STRUCTURE AND OPTOELECTRONIC PROPERTIES OF SINGLE CRYSTAL EPITAXIAL $Cu(In_{1-x}Ga_x)Se_2$ AND ORDERED DEFECT COMPOUNDS

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ABSTRACT

Epitaxial $CuIn_{1-x}Ga_xSe_2$ was grown on As-terminated (111) GaAs between 550 to 735°C with $0 \le x \le 1$. The Cu/[In+Ga] ratio, y, ranged from y=0.3 to 1.3. Analysis of the deposited films showed an ordered defect structure that was homogeneous throughout the epitaxial layers when group III rich for all Ga contents examined. Films grown with y=0.3 had energy gaps of ~1.2 eV and showed evidence by both cathodoluminescence and optical absorption of band tails. Stacking faults affect both the growth rate and the luminescence but can be converted to dislocations by rapid thermal annealing. The highest hole mobilities to date, >1500 cm^2 /V-sec, were measured at 50-75K by Hall-effect in near-stoichiometry samples. Room temperature hole mobilities were >200 cm^2/V-sec and increased at low temperatures. Hole concentrations showed evidence of a level 80 meV above the valence band edge at a concentration in excess of 10^{17} cm^{-3} in all p-type samples. A composition-dependent level at ~40 meV and type conversion at ~100K was also observed.

INTRODUCTION

One of the critical problems facing the $CuInSe_2$ solar cell community is a lack of fundamental understanding of $CuInSe_2$, related alloys (particularly Ga alloys), and ordered defect layers thought to result from segregation of excess group III constituents to the surfaces of $CuInSe_2$ polycrystalline layers. This work continues previous efforts to improve this understanding through characterization of single-crystal epitaxial layers of $Cu(In_{1-x}Ga_x)Se_2$ on GaAs substrates. A review article describing the properties and applications of $CuInSe_2$ in thin film photovoltaic devices may be found in Reference 1. Papers describing the critical issues in materials and devices based on $CuInSe_2$ and related compounds may be found in References 2 and 3. The principle goal of the work reported here is to study the effect of point, line, and planar defects in $CuIn_{1-x}Ga_xSe_2$ on the optical and electronic properties of the semiconductor.

EXPERIMENTAL

The single crystal $CuIn_{1-x}Ga_xSe_2$ layers investigated in this study were deposited directly on pieces of two-inch diameter epitaxy-ready (001) or Ga or As-terminated (111) GaAs wafers. The deposition process used magnetron sputtered Cu, Ga, and In fluxes and evaporated molecular Se. The depositions were carried out in a stainless steel vacuum system with a base pressure of $1x10^{-4}$ Pa ($1x10^{-6}$ Torr). Details of the vacuum system and growth procedures may be found in References 4-6. The GaAs substrates were cleaved into smaller pieces, clamped to silica or In-bonded to Mo plates, and inserted into the deposition system through a load lock. The backing plates and substrate holders were cleaned between each deposition. During sputter cleaning of the targets, the substrates were covered by a main shutter. An additional shutter isolated the Se source during warm-up. To initiate deposition, the target currents were raised to the appropriate values, the Se shutter was opened, and finally the main shutter was opened. Sputtering was carried out with 99.999% pure Ar at a pressure of 0.1-0.2 Pa (1-2 mTorr). Sputtering targets consisted of pure Cu and pure In targets as well as vacuum hot pressed Cu-Ga alloy targets mounted on Cu backing plates in each case. Two Cu-Ga targets were used with compositions of 20.0 and 42.5 atomic % Ga. The Ga content could not be controlled arbitrarily to select values of x. However, outdiffusion of Ga from the substrate did result in changes in Ga content depending upon the deposition temperature. The Cu or Cu-Ga target sputtering current ranged from 0.10 to 0.35 A, at voltages from 440 to 510 V, respectively. For the In target, the current and voltage were 0.10 to 0.40 A at 410 to 480 V, respectively, and were adjusted to obtain the desired stoichiometry. The Se effusion-cell temperature was 270 °C during deposition corresponding to a Se/metal atomic flux ratio [Se/(Cu+In+Ga)] > 5. The deposition rate was 10 to 50 nm/min (controlled by the Cu and In sputtering currents).

