GROWTH OF NOVEL MATERIALS BY GLOW DISCHARGE SPUTTERING: SINGLE CRYSTAL METASTABLE $(GaSb)_{1-x}Ge_x$ ALLOYS

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ABSTRACT

Epitaxial metastable $(GaSb)_{1-x}Ge_x$ alloys with compositions across the pseudobinary phase diagram have been grown on (100) GaAs substrates by multitarget rf sputtering. An essential feature allowing the growth of these metastable materials was low energy ion bombardment of the growing film during deposition to enhance surface diffusion, promote mixing, and preferentially sputter incipient second phase precipitates.

I. INTRODUCTION

Metastable phases have been produced in a large number of metallic alloy systems[1] by nonequilibrium growth techniques such as splat cooling,[2] vapor quenching,[3] and ion implantation.[4] Most of the work on semiconducting metastable phases has been devoted to investigating the growth and physical properties of amorphous materials; only a few crystalline metastable semiconductors have been reported. Zilko and Greene[5-7] have recently published the results of a detailed study on the growth of single crystal metastable $InSb_{1-x}Bi_x$ alloys on GaAs. Extended solid solutions of $InSb_{1-x}Bi_x$ with x up to 12 mole% were obtained, whereas the equilibrium solid solubility of tetragonal semimetallic InBi in zinc blend structure InSb is $\sim$2.6 mole%.

In the present paper we present some results on the growth, thermal stability, and electrical properties of single crystal $(GaSb)_{1-x}Ge_x$ alloys, which represent a different subclass of metastable materials. $(GaSb)_{1-x}Ge_x$ was chosen as a model system since, unlike the InSb-InBi system, GaSb and Ge have the same space lattice – GaSb is zinc blende while Ge is diamond cubic. The free energy difference between the metastable and equilibrium states is expected to be small (on the order of 20 to 30 meV/atom) while the kinetics of the phase transformation from the metastable to the two-phase equilibrium state should be slow due to the large activation barriers for self diffusion in GaSb and Ge. As we will show in section III, single crystal metastable alloys have been grown at compositions across the pseudobinary phase diagram while Duwez et al.[8] have estimated the equilibrium solid solubilities of Ge in GaSb and GaSb in Ge from splat cooling work to be "less than 2%".

II. EXPERIMENTAL PROCEDURE

All $(GaSb)_{1-x}Ge_x$ films were grown in a multitarget rf sputtering system which has been described in detail elsewhere.[9,10] The system allows separate discharges to be established under each of several targets and the substrate platten may be rotated at a programmed rate through the discharges. The purity of the targets used in these experiments, $Ga_{0.3}Sb_{0.7}$ and Ge, was better than 99.999%. The nonstoichiometric $Ga_{0.3}Sb_{0.7}$ target provided excess Sb during film growth at elevated temperatures.[11] The substrate rotation rate was 12 revolutions per minute to provide nominal deposition rates at target voltages of -550 to -1100 V of 0.1 to 1 monolayer per target pass. Average film thicknesses t were 1.5 μm but alloys with thicknesses up to t = 3 μm were grown.

The system base pressure was $\sim 10^{-7}$ Torr and sputtering was carried out in gettered Ar at a pressure of 15 mTorr. The substrates used in these experiments were Cr-doped semi-insulating (100) GaAs wafers and Corning 7059 glass slides. The reported film growth temperatures, T_s, are accurate to within ± 10°C and include the contribution from both the substrate heater and energetic particle bombardment from the plasma.[5] Film compositions were determined by wavelength dispersive analysis in a JEOL electron microprobe using elemental and compound reference standards. Matrix corrections were carried out using the MAGIC IV computer program.[12] The reported film compositions are accurate to ± 0.5 atomic %. The structure of as-deposited and isothermally annealed films was determined using x-ray diffractometry and Debye-Scherrer powder patterns. Prior to annealing, the films were encapsulated with a 1000 Å thick sputter-deposited layer of Corning 7059 glass which acted as a diffusion barrier against both oxidation and evaporation. Differential scanning calorimetry was also carried out on selected samples using a Dupont 1090 Thermal Analysis System.

