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Electronic Materials Engineering and AFOSR have demonstrated a new semiconductor materials technology for electronic and optoelectronic device applications: the Supermatrix Semiconductor (SMS). SMS makes possible the 3-dimensional superlattice and a new method for engineering the properties of semiconductor materials through the synergy of 3-dimensional microstructural ordering. A CrGaAs SMS has been produced in ingot form (2" long and 1" diameter) exhibiting a periodic rod-matrix microstructure over wafer-scale distances. Electronic, optical, and structural properties were characterized by PPL, SIMS, RBS, Auger, and x-ray diffraction and correlated to conditions of solidification. It was demonstrated that the cubic degeneracy of GaAs in the CrGaAs matrix is lifted as a result of anisotropic stress and leads to birefringence. Advances in practical processing of SMS materials, including polishing, have also been achieved to support future device development activities.

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by

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ABSTRACT

Electronic Materials Engineering and AFOSR have demonstrated a new semiconductor materials technology for electronic and optoelectronic device applications: the Supermatrix Semiconductor (SMS). SMS makes possible the 3-dimensional superlattice and a new method for engineering the properties of semiconductor materials through the synergy of 3-dimensional microstructural ordering. A CrGaAs SMS has been produced in ingot form (2" long and 1" diameter) exhibiting a periodic rod-matrix microstructure over wafer-scale distances. Rods were identified as CrAs, and the matrix, GaAs. Packing of the rods is hexagonal along the direction of solidification and the average density was about 5 million per square centimeter. Cause-effect relationships between material properties and microstructural defects were correlated to conditions of solidification. Results of Hall Effect measurements, polarized photoluminescence, and x-ray analysis, and secondary electron microscopy highlighted the anisotropy of material properties. Most important, the combination of materials in the supermatrix leads to anisotropic stress removing the cubic degeneracy of the GaAs and creating a biaxial optical material. Biaxial GaAs offers great potential as a nonlinear optic material. Advances in practical processing of SMS materials, including polishing, have also been achieved to support future device development activities.

Table of Contents

1.0 Introduction

Major advances in Air Force Systems such a C3I require ultra-high speed electronic and photonic devices for collecting, transmitting, storing, and analyzing vast amount of information in short periods of time. New materials with engineered quantum optoelectronic, nonlinear optic, electro-optic, and photorefractive properties are required to fabricate advanced devices.

Launched by EME in late 1990 with the support of AFOSR, the "Dynamics of Supermatrix Semiconductor Growth" Program was a unique and original effort to develop a new class of semiconductor materials to meet Air Force requirements. A specific objective of the program was to demonstrate a 3-dimensionally ordered, multi-phase semiconductor with regular microstructure over wafer-scale distances. A long-term goal was to open a broad new horizon of semiconductor materials research and device development.

Major objectives of the program were achieved during the previous reporting period.

A CrGaAs SMS consisting of a periodic, 3-dimensional array of CrAs rods in a GaAs matrix was demonstrated. The regular microstructure extended throughout ingots 2" long and 1" in diameter. EDAX (energy dispersive x-ray analysis) compositional analysis confirmed the identity of the materials. Microscopic investigations of axial and cross-sections showed hexagonal packing of the rods along the direction of solidification at a density of about 5 million per square centimeter.

Non-uniformities and defects in the microstructure, including branchin terminations, coalescence, and spacial variations of rod diameter were identified and correlated to conditions of solidification.

Electronic transport properties of the material were evaluated by Hall Effect measurements. These results were the first to show anisotropy of the material. Samples were prepared such that the magnetic field was parallel or perpendicular to the direction of rod alignment. Electron mobility parallel to the rods was found to be almost four times that in the perpendicular direction, while the apparent electron concentration in the perpendicular samples was greater by about a factor of four. These results were explained in terms of the interaction of Lorentz forces and the interphase boundary surfaces.

Finally, three new SMS materials systems with high potential for extended microstructure were discovered, including Ge/ZnGeP(2), Ge/GeAs, and SiGaAs. The diphosphide system is of particular interest due to the superior nonlinear optical properties of the ternary.

2.0 Progress

Based on the dramatic progress of the previous reporting period, work proceeded in three areas during the current reporting period; (2.1) Characterization; (2.2) Polishing Technology; (2.3) Improvements in SMS Processing. Results are presented and discussed in this section. In addition, the laboratory was moved to a new and larger facility during the current reporting period, as summarized in Section 2.4.

2.1 Characterization

Characterization of SMS materials during this reporting period focused on the CrGaAs system. Properties of both the surface and the bulk were investigated. Surface properties were evaluated in support of the polishing improvement activity, which is described in Section 2.2. Bulk properties were characterized by polarized photoluminescence (PPL), secondary ion mass spectrometry (SIMS), Raman backscattering (RBS), secondary electron microscopy (SEM), and x-ray diffraction.

2.1.1 Polarized Photoluminescence

Results of PPL analysis provided the most compelling evidence of the synergy of microstructural ordering whereby the SMS exhibits a new property not inherent to the respective components.

PPL of parallel and perpendicular samples were determined at 4.2 K. Two important features were observed. First, PPL of perpendicular samples were highly polarization dependent, whereas that of parallel samples was polarization independent. For example, PPL spectra of perpendicular material taken at two different orthogonal orientations of the plane of polarization of the laser with respect to the sample exhibited a factor-or-2 difference in intensity, as shown if Fig. 1. Similar spectra taken on parallel material were isotropic.

Second, a comparison of spectra of parallel and perpendicular samples demonstrated a shift of about 10 meV in peak position, as shown in Fig 2.

