisely as predicted by the van der Merwe model. To account for the shift in the interface peaks, we note from Figure 1 that their intensity falls below that predicted by the van der Merwe model by as much as a factor of 100. We have attributed this lowered intensity to random atomic displacements. If the atoms nearest the interface suffer the most displacement, the scattering will reflect primarily the atoms further from the interface. Since strain falls off rapidly with distance from the interface, the scattering will reflect the lower strain from the less displaced atoms further from the interface. Of the three models we have considered which will account for this shift in the scattering, only this last is physically plausible.

Finally, we compare use of CTR intensities to measure interface structure with other scattering techniques. The most direct measure of a periodic interface structure is given by the intensity of diffraction on the interface reciprocal lattice. While our model for the GaAs/Si lattice predicts a lattice of dislocations, we find no diffraction from this lattice, consistent with the high degree of disorder we measure at the interface.

X-ray standing wave fluorescence (XSWF) provides very much the same information as CTR intensities: the degree of registry and position of atoms are measured relative to the substrate lattice.¹⁸ By measuring fluorescence rather than diffraction, XSWF discriminates between substrate and film scattering, as only the film fluoresces. XSWF is effective however only when the film is very thin, as it provides no discrimination between film atoms near the interface and those further away: fluorescence from a 900 Å film would swamp the signal from interface

atoms.

Specular x-ray reflectivity, or diffraction from the (00t) CTR, gives a measure of interface roughness only -- it is not sensitive to the crystal lattices. As an added complication, the free surface and the interface must both be modelled. The sharpest GaAs/Si interfaces measured by this technique exhibit 10 Å roughness, somewhat greater than that calculated here.¹⁹

ACKNOWLEDGEMENTS

We thank F. J. Walker for helpful discussions. This research is sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., and under contract DE-AC02-76ER01198 with the University of Illinois. NSLS is supported by the U.S. Department of Energy under contract DE-AC02-76CH00016.

REFERENCES

1. J. H. van der Merwe, Proc. Phys. Soc. (London) **A63**, 616 (1950).
2. H. K. Choi, G. W. Tuner, and B-Y. Tsaur, IEEE Electron Device Lett. **EDL-7**, 271 (1986).
3. H. Shichijo and J. W. Lee in Materials Research Society Symposia Proceedings, Vol. 67, *Heteroepitaxy on Silicon*, edited by J.C.C. Fan and J. M. Poate (Materials Research Society, Pittsburgh, PA, 1986), pp. 173-180.
4. M. Akiyama, Y. Kawarada, and K. Kaminish, J. Appl. Phys. **23**, L843 (1984).
5. W. T. Masselink, T. Henderson, J. Klem, R. Fisher, P. Pearah, H. Morkoc, M. Hafich, P.D. Wang, and G. Y. Robinson, Appl. Phys. Lett. **45**, 1309 (1984).
6. R. Fisher, D. Neuman, H. Zabel, H. Morkoc, C. Choi, and N. Otsuka, Appl. Phys. Lett. **48**, 1223 (1986).
7. J. W. Lee in Materials Research Society Symposia Proceedings, Vol. 67, *Heteroepitaxy on Silicon*, edited by J.C.C. Fan and J. M. Poate (Materials Research Society, Pittsburgh, PA, 1986), pp. 29-36.
8. G. M. Metze, H. K. Choi, and B.-Y. Tsaur, Appl. Phys. Lett. **45**, 1107 (1984).
9. R. Fischer, H. Morkoc, D. A. Neumann, H. Zabel, C. Choi, N. Otsuka, M. Longerbone, and L. P. Erickson, J. Appl. Phys. **60**, 1640 (1986).
10. A. S. Bommannavar, C. J. Sparks, A. Habenschuss, G. E. Ice, A. Dhere, H. Morkoc, and H. Zabel, in Materials Research Society Symposium Proceedings, **102**, 223 (1988).
11. H. L. Tsai and J. W. Lee, Appl. Phys. Lett. **51**, 130 (1987).
12. I. K. Robinson, R. T. Tung, and R. Feidenhans'l, Phys. Rev. B **38**, 3632 (1988).
13. A. Habenschuss, G. E. Ice, C. J. Sparks, and R. A. Neiser, Nucl. Instr. and Methods **A266**, 215 (1988).
14. E. D. Specht, G. E. Ice, C. J. Peters, C. J. Sparks, N. Lucas, X.-M. Zhu, R. Moret, and H. Morkoc, to be published.
15. *International Tables for X-Ray Crystallography*, K. Lonsdale ed. (Kynoch Press, Birmingham, Eng., 1962), Vol. III, p. 204.
16. I. K. Robinson, Phys. Rev. B **33**, 3830 (1986).
17. N. Lucas, H. Zabel, H. Morkoc, and H. Unlu, Appl. Phys. Lett. **52**, 2117 (1988).
18. N. Hertel, G. Materlik, and J. Zagenhagen, Z. Phys. B, **58**, 199 (1985).
19. N. Lucas, H. Zabel, S. V. Iyer, and H. Morkoc, to be published.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

END

DATE FILMED

12 / 27 / 90