Carrier concentrations and mobilities were determined from resistivity and Hall effect measurements. For this purpose, ohmic contacts were made to the samples by alloying In for 10 minutes at 200°C in a H_2 atmosphere. Carrier type was checked using thermoelectric measurements.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Metastable single phase solid solution $(GaSb)_{1-x}Ge_x$ alloys were grown at compositions ranging across the entire pseudobinary phase diagram. Films deposited at $T_s > 400°C$, but less than the transition temperature, were epitaxial on GaAs substrates and exhibited strong (220) preferred orientation on Corning 7059 glass substrates. In both cases, measured lattice constants were found to obey Vegard's law and vary linearly with film composition. Selected Ge-rich and GaSb-rich alloy films were also analyzed using a Debye-Scherrer X-ray diffraction powder camera. All diffraction lines could be indexed as due to single phase alloys.

Figure 1 shows a typical series of x-ray diffractometer (XRD) spectra taken from $(GaSb)_{0.37}Ge_{0.63}$ films grown on (100) GaAs substrates at progressively higher substrate temperatures. Only (200) and (400) alloy diffraction peaks were observed for films grown at $T_s = 470°C$ and the peak widths were limited by instrumental broadening indicating good quality single crystals. The diffraction pattern in Figure 1b shows evidence for precipitation of Ge and GaSb phases in films grown at 507°C. The matrix alloy, represented by the central peak, has become more Ge-rich with a composition of $(GaSb)_{0.31}Ge_{0.69}$. As the growth temperature was increased above 507°C, more and more precipitation was observed with the central alloy peak continuing to diminish in intensity and becoming every more Ge-rich. The side peaks, corresponding to supersaturated GaSb in Ge and Ge in GaSb phases, also moved towards the expected positions for the pure equilibrium phases as T_s was increased. At $T_s = 540°C$, Figure 1c, the side peaks dominate but a central alloy peak is still contributing.

As was the case for $InSb_{1-x}Bi_x$,[6,7] the maximum growth temperature, T_g, at which single phase epitaxial alloys could be obtained depended strongly, for a given alloy composition, on the degree of ion bombardment of the growing film during deposition. Even with no applied negative substrate bias, V_a, the induced negative potential, V_i, on the growing film with respect to the positive space charge region in the discharge was 75 V at P_{Ar} = 15 mTorr.[13] Experiments were carried out in which the net negative bias V_b on the growing film, $V_i + V_a$, was increased by either decreasing P_{Ar}, and hence increasing V_i,[14] or by increasing V_a directly. In both cases, T_g was found to increase.

Figure 2 shows XRD spectra from films with an average composition $(GaSb)_{0.49}Ge_{0.51}$ grown on Corning 7059 glass substrates at P_{Ar} = 15 mTorr and T_s = 508°C. The film represented by the spectra in Figure 2a was grown with V_a = 0 while that in Figure 2b had V_a = 45 V. In the former case, the film exhibited a three phase structure with some loss in (220) preferred orientation as evidenced by the (111) alloy peak. On the other hand, films grown under the same conditions except for the imposition of V_a = 45 V were single phase with a strong (220) preferred orientation as shown in Figure 2b. Similar effects were observed when V_a was maintained constant and P_{Ar} decreased.

Structural data on a large number of as-deposited films have been combined in a phase map plotted as a function of film growth temperature and average film composition as shown in Figure 3. At sufficiently high values of T_s, all single phase metastable alloys transform first to a three phase structure – $(GaSb)_{1-x}Ge_x$, a GaSb-rich phase, and a Ge-rich phase – and, at even higher temperatures, to an equilibrium two phase structure – GaSb saturated with Ge and Ge saturated with GaSb. The width of the boundary region between the single phase metastable and the equilibrium phase regions was only ~25°C, indicative of a large activation energy for the transformation. A minimum in the transition temperature occurs near x = 0.5 as would be predicted from the thermodynamics of regular solutions.