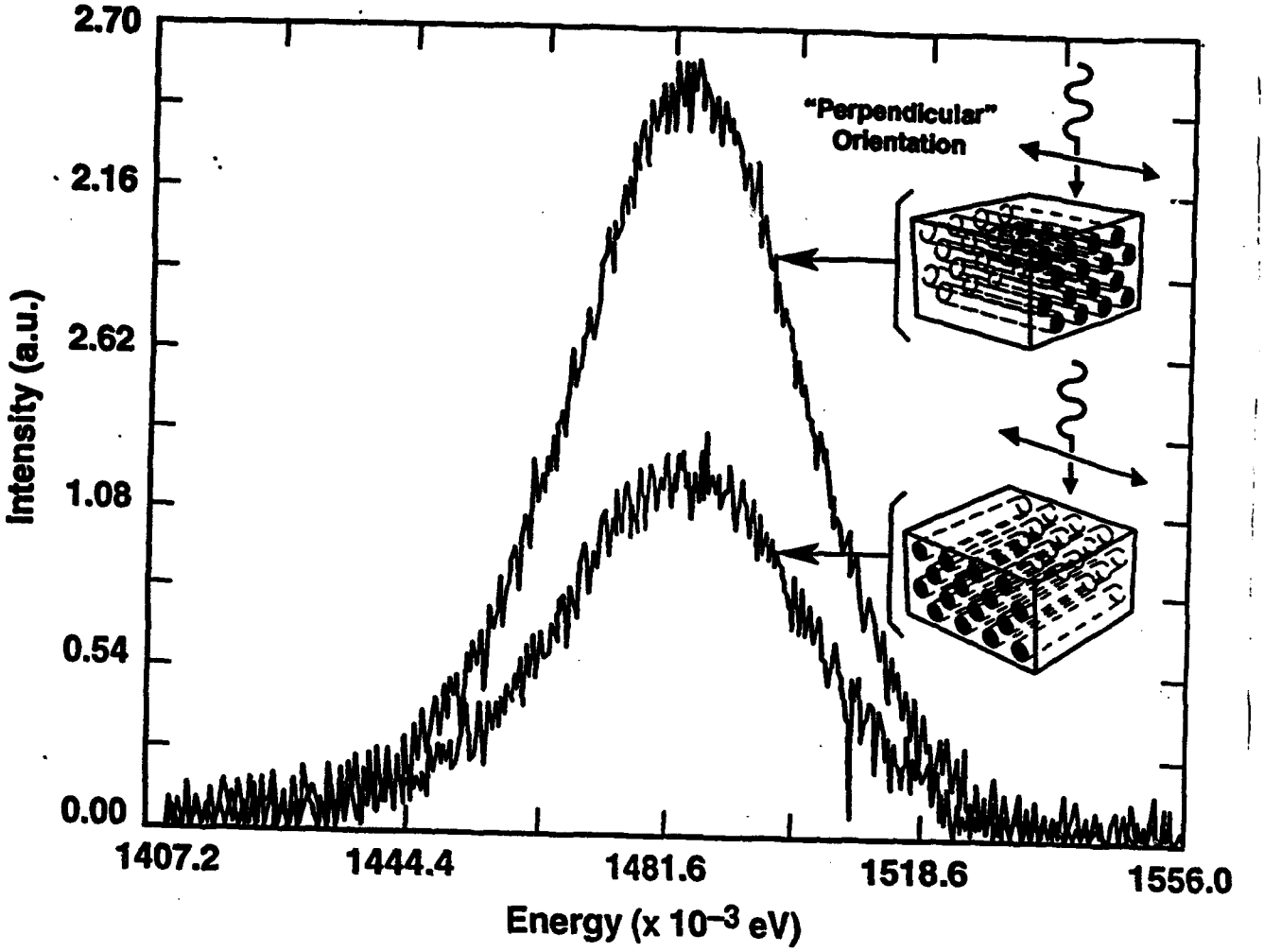

Fig. 1. PPL spectra of "perpendicular" CrGaAs SMS showing polarization dependence of PL intensity.

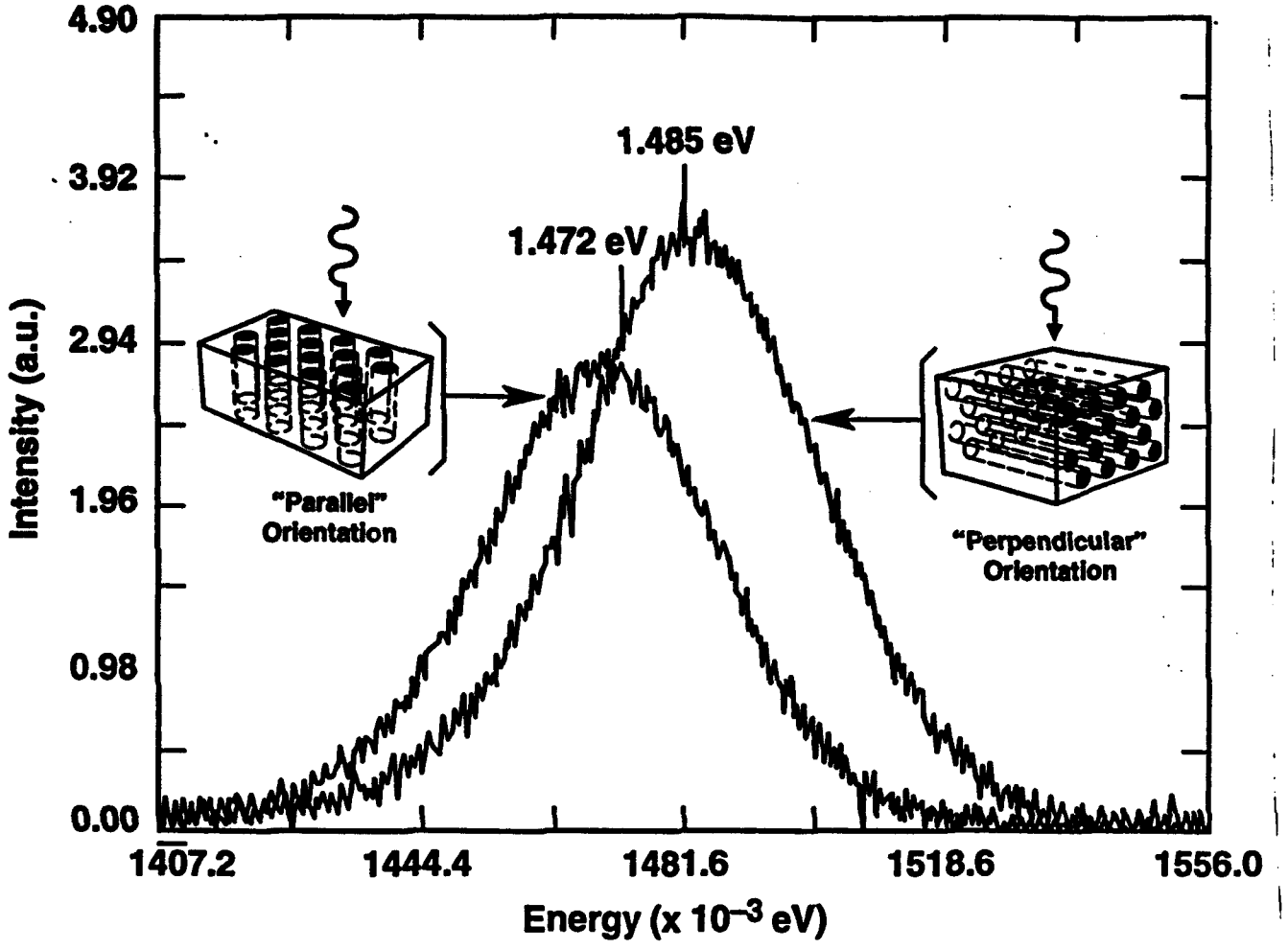

Fig. 2. Comparison of PPL spectra of "parallel" and "perpendicular" CrGaAs SMS demonstrating shifting of peak position.

