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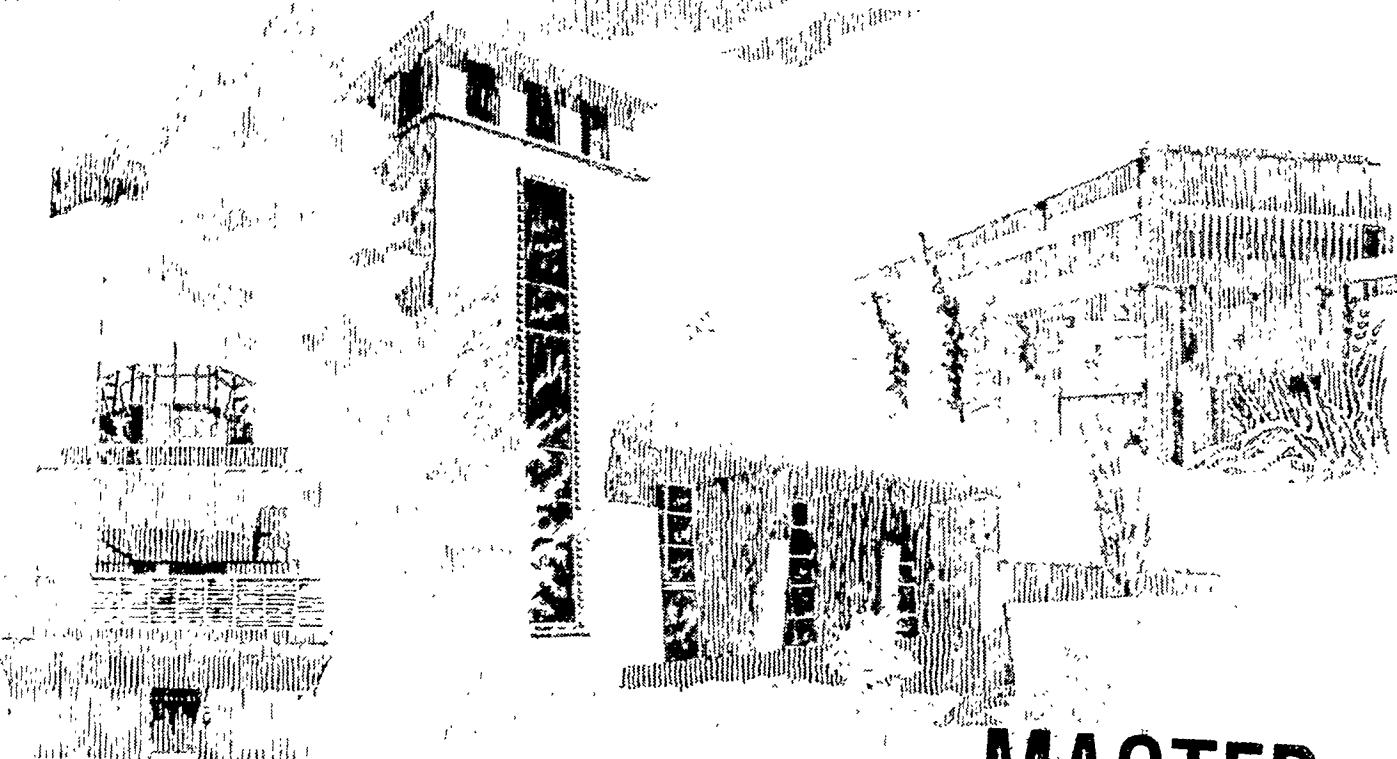
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Advanced Materials Development for Multi-Junction Monolithic Photovoltaic Devices

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**ADVANCED MATERIALS DEVELOPMENT FOR MULTI-JUNCTION
MONOLITHIC PHOTOVOLTAIC DEVICES**

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Abstract

We report results in three areas of research relevant to the fabrication of monolithic multi-junction photovoltaic devices. (1) The use of compliant intervening layers grown between highly mismatched materials, GaAs and GaP (same lattice constant as Si), is shown to increase the structural quality of the GaAs overgrowth. (2) The use of digital alloys applied to the MBE growth of $\text{GaAs}_x\text{Sb}_{1-x}$ (a candidate material for a two junction solar cell) provides increased control of the alloy composition without degrading the optical properties. (3) A nitrogen plasma discharge is shown to be an excellent p-type doping source for CdTe and ZnTe, both of which are candidate materials for a two junction solar cell.

