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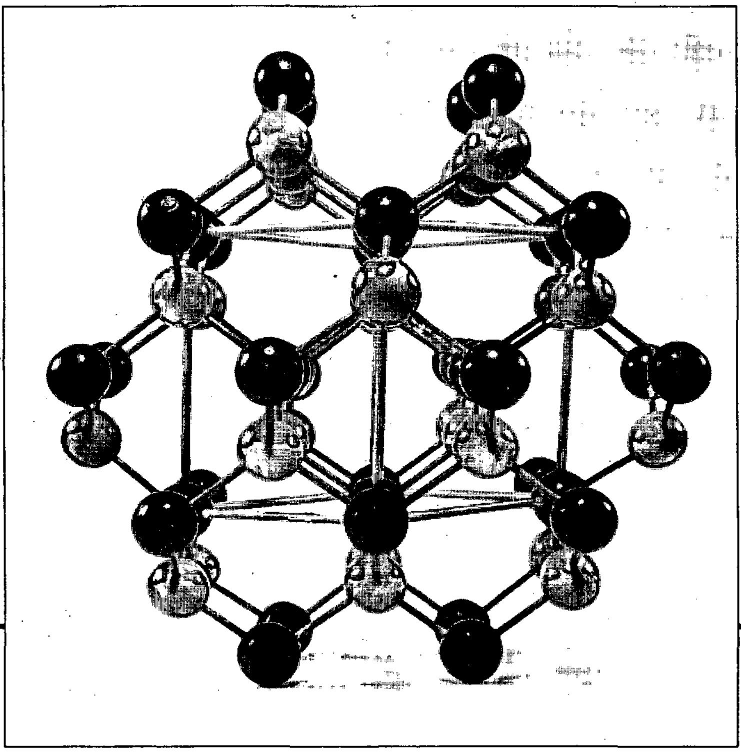
Electronic Materials

Basic Studies of Defects and Impurities in III-V Semiconductors
Bulk Crystal Growth • Thin Films and Interfaces • Interconnects



Center for Advanced Materials
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory • University of California

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Center for Advanced Materials

Annual Report • 1989

ELECTRONIC MATERIALS

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Cover and page 3: View of GaAs crystal lattice in (110) direction. (CBB 791-812)

Basic Studies of Defects and Impurities in III-V Semiconductors
Bulk Crystal Growth
Thin Films and Interfaces
Interconnects/Interfaces

Electronic Materials

The CAM Electronic Materials Program concentrates on scientific problems impeding the development of large scale digital integrated circuits and optoelectronic devices based on gallium arsenide and related III–V semiconductors. Research is focused in four main areas.

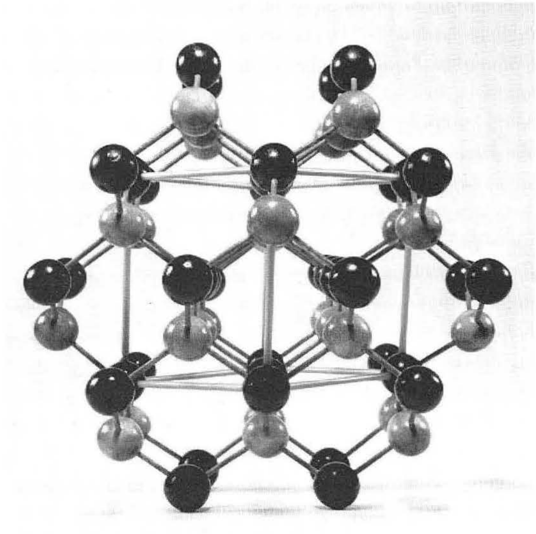
BASIC STUDIES OF DEFECTS AND IMPURITIES IN III-V SEMICONDUCTORS—the study of the structural and electronic properties of defects and impurities and the mechanisms of their incorporation. Many of the properties of compound semiconductors are determined by intrinsic imperfections of the crystal lattice introduced during crystal growth and processing. These must be understood and controlled. Recent results in this area include:

- First measurements of magnetic properties of deep DX donors in $Al_xGa_{1-x}As$ semiconductors. These strongly indicate that the deep donors bind only one electron rather than two.
- Demonstration that native defects play an important role in electron scattering in semiconductor structures. Calculations of the native defect scattering provide for the first unified explanation of an abrupt mobility reduction in heavily, uniformly doped GaAs and in two-dimensional inverted modulation doped GaAs/AlGaAs heterostructures.

BULK CRYSTAL GROWTH—the development of advanced techniques for the growth and characterization of gallium arsenide crystals. Studies rely on the close coupling of crystal growth and the characterization of those crystals in order to gain an understanding of the relationships between growth conditions and the structural and electronic properties of the crystals.

Results achieved during the past year include:

- The vertical gradient freeze growth of GaAs crystals using total liquid encapsulation with B_2O_3 was achieved. The process eliminated detrimental effects of PBN crucible wetting by liquid GaAs.



THIN FILMS AND INTERFACES—the study of dislocations, interfaces and point defect structures in thin films and solid state devices, their origin, processing dependence, and effect on properties. The approach emphasizes high resolution electron microscopy combined with microanalytical techniques. Recent results include:

- Significant reduction of defect densities in MBE-grown GaAs on Si by incorporation of Al; rapid thermal annealing; substrate patterning; use of strained layer superlattice buffers; periodically varying the Ga flux during growth.
- Determination of new phase formation and thermal stability for the Pt/InP metal contact for a range of temperatures.
- Development of a convenient technique for identification of inversion boundaries that arise from growth of a polar film on a nonpolar substrate and of techniques for elimination of such defects for GaAs on Si.

The *ELECTRICAL INTERCONNECTS/INTERFACES* project studies the microstructural, chemical and mechanical features of interfacial adhesion, pertinent to the fabrication and reliability of microelectronic interconnects and packages. These efforts study fundamentals of interfacial decohesion and also seek microstructures that yield more durable interfacial bonds under both sustained and cyclic loading patterns. Related work with thin films addresses microstructures, stress states, degradation and electromigration. Notable results this year include:

- Identification of surprising nature of the plastic deformation field resulting from crack extension at a ceramic-metal interface as reflected by compressive stresses in the crack wake.
- Elucidation of complex delamination mechanism for vapor deposited tantalum thin films caused by tensile and compressive stress components induced by displacive transformation of initial bct phase to the bcc phase. Variants of a simpler mechanism are shown to describe splitting and delamination driven by tensile growth stresses for many other film/substrate combinations.
- New theoretical criteria for damage formation due to interfacial rupture induced by stresses generated while sintering multicomponent materials.

BASIC STUDIES OF DEFECTS AND IMPURITIES IN III-V SEMICONDUCTORS

CARRIER SCATTERING BY NATIVE DEFECTS IN UNIFORMLY AND MODULATION-DOPED SEMICONDUCTOR STRUCTURES

W. WALUKIEWICZ

Many device applications of semiconductors require preparation of very low resistivity, high mobility materials. Charge carrier mobilities in semiconductors are limited by intrinsic, or phonon scattering, and extrinsic scattering processes such as ionized impurity and native defect scattering. In most semiconductors the phonon and impurity scattering mechanisms are now well-understood and their contribution to the total scattering can be evaluated. The scattering by native defects, on the other hand, is difficult to calculate since in general, neither the microscopic nature of the defects nor their concentrations are known in semiconductors.

We have demonstrated that our previously proposed amphoteric native defect model provides the basis to identify the microscopic nature and calculate abundances of the defects incorporated in semiconductors. We have shown that the Fermi level induced enhancement of defect incorporation explains the mobility reduction in heavily, uniformly doped n-type GaAs, as well as in modulation doped GaAs/AlGaAs heterostructures.