It has not yet been determined definitively whether the PL peaks are impurity-related or band-to-band, and further work needs to be done. The low temperature bandgap for bulk GaAs is 1.518 eV, and the PL bandwidth is typically about 0.1 meV. The half width for an MBE film on GaAs is typically 1.0 eV. A carbon-related neutral donor-acceptor emission occurs at 1.493 eV in GaAs and the bandwidth is typically 15 meV. Carbon is the shallowest acceptor in GaAs and the bound emission is nearly full gap. Although from bandwidth considerations it might be concluded that the PL line is impurity related, there is no evidence of significant levels of carbon in the material. Furthermore, it is questionable as to how to assign the peak position due to the shifting.

Polarization dependence of the PL peak position is interpretted as the result of anisotropic compressive stress induced in the GaAs due to the presence of aligned rods in the microstructure. Assuming that the peaks are band-to-band, the corresponding shift of the bandgap could be as large as 32.6 and 45.5 meV for the perpendicular and parallel materials, respectively. These shifts correspond to compressive strain of 0.514% and 0.716% for perpendicular and parallel orientations, respectively. Corresponding lattice constants would be 5.621 A and 5.610 A compared to GaAs at 5.650 A. The assumption that the PL transitions were impurity related would lead to somewhat lower stress levels and larger lattice constants. However, the behavior is fundamentally the same.

Polarization dependence of the PL peak position provides compelling evidence of the synergy of SMS technology through microstructural ordering whereby the SMS exhibits a new property not inherent to either component. Due to the anisotropic stress created in the matrix, the cubic degeneracy of the GaAs has apparently been removed. In effect, the SMS is a 3-dimensional, anisotropically strained superlattice in which the valence and conduction bands of the matrix become split. It can therefore be anticipated that the matrix is optically birefringent, whereas normal GaAs is not.

This finding is important not only for its fundamental scientific value, but for the technological implications, as well. For example, there are three basic requirements for the application of nonlinear optical materials to second harmonic generation and optical parametric oscillators. These are transparency, high Chi2, and birefringence. Normal GaAs has two of the three, and would actually be one of the best NLO materials if it were not for the fact that it is not birefringent. SMS technology could now make it possible to exploit GaAs for these applications.

The origin of stress in the SMS is most likely the post-solidification cooling process. Boundaries between the CrAs rods and the GaAs matrix are probably coherent if the behavior of metal-metal composites is any indication of the behavior of semiconductor systems. As a result of differences between the thermal expansion coefficient of the materials, compressive stresses are induced in the GaAs while the CrAs is placed under tension during post-solidification cooling. The

matrix is "squeezed" in between the rods and can relax only along the direction of the rods. Therefore, compression is greatest in direction perpendicular to the rods.

It is also noted that, as discussed in the following section on polishing; perpendicular samples have been found to be difficult to polish due to chipping-out of the ends of rods, which leaves imprints of th rods in the matrix. The susceptibility to chipping could be indicative of the general state of residual stress in the material.

2.1.2 RBS

RBS of GaAs has been widely investiged, while no work is known to have been reported for CrAs. Consequently, this RBS characterization effort concentrated on the GaAs matrix.

RBS spectra are shown in Fig. 3. A very large TO phonon peak and a relatively small LO phonon signture were found to be the primary modes. These modes are considered typical of GaAs. Enhancement of the TO (w-) peak corresponds to a high electron concentration causing a plasmon-phonon (polariton) mode. From published data in the literature, the total ionized impurity concentration would be estimated at greater than $10^{20}cm^{-3}$. This concentration level could correspond to the total concentration of silicon donors, as discussed in the section of SIMS. Additional work needs to be done on the w+ peak, which would provide an indication of the actual electron concentration. Also, the polarization response of the material and stresses at the rod-matrix interface need to be investigated.

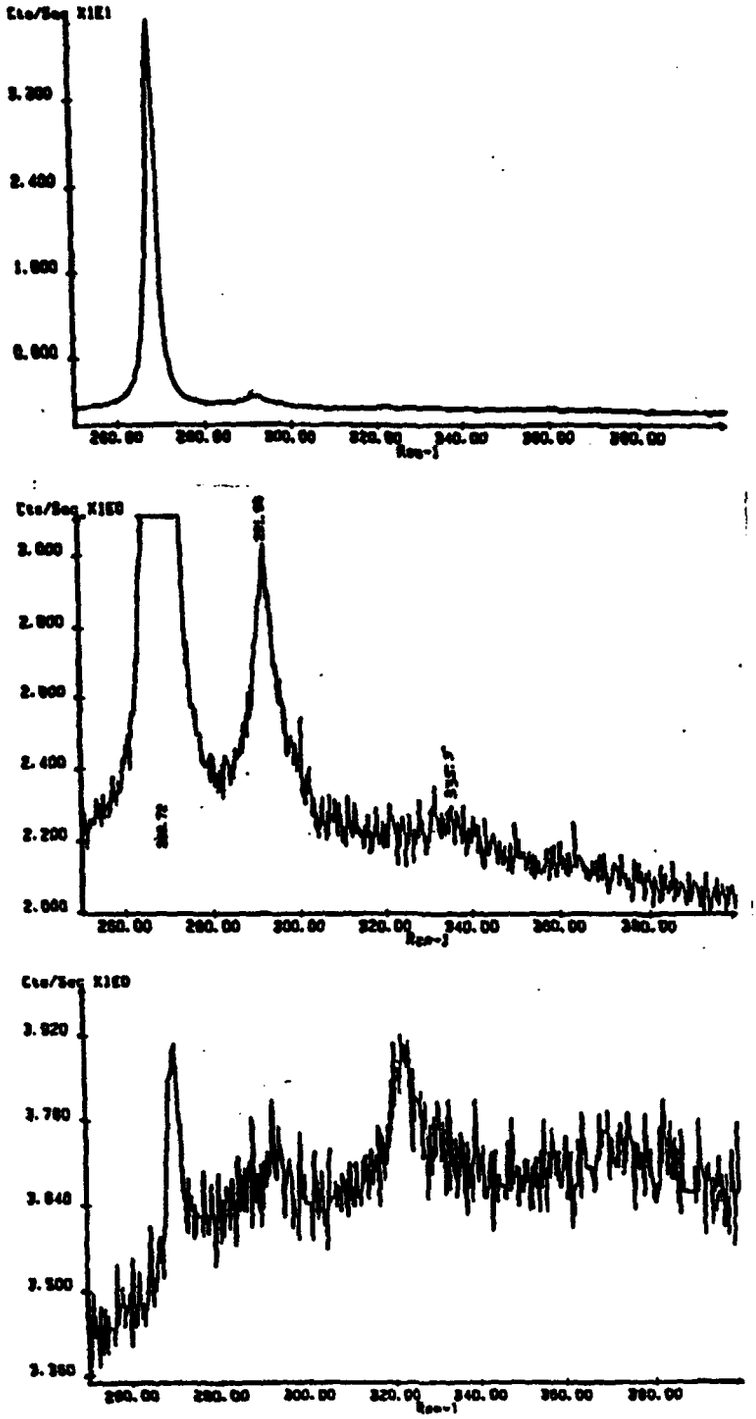

Fig. 3. RBS spectra of CrGaAs SMS.

