Cadmium germanium diarsenide glasses were synthesized in bulk form (~2.4 cm³) using procedures adapted from the literature. Several issues involved in the fabrication and quenching of amorphous CdGe₂As₂ (x = 0.45, 0.65, 0.85, and 1.00, where x is the molar ratio of Ge to 1 mol of Cd) are described. An innovative processing route is presented to enable fabrication of high-purity, vitreous, crack-free ingots with sizes up to 10 mm diameter, and 30–40 mm long. Specimens from selected ingots were characterized using thermal analysis, optical microscopy, scanning electron microscopy, energy dispersive spectroscopy, particle-induced X-ray emission, Rutherford backscattering, secondary ion mass spectrometry, X-ray diffraction, density, and optical spectroscopy. Variations in properties as a function of processing conditions and composition are described. Results show that the density of defect states in the middle of the band gap and near the band edges can be decreased three ways: through suitable control of the processing conditions, by doping the material with hydrogen, and by increasing the concentration of Ge in the glass.

I. Introduction

Amorphous semiconductors are the key functional material in several important technological areas such as xerography,1 photovoltaics,2 medical imaging plates,3 and TV vidicon tubes.4 For many applications, thin films are optimal and can be easily fabricated. However for some uses, such as radiation detection, bulk materials are required. Single crystal materials (e.g., Si, Ge, and CdZnTe) are typically preferred for these applications, but enough for fragile glass formers, accomplishing this without quenching molten compounds into a vitreous state17 is difficult. We have found that this is actually a fragile glass-forming system and that it is very difficult to water quench even modest volumes (10 mm diameter, 30–40 mm tall) of the molten liquid into a bulk vitreous ingot without fracturing it. Although quenching molten compounds into a vitreous state is difficult enough for fragile glass formers, accomplishing this without fracturing the material because of excessive thermal stresses is even more challenging.17 Consequently, it was necessary to develop new processing techniques in order to produce bulk, crack-free, vitreous specimens. The major modification (from typical anoxic material processing procedures that involve evacuated fused quartz ampoules) was the development of a double containment (DC) ampoule method as described below.

II. Experimental Procedures

(1) Synthesis

Thermal analysis experiments were used to study the elemental reactions involved with forming CGA compounds and also to measure important glass properties. Reported literature information was used as a starting point to guide experiments.14 Batching reactions of the constituent elements were studied to identify key thermodynamic events. These experiments were conducted using a Seiko TGA/DTA320 (Northridge, CA), which is a combination of thermogravimetric analyzer (TGA) and differential thermal analyzer (DTA). Hermetically sealed aluminum pans were used to minimize material loss because of volatilization. A total sample mass between 20 and 30 mg was used, at a heating rate of 10°C/min up to 620°C, and with a 150 cm³/min purge flow of ultra high purity Ar gas. Glass
transition and crystallization temperature experiments of selected quenched-CGA glass specimens were performed using a Netzsch Jupiter simultaneous thermal analyzer (STA) (Exton, PA). Hermetically sealed stainless-steel pans were used to hold the specimens (approximate mass of 120 mg), which were heated at a rate of 10°C/min up to 300°C, while under a 50 cm³/min purge flow of nitrogen gas.

Bulk specimens of CGA glass were prepared with varying concentrations of Ge according to the following formulation: CdGe₄xAs₅x, where x = 0.45, 0.65, 0.85, and 1.00. These compositions were chosen to complement other reported research on this system. All elements were stored and batched in a nitrogen-purged, atmosphere-controlled glove box (M-Braun, Stratham, NH) where water and oxygen levels were maintained at <0.1 ppm. Reaction vessels (ampoules) were made from 10 mm ID fused quartz tubing with 1 mm wall thickness (GE214, GM Associates, Inc., Oakland, CA). They were prepared by sealing one end of a ~30-cm-long tube with an oxygen–propane torch and set aside. After cooling, each tube was cleaned using a RCA1 etch where the tubes were filled with a solution of NH₄OH:H₂O₂:deionized water (DIW) at a 1:1:5 ratio by volume and set in a 70°C oven for 2 h. When the RCA1 etch was complete, the solution was discarded and the tubes were rinsed with DIW and then etched in a 5% HF solution at room temperature overnight. The tubes were rinsed again with DIW and then baked out and annealed at 1160°C inside of a box furnace located within the atmosphere-controlled glovebox. This bake-out/annealing step helped to reduce the thermal stresses in the ampoule as well as desorb all water on the ampoule interior further reducing processing-induced impurities.