Uniformly doped GaAs

According to the amphoteric defect model, the upward shift of the Fermi level in heavily doped GaAs n-type induces an increase in the formation of gallium vacancies. These acceptor-like native defects not only compensate intentionally introduced donors but also act as very efficient carrier scattering centers leading to a reduction of the electron mobility. We have used a variational procedure to calculate the electron mobility in n-type GaAs in the presence of ionized gallium vacancies. For electron concentrations exceeding ~ 5×10^{18} cm^{-3}, the electron mobility is abruptly reduced due to the scattering by native defects (Figure 1). The

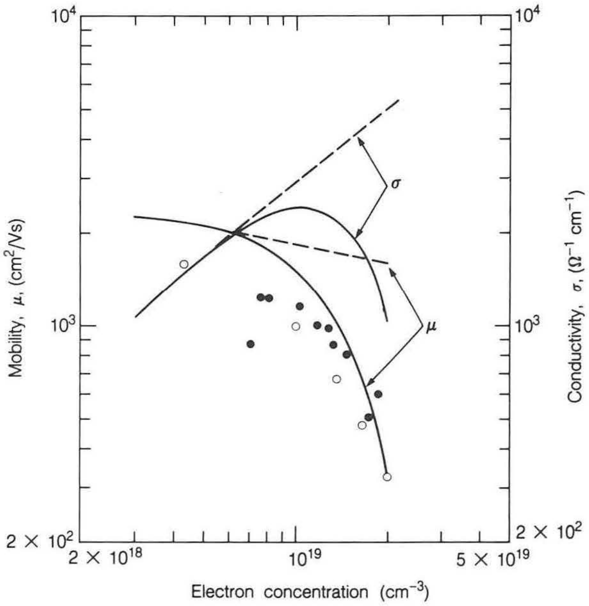


Figure 1
Electron mobility and conductivity in heavily doped n-GaAs. The solid lines represent the calculations in which effects of native defects were included. The broken curves correspond to the standard case in which the concentration of charged scattering centers is equal to the carrier concentration. The points represent typical experimental data. (XBL 885-1895)

reduction of the mobility results in a non-monotonic dependence of the conductivity on the electron concentration. The calculations show that a maximum conductivity of $\sigma \sim 2.5\text{x}10^{-3}\ \Omega^{-1}\text{cm}^{-1}$ is achieved for a carrier concentration of ~ 10^{19} cm^{-3}. This is an important finding since it points out that in order to increase conductivity of n-type GaAs one has to reduce the incorporation of native defects by invoking non-equilibrium incorporation of donor impurities or by inducing agglomeration of the impurities and native defects into neutral complexes which are inefficient as electron scattering centers.

Modulation Doped Heterostructures

In modulation doped heterostructures the donor impurities located in the barrier-forming layer are spatially separated from the 2-dimensional carrier gas in the quantum well. This configuration has been shown to reduce the impurity scattering and lead to ultra-high carrier mobilities. Thus, in n-GaAs/AlGaAs modulation doped heterostructures (MDH) mobilities in excess of 10^7 cm^{-2}/V·s were reported. This is orders of magnitude higher than the mobility observed for the equivalent carrier densities in uniformly doped GaAs. Such high mobilities could be obtained only in so-called normal modulation doped heterostructures (N-MDH), in which undoped quantum well forming GaAs is grown prior to the heavily doped AlGaAs barrier. In inverted-MDHs in which the growth sequence is reversed, i.e., the heavily doped AlGaAs barrier is grown first, followed by growth of the GaAs well, much lower mobilities are observed. Since I-MDHs are better suited for some device applications, a significant effort was directed towards understanding of the physical mechanism responsible for the mobility reduction in these structures. We have shown that the difference between N-MDH and I-MDH lies in much different conditions for native defect incorporation during preparation of these structures. In I-MDH the quantum well is grown in the presence of electrons transferred from the heavily doped AlGaAs. According to the amphoteric defect model such conditions enhance the formation of native defects in the quantum well. We have calculated the Fermi energy induced enhancement of the native defect formation in a typical I-MDH. It is found that although the concentration of the defects is very low, below 10^{15} cm^{-3}, the fact that the defects are located in the quantum well in the vicinity of 2-D electron gas leads to a substantial reduction of the electron mobility. Calculations of temperature dependent electron mobilities of 2-D electron gas in N- and I-MDH can be seen (Figure 2). In I-MDH low temperature mobility is about one order of

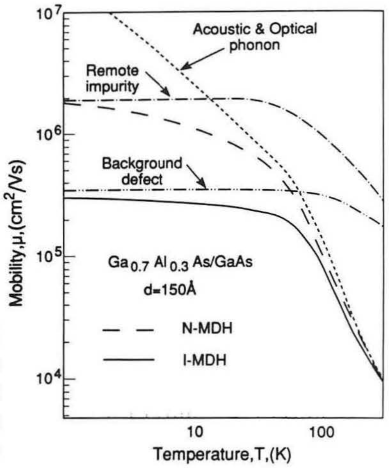


Figure 2

Temperature dependent 2-D electron gas mobilities in $Al_{0.3}Ga_{0.7}As/GaAs$ MDHs with the spacer width d = 150Å. The broken and solid lines represent electron mobilities in normal- and inverted-MDHs, respectively. Contributions to the total mobilities resulting from different scattering mechanisms are also shown. (XBL 899-3381)

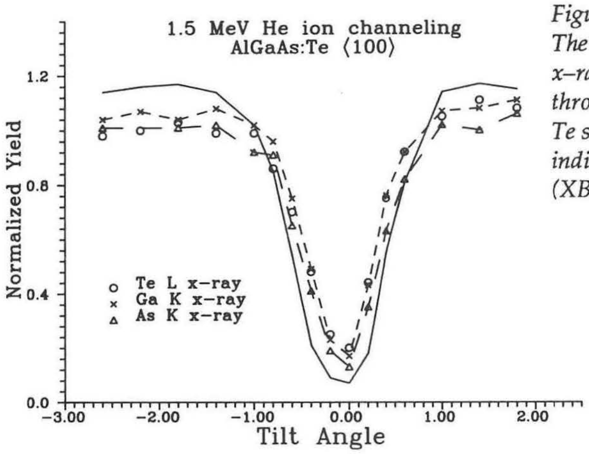


Figure 3
The angular scans of the TeL (o), GaK$_\alpha$ (x), and AsK$_\beta$ (Δ) x-rays and the RBS signal (full line) excited by 1.5 MeV ^{4}He$^+$ through a <100> axis for the AlGaAs:Te sample. Note that the Te scan follows the lattice Ga and As scans almost exactly, indicating good substitutionality of the Te atoms in the AlGaAs. (XBL 897-2727)

magnitude lower than the mobility in an equivalent N-MDH. On the basis of the present model of defect formation we have proposed a strategy to reduce the native defect concentration in I-MDH. This can be achieved by reducing the doping level in the AlGaAs barrier, and by controlling the 2–D electron gas density by the gate voltage applied to the structure.

The model presented is quite general and can be applied to any semiconductor system. We have shown that there is no enhancement of defect generation in p-type GaAs. Therefore, we predict the mobilities of 2–D hole gas in p-type I and N-MDHs.

LATTICE LOCATION OF DOPANT ATOMS IN III-V COMPOUND SEMICONDUCTORS

L.Y. Chan, E.E. Haller, J.M. Jaklevic, K. Khachaturyan, H.P. Lee, W. Walukiewicz, E.R. Weber, K.M. Yu

Unlike elemental semiconductors, compound semiconductors in general exhibit lower dopant activation efficiency. In the case of III-V semiconductors, e.g., GaAs and InP, there exist upper limits to the free electron or hole concentrations. Several theoretical models have been proposed to explain this free carrier saturation phenomenon in compound semiconductors. However, experiments directly addressing the local environments of the dopant atoms in highly doped III-V semiconductors are scarce. It is therefore of particular interest to investigate the substitutionality of dopant atoms in III-V semiconductors which are highly doped with dopant concentrations exceeding the free carrier saturation level. Our experiments were carried out on highly doped III-V compound semiconductors using ion channeling methods. N-type (Sn,Te), and p-type (Zn), as well as isoelectronic (In) dopants in GaAs, InP, and AlGaAs substrates were studied.

Highly doped GaAs:Zn and InP:Zn samples were obtained by closed ampoule diffusion with a Zn solid source. Combined Particle Induced X-ray Emission (PIXE) and ion channeling experiments on GaAs:Zn ($\sim 10^{21}$cm^{-3}) show a high level of substitutionality (≥90%) of the Zn atoms in the GaAs lattice. However, for InP:Zn ($\sim 10^{19}$cm^{-3}) only about 50% of the Zn atoms are found to be substitutional. From the channeling results, the nonsubstitutional Zn atoms are believed to form clusters or precipitates. Detailed electron microscopy studies on these Zn precipitates are planned.