2.1.3 SIMS

Primary impurities in the CrGaAs SMS were determined by SIMS compositional profiling, as shown in Fig. 4. Primary impurities are Al and Si. Al is a common impurity in GaAs, the source of which is the Ga starting material, so the presence of Al is not unusual. Al is isovalent with Ga and is not electrically active. On the other hand, Si is a donor. Although the SIMS profile is not calibrated, it is estimated that the concentration of Si is in the low 10(20)cm(-3) range. This is a considerable amount of Si. It is noted that this estimated concentration of silicon is consistent with the estimate of ionized impurities obtained from the RBS analysis.

It is important to emphasize that while chemical analysis of the material indicated impurity levels in the 10(20)cm(-3) range, Hall Effect measurements showed that the free electron concentration was about two orders of magnitude lower. It is believed that this apparent discrepancy is due to compensation of the silicon by chromium. Chromium is present in the GaAs due to counterdoping. That is, although most of the chromium from the melt incorporates in the CrAs, a certain fraction segregates to the GaAs phase where it has a finite solubility. Further work needs to be done to quantify the concentration of impurities in the material and to reconcile the chemical composition and the free carrier concentration.

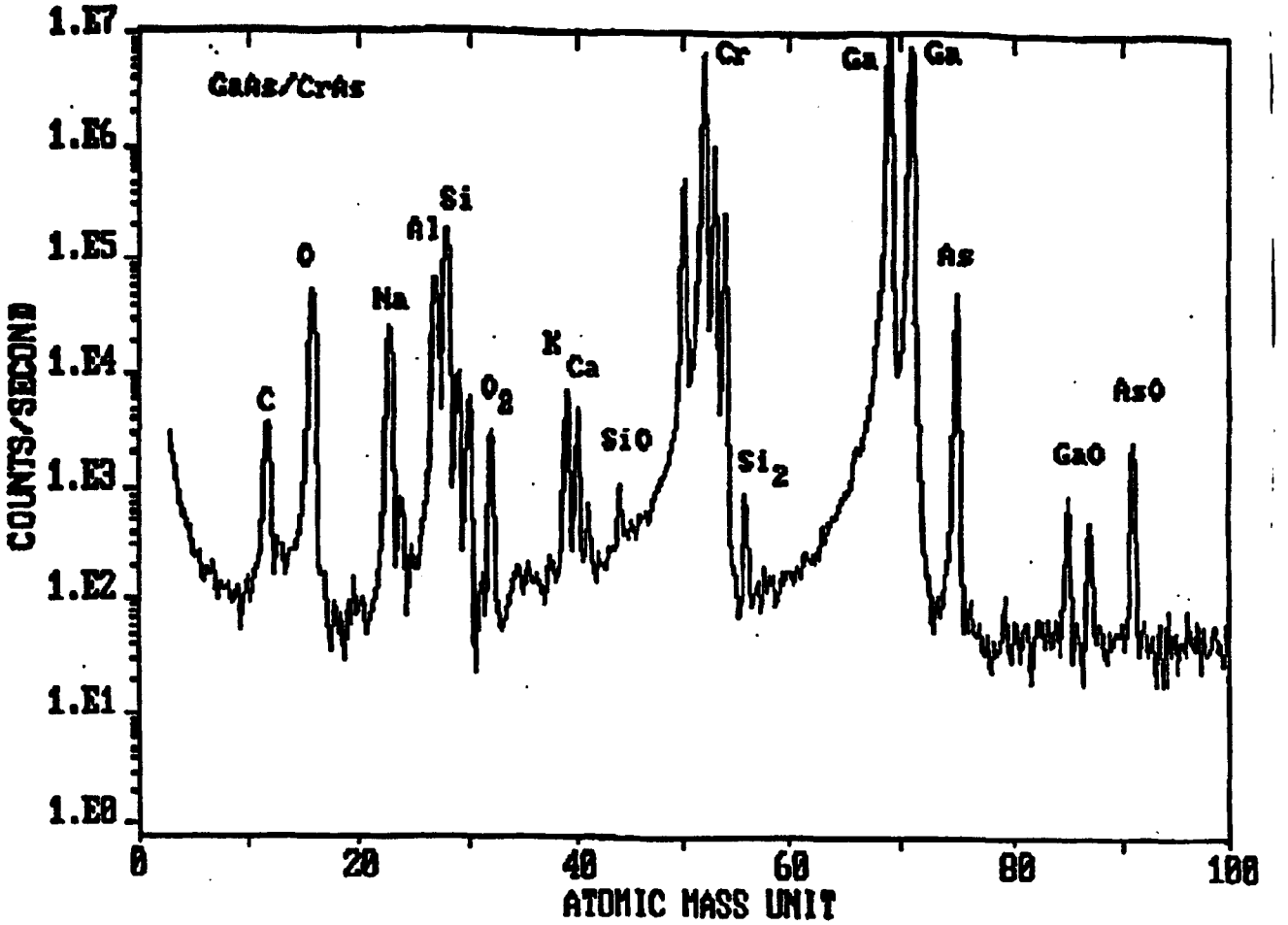

Fig. 4. SIMS compositional profile of CrGaAs SMS.

It is equally important to emphasize that the high concentration silicon in the SMS material is probably not an intrinsic property. In fact, silicon undoubtedly incorporated during the solidification process where the source was the quartz crucible liner. Techniques for limiting silicon incorporation in GaAs crystal growth are available and should be applicable to the SMS. We anticipate that the CrGaAs SMS can be produced with silicon in the 10(15)cm(-3) range by using these techniques. Much higher resistivity in the GaAs matrix would therefore be achievable.

2.1.4 Structural Characterization

Confirmation of anisotropic stress in the GaAs matrix was the initial motivation for investigating the SMS by x-ray diffraction.

X-ray Laue photographs taken of a parallel sample showed multiple spots, such as shown in Fig. 5, which is indicative of polycrystalline material. It did appear that the sample had a preferred orientation (texturing) possibly in the <400> direction, but this is not certain. Furthermore, the axis of the sample, which was parallel to the direction of solidification, does not coincide with any low index crystallographic direction of GaAs.

SEM micrographs strongly suggested that the matrix is twinned rather than polycrystalline. Twinning was indicated by contrast observed in the matrix, as shown in Fig. 6. This contrast was not observed in optical micrographs indicating that the origin is a variation of secondary electron emission. Secondary electron emission is dependent on crystallographic orienation. Furthermore, the banded morphology of the contrasting regions is consistent with micro-twins.