Isothermal annealing studies were also carried out in order to investigate the thermal and temporal stability of single phase $(GaSb)_{1-x}Ge_x$ films. All samples used in this study were single phase as-deposited and were grown at relatively low temperatures in order to prevent annealing effects during deposition. The general sequence of events can be illustrated using $(GaSb)_{0.38}Ge_{0.62}$ films deposited on Corning 7059 glass substrates as an example. XRD spectra from films grown at 425°C exhibited only a single sharp (220) diffraction peak. After a 1.5 h anneal of 500°C, the diffraction peak broadened as (220) peaks from GaSb-rich and Ge-rich phases began to appear. With continued annealing, the side peaks grew in intensity while their angular positions shifted towards the respective values for pure GaSb and pure Ge. After 7 h of annealing, the strong (220) preferred orientation was lost with the appearance of (111) reflections from GaSb-rich and Ge-rich phases. Continuing to anneal for ≥ 50 h resulted in the complete disappearance of the central peak with the side peaks reaching their equilibrium positions and giving solid solubility limits of ~5% Ge in GaSb and ~2% GaSb in Ge at 500°C.

The variation of the intensity ratio of the (220) Ge-rich peak to the (220) alloy peak was determined as a function of annealing time for films annealed at 475, 500, and 525°C. Analysis of this data prior to the appearance of the strong (111) diffraction peaks was used to obtain the activation energy E_a for the metastable to equilibrium transformation. For $(GaSb)_{0.38}Ge_{0.62}$

alloys, E_a was 3.1 eV. This is reasonable in view of the high self-diffusion activation energies, E_d, in the GaSb-Ge system. E_d for Ge is 2.98 eV[15] and the values of Ga and Sb in GaSb are 3.14[16] and 3.45,[16] respectively.

Differential scanning calorimetry (DSC) studies were carried out on a series of alloys using heating rates from 10 to 80°C/min. Figure 4 shows a typical DSC scan at 40°C/min from a $(GaSb)_{0.36}Ge_{0.64}$ alloy. The exothermic peak which occurred at 606°C is due to the metastable to equilibrium phase transformation. The position of the peak was found to depend strongly on the heating rate as is true for all thermally activated transformations. From the integrated area under the peak, the enthalpy of the transformation was determined to be 27 ± 1 meV/atom. The onset temperature for the transformation in this case was 553°C which is in reasonable agreement with the annealing results. The endothermic peak in Figure 4 was due to the onset of melting at the eutectic temperature. The value which we obtain for the eutectic temperature, 648°C, is in very good agreement with that predicted by Duwez et al.[8] from early splat cooling experiments.

Under the assumption that metastable $(GaSb)_{1-x}Ge_x$ alloys are regular, and using the equations developed by Stringfellow[17], the interaction parameter and the Gibbs free energy difference ΔG between the metastable and equilibrium states for alloys with $x = 0.5$ have been calculated to be 144 and 18 meV/atom, respectively, at 300°K. This is in reasonable agreement with known values of ΔG for transitions between metastable amorphous and crystalline phases which are typically from 10 to 100 meV.[1] In addition, the calculated value of ΔH for the transition in $(GaSb)_{0.36}Ge_{0.64}$ at 606°C is 33 meV/atom which agrees very well with the value obtained by DSC as shown in Figure 4. Thus the thermodynamic driving force for the metastable to equilibrium phase transition is relatively small while the kinetic barrier, ~3 eV, is quite large due to the low self-diffusion coefficients in these alloys. This explains why the metastable phase, once formed, is stable at quite high annealing temperatures. In fact, the lifetime of these alloys at room temperature is calculated to be $\sim 10^{29}$ years.