The lattice location of Sn atoms in MBE grown GaAs and Al$_x$Ga$_{1-x}$As

($x \approx 41\%$) layer ($\approx 3.5\ \mu m$ thick) were also studied by ion channeling. The concentration of Sn in the layers was measured by PIXE to be $\approx 6x10^{18}$ atoms cm^{-3}. Results show that the Sn atoms are all substitutional in both the GaAs and AlGaAs layers with the displacement from the Ga or Al site smaller than 0.1Å. An accumulation of Sn atoms near the surface of the layers is detected. This surface Sn accumulation effect is consistent with previous reports on MBE grown GaAs:Sn layers. Te doped $Al_xGa_{1-x}As$ ($x \approx 42\%$) with $N_{Te} \approx 3x10^{18}cm^{-3}$ grown by metal organic vapor phase deposition technique was also studied. The Te atoms are found to be 95% substitutional in the layer with no detectable displacement from the As lattice site (Figure 3).

The results of the Te and Sn doped AlGaAs layers have important implications for theoretical models proposed for the formation of DX centers in AlGaAs. Our channeling results with the AlGaAs:Te system do not contradict the recent theoretical calculations on a group VI dopant, S in AlGaAs, which showed that one of the nearest neighbor Ga (or Al) atoms of the S dopant moves by 1.13 Å into the interstitial position. The S atoms remain substitutional in the As sites. The AlGaAs:Sn results, however, do not agree with any theoretical model that predicts a large lattice relaxation involving the movement of the dopant atoms into the interstitial positions.

BISTABLE DONORS ("DX-CENTERS") IN COMPOUND SEMICONDUCTORS

K. Khachaturyan, E.R. Weber, D.O. Awshalom*, J.R. Rosen*

Many donors in compound semiconductors show bistability, connected with a lattice relaxed, deep ground state. The so-called "DX-Centers" in AlGaAs are the most well-known examples for this class of defect. The bistability has detrimental effects on device performance, such as high noise figures and slow transients.

Recent pseudopotential calculations have suggested that the formation and metastable properties of the DX center can be explained by redistribution of electrons according to the reaction $2D^0 \Rightarrow D^+ + D^-$, where rather than all donors being neutral (D^0), half of the donors have two electrons and become negatively charged (D^-) in a lattice relaxed state, whereas the other half have none and are positively charged (D^+) (negative U model) (Figure 4). According to this model, the DX centers should be diamagnetic.

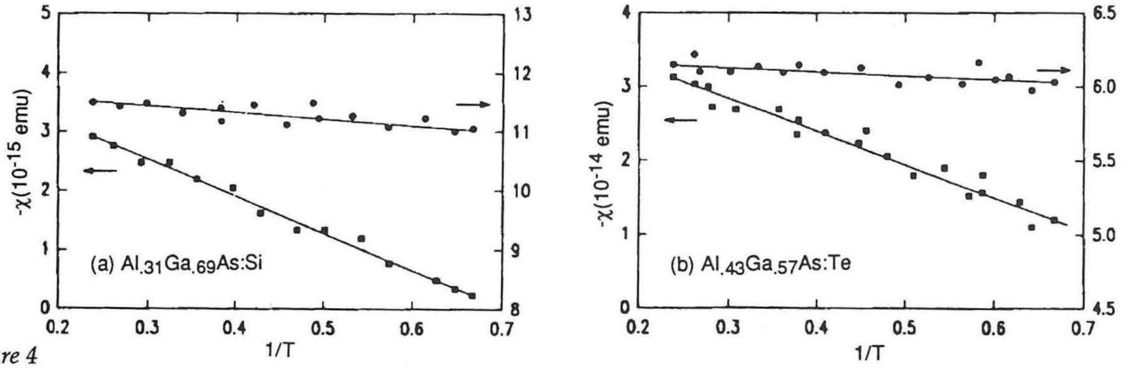


Figure 4

Diamagnetic susceptibilty of the epilayers vs inverse temperature before (squares) and after (circles) illumination in a field of 3.7 G. Illumination was made with 500 μW at E = 1.6 eV. The data offset is arbitrary but the same for the plots before and after illumination. (a) $Al_{0.31}Ga_{0.69-}$ *As: (*$3x10^{17}$*Si). (b)* $Al_{0.43}Ga_{0.57}$*As:(*$3.6x10^{18}$*Te). Before illumination, the paramagnetism of the bistable donors is visible; after illumination, the much weaker paramagnetism of free electrons producing persistent photoconductivity is measured. (XBL 901-121)*

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* IBM Research Center, Yorktown Heights.

This negative U model is in disagreement with magnetic susceptibility measurements on DX centers in AlGaAs and GaAsP. In these measurements, the concentration of paramagnetic defects was determined from the temperature dependent part of the magnetic susceptibility. Using a wide variety of samples with different doping and composition, the concentrations of paramagnetic impurities were found to be equal to the concentrations of DX centers obtained from electrical measurements. The DX center paramagnetism disappeared after 1.6 eV illumination. Even though DX centers are paramagnetic donors, no electron paramagnetic resonance signal can be detected from the ground state of DX centers in bulk GaAsP:S, grown by chloride vapor phase transport. However, a very large EPR signal from the light induced metastable X-like hydrogenic state of S in GaAsP can be seen. The mechanism of lattice relaxation was further investigated by PIXE-channeling measurements on Sn:AlGaAs. No relaxation of Sn atoms from the substitutional site could be detected. This observation is also in disagreement with the negative U model of the DX center.

ARSENIC ANTISITE DEFECTS IN GaAs

M. Hoinkis, E.R. Weber

Arsenic antisite defects (As atoms on Ga sites) in GaAs produce the so-called EL2 midgap donor level, which dominates the electrical properties of semi-insulating GaAs. The EL2 defect shows a characteristic metastability: illumination at low temperatures can bring this defect into a metastable state, bleaching all optical absorption due to EL2 and removing the EL2 energy levels from the band gap. The origin of this metastability is not yet unambiguously established; a model developed independently by two groups of theoreticians suggests the atomic motion of the As atom from a Ga substitutional site into an interstitial position.

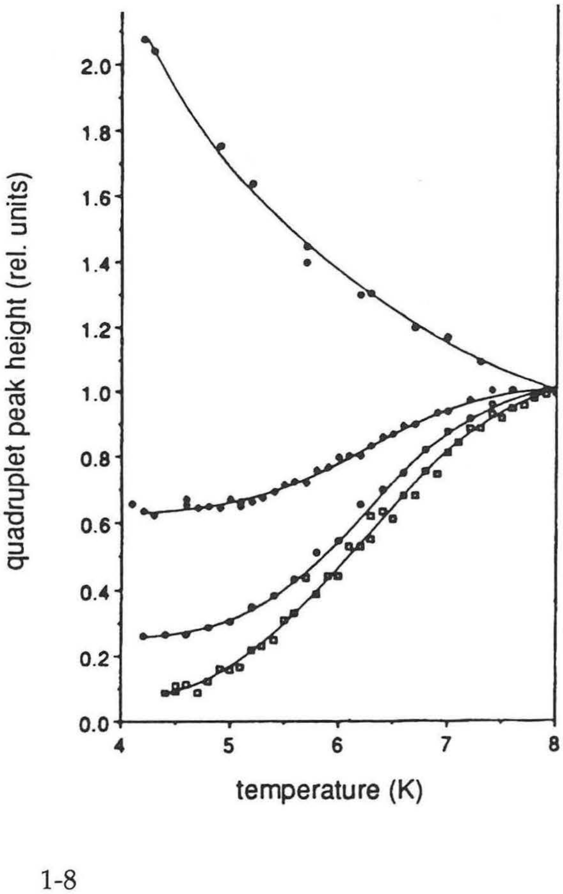

Figure 5
The quadruplet peak height as a function of temperature is shown for the neutron-irradiated sample (filled circle), the optically nonquenchable quadruplet in the plastically deformed sample (diamond), the optically quenchable quadruplet in the plastically deformed sample (open circle) and the quadruplet in the ITC + 800 sample (square). The quadruplet peak height at 8.0K in all four curves has been set equal to unity in order to display their qualitative features. (XBL 901-116)

Our previous work on the characteristic quadruplet Electron Paramagnetic Resonance (EPR) signals of positively charged antisite defects in as-grown GaAs crystals showed unambiguously that these signals arise from the positive charge state of EL2. EPR measurements from plastically deformed or neutron irradiated GaAs showed a strong enhancement of this quadruplet signal. However, the newly formed antisite defects did not show the metastability characteristics of EL2.