Stoichiometric quantities of the elemental constituents were weighed out to 0.1 mg accuracy and loaded into the ampoules. Each batch contained approximately 12–15 g of raw elements so as to yield an ingot with a 10 mm diameter that was 30–40 mm tall. The elements were loaded into the ampoule according to the order of their melting or sublimation temperatures Cd (Tm = 321.069°C) at the bottom, As (Tm = 616°C) in the middle, and then Ge (Tm = 938.25°C), as the top layer. This order was chosen for several reasons. Germanium, which has the highest melting point, was used as the top layer to minimize volatilization of the batch due to ampoule heating during the sealing operation. Cadmium was placed at the bottom to keep it as far away as possible from the heat during sealing of the ampoule. The ampoule was then sealed, the nitrogen-purged, atmosphere-controlled glove box (M-Braun, York, PA). Hermetically sealed stainless-steel pans were used to hold the specimens (approximate mass of 120 mg), which were heated to 800°C in an oxygen–propane torch. The gate was sealed at 100°C, the tube was transported to the furnace, and the gate was sealed again by nitrogen-purged, atmosphere-control to prevent crystallization during quenching. Rocking was not initiated until the melt was at 650°C and the rocking point of the composition as interpolated from DTA/DSC data (eq. 1) was usually ~20°C above melting point of the composition as interpolated from DTA/DSC data reported in the literature. Selecting the correct value for Tq was essential at preventing crystallization during quenching. Rocking was terminated while holding at Tq, the rocking arc, the rocking rate, and the dwell time at each end point were controllable.

Once constructed, the ampoules were quenched into a water bath (RT) or liquid gallium (T = 50–150°C). Heating the Ga followed the approach of Hruby and colleagues who reported success with Ar/H₂ gas (Matheson Argon ULSI 6N purity, with 2.6% H₂). This purge/evacuation procedure was repeated at least three times. (Selected ingots were doped with hydrogen by back filling the ampoule with the Ar/H₂-blended gas to a final pressure of ~13 kPa (110 torr) in lieu of a final purge.) After the final purge, a final evacuation step to ~10⁻¹⁰ Pa (~10⁻¹² torr) was used before sealing the ampoule with an oxygen–propane torch.

Double containment (DC) ampoules were made by inserting and centering a SW ampoule into a separate, larger diameter (19 mm ID), fused quartz tube with a closed bottom and filling the gap between them with copper powder (~16–25 g) to a height near that of the predicted height of the solid amorphous ingot. The outer ampoule was then evacuated and sealed using the same process as with the inner ampoule. The outer ampoule provided an additional level of protection in case the inner ampoule failed. The copper powder (k = 366 W/(m·K) at 800 K) was used to improve the thermal conductivity of the region of the assembly containing the ingot. The added thermal mass of the system was used to keep the melt above the nucleation temperature during ampoule transfer from the furnace to the quench bath, as well as moderate the cooling kinetics (vitrify without thermally shocking and fracturing the ingot) during the quench process itself.

Once constructed, the ampoules (either SW or DC) were attached to a quartz ampoule holder and loaded into the containment assembly of a custom-designed rocking furnace. The quartz holder was designed to perform three functions: (1) hold the ampoule at a fixed location in the hot zone of the furnace, (2) facilitate rapid removal of the ampoule from the furnace for quenching, (3) maximize cooling rate by not thermally interfering with the quench. The rocking furnace consisted of a small, clam-shell tube furnace (DeTech, Denver, CO) mounted on a motor-driven pivoting platform such that the furnace could be tilted to ±30° from horizontal. The pivoting motion was used to facilitate homogeneous mixing and reaction of the elements in the ampoule during thermal processing. The furnace was fitted with a secondary containment system composed of 50 mm diameter stainless-steel tubing with a baffled vent that was designed to contain the contents of an ampoule and vent the released pressure, should an ampoule fail during thermal processing. The rocking arc, the rocking rate, and the dwell time at each end point were controllable.