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Nomenclature

MBE	Molecular Beam Epitaxy, a crystal growth technique
GaAs	Gallium Arsenide
ZnSe	Zinc Selenide
CdTe	Cadmium Telluride
InSb	Indium antimonide
GaSb	Gallium antimonide

Introduction

The design and fabrication of a cost effective, high conversion efficiency photovoltaic cell requires the monolithic integration of two or more p-n junctions in materials of differing energy gaps to absorb photons of varying wavelength ranges without an unacceptable decrease in the output voltage. One combination of materials receiving recent attention is Si/GaAs. Each of these materials has been the subject of intense photovoltaic research and development in recent years, leading to the fabrication of excellent high efficiency, single junction cells. The photovoltaic technology of these two materials is nearing maturity. However, the monolithic integration of cells made from these two materials depends upon the ability to grow high quality (low dislocation density, crack-free, high purity) GaAs on Si. Although early progress was reported in this difficult area, recent results have shown only modest improvements, leaving much to be desired in the quality of GaAs grown directly on Si. The remaining major difficulties are related to substantial differences in 1) lattice constant, and 2) thermal expansion coefficient. The first leads to a high density of dislocations and other defects in the epitaxial overgrowth and the second leads to severe cracking and additional dislocating of the overgrowth when cooled from the growth temperature to room temperature. These problems can be minimized by using a novel growth approach involving the insertion of a highly compliant (weakly bonded), low melting point material, such as InSb, between the two mismatched materials of interest, Si and GaAs. The growth of such structures is reported here.

A second area of investigation addresses the need for an ideal pair of materials for the monolithic dual junction cell. While Si and GaAs are good choices based on their mature materials technologies, an ideal combination should have materials with somewhat different energy gaps, about 1.6 eV and 0.95 eV. One candidate for the narrow gap material is GaAsSb. This research explores the MBE growth of materials in this alloy system.

A third area covered in this report is the doping of II-VI materials, such as ZnTe and CdTe. These materials and their alloys are candidates for the wide bandgap member of ideal dual junction cells, but are severely limited by the absence of reproducible doping procedures, especially for p-type material. This study includes the MBE growth of these materials on candidate substrates and establishes procedures for successful p-type doping of both ZnTe and CdTe.

Compliant Layers for Mismatched Structures

The problems encountered in the monolithic growth at elevated temperature of materials having substantial differences in both lattice constant and thermal expansion coefficient can be minimized by a novel growth approach involving the insertion of a highly compliant (weakly bonded), low melting point material, such as InSb, between the two mismatched materials of interest, such as Si and GaAs. Using molecular beam epitaxy (MBE) one can initially grow, at a relatively low temperature, a thin layer of InSb on a Si substrate, followed by a thin layer of GaAs. At this stage both layers are likely to be highly dislocated. This structure is then annealed *in situ* at a temperature near or slightly above the melting point of InSb (525 C). The weak bonding in the InSb is expected to facilitate the rapid diffusion of defects in the overlying GaAs (melting point =1238 C) and lead to substantial decrease in defect density. During this annealing period some diffusion of the various constituents is likely to occur, causing the InSb binary material to become the ternary InGaSbAs. While diffusion of As and Ga into the InSb will raise the melting point of the resulting material, it is known that the Sb-rich alloys are extremely thermodynamically non-ideal alloy systems, and their melting points do not rise quickly with changing composition. Hence, substantial diffusion can take place without drastic increase in the melting point or the bond strength. After a suitable annealing time, the temperature is further raised to the optimum growth temperature for GaAs, ~600 C, and further growth of high quality GaAs can be achieved. For a high efficiency GaAs solar cell, it is likely that the growth temperature will need to be raised to ~700 C for the growth of an Al_{0.9}Ga_{0.1}As window layer. At the termination of growth the cooling of the structure will produce no additional strain in the GaAs/AlGaAs until the freezing point of InSb, 525 C, is reached. Thus problems due to differences in thermal expansion coefficients will be mitigated by limiting the range of differential cooling to ~500 C as opposed to ~700 C when the GaAs/AlGaAs structure is grown directly onto a Si substrate. In addition, it is highly likely that the strain produced by cooling the structure from 525 C down will be preferentially accommodated by the weak bonds in the compliant InSb layer, further mitigating any detrimental strain effects in the GaAs/AlGaAs.