Measurements of the temperature dependence of the EPR signals in as-grown, plastically deformed and neutron irradiated GaAs allowed us for the first time to distinguish the EPR quadruplet spectra of arsenic antisite defects producing metastable EL2 levels from those which do not show metastability. Metastable antisite defects show saturation at low temperatures because of long spin-lattice relaxation times indicative for undisturbed defects, whereas antisite defects which are not metastable exhibit less saturation at low temperatures and thus shorter spin-lattice relaxation times (Figure 5). This result allows us to conclude that lattice distortions such as dislocation strain fields can suppress the metastability of antisite defects. Our findings are an important contribution towards the microscopic understanding of the EL2 defect in GaAs.

DONOR EXCITED-STATE SPECTROSCOPY OF ULTRA-PURE GaAs

J. Wolk, E.E. Haller, S.E. Bauser*

The electronic states of defects in semiconductors can conveniently be studied using far-infrared Fourier transform spectroscopy. One of the inherent difficulties in such studies is that there are several effects which broaden the spectral lines produced by transitions between the ground state and excited states. One important cause of broadening is impurity wave-function overlap. This is particularly important in GaAs, where the spatial extent of the donor ground state is $r_d \approx 100$ Å. In order to reduce overlap broadening, spectroscopy is often performed in a magnetic field. This squeezes the donor wave function and therefore reduces overlap, but the magnetic field represents a strong perturbation. If $nr_d^3 << 1$, where n is the concentration of impurities, then impurity wavefunction overlap is no longer important. There are two further types of line broadening, however, that play important roles even in pure samples. Both result from the electric fields due to ionized impurities. These electric fields limit the lifetime of a carrier in a bound excited state, which results in line broadening. The fields also shift the energies of the transitions (Stark shift) and this results in Stark broadening. The effect of Stark broadening is usually not observed in GaAs, because it is less important than lifetime broadening except in extremely pure samples. These last two effects can be diminished by shining "band edge light" on the sample. Light with photon energies just above the bandgap creates large numbers of electrons and holes which can neutralize ionized impurities. To study Stark broadening of shallow donor states we have used ultra-pure n-type GaAs epilayers with mobilities over 200,000 cm^2/Vs at 77 K and electron concentrations ranging from 2-4×10^{12} cm^{-3} grown by liquid phase epitaxy at the Max-Planck-Institute in Stuttgart. These samples are pure enough that no magnetic field is necessary to reduce wavefunction overlap. Stark broadening is expected to be the dominant type of line broadening. We have observed the excited state structure of the shallow donors at high resolution with photothermal ionization spectroscopy using a far-infrared Fourier transform spectrometer. Samples have been studied both with and without band

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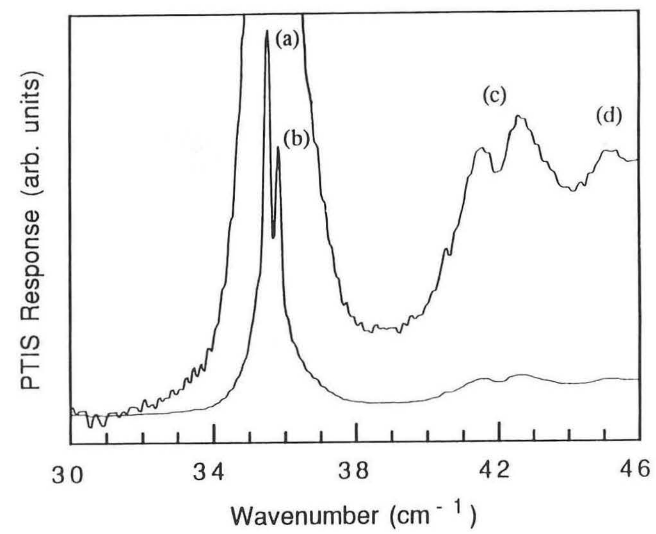

Figure 6
Two different magnifications of the PTIS response of an ultra-pure GaAs epilayer under illumination by band edge light. The features (a) and (b) are the 1s-2p peaks of silicon and sulfur donors, respectively. The double peak of feature (c) is the Stark split 1s-3p peak, and feature (d) is the 1s-4p peak. (XBL 901-122)

edge illumination (BEI). Under BEI, the 1s-2p transitions of S and Si are resolved and have a FWHM as low as 0.025 meV. The extreme narrowness of these lines has stimulated interest in using this material as photoconductors for astronomical observation. Both with and without BEI, the 1s-3p peaks of the two kinds of donors are too broad to be separated. However, the single 1s-3p peak is split (Figure 6). This splitting is in agreement with the theory which predicts that for n odd, the 1s-np transitions would be split by the Stark effect, and that this splitting should increase as $n^{2/3}$. Shining band edge light on the sample reduces the concentration of ionized impurities and therefore should also decrease the splitting. This effect is clearly observed in our study.

BULK CRYSTAL GROWTH RESEARCH

SEMI-INSULATING GaAs SINGLE CRYSTALS

E. Bourret, M. Galiano, R. Mih, J. Guitron

The vertical gradient freeze method for the growth of single crystals of GaAs offers great promise for crystals of improved electrical homogeneity and low dislocation density. Significant research is required before a reliable method can be developed by industry. Defects that still impair the success of this approach are most often generated by nucleation on the crucible wall and/or by very small inhomogeneities in the thermal field. Basic research for identification of the causes for non-reproducibility and means to prevent them has been the recent focus of our program. The electrical properties of the crystals have been further investigated to achieve a complete understanding of the compensation mechanism in these crystals. These studies were conducted for crystals 2" in diameter grown in Pyrolytic Boron Nitride (PBN) crucibles.

PBN crucibles are widely used for the growth of GaAs by the Czochralski technique because they are essentially non-reactive with the GaAs melt, and structurally stable up to high temperatures. In the vertical gradient freeze technique, the crystal grows in contact with the crucible wall. Therefore, in addition to being nonreactive, the crucible must not be wetted by the GaAs melt. Clean PBN is partially wetted by GaAs and reproducible growth cannot be achieved. Total liquid encapsulation with B_2O_3 has been found to be an efficient way to prevent random nucleation

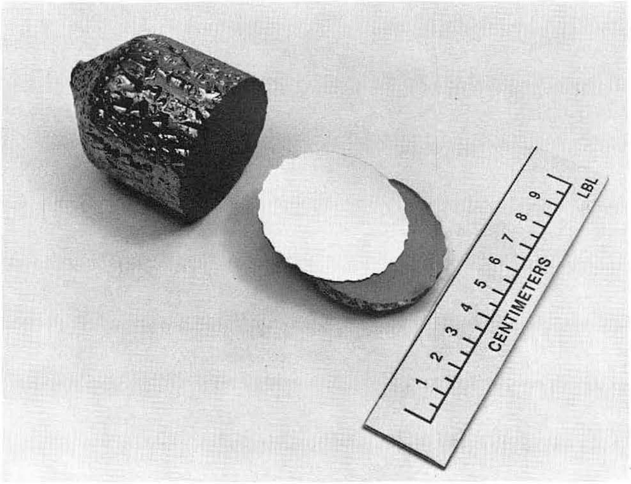

Figure 7
GaAs single crystal 2" in diameter, grown in a Pyrolytic Boron Nitride crucible fully encapsulated in wet B_2O_3 (about 1200 ppm H_2O). Imprints of water vapor bubbles are seen on the surface of the crystal. (BBC 892-899)

Figure 8
GaAs single crystal 2" in diameter, grown in a Pyrolytic Boron Nitride crucible fully encapsulated in dry B_2O_3 (about 400 ppm H_2O). The surface of the crystal is smooth and shiny. (CBB 893-2639)

on the PBN crucible wall. A thin layer of liquid B_2O_3 coats the crucible wall and separates the melt and growing crystal from it. Complete wettability between B_2O_3 and PBN is critical. Two processes have been successfully developed to uniformly coat the crucibles with B_2O_3. The residual water content of the B_2O_3 determines its wetting behavior and the surface morphology of the GaAs crystal. High water content increases wetting; however, at high temperatures, water vapors condense into bubbles which are trapped between the crucible and the GaAs melt. Traces of these bubbles appear on the surface of the crystals (Figure 7). They do not induce nucleation even though the resulting holes can be up to 3 mm deep. When dry B_2O_3 is used, the gas bubbles do not form (Figure 8). The smooth surface is advantageous for reducing grinding waste during further processing.