Specimens were thermally processed by slowly heating them up in the rocking furnace according to the schedule shown below. They were loaded into the furnace with the platform at its maximum tilt (~30°), so that the Cd end of the ampoule was at the bottom. The thermal treatment consisted of the following (R, ramp segment; D, dwell segment)

1. R@3°C/min 400°C → (2) D2 h → (3) R@3°C/min 650°C →
2. D2 h → (5) R@3°C/min (Tq)m → (6) D2 h (rocking) →
3. R@10°C/min Tq → (8) D0.5 h → quench

The melt was typically processed at 800°C–850°C (Tq) and the quench temperature (Tq) was usually ~20°C above melting point of the composition as interpolated from DTA/DSC data reported in the literature. Selecting the correct value for Tq was essential at preventing crystallization during quenching. Rocking was not initiated until the melt was at 650°C and the rocking proceeded until ~20 min before the temperature was ramped to Tq. Rocking was terminated while holding at Tq, with the furnace tilted at ~30° so the glass could settle to the flat end of the ampoule.

SW ampoules were quenched into either a water bath (RT) or liquid gallium (T = 50–150°C). Heating the Ga followed the approach of Hruby and colleagues who reported success with
using liquid Ga (70°–150°C) as a quenchant. In their work, quenching in warm liquid Ga was supposed to provide some annealing of the sample during the quench and reduce thermal shock. Although expensive, liquid Ga was an appealing quenchant because of its low melting point (29.76°C), very high boiling point (2204°C), and low vapor pressure. DC ampoules were typically quenched in a water bath at room temperature. After quenching, the ingots were annealed at −50°C < Tg for that composition (as determined by DTA/TG/A/DSC) for ~8 h in a vacuum to aid in reducing thermally induced stress in the glasses. After cooling, the ingots were cast into thin acrylic (Buehler VariKleer®, Lake Bluff, IL) to reduce fracture during sawing. They were then sectioned into thin wafers 1–3 mm thick, polished, and analyzed.

(2) Characterization

Specimens were sectioned from the ingots and characterized using a variety of techniques to determine processing-property as well as composition-property relationships. Optical microscopy was performed with a Leitz Orthoplan optical microscope using reflected cross-polarized light, a 1/4 λ calcite wave plate and a rotating stage. This enabled the rapid detection of crystalline phases as the variations in birefringence and crystallographic orientation caused the different grains to go in and out of extinction at different angles as the stage was rotated. X-ray diffraction experiments were conducted with a Scintag PAD V diffractometer using CuKα radiation (λ = 0.15406 nm, 45 kV, and 40 mA) and equipped with a Peltier-cooled Si(Li) solid-state detector in a 0–2θ geometry. Samples were analyzed in a step-scan approach, typically from 10° up to 110° 2θ with a step size of 0.04° 2θ and a dwell time of 6 s/step. Each sample was mounted on a holder that rotated in the θ–2θ plane to minimize preferred orientation effects. Samples were analyzed to detect and identify the presence of any crystalline phase(s) and for radial distribution function analysis. A JEOL 5900 (Joel Ltd., Peabody, MA) scanning electron microscope with a Robinson Series 8.6 backscattered electron (BSE) detector and EDAX Genesis energy dispersive spectrometry (EDS) system were used to analyze selected specimens for homogeneity and phase separation. Density measurements were accomplished using a Microceramics AccuPyc 1330 (Norcross, GA) helium pycnometer. Contamination experiments were performed using particle-induced X-ray emission (PIXE) spectroscopy and Rutherford backscattering spectroscopy (RBS) on the linear accelerator at the Environmental Molecular Sciences Laboratory (EMSL, Richland, WA). PIXE measurements were carried out with a 2.5 MeV H+ beam, and the X-rays emitted during the de-excitation process were analyzed using a Li-drifted Si detector positioned at an exit angle of 39°. The system was calibrated using a standard from the National Institute for Standards and Technology. The GUPIX computer code, developed at the University of Guelph, Canada, was used to fit the experimental data. Background subtraction to remove bremsstrahlung effects was performed and the areas under each peak were converted into concentrations using experimental parameters such as energy, incident and exit angles, charge, solid angle of the detector, absorber thickness, and detector response functions. The experimental parameters were then calibrated against the known concentrations of the standard. Following calibrations, PIXE measurements were collected on CdGe1–xAsx2 samples.

Rutherford backscattering experiments were performed with 2.0-MeV He+ ions at a scattering angle of 165°. The SIMNRA simulations code was used to fit the RBS data. These experiments were performed to determine absolute concentrations of the major constituent elements. Instead of detecting characteristic X-rays, the incident ions that are subsequently scattered from target atom nuclei are detected and measured. This provides information on the mass and depth of the target atoms.

Additional compositional analyses were conducted using secondary ion mass spectroscopy (SIMS). These measurements were performed with a Cameca IMS-5f instrument using an O2 ion beam. This analysis condition is highly sensitive to electropositive species and to a broad range of transition and other metals. The results were used to corroborate compositional data obtained by PIXE and RBS.