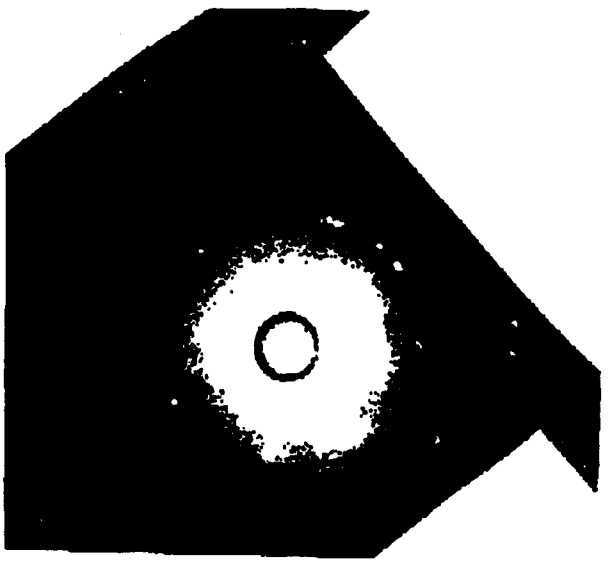

Fig. 5. Laue photograph of parallel CrGaAs SMS showing multiple diffraction spots.

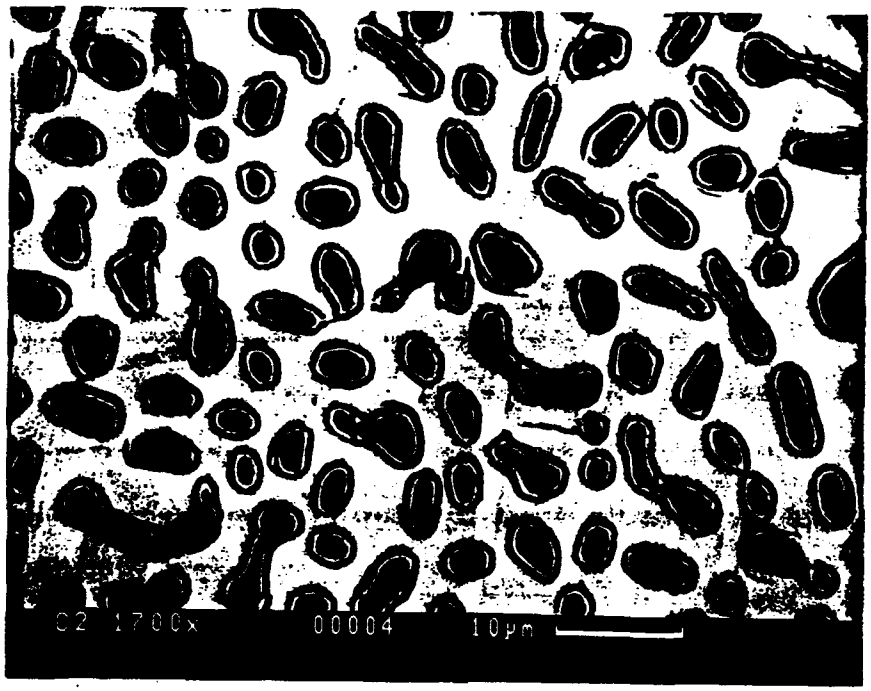

Fig. 6. SEM micrograph showing twinned GaAs matrix.

2.2 Polishing Technology

Polishing of SMS materials is important for several reasons. First, good polishing has been required to support the characterization activities of the program. Quality optical and SEM microscopic investigations require damage-free surfaces. In addition, accuracy of bulk electronic and optical measurements depends on minimal surface damage. Finally, recognizing that surface preparation would ultimately have to be addressed to support device development, it was decided that early action at a reasonable level of effort was justified to benefit the SMS technology over the long term.

Conventional semiconductor methods were used to slice and polish samples during early stages of the program. For example, the CrGaAs ingots were sliced by using an annular I.D. saw. Prior to polishing, surfaces were lapped with 9 um SiC grit to remove saw damage and produce a flat starting surface for polishing. Polishing proceeded by lapping with suspensions of alumina with successively smaller partical size starting with 5 um and ending with 0.1 um. Final polishing was conducted by machine using colloidal silica. A partial list of supplies used for polishing is presented in Table 1.

Table 1

Materials Used in Polishing Development

Polishing Pads	Lapping Materials	Polishing Fluids
Polytex Supreme	Struers 9 um SiC	Nalco 2360, 2355
Rodel 750	5 um, 1 um	colloidal silica
Rodel 204	0.5 um, 0.3 um alumina suspension	

Generally, samples sliced perpendicular to the direction of solidification (parallel orientation) polished well by using the above-mentioned procedure. However, samples sliced along the direction of solidification (perpendicular orienation) invariably showed damage, as shown in Fig. 7. It was established that the damage consisted of holes in the GaAs matrix left behind when ends of CrAs rods fractured as they were pulled out of the surface. Fracturing of the rods was also identified, as shown in Fig. 8.

It was found through experimentation that the best polishing results in terms of minimal fractured rods were obtained by eliminating all lapping procedures and proceeding with machine polishing with colloidal silica immediately after slicing. Disadvantages of this method

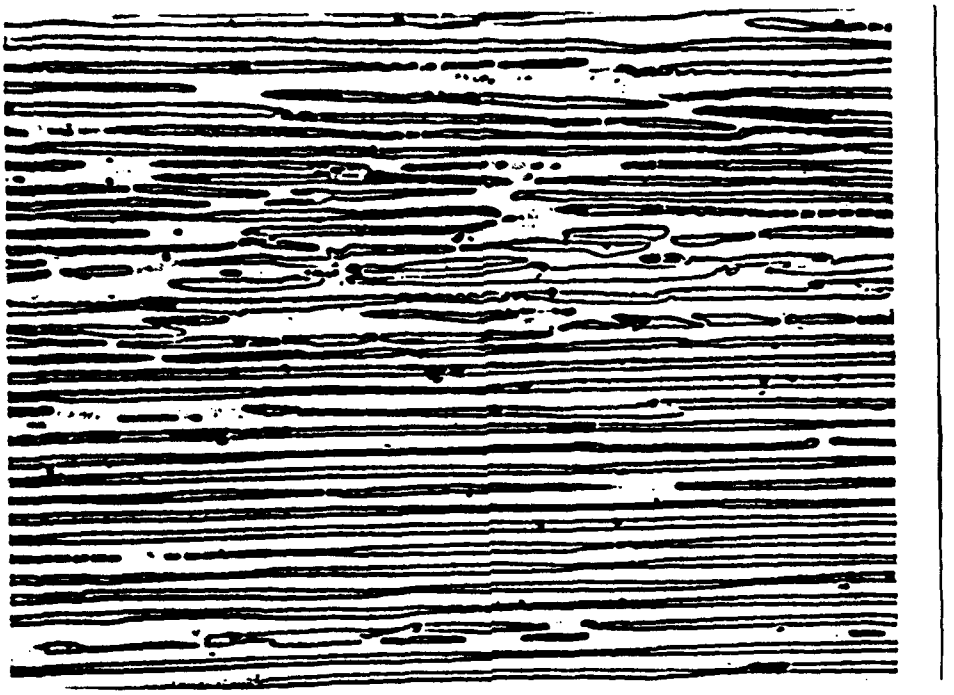

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Fig. 7. Optical micrograph showing imprints of CrAs rods resulting from chip-outs during lapping operations.