For the initial phase of this work the substrate material chosen for growth was GaP, which has a lattice constant nearly identical to that of Si. Since GaP and GaAs have similar thermal expansion coefficients, this approach has allowed the study of effects due to lattice mismatch alone.

GaP Substrate Preparation

Growth on GaP using the molecular beam epitaxy (MBE) technique, for which there is relatively little previous experience by these workers or in the literature, was begun by establishing a procedure for producing a clean surface on which to begin epitaxial growth. A sulfuric acid/hydrogen peroxide etch similar to that used for GaAs was designed and tested. We verified by Auger analysis that the GaP surface was free of any contaminant other than an intentional protective oxide coating. The protective oxide was then thermally desorbed by annealing the substrate at an elevated temperature in the MBE system immediately prior to growth. In-situ Auger and RHEED analysis showed that the oxide was removed by annealing at 600 C for < 10 minutes. This was confirmed by comparison of InSb growth on substrates annealed at 570 C and 600 C. The former produced a rough, hazy surface typical of oxide-contaminated surfaces on other III-V materials (such as GaAs), while the latter resulted in a very smooth, highly specular surface. Once the method to prepare the substrate was determined, we proceeded to grow layers of InSb, CdTe, and ZnTe on GaP.

X-ray diffraction was performed on each of the layers grown on GaP. InSb was found to be a single crystal epitaxial layer. CdTe was also found to be a single crystal epitaxial layer but with an interesting variation. The GaP substrates had a (100) orientation. In contrast to the InSb which maintained this orientation, the CdTe grew with a (111) orientation. The mechanism for this change in orientation is not known at this time. We also do not know if it is possible to grow CdTe on GaP in the (100) orientation. X-ray diffraction showed the initial ZnTe layer to be polycrystalline but with more care in the substrate preparation we have obtained single crystal epitaxial ZnTe layers. The growth of CdTe and ZnTe on GaP was achieved for the first time ever as part of this project.

Strain Relief Structure

Structures of the form shown in Figure 1 were grown in a Vacuum Generators MBE system using elemental Ga and In sources, a Knudsen cell Sb source operating at temperatures yielding primarily the tetramer species, Sb₄, and a thermal cracking source for As yielding primarily the dimer species, As₂.

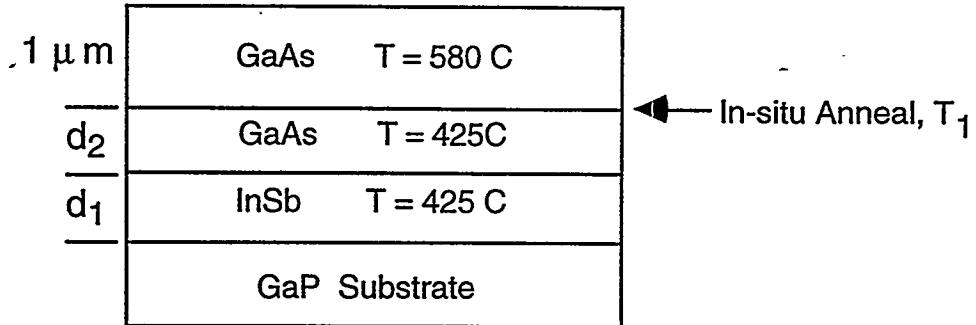


Figure 1. Structure for GaAs on Si with intervening compliant InSb layer.

Numerous multi-layer structures of GaAs/InSb were grown on GaP substrates with a wide range of layer thicknesses, d_1 and d_2 , and annealing conditions. X-ray diffraction verified that both constituents of the structure, InSb and GaAs, are single crystal epitaxial layers of the same orientation as the GaP substrate (100). This is true in spite of the very large lattice mismatch of the materials ($\Delta a/a = 0.19$ for GaP/InSb). For unannealed samples, in all cases the surfaces are smooth and highly reflective. No cross hatching or cracking is visible under optical microscopy. This capability demonstrates the control of the growth process necessary to proceed with annealing experiments designed to minimize point and line defects in the GaAs layers. GaAs/InSb/GaP structures have been grown with the thickness of the intermediate InSb layer, d_1 , varied from 250 to 500 Å. Several of these structures were annealed in-situ immediately after growth, under As_2 flux, at temperatures ranging from 475 to 550 C. This temperature range encompasses the melting point of InSb, 525 C. Thicker layers (500 Å) annealed at higher temperatures showed poor surface morphology. For other combinations of layer thickness and annealing temperature the surfaces were very smooth and free of surface defect structure.