Current–voltage curves as a function of temperature were measured with a Hall effect testing device consisting of a MMR Technologies analysis head and H-50 van der Pauw controller. The sample temperature was controlled by a heater and a CTI Cryogenics refrigerator with a base temperature of ~259°C. The sample was mounted on the refrigerator and reheated with the heater power controlled by a Lake-shore 320 autotuning temperature controller to a set point temperature. A magnetic field of 1 T (Varian Associates electromagnet) could be applied to the sample for Hall effect. Data was taken and analyzed using a custom Labview program. Ohmic contacts were made by evaporating high work-function metals such as Ti, Au, or Pd onto polished CGA disks. Four contacts were applied in a Van der Paw geometry. Indium-coated wires were attached to the contacts using indium solder. Voltages applied to the samples depended upon the current to be driven and this current was minimized based on signal-to-noise requirements as this produced the most reliable results. Typical currents were of the order of 1 nA for most measurements. The conductivity of the sample was calculated from the I–V data based on the geometry of the test.

The optical bandgap of these materials were characterized using a Varian Cary 5 G UV–Vis–NIR spectrophotometer with a spectral range of 175–3300 nm and an out-of-plane double Littrow Monochromator. Infrared (FTIR) spectroscopy and UV–Vis–NIR spectroscopy were performed on all samples using a Thermo 6700 FTIR and a Varian Cary 500 spectrometer, respectively. Polished windows of each composition were mounted and transmission measurements were collected from 2.5 to 25 µm and 300 to 2500 nm on the Thermo and Varian instruments, respectively.

III. Results and Discussion

Thermal analysis studies of the batch reactions between the three elements detected three significant endotherms: the melting point of Cd (observed at 325°C) and two additional endotherms at 573° and 592°C. Neither of these corresponded to an obvious phase transition for one of the elemental constituents. However, the As–Cd phase diagram24 showed several phase transitions associated with the As2Cd3, α, γ, and β phases, with one at 578°C. Furthermore the CdAs2–As2Cd3 eutectic is given as melting at 610°C. We hypothesize that the endotherms at 573° and 592°C represent phase transitions in a Ge-poor As–Cd compound or in the ternary CdGe2As3 itself. A distinct, exothermic reaction to form CdGe2As3 was not obvious in the DTA data but may have been obscured by the rise in the data beginning at the 573°C endotherm and continuing on to the end of the experiment. The use of hermetically sealed-Al pans limited the experiments to 620°C. Even at that temperature, reactions between the molten Cd, As and/or Ge with the Al pan were noted based on ex situ observations of chemical attack on the pan. Therefore, the observed rising slope in the DTA data above 573°C probably also included a significant component of reaction with the Al pan.

Subsequent thermal analysis experiments of quenched CGA glasses of various compositions were able to detect both the glass transition temperature and the crystallization temperatures. The results from all of the tests are shown in Table I. The data from the batch reaction and the glass measurement experiments were used to develop the heating rate profile used to process, quench, and anneal the CGA specimens. The results were similar to the values of a more extensive study by Hong, et al.9,25 Variations between the data sets may be attributed to differences in sample volume (smaller with Hong and colleagues) and purity (e.g., final ampoule sealing pressure was higher with
Table 1. Glass Transition ($T_g$) and Crystallization ($T_c$) Temperatures for Various Cadmium Germanium Diarsenide Glasses

<table>
<thead>
<tr>
<th>Name</th>
<th>Quench method</th>
<th>Composition</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\rho_{pycn.}$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G 0.45</td>
<td>DC</td>
<td>CdGe$_{0.45}$As$_2$</td>
<td>353</td>
<td>440</td>
<td>5.8094</td>
</tr>
<tr>
<td>G 0.65</td>
<td>LG</td>
<td>CdGe$_{0.65}$As$_2$</td>
<td>372.2</td>
<td>463.9</td>
<td>5.7774</td>
</tr>
<tr>
<td>G 0.85</td>
<td>DC</td>
<td>CdGe$_{0.85}$As$_2$</td>
<td>373.7</td>
<td>448.5</td>
<td>5.7405</td>
</tr>
<tr>
<td>G 1.00</td>
<td>LG</td>
<td>CdGe$_{1.00}$As$_2$</td>
<td>390</td>
<td>448</td>
<td>5.7171</td>
</tr>
</tbody>
</table>

Hong’s vs. This study: $10^{-3}$ vs $10^{-5}$ Pa, or $10^{-5}$ vs $10^{-7}$ (orr, respectively).