The cathodoluminescence system used in this study is based on a Zeiss scanning electron microscope (SEM) and employs a Ge detector and a liquid-He cooled stage for low temperature measurements (≥4.3 K). Optical absorption, transmission, and reflection measurements were carried out at room temperature using a Perkin Elmer Lambda-9 double beam spectrometer equipped with an integrating sphere. Surface morphologies and compositions of the epitaxial layers were examined using a Hitachi S-800 SEM equipped with an energy dispersive X-ray spectroscopy (EDS) system. Standard specimens with a known composition were used to quantify the EDS data when determining the film compositions when possible. When standards were not available the "ZAF" numerical corrections alone were used. Chemical composition depth profiles were obtained by secondary

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ion mass spectrometry (SIMS) in a Cameca IMS 5f instrument. Microstructural studies (electron diffraction and bright- and dark-field imaging analyses) were carried out in Philips EM420 and CM12 transmission electron microscopes (TEMs). High resolution TEM studies were performed using a Hitachi 9000 TEM operated at 300 kV. Plan-view and cross-sectional TEM samples were prepared by mechanical thinning to 50-80 μm and then were ion milled to perforation on a (77 K) cold stage using 3 kV Ar^+ ions. Hall-effect measurements were carried out in an evacuated chamber that could be cooled by a closed-cycle refrigerator to ~15 K. The temperature was measured by a thermistor mounted beside the sample and was controlled to ±1°C by a small heater. The magnetic field was 1 Tesla. Contacts were In dots or sputtered Au-Pd. The electrometer and current source were computer controlled as was data acquisition and analysis.

RESULTS

Single crystal epitaxial layers of $Cu(In_{1-x}Ga_x)Se_2$ with x~0.1, ~0.3, ~0.6, and 1 with Cu/(In+Ga) ratios, y, of 0.7 to 1.0 and with x~0 and $0.3 \le y \le 1.2$ were deposited on GaAs (001), $(111)_{Ga}$, and $(111)_{As}$ at temperatures ranging from 550 to 735°C and at a rate of 10 to 50 nm/min. The thickness of the grown layers was typically ~1 μm. All compositions lay close to a "tie-line" connecting Cu_2Se and $(Group\text{-}III)_2Se_3$ on a pseudo-ternary phase diagram. Cu-rich films showed evidence of coherent second phase precipitates in the chalcopyrite matrix. The basic growth mechanism and structural and surface defects were similar to those of near stoichiometry $CuInSe_2$ described previously.[4-6] The surfaces showed rippling with a tendency to facet to form the $(112)_{Se}$ surface although at high growth temperatures very smooth surfaces were obtained on GaAs (001). Surface pits were found on Cu-rich samples and samples for which the GaAs surface was damaged during sample preparation. Triangular islands were often found on the surfaces of group-III-rich films.

Films containing little or no intentionally added Ga all included significant Ga near the substrate interface due to Ga out diffusion from the substrate. Diffusion of this Ga into the remainder of the films increased with increasing growth temperature. Concurrent vacancy in-diffusion generally led to the formation of highly (112)-faceted Kirkendall voids at the interface extending into the GaAs. For very high deposition temperatures and with no Ga intentionally added to the films, outdiffusion was so strong that homogeneous high Ga contents were found in the samples. Delamination from the substrates was common in this case due to coalescence of the Kirkendal voids.

Group-III-rich single crystals showed evidence of ordered defects (as determined from electron diffraction patterns obtained in the TEM). Unlike the polycrystalline films, epitaxial layers showed no surface segregation of the ordered defect layer. Ordered defects varied in concentration from sample-to-sample but were homogeneous within a sample. A $CuIn_3Se_5$ sample had an increased energy gap (>1.8 eV) compared to $CuInSe_2$ with significant subgap densities of states giving rise to both absorption and luminescence over a range of energies.

Figure 1a shows the cathodoluminescence spectrum for the $CuIn_3Se_5$ sample. The subgap absorption and luminescence decreased with a characteristic slope of 80meV (from absorption measurements at room temperature) to 70 meV (from cathodoluminescence at 8K).