Fig. 8. SEM micrograph showing cracking of CrAs rods in polished surface.

included greatly extended polishing times (one hour or more per sample and poor macroscopic flatness. However, for microscopic studies, this process produced the best polish.

These results highlight an interesting issue concerning surface preparation in that fracturing of the rods is probably not caused by slicing, as was originally expected, but by lapping compounds. Particles with diameters on the order of the rod diameters appear to be the cause.

Another important general requirement of polishing is the production of flatness over large areas in a reasonable length of time. This requirement can probably not be accomplished without intermediate lapping unless the slicing operation is under extremely good control.

Surfaces of polished samples were characterized by Auger analysis to evaluate the surface chemistry. Auger spectra of "as polished" and "oxygen sputter cleaned" surfaces, shown in Figs. 9 and 10, show a carbon, oxygen, and silicon as major contaminants residing after polishing. Only the major elemental components of the SMS are detected after cleaning the surface by oxygen sputtering. Although carbon and oxygen are commonly observed on the surfaces of semiconductors, these levels were noted to be relatively high. Furthermore, the presence of silicon is unusual.

The source of silicon is believed to be residue from the colloidal silica. Although it is not clear at this time, the presence of high

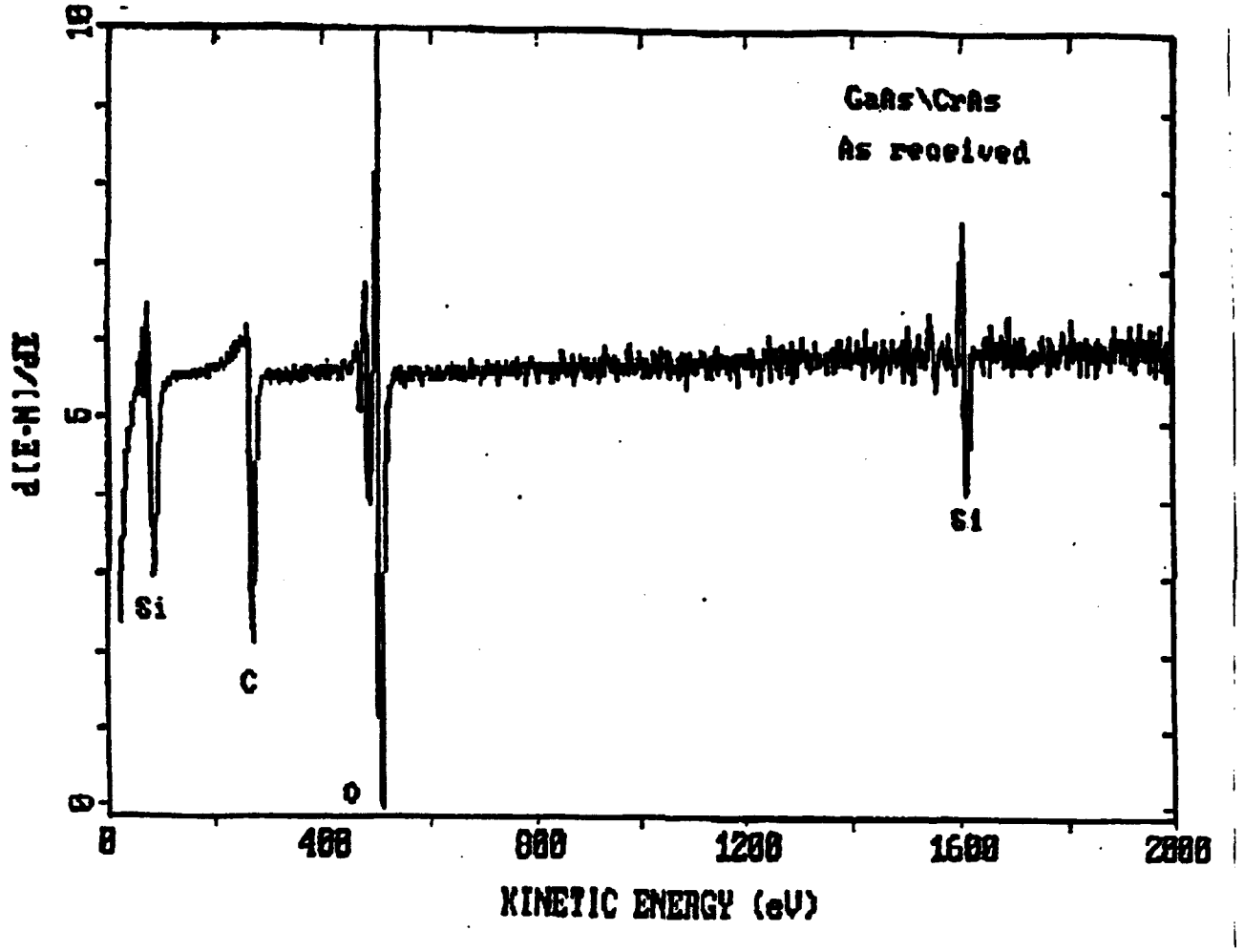

Fig. 9. Auger spectra of as-polished surface.