Structural Quality

The crystalline quality of as-grown and in-situ annealed GaAs/InSb/GaP epitaxial structures was evaluated using x-ray linewidth measurements. For several combinations of layer thicknesses and annealing conditions, the x-ray linewidths from the GaAs layers were somewhat narrower than linewidths from GaAs layers grown on GaP with no intervening InSb layer, confirming that the presence of the compliant layer is beneficial in reducing structural defects in the severely mismatched layers. However, linewidths from a 1 μm GaAs overlayer in standard comparison structures are large

compared to that of bulk GaAs or GaAs grown epitaxially (and unstrained) on GaAs substrates, indicating that multiple layers of InSb/GaAs may be needed to improve the quality of the GaAs grown on a GaP(or Si) parent substrate to the point that it will be of technological importance.

Multi-layer structures of the form show below have been grown to compare directly the use of GaAs and AlAs as the annealed layer upon which the ensuing GaAs active layer is grown.

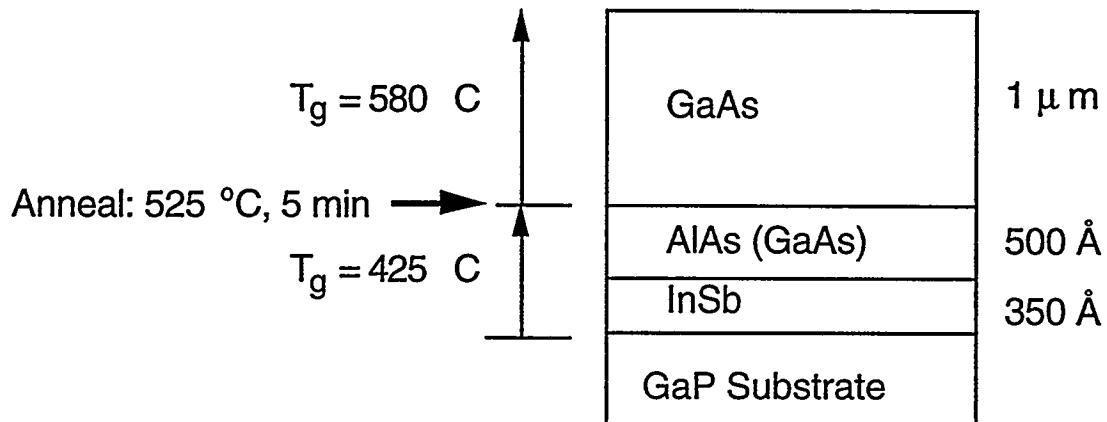


Figure 2. Structure for GaAs on Si with intervening compliant InSb layer plus AlAs layer.

In these structures, after thermally desorbing the oxides from the GaP substrate at 580 C under an As₂ stabilizing flux, the temperature was lowered to 425 C for growth of the InSb and AlAs (or GaAs) layers, followed by an anneal at 525 C for 5 minutes under As₂ flux. The thick GaAs reference layer was then grown at 580 C, an optimum growth temperature for GaAs. X-ray linewidths for the GaAs reference layer grown on an AlAs annealing layer are much larger than those grown on a GaAs annealing layer. One possible reason for this is that the stronger Al-As bond (compared to Ga-As) does not permit defect migration and subsequent defect annihilation. A second possibility is that during the annealing process the static AlAs surface is contaminated with oxygen, causing degradation in the growth of the GaAs overlayer.

MBE Growth of Antimony-Based Materials

The work on GaAsSb is focused on providing materials for the low energy gap member of a multi-junction device. Extensive MBE growth of $\text{GaAs}_x\text{Sb}_{1-x}$ has shown difficulty in controlling the composition, x , of the material grown using a conventional Knudsen cell source for Sb, which yields the tetramer Sb_4 as the evaporating Sb species, and thermally cracked As, which yields the dimer As_2 as the evaporating As species. Small but significant drift of the Sb_4 and As_2 flux rates during MBE growth make it very difficult to control the composition, as would be required for lattice match to an InP substrate, for instance. It is not likely that these flux rates, especially that of Sb_4 , can be stabilized well enough to achieve good composition control. Some improvement was realized by replacing the Sb source with a thermal cracker yielding Sb_1 as the dominant Sb species. Much greater progress was made by using digital alloys, in which thin layers of the binary materials GaAs and GaSb are grown repetitively to simulate the material properties of the ternary alloy. The average composition is controlled by the relative thickness of the two binary layers. This method shows excellent promise for the growth of high quality ternary material with closely controlled composition. Such materials show optical properties very similar to that of bulk ternary alloys.¹