The effects of liquid encapsulation on the electrical properties of the crystals are being investigated. B_2O_3 can getter silicon, and carbon impurities present in the GaAs melt. The gettering ability also depends on the water content of the B_2O_3 encapsulant. Crystals are being grown using partial encapsulation (coated crucible wall only), total encapsulation (coated wall and B_2O_3 layer on top of the melt), and wet and dry encapsulant. Preliminary results indicate that carbon is efficiently gettered by wet B_2O_3. Due to a shift in the balance of donors and acceptors, undoped crystals with very low residual carbon concentration (less than $10^{14}cm^{-3}$) show a relatively low resistivity in the $5x10^5$ to $5x10^6$ Ω cm range. This point is being investigated further. Semi-insulating crystals of a resistivity up to $3x10^8$ Ω cm and a mobility of about 5500 $cm^2/V{\cdot}s$ have been obtained using dry B_2O_3 as the encapsulant.

n-TYPE Te-DOPED CRYSTALS

E. Bourret, R. Mih, J. Guitron

The vertical gradient freeze technique developed for undoped crystals has been adapted for growth of Te-doped GaAs single crystals. These crystals are used for optoelectronic devices such as high efficiency LED's.

Low dislocation density and uniformity of dopant concentration must be achieved to assume a high yield for device manufacturing. Two-inch-diameter single crystals have been obtained with dislocation densities about 10 times lower than those in crystals grown by the more traditional Czochralski technique. The crystals are doped at 10^{17} Te cm^{-3}. A new experimental setup is being implemented to grow three-inch-diameter crystals, which is the size needed for competitive manufacturing of the devices. Defect formation in three-inch-diameter crystals will be studied in relation to the new growth conditions.

THIN FILMS AND INTERFACES: METAL CONTACTS TO III-V SEMICONDUCTORS

PHASE FORMATION IN THE Pt/InP THIN FILM SYSTEM

D. A. Olson, K. M. Yu, J. Washburn, T. Sands

The stability and reproducibility of metal contacts to compound semiconductor devices are critical for proper device operation. These characteristics generally depend on the formation of interfacial phases and their morphology. Binary phase diagrams (e.g., PtIn and PtP) do not fully describe the nature of possible reaction products in these systems. Phase formation for thin Pt films on chemically cleaned InP substrates has been studied as a function of temperature. This information will be useful in predicting the suitability of this metal for use as a contact material.

InP substrates with 40nm metal films of Pt were encapsulated in SiO_2, and isochronally annealed up to 600°C in flowing forming gas. The composition and morphology of the phases that formed were studied using x-ray diffraction, Rutherford backscattering, transmission electron microscopy, and energy-dispersive spectroscopy.

Results show that the Pt/InP system begins interacting at 300°C. The Pt layer has been completely consumed by 400°C, with a uniform reacted layer indicated by RBS. At high temperatures (between 500°C and 600°C), the reaction products are $PtIn_2$ and PtP_2. The two phases are layered, with PtP_2 at the InP/reacted layer interface. The phosphide phase also shows a preferred orientation relationship with the substrate.

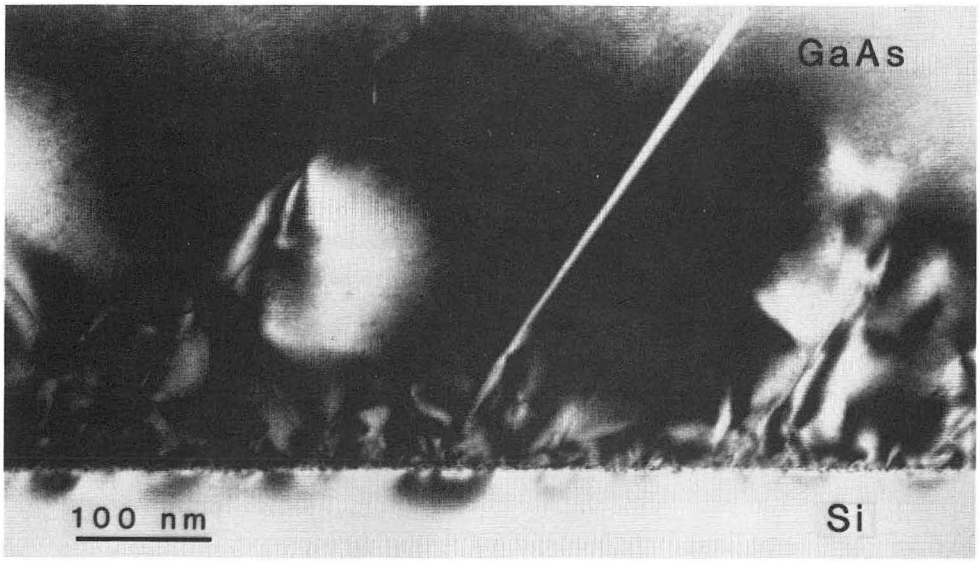

Figure 9
Cross-section TEM micrograph showing an inversion boundary. The boundary is faceted on {110} even though its average orientation is near that of the microtwin, {111}, to its right. (XBB 894-9410)

CHARACTERIZATION OF GaAs EPITAXIAL LAYERS

GaAs/Si Heterostructures

Z. LilientalWeber, J. Washburn

Recent developments in the field of GaAs/Si heteroepitaxy have been spurred by the possibility of combining high-speed GaAs material with well-established Si technology, thus gaining better thermal conductivity, higher fracture toughness, smaller weight and larger diameter wafers offering the possibility for integration of optoelectronic and digital devices. Unfortunately, many problems are encountered in growth of GaAs on Si, such as growth of polar crystal on nonpolar substrate, lattice mismatch of 4.1%, and a considerable difference in thermal expansion coefficient between epilayer and substrate. As a consequence of these problems, the quality of GaAs epilayers on Si substrates is very poor. The dominant defects in the GaAs epilayer are misfit dislocations formed at the interface with Si, stacking faults, microtwins and threading dislocations which propagate through the epilayer, and inversion boundaries (IBs).

Inversion Boundaries

Z. Liliental-Weber, J. Washburn, H. Kroemer*

Presence of inversion boundaries was confirmed by transmission electron microscopy (TEM) using the convergent beam electron diffraction method (Figure 9). Electrical and optical properties of the boundaries were investigated using cathodoluminescence, electron beam induced current and scanning deep level transient spectroscopy (in cooperation with Hewlett-Packard). It was found that IBs reduce near-bandgap luminescence and minority carrier lifetime. In contrast to the recombination at threading dislocations in GaAs films, the nonradiative recombination process at IBs is not due to deep traps but rather to a continuum of bandgap states. Drastic changes in IB densities were observed upon changing the growth parameters. After postgrowth annealing IB-free layers even as nominal (100) substrates were found.

Reduction of Defect Density

Z. Liliental-Weber, J. Washburn, S. Wang*, H. Kroemer*, P. Umeno*, H. Lec*

Several methods have been found for reduction of overall defect density. The defect density was determined by TEM. It was found that the cleaning of the Si substrate before GaAs growth played a crucial role in the formation of new defects at the interface (Figure 10). The work showed that high

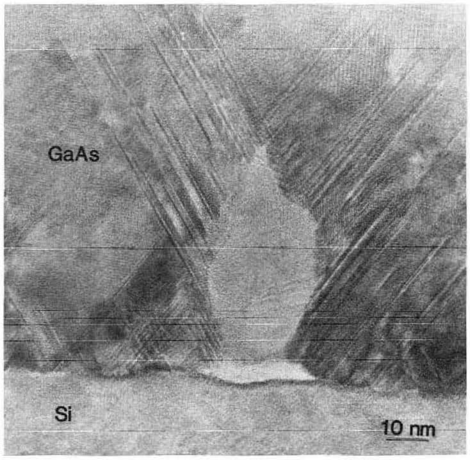

Figure 10
High-resolution image of the GaAs on Si interface taken in {110} projection. Note that interface contamination is the source of polycrystallinity and other defects. (XBB 870-3155)

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*University of California, Santa Barbara temperature substrate annealing steps currently used should be avoided. Such high annealing temperatures result in roughening of the Si surface and are incompatible with patterned epitaxy. A promising approach is the use of Ga reduction (proposed by H. Kroemer) or growth of ternary Al-containing buffer layers (in cooperation with Prof. Umeno's group). It was shown that addition of small amounts of Al results in perfect two-dimensional growth (Figure 11). This may be due to the high affinity of Al for oxygen, allowing growth of Al-containing compounds on both clean and contaminated surface areas.