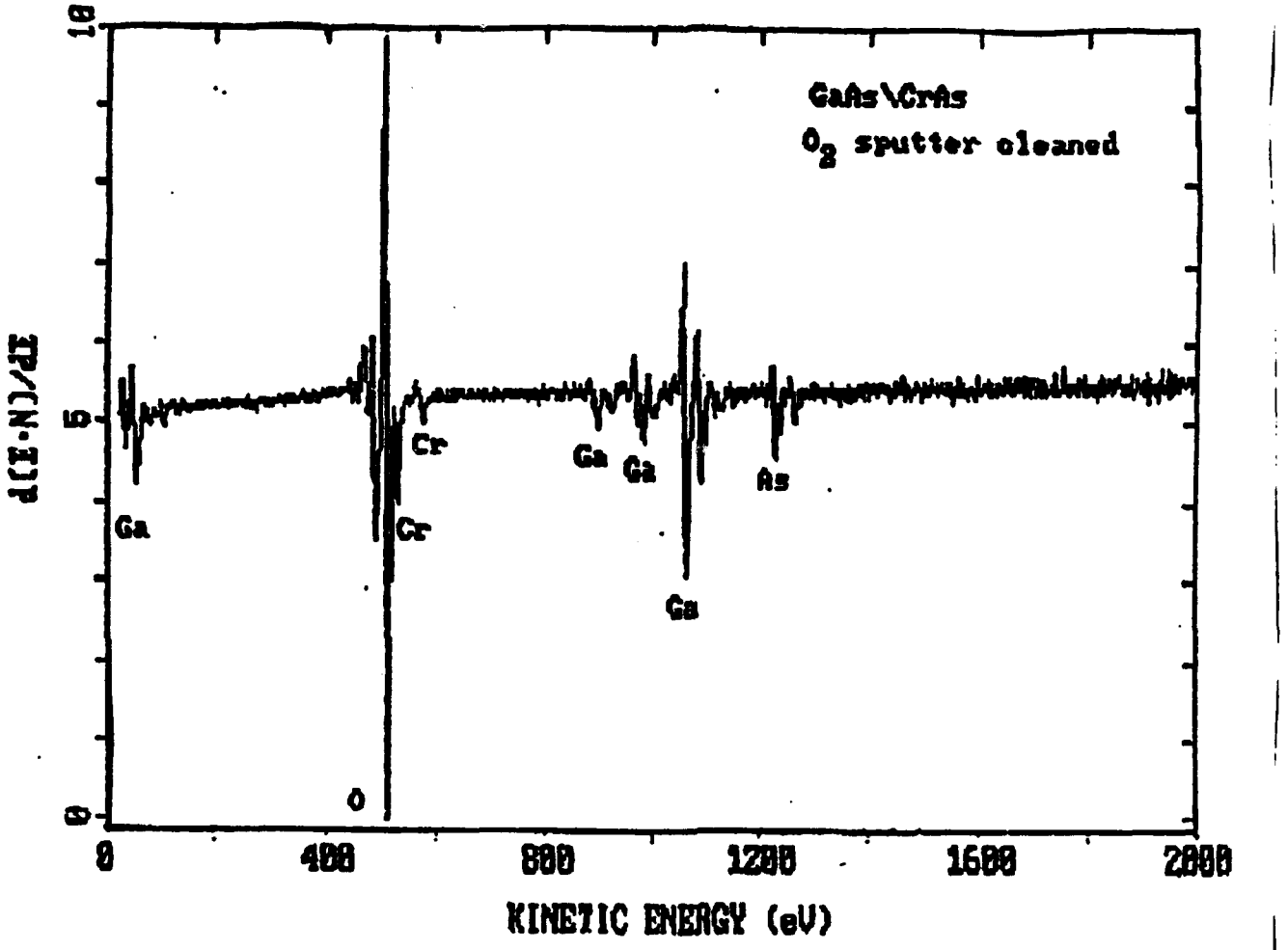

Fig. 10. Auger spectra of oxygen sputter-cleaned surface.

concentrations of carbon and oxygen combined with silicon could indicat that the final stages of polishing of SMS materials will require special attention in the future. For example, it seems likely polished surfaces of SMS materials may not be perfectly flat. Instead, because the softer component (either the rod phase or the matrix) would abrade more quickly during polishing, the surface topology may exhibit relief corresponding to the microstructure. Such a surface might tend to retain polishing materials during finishing and rinsing operations.

It is anticipated that SMS materials with parallel configurations will eventually have greater device applications. The fact that parallel surfaces polish relatively easily bodes well for the future. Polishing technology for perpendicular samples will require further development.

2.3 Improvements in SMS Processing

In general, controlled growth of SMS materials with uniform properties over extended distances requires a high axial temperature gradient, relatively low solidification rate, and minimal convection in the melt. High gradients are required to stabilize the solid-liquid interface against constitutional supercooling, which leads to breakdown of a smooth interface in polyphase solidification in a manner analogous to that in single crystal growth. Low solidification rates have a similar stabilizing effect. However, characteristic dimensions of the microstructure (i.e., rod diamter, inter-rod spacing, etc.) are also controlled by this parameter. As a results, solidification rate is not always an independent parameter available for interface stabilization,

and higher-than-normal gradients might be required to offset constraint on rate established for reasons of dimensional control.

Minimal convection is a requirement because, as we have shown during the previous reporting period, microscopic variations of the solidification rate and momentum boundary layer thickness lead to corresponding spacial variations of rod diameter across an ingot.

A vertical directional solidification system was built during the first phase of the program, and details have already been reported. Major modifications were made to this system during the current reporting period to achieve improved control over the SMS process.

Two major objectives of the modification engineering were the following.

First, it was found in the original system that both the axial temperature gradient and the solidification rate were time and spacially dependent. The former decreased and the later increased, respectivley, with solidification time and as the position of the solid-liquid interface rose during growth. Our objective was to provide constant and controlled solidification parameters over the duration of solidification.

The second objective was to decouple the axial temperature gradient from the solidification rate to enable independent control of each.

To achieve both objectives, a translating ampoule support shaft was added to the system. This water cooled shaft suspends the sample

(contained in a sample holder) in the hot zone. Rather than controlling solidification by power reduction with a stationary sample, the new approach involves lowering the ampoule through the hot zone with a constant and controlled thermal profile.

The shaft extends from the heater coil, down through a port in the baseplate of the vacuum chamber, to the translation assembly mounted to the bottom of the baseplate (see Fig. 11). The translation assembly has two drive servo motors. One controls the vertical translation of the ampoule and, therefore, the solidification rate. Steady rates as low as 5 millimeters per hour are achievable. The second rotates the shaft to promote as smooth a motion as possible. Rotation will also be beneficial by improving radial thermal symmetry around the ampoule, which should help to promote lower thermal convection. Our engineering estimates combined with measurements of axial temperature profiles indicates that gradient-to-growth rate ratios on the order of 1x10(6)(C-sec/cm(2)) are achievable providing a very wide lattitude over which to vary solidification parameters and melt composition under conditions of morphological stability.

The RF coil was also rebuilt (see Fig. 12) during this reporting period to improve the uniformity of heat delivery. In addition, an alignment system for the coil inside the vacuum chamber was designed and built. This system enables precise concentricity of the ampoule and the coil.

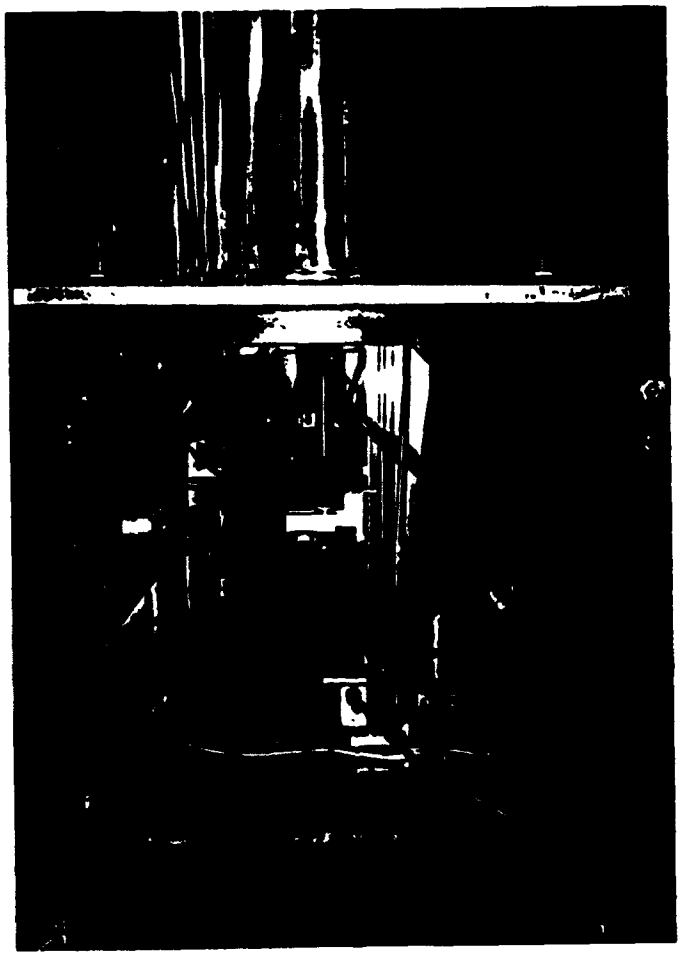

Fig. 11. Photograph of new translation/rotation assembly.