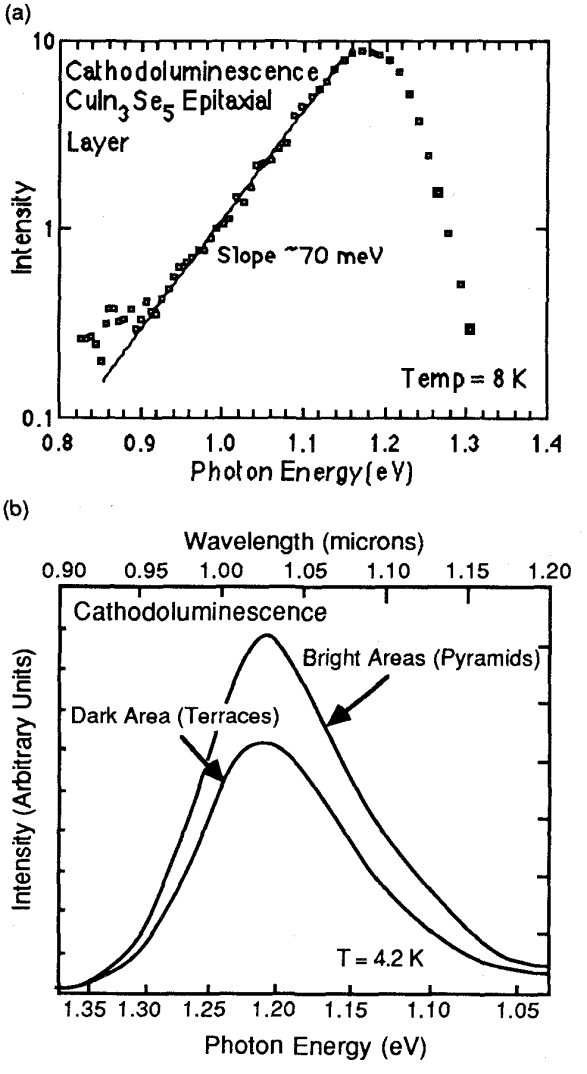

Figure 1. Cathodoluminescence spectra for (a) $CuIn_3Se_5$ and (b) from a flat surface region and from a pyramidal island on an epitaxial layer with x~0.3. Both samples were grown on GaAs $(111)_{As}$.

The diffraction results taken together with the observed composition and very high resistivity of the samples suggest the presence of ordered valence compensating defects on (001) planes, probably In on Cu site antisite defects and Cu vacancies. While the defects are ordered on (001) planes, they are disordered within these planes. The disorder within the planes should give

rise to local variations in defect density. This should cause local variations in energy gap due to a range of subgap states. A more complete characterization of $CuIn_3Se_5$ may be found in Reference 7.

Cross-sectional TEM analyses showed the presence of stacking faults and microtwins in all films. The density of stacking faults was higher for high Ga content films but may have been due to an apparently greater sensitivity of high-Ga-content layers to the preparation of the GaAs surface prior to growth and growth conditions.

In dark field cross-sectional images, stacking faults were observable near the surface of the layers adjacent to but not underlying islands (see Figure 2). Apparently, when a stacking fault occurs during growth the surface polarity may be reversed (i.e., the surface changes from metal to Se terminated or vice-versa) and the growth rate of the crystal decreases abruptly. In the surrounding area where there is not fault the growth continues giving rise to a triangular island. Cathodoluminescence measurements showed increased luminescence from the islands (Fig. 1b) but little change in the spectrum shape. This implies that luminescence and minority carrier lifetime are quenched by the stacking faults just below the surface. Where there is an island, a larger volume exists near the surface that is fault free and thus provides stronger luminescence. Eventually another fault occurs and rapid growth resumes. The stacking faults were commonly a multiple of six (112) plane spacings wide, consistent with the repeat distance of the $CuInSe_2$ chalcopyrite unit cell.

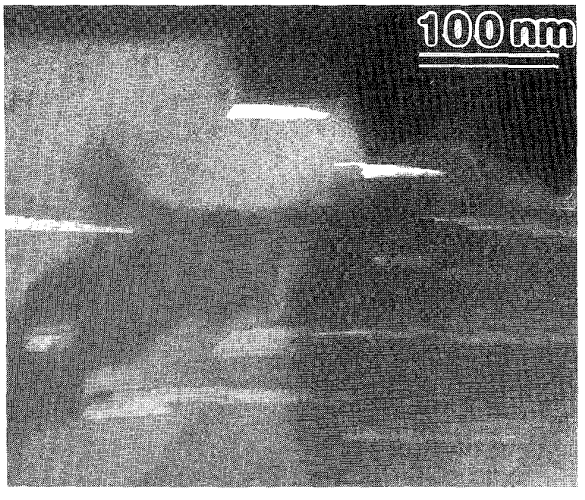

Figure 2. A cross-sectional dark-field TEM image of a $CuIn_{0.7}Ga_{0.3}Se_2$ sample. The bright areas are stacking faults.

Hall effect measurements on stoichiometric and slightly group-III-rich epitaxial films deposited on semi-insulating GaAs substrates showed the films to be p-type with carrier concentrations of ~10^{17} cm^{-3} and mobilities of >200 cm^2/V-sec at 25°C. Cu-rich and stoichiometric ($y \geq 1$), films had resistivities of the order of 10^{-1} Ω-cm while group-III-rich resistivities were >10^1 Ω-cm. Strongly group-III-rich samples were n-type with resistivities of >10^5 Ω-cm. The results of temperature-dependent Hall effect measurements are shown in Figures 3 and 4. For clarity the number of data sets shown on each graph is limited. Different symbols correspond to different samples. Most samples could not be measured reliably below temperatures ranging from 90 to 140 K because of a large increase in resistivity accompanying a conversion to n-type conduction. The hole mobility increased and the carrier concentration decreased for all samples measured as the temperature was decreased. A remarkable similarity in the hole concentration (less than a factor of 4 variation) and mobility (less than a factor of two variation) was found over a wide range of samples with compositions ranging from stoichiometric to slightly group-III rich and for which x~0.3 (see Figs. 3 and 4).