Another promising method has been migration-enhanced epitaxy in which the Ga and As flux is alternated or modulation-enhanced epitaxy with continuous As flux but intermittent Ga flux. It was demonstrated that this kind of growth enhances two-dimensional growth and results in very narrow PL lines (in cooperation with H. Lec from S. Wang's group). Post-annealing of GaAs on Si was also shown to improve the quality of the GaAs layer.

Noticeable improvements in the quality of GaAs/Si epilayers grown by MBE were observed after rapid thermal annealing (RTA) at 800°C for 10 seconds by the capless close proximity method in a commercial heat-pulse furnace. The density of stacking faults after this treatment was very low, possibly because of the rapid cooling rate compared to furnace annealing. RTA was found to be beneficial for the removal of stacking faults, but it inhibits stress relief; this was evidenced by cracking of GaAs epilayers. The heterointerface was also observed to be more undulated after RTA, compared to the as-deposited samples. Independent electrical measurements of devices after RTA showed noticeable improvement for forward and reverse bias characteristics. Leakage currents were reduced by more than two orders of magnitude after this treatment.

Patterned or island growth was also shown to be effective for reduction of defect densities. Growth of a mismatched heteroepilayer with a network of misfit dislocations confined to the interface and no threading dislocations in the epilayer requires glide of the threading "arms" of misfit dislocations across the whole wafer without being blocked by other threading dislocations. It is much easier to achieve this goal if the growth

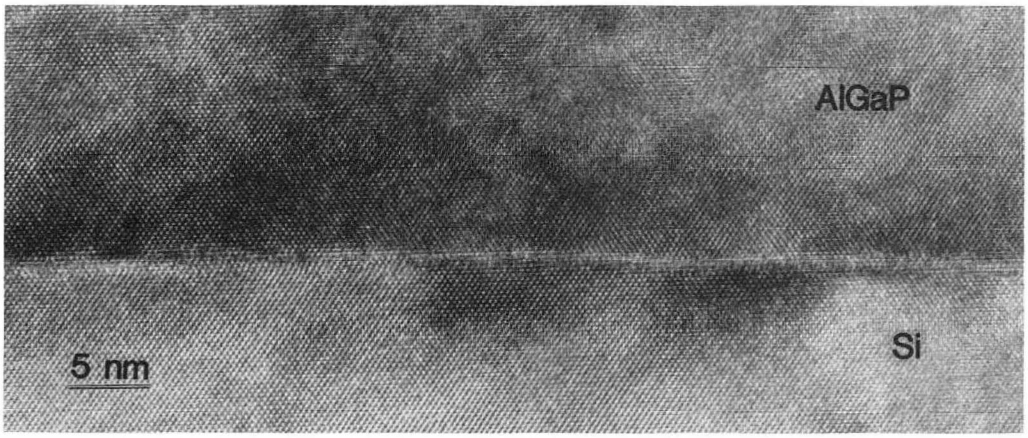

Figure 11
For growth of GaP on Si it has been shown that addition of small amounts of Al promotes perfect layer by layer growth resulting in very few defects compared to the more typical island growth mode. (XBB 894-3163)

areas are confined to small parts of the substrate, e.g., by patterning lines or mesas on the substrate.

Growth of GaAs on Si through openings in an oxide or nitride mask was studied. Above the SiN mask the GaAs was polycrystalline, but in the open areas where the nitride was removed, monocrystalline GaAs was found with much lower dislocation density than in typical two-step growth. The stacking fault density was also much lower in the entire pattern, inceasing only at the border with the nitride. This decrease in defect density was probably connected with stress released at the periphery of patterns in the polycrystalline areas. Post-growth annealing at 850°C in arsenic overpressure resulted in significant grain growth in the polycrystalline GaAs overgrown on the amorphous oxide or nitride, and elimination of the defects at the transition region between polycrystalline and single crystal growth. An increase of Hall mobility of 30% was achieved in these annealed samples.

Another promising method for obtaining device-quality epitaxial GaAs which was investigated is the use of strained-layer superlattices (SLSLs), which increase dislocation annihilation by causing them to bend into the strained interface.This investigation found that by application of SLSLs of InGaAs/GaAs with 10nm-thick periods grown on Si(211), blocking of dislocation propagation occurred almost entirely at the uppermost interface between the strained layers and the final thick GaAs layer. It was concluded that reduction of dislocation density was only weakly dependent on the number of periods of the strained-layer superlattice. InGaAs/GaAs superlattices proved to be more efficient in dislocation bending than InGaAs/InGaP SLSLs. Because it was recognized that only the upper interface of the SLSL was efficient in dislocation bending, packages consisting of 5 periods of SLSL (InGaAs/GaAs) were tried. Indeed, each set of SLSLs was found to cause dislocation bending, but in some areas these dislocations were also formed at the lower interface between the buffer layer and the SLSL. On the average, the dislocation density in this sample was in the $\sim 2 \times 10^7/\text{cm}^2$ range, which is very low taking into account that all misfit dislocations in the GaAs grown on Si(211) are 60° dislocations with Burgers vectors inclined to the interface.

Further defect reduction strategies, such as thermal cycling during growth, post-growth annealing, and the use of strained-layer superlattices, need to be optimized. Combined use of some of these methods together with the possibilities of pattern epitaxy appear to make high-quality growth of lattice mismatched heterostructures such as GaAs/Si achievable. Only such optimized low-defect material will allow practical use of the numerous devices possible with this technology, including minority carrier devices, the feasibility of which have already been demonstrated in GaAs/Si heteroepitaxy.

Ultra-High-Speed Metal-Semiconductor-Metal Photodetectors

Z. Liliental-Weber, J. Washburn, J. Mariella*

In some applications a high defect density can be an advantage. The possibility of using GaAs grown on Si to fabricate ultra-high-speed metal-semiconductor-metal (MSM) photodetectors was investigated. Optimum performance of such detectors requires a combination of high sensitivity with short minority carrier lifetime. In earlier work, neutron-damaged GaAs has been used in MSM devices but sensitivity was sacrificed for the

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* Lawrence Livermore National Laboratory.

increased speed. Our approach was to use molecular beam epitaxy (MBE) to grow GaAs on Si substrates. The planar thin film geometry allows good carrier mobility parallel to the GaAs/Si interface, while the expected high density of crystal defects at this interface could reduce the carrier lifetime. Two kinds of samples were compared: GaAs grown on a 15 Å Si epilayer grown on GaAs, and GaAs grown at low temperatures (300 °C) on conventional Si substrates. It was shown that the GaAs epitaxial layer grown on a thin Si layer had reverse polarity to the substrate (antiphase relation), which is consistent with preferential bonding of As to Si. The density of defects formed in the GaAs grown on a conventional (001) Si substrate was higher compared to the GaAs/Si/GaAs(001) structure and was found to correlate with increased device speed.

GaAs Grown on InP

Z. Liliental-Weber, J. Washburn

Characterization of 3 µm-thick GaAs films grown on (100) InP substrates by MBE employing different buffer layer structures during the initial deposition was performed. Three buffer layer structures were under study: 1) GaAs layer grown at low temperature; 2) GaAs layer grown at low temperature plus two sets of $In_{0.08}Ga_{0.92}As$/GaAs strained layer superlattices and 3) a transitional compositionally graded $In_xGa_{1-x}As$ layer between the InP substrate and the GaAs film. After the buffer layer deposition, the growth was continued by conventional MBE to a total thickness of 3 µm for all samples. From the 77K photoluminescence (PL) measurement, it was found that the sample with SLSL layers had the highest PL intensity and the narrowest PL line width. Cross-sectional TEM studies showed that the SLSL was effective in reducing the propagation of threading dislocations and explains the observed superior optical quality from the PL measurement. The effect of InGaAs/GaAs SLSL in bending threading dislocations was thus applicable to GaAs/InP heteroepitaxy as in the case of other heteroepitaxial systems such as GaAs/Si, although the average lattice constant of SLSL is not matched with either the films or the substrates.