Anecdotally, greater success was experienced in obtaining crack-free, crystal-free CdGe$_{x}$As$_2$ ingots for $x = 0.45$ and 0.85 than for the other compositions. In contrast, a greater percentage of ingots for compositions with $x = 0.65$ and 1.0 failed due to either cracking or crystallization or both. This was in contrast to the findings of Hong et al.,$^{10}$ where they computed a maximum in glass formation tendency between $x = 0.3$ and 0.6 based on thermal analysis data. Additional thermal analysis experiments at finer compositional intervals are needed to better characterize these variations in glass formability. In addition to thermal glass formability criteria (based on differences between the crystallization and glass transition temperatures) variations in residual oxygen content have also been reported to affect glass formability. Hruby et al.$^{27}$ stated that when they took the effort to remove oxygen and water contamination from their starting materials and ampoule walls it was much more difficult to form bulk As–Te glasses. Because these Cd–Ge–As glasses were processed at significantly lower oxygen and moisture contamination levels than reported previously, it is possible that a similar effect is at work. To our knowledge, the influence of trace oxygen content on glass formability in Cd–Ge–As glass has not yet been rigorously examined.

Initial experiments synthesizing bulk CGA glasses were not successful because of failed and cracked ampoules. The source of the cracking was attributed to Cd attack of the fused quartz wall. Pyrolytic graphite coatings (described previously) were attempted as a means to address this problem, but yielded mixed results. They were effective in eliminating the problem of ampoule failures because of Cd attack of the fused quartz, but they introduced several additional problems. We observed that the CGA melts had a tendency to wet and adhere to the walls of the pyrolytically coated ampoules. This reduced ingot yield, because a film of the CGA glass remained along the ampoule wall rather than pool and collect as a bulk ingot. Additionally, the pyrolytic coatings themselves were not sufficiently adherent to the ampoule wall, but became incorporated into the melt. SEM examination of polished cross-sections from ingots made in pyrolytically coated ampoules showed evidence of carbon contamination in the ingot. Electrical characterization tests performed by measuring the conductivity as a function of temperature showed that an ingot synthesized in a pyrolytically coated ampoule was over an order of magnitude more conductive than the ingot made in a bare ampoule and its conductivity also had significantly lower temperature dependence. Consequently, pyrolytical coatings had to be abandoned. As a result, the specific element loading sequence described previously was developed, and proved to be an effective means to address the problem of Cd reacting with fused silica.

Development of an effective quenching process to form bulk, amorphous, crack-free ingots proved to be challenging. Optical microscopy (Fig. 1) and XRD (see later discussion) were the primary analytical techniques used to evaluate different quenching methods. Polished cross-sectioned specimens were imaged using cross-polarized reflected light microscopy (Figs. 1(A) and (B)). Air quenching, though reported in the literature to be effective,$^{17}$ yielded only polycrystalline ingots. Water quenching was somewhat more effective, but it was only able to produce ingots that were partially amorphous around the perimeter (Fig. 1(B)) or cracked. However, by using the DC ampoule method, and reducing the Ge content, it was possible to form crack-free, amorphous ingots (Fig. 1(C)). The improvement in glass formability by reducing Ge content was anticipated, based on reports by Hong and colleagues.$^{14,28}$ Quenching in liquid Ga was also effective, and an example of a Ge = 1.0 ingot is shown in Fig. 1(D).

Extensive materials characterization was necessary in order to validate that the processing methodology was not introducing contamination or producing artifacts that would obscure or interfere with analyzing performance data. Stoichiometric control of the batching and synthesis of CGA glass was validated using RBS and PIXE in a complimentary fashion. The absolute elemental concentration of Cd was measured with RBS (Fig. 2). Unfortunately, overlap of the data for As and Ge interfered with precise measurement of their individual concentrations. Consequently, PIXE was used to identify the elemental ratio of As:Ge while normalizing to the RBS measurement for Cd. This method was used to provide accurate compositional measurements (Fig. 2). Specimen homogeneity was evaluated by translating the specimen and making measurements at $\sim 1.2$–1.5 mm intervals across the diameter of the disk. Different slices taken from the same ingot were also analyzed to establish homogeneity along the axis of the ingot. The experimental results are shown in Table II and indicate that stoichiometry was maintained within $\pm 1$ at.%. The extra, unlabeled peaks in the PIXE plot were attributed to pulse pile-up and escape peak artifacts, based on complementary analysis of these specimens by SIMS.