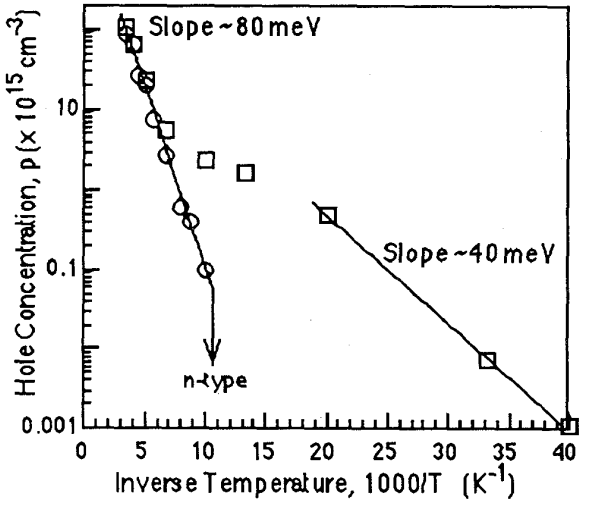

Figure 3. Temperature dependent hole concentrations for two epitaxial layers of $CuIn_{1-x}Ga_xSe_2$ for which x~0.3.

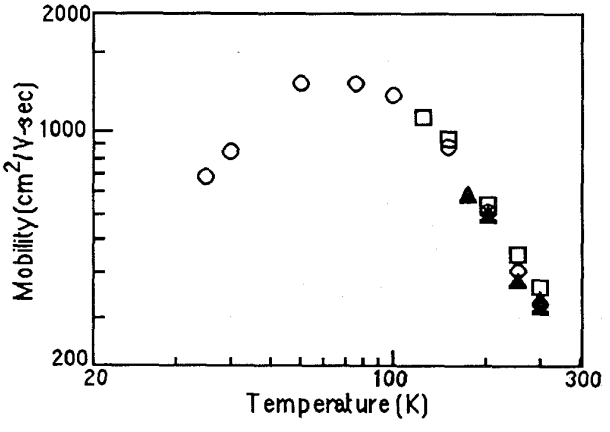

Figure 4. Mobility results for three p-type epitaxial layers for which x~0.3.

For higher temperatures (> ~150 K), all samples were dominated by a defect level at ~80 meV above the valence band edge at a concentration in excess of $2x10^{17}$ cm^{-3}. The sample with the highest value of y (very near stoichiometry) showed the presence of a second defect state at 40 meV with respect to the valence band edge and a concentration of ~$3x10^{15}$ cm^{-3} (see Fig. 3). No other samples showed this state but none was as close to stoichiometry. The absence of a type conversion and a shallow acceptor in this sample is consistent with a change from an n-type to a p-type minority defect associated with a change in stoichiometry. The hole concentration at which type conversion was observed suggests that the n-type minority defect concentration was ~10^{15} cm^{-3}. The high resistivity of strongly group-III-rich samples indicates that very far from stoichiometry the concentration of the donor defect rises and eventually fully compensates the 80 meV p-type defects. This explains the conversion from n to p-type on the group-III-rich side of stoichiometry generally found in polycrystals.

For the sample closest to stoichiometry the absence of type conversion allowed measurement of the mobility down to 20 K. The mobility curve follows a classic semiconductor behavior, increasing with decreasing temperature as ionized impurity scattering decreases; passing through a maximum; and then decreasing as neutral impurity scattering becomes more significant.

CONCLUSIONS

Epitaxial growth of $CuIn_{1-x}Ga_xSe_2$ across a wide range of compositions has been accomplished on GaAs. There is no evidence of significant general optical, electronic, or morphological differences other than changes in energy gap in $CuIn_{1-x}Ga_xSe_2$ as a function of x. The results indicate that point defect ordering occurs in group-III-rich samples on (001) planes. The defects give rise to increased energy gaps and band tail states below the band edge. Stacking faults can cause significant reductions in the growth rate along (112) directions and decreases in the cathodoluminescence intensity, presumably by radiative recombination of carriers. The very high hole mobilities observed indicate that the epitaxial layers are of high quality. Corresponding carrier concentrations indicate the presence of defect states at ~80 meV and ~40 meV with respect to the valence band edge. The former was present in all samples while the latter was only present in one sample with a composition very close to stoichiometry. Samples containing a larger group-III elemental composition showed type conversion to n-type upon cooling. The variation in the hole concentration at which this type conversion occurs suggests a composition-dependent n-type doping level.

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