MBE GaAs Grown at Low Temperatures on GaAs Substrate

Z. Liliental-Weber, E. R. Weber, J. Washburn

GaAs layers grown by MBE at very low substrate temperatures have gained considerable interest as buffer layers for GaAs metal-semiconductor field effect transistors (MESFETs) due to high resistivity and excellent device isolation. However, the structure and the electronic properties of such layers have not yet been investigated in detail. We have studied unannealed low temperature (LT) MBE layers grown at 200 °C using TEM, analytical TEM, x-ray diffraction, the Hall effect, and electron paramagnetic resonance (EPR) techniques.

For TEM studies, cross-sectional samples in the (110) orientation were prepared from unannealed LT GaAs MBE layers grown on a Si LEC GaAs substrate at 200 °C. Bright and dark field micrographs were taken in the two-beam condition for the (200) reflection, which is the most sensitive to changes in the structure factor. As reported previously, contrast is found at the interface between GaAs substrate and epilayer. This contrast suggests either different stoichiometry of the LT layer as compared with the substrate or stress built into the layer during the low-temperature growth. Analytical electron microscopy showed ~1% to 1.5% excess arsenic for unannealed LT GaAs MBE layers in comparison with the substrate. Moreover, analytical TEM studies revealed nonuniformity of the distribution of excess arsenic within the same layer, varying between 1% and 1.5%. This is a two order of magnitude higher deviation from stoichiometry towards arsenic-rich composition than ever observed for other GaAs crystals.

CHARACTERIZATION OF STRAINED InGaAs SINGLE QUANTUM-WELL STRUCTURES

K.-M. YU, K.T. CHAN[*]

Pseudomorphic strained single quantum well (SSQW) structures of $In_xGa_{1-x}As$ on both GaAs and InP substrates have demonstrated excellent performance in modulation-doped field effect transistors and optoelectronic devices. Since device characteristics are strongly affected by the SSQW properties, such as strain and well thickness, it is important to be able to measure those parameters in order to understand their correlation with device performance.

$In_xGa_{1-x}As$ SSQW structures on GaAs substrates were investigated using ion beam methods. The SSQW's were fabricated by molecular beam epitaxy[†]. The composition and well size were measured with combined Rutherford backscattering spectrometry (RBS) and particle induced x-ray emission (PIXE). The crystalline quality of the SSQW was also investigated using ion channeling methods (Figure 12).

For an InGaAs layer below the critical thickness, the lattice constant perpendicular to the layer will be increased due to the Poisson effect. This distortion in the lattice parameter of the film can be detected when the substrate is aligned with the ion beam at a tilted axis. We have investigated this lattice strain in InGaAs SSQW structures by ion channeling combined with PIXE and RBS across the <112> axis. The In content in the SSQW's was also evaluated from the lattice strain measured according to Vegard's law. The In fractions measured this way agree very well with those obtained by RBS and PIXE.

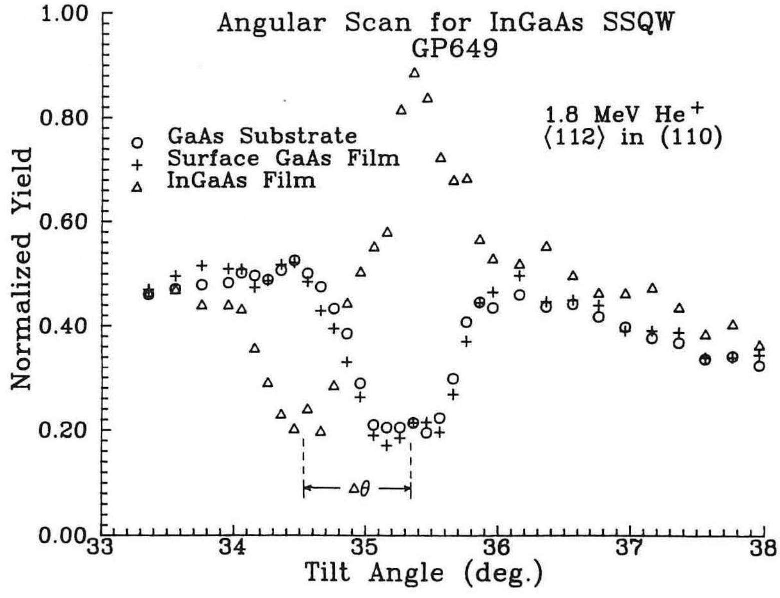

Figure 12
The angular scan profiles of the GaAs substrate, the GaAs capping layer, and the $In_xGa_{1-x}As$ layer obtained by a 1.8 MeV $^4He^+$ beam across the {112} axis along a (110) plane. Note that the profiles for the GaAs substrate and the capping layer follow exactly, indicating that the capping layer is grown without observable strain on the In_xGa1−x As layer. The dip in the $In_xGa_{1-x}As$ profile deviates from that in the substrate profile by Dq=0.84, which arises from the strain in the $In_xGa_{1-x}As$ layer. (XBL 896-2740)

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[*] CAM Industrial Fellow, Hewlett-Packard Corporation, Microwave Technology Division.

[†] Hewlett-Packard Corporation, Microwave Technology Division.

The structural properties of the InGaAs SSQW's grown by MBE with various growth parameters were studied by the ion beam methods. Results indicate that there is little variation of In mole fraction and SSQW thickness by varying the substrate temperature T_s in the range of 375 to 510°C during film growth. Ion channeling also revealed that the crystal quality of the SSQW degrades as T_s increases. This degradation in crystal quality is accompanied by a decrease in electron mobility measured by Hall effect. The electrical and structural degradation of the SSQW due to high T_s (~510°C) can be prevented by increasing the As_4/Ga beam equivalent pressure ratio during MBE growth. More detailed studies on the relationship between MBE growth parameters and the electrical as well as structural properties of SSQW structures on GaAs are underway.