SIMS was chosen for the purpose of corroborating the RBS and PIXE results as well as to analyze specimens for trace elemental contamination. Four different specimens were examined. There was no evidence of any transition metals. Transition metal contaminants have been shown to have a measurable effect on electrical transport properties in CGA glass.$^{29,30}$ Consequently, this type of contamination could seriously interfere with electrical characterization experiments, and prevent unambiguous correlations between processing, composition, and property relationships. This data combined with the results...
from RBS and PIXE substantiated that the synthesis process was able to accurately achieve the specified stoichiometry and that the process was clean, and essentially free of trace contamination down to ppm levels.

X-ray diffraction results of a CGA glass with 0.85 Ge content are shown in Fig. 3(A), and are typical of all compositions. Short range order in the CGA glasses was evaluated by calculating the atomic pair distribution function (PDF) from the amorphous XRD spectra. For PDF calculations, XRD spectra were collected from 5°–144° 2θ at a step interval of 0.05° with a dwell time of 3 s/step, and summing up the results of three scans. The spectra were collected using the same diffractometer described previously. Atomic PDF calculations were performed using the computer program “PDFgetX2”. The results are shown in Fig. 3(B). Detailed measurements of the PDF nearest neighbor (NN) peak heights for four CGA glasses, and the crystalline reference are shown in Table III. The PDF plots for all of the CGA glasses were very similar with the individual peaks being located within ±0.1 Å of each other. The trend is that the NN distances increased slightly from 0.45 to 0.65 Ge for four measurable NN peaks. However, at 0.85 Ge, the NN distances decreased below the value for 0.45 Ge for the first 3 NN peaks but increased steadily at the fourth NN peak. Overall, the PDF’s show that the amorphous CGA glasses have a high degree of short range order out to the third NN. In comparison to the computed PDF plot for the crystalline reference, the G(r) plot for the amorphous CGA was shifted to the right, had shorter NN distances, broader peaks, and lost coherency after the third NN at 6.3 Å.

The PDF computed from the crystal structure model of CdGeAs$_2$ consisted of four prominent peaks with a shoulder on the third one. Peak assignments were based on measurements

| Table II. Summary of Line Scan Compositional Data Computed from Combined RBS and PIXE Analysis for CdGeAs$_2$ Glass (Measurement Accuracy, ±0.5%) |
|---|---|---|---|
| Spot | Cd (at.%) | Ge (at.%) | As (at.%) |
| 0 | 25.6 | 24.7 | 49.6 |
| 1 | 25.9 | 24.6 | 49.5 |
| 2 | 25.9 | 24.6 | 49.5 |
| 3 | 26.0 | 24.6 | 49.4 |
| 4 | 25.9 | 24.6 | 49.4 |
| 5 | 25.9 | 24.7 | 49.3 |
| 6 | 25.7 | 24.8 | 49.5 |
| Average: | 25.9 | 24.7 | 49.5 |

| Table III. Summary of Atomic Pair Distribution Data for CdGe$_{x}$As$_2$ |
|---|---|---|---|---|
| Ge:Cd ratio | First NN | Second NN | Third NN | Fourth NN |
| 0.45 | 2.56 | 4.09 | 6.34 | 7.45 |
| 0.65 | 2.57 | 4.10 | 6.40 | 7.49 |
| 0.85 | 2.55 | 4.06 | 6.32 | 7.51 |
| 1.0 | 2.56 | 4.10 | 6.36 | 7.46 |
| CdGeAs$_2$ reference | 2.53 | 4.35 | 6.32$^*$ | 7.23$^*$ |

$^*$Shoulder on the third prominent peak. NN, nearest neighbor.
made of the crystal structure model of CdGeAs$_2$ (as published by Marenkin$^{35}$) using the computer program “CrystalMaker”$^a$. The first peak was located at 2.52 Å and was attributed to the convolution of the As–Ge and As–Cd bonds at 2.425 and 2.633 Å, respectively.$^{4,25}$ The second peak was at 4.35 Å and was assigned to As–As second NN at distances of 4.219 and 4.459 Å. Atom pair distances between Cd–As and Ge–As exist at 6.33 and 6.35 Å, thus the shoulder in the crystalline PDF at 6.32 Å was assigned to these atom pairs. The third prominent peak in the crystalline PDF was located at 7.23 Å and was assigned to As–As atom pairs, since several As–As atom pair distances were measured at 7.14, 7.43, and 7.91 Å. The fourth peak was located at 8.64 Å and most likely corresponds to several different atom pairs (Cd–Cd, Ge–Ge, and As–As) that all occur at 8.402 Å in the crystal model.