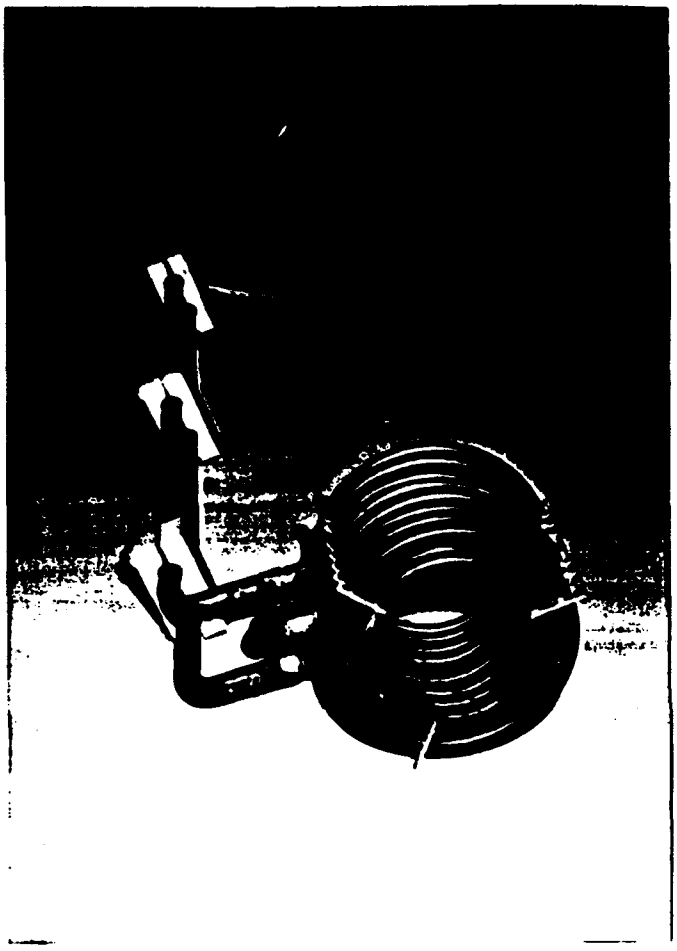

Fig. 12. Photograph of redesigned and fabricated RF coil.

2.4 New Facility

The laboratory of Electronic Materials Engineering was moved during the summertime of 1993 from its old address at Tourmaline Drive in Newbury Park, CA, to 829 Flynn Road, in Camarillo, CA. A photograph of the new facility is shown in Fig. 13. The facility includes vacuum, high-pressure nitrogen, high-pressure air, DI water, and city water.

In addition to crystal growth and polishing capabilities, we are adding slicing with the inclusion of an MRC Microslice annular I.D. saw. This capability completes our plan of achieving self-sufficiency in the area of sample preparation and thus strengthening our ability to move as efficiently as possible in the research of SMS materials.

3.0 Summary

Electronic Materials Engineering and AFOSR have demonstrated a new semiconductor materials technology for electronic and optoelectronic device applications: the Supermatrix Semiconductor (SMS). SMS makes possible the 3-dimensional superlattice and a new method for engineering the properties of semiconductor materials through the synergy of 3-dimensional microstructural ordering.

Major achievements of the program include the following.

1. Demonstrated a 3-dimensional superlattice exhibiting regular, rod-matrix microstructure over wafer-scale distances (CrGaAs).
2. Demonstrated that SMS material can have new property not intrinsic to components. Specifically, GaAs matrix in CrGaAs SMS is birefringent.
3. Identified three new SMS systems.
4. Developed vertical directional solidification system with high gradient-to-solidification-rate ratio and other features for controlled preparation of SMS materials.
5. Correlated structural defects to solidification parameters.
6. Correlated impurity levels to conditions of solidification.
7. Assessed requirements for SMS polishing technology.

We believe that our results have very high scientific value by having opened the door to a new thrust in semiconductor materials focused on 3-dimensional superlattices. Furthermore, technological value of the SMS is also becoming clear from the standpoint of engineering new materials for electronic and optoelectronic applications.

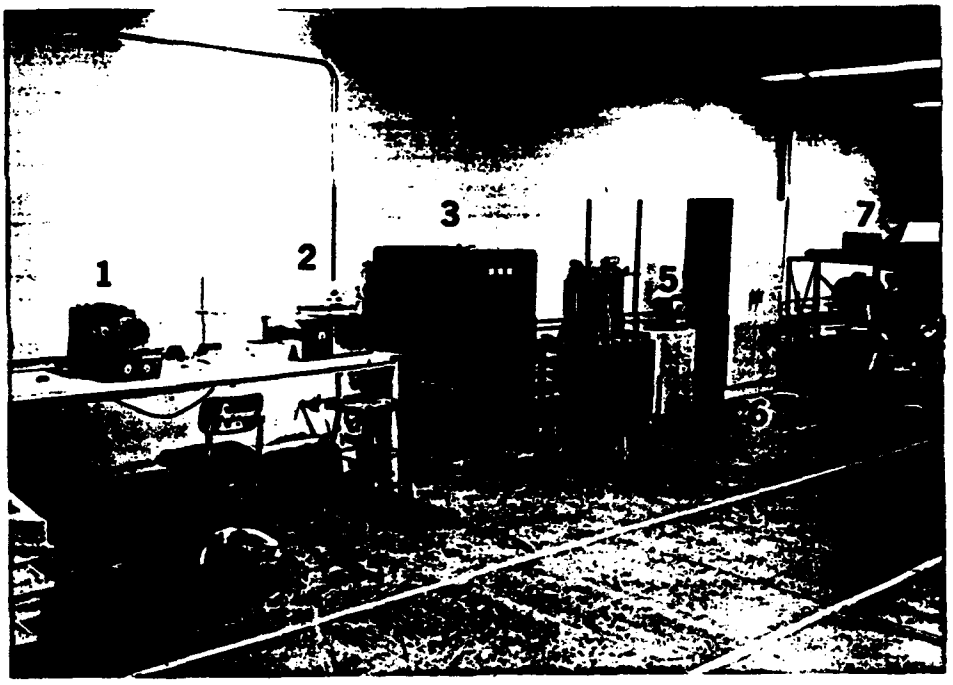

Fig. 13. Photograph of new facility:

1) slicing; 2) polishing; 3) RF generator;

4) vertical directional solidification system;

5) controls; 6) and 7) storage.

Acknowledgements

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