Ion bombardment of the growing film during deposition is an essential feature which stabilizes the growth of these alloys. Eltoukhy and Greene[18] showed that low energy (≤ 300 eV) ion bombardment during deposition of InSb/GaSb heterojunctions can lead to enhanced interdiffusion coefficients which are several orders of magnitude larger than thermal values. In addition, it has been found not only in the case of $InSb_{1-x}Bi_x$,[6,7] but also in the case of InSb and GaSb films grown under conditions which would normally lead to second phase precipitation,[13] that ion bombardment of the growing film inhibits second phase formation due to preferential sputtering of incipient precipitates. This can be understood from sputtering theory[19] which shows that the sputtering yield depends not only on momentum transfer coefficients between incoming projectiles, lattice knock-ons, and sputter ejected species but also on the surface binding energy which is lower for incipient second phase precipitates than for the bulk alloy. The net result of these ion bombardment effects is to provide excellent mixing in the near-surface region of the growing film. The ion bombardment enhanced diffusion coefficient falls off very rapidly with depth[18] however, and because of the high activation barrier for thermal diffusion in these alloys, the as-deposited metastable phase is stable against second phase formation at growth temperatures within ~20°C of the lower boundary temperature shown in Figure 3.

Hall measurements carried out on single crystal $(GaSb)_{1-x}Ge_x$ films show that all samples were p-type. Room temperature carrier concentrations ranged from 10^{17} cm^{-3} for 1.5 μm thick GaSb films on GaAs to 10^{19} cm^{-3} for $(GaSb)_{0.5}Ge_{0.5}$

alloys to 10^{16} cm^{-3} for Ge on GaAs. For these same samples, room temperature hole mobilities ranged from 115 to 10 to 720 cm^2/V-sec. Previous work on p-type sputter deposited single crystal GaSb[(11)] films grown on GaAs showed that the dominant acceptor was due to Sb-deficient point defect complexes and that the dominant charge carrier scattering mechanism was dislocation scattering due to the large lattice mismatch. Such dislocations were associated with deep levels at 80 meV above the valence band edge. The relatively high hole mobilities and low carrier concentrations indicate that these materials are unique alloys and cannot be described simply as self-compensated degenerate Ge-doped GaSb or high compensated degenerate Ga and Sb-doped Ge.

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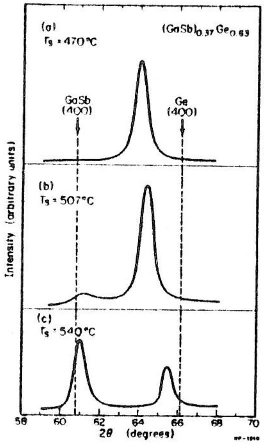

Figure 1. X-ray diffraction patterns from $(GaSb)_{0.37}Ge_{0.63}$ alloy films grown on (100) GaAs at the temperatures, T_s, indicated. The peak in (a) and the central peak in (b) are the (400) alloy reflections. The expected positions of the (400) GaSb and Ge reflections are shown.

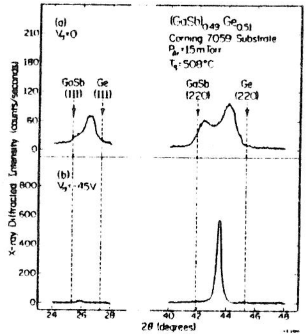

Figure 2. X-ray diffraction patterns from $(GaSb)_{0.49}Ge_{0.51}$ alloy films grown on Corning 7059 glass substrates at 508°C and an Ar sputtering pressure of 15 mTorr (2 Pa) with an applied substrate bias of (a) $V_a = 0$ and (b) $V_a = -45$ V.

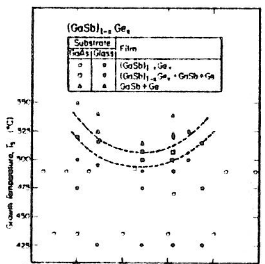

Figure 3. A phase map plotted as a function of growth temperature and film composition for as-deposited $(GaSb)_{1-x}Ge_x$ films grown on both (100) GaAs and Corning 7059 glass substrates.

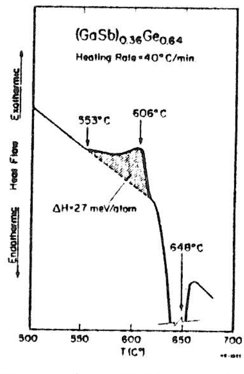

Figure 4. Differential scanning calorimetry spectrum from a $(GaSb)_{0.36}Ge_{0.64}$ sample heated at 40°C/min.