The first peak of $G(r)$ for the CGA glasses was located at 2.56 Å and was at a slightly farther distance than in the crystal PDF. The farther NN distance in the CGA glass is probably due to the fact that most of the glasses have a lower Ge content than the crystal, thus causing a slight peak shift toward the longer As–Cd bond distance of 2.633 Å. The second NN peak was located at approximately 4.09 Å for the amorphous $G(r)$, and its position was 5.6% shorter than the second NN distance for the crystalline specimen. These peaks were assigned to As–As second NN distances as was the same for the perfect crystal. The higher relative intensity of this peak is consistent with the fact that these compounds contain at least 50% As. Additional corroborating data are needed to make a definitive assignment of specific atom pairs to the PDF peaks in the amorphous CGA glasses beyond the second NN. For example, it is not clear whether the third peak in the amorphous PDF at 6.35 Å corresponds to the shoulder in the crystalline PDF at the same location (e.g., Cd–As and Ge–As atom pairs), or to the prominent third peak due to As–As atom pairs located almost an angstrom farther away, or possibly the convolution of other possible atom pairs. Because the glasses contain at least 50% As, and since the amorphous PDF peak at 4.09 Å was shifted to the right, the third peak in the amorphous PDF may be due to As–As atom pairs, but a peak shift of approximately 0.88 Å seems unusually large. The fourth peak for the amorphous specimens occurred from 7.4–7.5 Å, and was very diffuse. Again, definitive assignment of this peak was not possible. Several As–As atom pair distances in the single crystal structure at 7.14, 7.43, and 7.91 Å, so this peak may be due to a convolution of those atom pairs.

The macroscopic bulk densities (g/cm$^3$) of the samples were measured using He pychnometry and were found to vary as a function of Ge content, processing method, and structure (i.e., crystal vs. amorphous); see Fig. 4. The density for crystalline compounds decreases going from 5.86 g/cm$^3$ for CdAs$_2$ to 5.62 g/cm$^3$ for CdGeAs$_2$ (a pseudo trend-line was drawn as a guide to the eye).$^{12,35,36}$ A similar variation in density with Ge content was observed for the amorphous specimens fabricated in this study, however, the amorphous compounds were approximately 2% more dense than their crystalline counterpart at $x = 1.0$. This was consistent with data reported elsewhere.$^{12,14}$ The shift in NN distances to shorter values as observed in the amorphous PDF (Fig. 3(B)) also illustrates this relationship. The variation in density with phase was important to note while interpreting failed experiments, so as to make appropriate processing adjustments. Density variations with processing method indicated that the DC-quenched specimens were slightly denser than the LG-quenched specimens. Because the amorphous phase was denser than the crystalline phase, the higher density may have been due to the additional constraint imposed by the annular Cu ring in the DC ampoule, or it may be an indication that the DC quench method was slightly faster than the LG method. Although the macroscopic bulk density decreases with increasing Ge content, it is important to point out that the atomic density (atoms/cm$^3$) increases with Ge content. This is explained by the change in average atomic mass and in covalent or atomic radius of the atoms as the alloy changes composition.

The electronic structure of crystalline semiconductors is modeled as having a distinct conduction and valence band edge with a well-defined band gap. Amorphous semiconductors typically exhibit bands of extended states with band edges similar to those of the crystalline materials combined with increasingly localized states below the band edge whose density decays exponentially with energy away from the band edge. The exponentially decaying density of states is referred to as a band tail. Finally, there are isolated states in the energy gap (properly the mobility gap), which give rise to a typically constant density of states. The optical absorption coefficient of the material reflects the product of the density of states in the valence and conduction bands. Therefore, the absorption coefficient typically shows a quadratic decrease near the energy separating the two sets of extended states, an exponentially decaying behavior resulting from the band tails, and a constant absorption for energies where only isolated defect states occur.