Growth and Doping of II-VI Materials

MBE Growth and Doping

Both CdTe and ZnTe have been successfully and reproducibly grown on GaP. The crystal quality of the layers has been investigated by x-ray diffraction. Standard θ - 2θ scans have shown both materials to be single crystal and epitaxial. High resolution double crystal measurements have also been performed. While the structural quality of the ZnTe is poor, that of the CdTe is very good. The quality of the CdTe is equivalent to that grown on GaAs substrates in spite of the larger mismatch. The CdTe is of better quality than the ZnTe due to a change in orientation. CdTe prefers to grow in the (111) orientation on GaP(100). This orientation switch lowers the mismatch from over 17% to less than 3% in one of the in-plane directions while leaving the other unchanged. This same switch in orientation has been seen in CdTe on GaAs.

The investigation of the n- and p-type doping of CdTe and ZnTe has been the primary focus of the II-VI component of this project. Indium has been investigated as a possible n-type dopant for both CdTe and ZnTe. For bulk crystals of CdTe, In has been shown to act as

an n-type dopant. By MBE we have found that In is not an appropriate n-type dopant. While there are some indications that it may successfully dope CdTe to a very limited degree, its use as a possible dopant for ZnTe has been completely unsuccessful. Our initial work to determine a p-type dopant was focused on the use of arsenic. We were not successful in achieving p-type doping in either CdTe or ZnTe with As. The failure of these initial investigations caused us to pursue other options for doping these materials. We obtained and installed new MBE sources that allowed us to test chlorine as an n-type dopant and nitrogen as a p-type dopant. These particular elements have been shown to be successful dopants in another II-VI material, ZnSe, and are likely prospects for CdTe and ZnTe. The nitrogen source uses a plasma discharge to convert N_2 into neutral N atoms. Epitaxial layers grown while exposed to this N plasma are doped p-type with a carrier concentrations in the low $10^{19}/cm^3$ range.

Ohmic Contacts

One of the difficulties in the investigation of the doping of CdTe and ZnTe has been achieving ohmic contacts to the material. Ohmic contacts are required for both the characterization of the material by Hall effect and for the use of these materials in n-p junctions and solar cells. An ohmic contact for p-type ZnTe has been developed. It consists of sequential deposition by e-beam evaporation of palladium and gold. This contact has been shown to have a very low contact resistance with p-type ZnTe and has allowed us to perform Hall measurements on the p-type ZnTe.

Conclusion

It has been demonstrated that the insertion of a compliant material, such as InSb, between highly mismatched materials, such as GaAs and GaP, increases the structural quality of the overgrown layer without degrading the surface quality. We have also shown that the use of digital alloys improves the composition control in GaAsSb alloys while maintaining normal bulk-like optical properties. In addition, we have determined conditions for MBE growth of CdTe and ZnTe on GaP substrates and have demonstrated the efficient use of N plasma sources for p-type doping of these materials.

References

1. Digital alloy AlAsSb/AlGaAsSb distributed Bragg reflectors lattice matched to InP for 1.3 - 1.55 μ m wavelength range, O. Blum, I. J. Fritz, L. R. Dawson, and T. J. Drummond, Electronics Letters, 1995, 31, (15), pp. 1247-1248.

APPENDIX

LDRD Data

Refereed Publications:

Digital alloy AlAsSb/AlGaAsSb distributed Bragg reflectors lattice matched to InP for 1.3 - 1.55 μ m wavelength range, O. Blum, I. J. Fritz, L. R. Dawson, and T. J. Drummond, Electronics Letters, 1995, 31, (15), pp. 1247-1248.

Oral Presentation:

MBE Growth of AlGaAsSb Using Digital Alloys, L. R. Dawson and O. Blum, 1995 Fall Meeting of the Materials Research Society, Symposium EE, November 30, 1995, Boston.

Patent Disclosures: 0

Patent Applications: 0

Patents: 0

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Awards: 0

Follow-on work: The digital alloy technique applied to GaAsSb materials has been adapted for use with other Sb-based alloys and will be applied to the growth of Mid-IR lasers (LDRD).

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