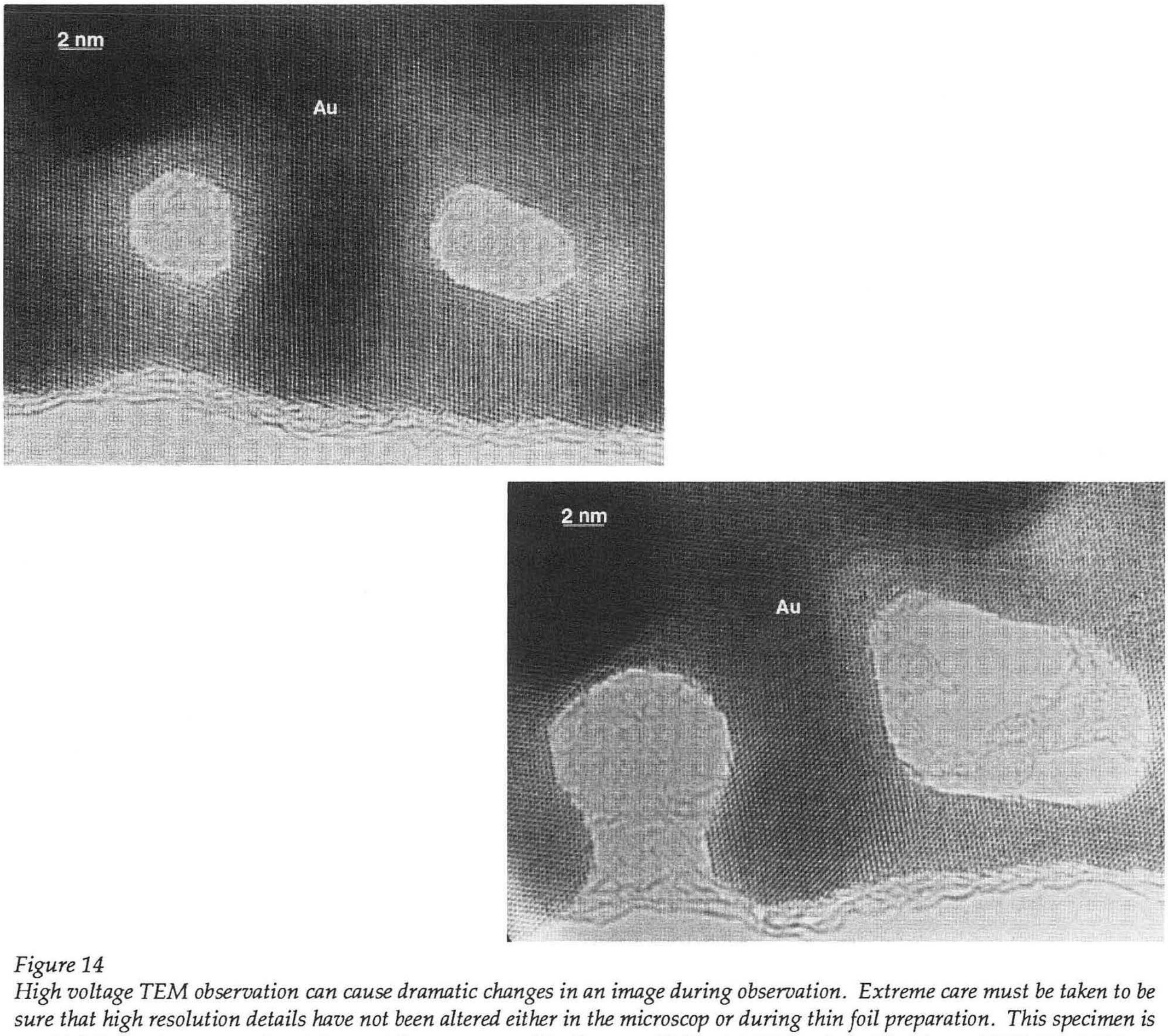

Figure 14
High voltage TEM observation can cause dramatic changes in an image during observation. Extreme care must be taken to be sure that high resolution details have not been altered either in the microscop or during thin foil preparation. This specimen is a gold foil showing successive pictures of the same area. Washburn and Liliental–Weber, J. de Physique. *(XBB 893-2487)*

INTERFACIAL FRACTURE ENERGIES

R. Cannon, A. Fox

The events associated with fractures along interfaces between copper thin films and glass substrates were investigated by X-ray diffraction and transmission electron microscopy (TEM). In as-bonded films, the Bragg diffraction lines were shifted and broadened (relative to strain-free Cu) due to residual in-plane tensile strains arising from differences in thermal contraction after bonding; TEM studies showed that these stresses had been relieved somewhat by dislocation densities in the Cu as high as $10^{10}cm^{-2}$ for Cu/SiO_2. The passage of an interfacial crack led to a marked reduction in line shift and a slight reduction in the broadening. Thus, dislocations generated by the fracture "plasticially relaxed" the stresses in the as-bonded Cu by superposing a compressive component onto the pre-existing in-plane tensile strains. This dislocation generation was confirmed using TEM. The results indicated that greater numbers of dislocations were generated in the Cu by fracture along interfaces of higher toughness (i.e., bond strength). These stresses are opposite in sign to those expected from a ductile crack in a metal and provide a basis for developing models for the bond rupture and deformation near an advancing interfacial crack.

Fracture energies of such interfaces and others designed to have enhanced fracture energy by virtue of near-interfacial microstructures that induce crack-tip shielding are being studied in conjunction with R.O. Ritchie of the CAM Structural Materials Program. The fracture resistances, under tensile and mixed mode loading, and under static and cyclic loading, pertain to studies of thin film adherence and reveal methods to increase the integrity in such interface dependent applications.

FRACTURE AND DELAMINATION OF THIN FILMS

R. Fisher, J.-Z. Duan, A. Fox

Studies of vapor-deposited chromium films on glass, silicon or polymer substrates, with and without prior deposition of a thin copper layer, have been extended to tantalum. Differences in microstructures, stress states and the events leading to film cracking and spalling have emerged. A very fine dendritic structure forms during Ta deposition, rather than the aligned columnar structure of Cr films. This trend with homologous deposition temperature, which for Ta on a room temperature substrate is even lower than for Cr (0.084 vs 0.127), coincides with trends seen elsewhere and here for Cr films. In Cr, the columnar grains are finer, more branched and less textured crystallographically when deposited on Si than on glass, apparently owing to less film heating with the more conductive Si. More importantly, vapor-deposited Ta forms initially as a bct phase and then transforms to the denser bcc phase at a critical thickness of roughly 100 nm that depends somewhat upon substrate features.

Study of various film/substrate combinations has yielded a coherent understanding of splitting and delamination for films with internal tension and of the several crack morphology regimes, dictated by the relative interfacial, film and substrate fracture resistances that these exemplify. Extant fracture mechanics models plus film stresses and stress gradients deduced by x-ray diffraction are used to compute driving forces for the various cracks; these are compared with interfacial fracture energies from macroscopic tests for interfaces that fracture and with bulk fracture energies where appropriate. For Cr deposition, tensile "growth" stresses become high enough as the thickness increases to crack the film into small "islands." If the Cr exceeds a critical thickness, spontaneous delamination occurs as cracks spread from the splits. The delamination can be at an interface that is less tough than the substrate, e.g., Cr with a Cu prelayer on glass, or fully within the substrate several film thicknesses below the interface, as occurs for Cr/Si. A common, intermediate situation, e.g., Cr or Ta on glass, in which the delaminating crack first spreads along the interface and then penetrates into the substrate, results if the environmentally induced subcritical crack velocity curves for the interface and substrate cross, as found from macroscopic tests on Cu/glass interfaces of suitable purity. Several issues, such as the extent that splitting cracks penetrate into the substrate deeper than the delamination cracks, and the role of shear loading on interfacial fracture energies, are subjects of ongoing analysis.

More complex stresses occur in Ta films due to anisotropic strains associated with the martensitic transformation that can yield failure modes representative of both tensile and compressive stress components when a Cu sublayer is present and adhesion is reduced. For more adherent films, as on bare glass, the transformation is surpressed and significant cracking does not occur until the film is thicker and stresses are dominantly tensile, leading to failure modes described above.

INTERFACIAL WETTING AND RUPTURE DURING SINTERING

R. Cannon, C. Carter

Mechanisms causing damage, by interfacial rupture, during fabrication by sintering of heterogeneous materials, such as multicomponent electronic packages, are being analyzed theoretically. To establish concepts, a linear row of sintering particles has been used that permits highly precise treatments based on previously computed, equilibrium grain shapes. Under constraint, mechanical forces develop which can induce rupture by a process analogous to differential densification in a three dimensional compact. The morphological stability analyses address both thermodynamics and kinetics and, thereby, apply to a wide range of constraining conditions. Results delineate loads under which the rod would either extend or shrink. The new feature is that regimes were identified wherein strain would tend to be homgeneous or susceptible to localization leading to grain boundary fracture. Moreover, much greater loads can apparently be borne without damage, for certain small displacements, than are predicted from solely thermodynamic treatments.

Equilibrium shapes were also calculated for axisymmetric fluid bridges between two solids having arbitrary radii of curvature and contact angles. Results are being used to assess the stability of powder compacts containing liquids, as occur during liquid phase sintering and drying of powder compacts. They also pertain to tribology issues involving the interaction of a protrusion (even an STM tip) with a substrate in the presence of a lubricant or condensate fluid.

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AWARDS

- David Bliss received an IBM Fellowship.
- Amy Moll received a Fellowship from the Office of Naval Research.

INDUSTRY INTERACTIONS

Industrial Fellows

- Grant Elliot, Hewlett-Packard Optoelectronics Division, collaborated on a study of the growth of n^+ type GaAs single crystals in vertical gradient freeze furnaces. The focus is on low defect density crystals for optoelectronic applications. The furnaces in use were donated to CAM by Hewlett-Packard.
- Kam T. Chan, Hewlett-Packard Microwave Technology Division, is collaborating with the Semiconductor Processing and Characterization Project on studies of structural defects in epitaxially grown GaAs and GaInAs strained heterostructures and on investigations of defects in GaAs grown at low temperatures.
- Roy Crooks, Rockwell International Science Center, is working with the Interconnects Project on the adhesion of thermal barrier coatings for advanced aircraft. The focus of the work is on mechanisms to limit delamination and spalling during supersonic flight.

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Contracts

- IBM provided support for the Interconnects project for research on ceramic-metal interfacial fracture resistance and thin film adhesion.

Gifts

- Gifts from Bertram Laboratories and AKZO Corporate Research America, Inc., to the Semiconductors Project were used to intensify research in the area of crystal growth by the vertical gradient freeze method.

Technology Transfer

- A patent application was filed for a process to prepare non-melting surface of pyrolytic boron nitride crucibles for vertical Bridgeman growth of GaAs.

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