Optical absorption spectroscopy and ellipsometry were used to characterize the transition from the band edge toward the middle of the mobility gap. At the band edge, the material is relatively opaque, and the optical absorption coefficient becomes very large. Therefore a simple transmission/reflection model will not work. Ellipsometry, however, provides a measure of the absorption coefficient out to much lower transmission values. Toward the middle of the mobility gap, the material is more transparent and optical transmission measurements suffice. The greater the density of defect states in the material, the more gradual the transition will be from the band edge to the mobility gap, and the higher the absorption coefficient will be in the gap region. Consequently, improved electrical conduction properties depend on minimizing the density of defect states. Ideally the material should be characterized by (1) a steep slope of the absorption coefficient curve at the mobility edge and (2) minimizing the low-energy absorption coefficient. The effects of composition and processing conditions on the density of defect states was thus evaluated.

Optical absorption coefficient measurement results for a variety of CGA glasses and processing methods are shown in Fig. 5 and combined optical absorption and ellipsometry results are given in Fig. 6. The effect of composition on the density of defect states was evaluated for both the DC and the LG quench methods. The variation for both processing methods was similar, increasing the Ge content resulted in a reduced optical absorption coefficient (Figs. 5(A) and (B)). There was about a 50% reduction in the absorption coefficient upon changing the Ge content from $x = 0.45–0.85$ Ge for the DC process, whereas for the LG process, there was over a factor of 4 reduction in the absorption coefficient for changing the Ge content from 0.65 to 1.0.
The effect of processing method (DC vs LG) on the density of defect states was also evaluated. Two different Ge compositions were selected (0.65 and 0.85 Ge), and ingots were made from each composition using both of the processing methods. Optical absorption coefficients were measured as a function of energy for samples taken from each ingot, and the results for 0.85 Ge are shown in Fig. 5(C). For both compositions the results were the same; the DC quench process yielded a lower optical absorption coefficient curve than the LG quench process. For a composition of 0.65 Ge, the DC process resulted in approximately a threefold reduction in the absorption coefficient from the maximum value measurable to the constant value far below the absorption edge. For the 0.85 Ge composition, the absorption coefficient data were lower by over a factor of two in the gap compared with the highest measurable value. The results were similar for samples thinned as much as the mechanical properties of the material would permit.

Reducing the density of defect states in amorphous semiconductors is a common concern. Amorphous silicon (a-Si) is one of the most prevalent amorphous semiconductors and is widely used in photovoltaic applications. One strategy used to reduce the density of defect states in a-Si is to dope it with hydrogen during thin film deposition. The hydrogen acts to passivate dangling bonds. Because CGA glass is a tetrahedrally bonded material just like a-Si, hydrogen doping (as described in the experimental section) was evaluated to determine if it could have a similar positive effect on reducing the density of defect sites. A comparison was made between two different specimens, both having the same composition (0.85 Ge) and both processed in the same method (LG), but one was doped with hydrogen. The optical absorption coefficient measurement results are shown in Fig. 5(D). Hydrogen doping was able to reduce the absorption coefficient values in the midgap energy range by almost a factor of two.

The results of the optical absorption data indicates that it is possible to reduce the density of defect states in CGA glass both near the mobility edge as well as in the middle of the mobility gap. This can be achieved by controlling composition, processing conditions, and by doping the material with hydrogen.

Hall conductivity measurements as a function of temperature were made on several different CGA glasses. In general, the Hall conductivity trends paralleled those of the absorption coefficient data: specimens with lower optical absorption coefficients had lower Hall conductivity values. Increasing Ge content resulted in lower conductivity and DC-quenched specimens had lower conductivity values than LG-quenched specimens with the same composition.
IV. Conclusions

Two different methods for synthesizing bulk, crack-free ingots of CGA glass were developed. The use of pyrolytic coatings lining the process ampoules was dismissed due to problems associated with reduced ingot yield, contamination of the melt by the coating, and degradation of the resulting electrical properties. Stoichiometry control, homogeneity, and minimal trace elemental contamination of the synthesized ingots validated the ability of both processes to yield good quality, high-purity amorphous materials. PDF analysis of CGA glasses showed that they retained NN atomic coherency out to the third NN. The PDF peaks were broader and located at shorter distances than in the crystal, but tended to increase in distance with Ge content. Composition-property and processing-property relationships were demonstrated using optical absorption spectroscopy and Hall conductivity. The results indicate that the density of defect states in the material near the band edges and in the middle of the mobility gap can be reduced three different ways: (1) by increasing the Ge concentration, (2) using the DC quench process, and (3) by doping with hydrogen. The variation in properties with composition was attributed to the effect of Ge on the short-range order in the material. Thus, we have been able to demonstrate broad control of semiconductor properties for Cd–Ge–As glasses by manipulating composition and processing parameters, and have been able to achieve an increase in room temperature resistivity over an order of magnitude greater than previously reported.

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