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Luminescence and optical absorption study of p-type $CdGeAs_2$

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Abstract
A photoluminescence (PL) study has been performed at liquid-helium temperature on a set of over 50 p-type bulk single-crystal samples of $CdGeAs_2$. As part of the study, the effect of surface preparation on PL emission was evaluated. Room-temperature optical absorption measurements that monitored the intensity of the intervalence band transition peaking near 0.22 eV (i.e. 5.5 μm) were compared with the low-temperature PL data. Every sample exhibited a PL band near 0.35 eV related to a deep acceptor. A second PL band near 0.55 eV was present in all of the samples having a large absorption band, but was observed in only a few samples with an absorption coefficient less than 3 cm^{-1} at 0.22 eV. We attribute this second band to donor–acceptor-pair recombination involving a shallow 120 meV acceptor and residual donor impurities. To produce low-absorption material for use in nonlinear optical devices, it is necessary to reduce the concentration of both acceptors or, alternatively, to dope with donor impurities that provide compensation.

1. Introduction

Cadmium germanium arsenide ($CdGeAs_2$) is a nonlinear optical material suitable for use in a variety of infrared frequency conversion applications. At room temperature, the transparency range of this material extends from about 2.3 μm to beyond 17 μm. Single crystals of $CdGeAs_2$, of ample size for fabricating optical devices, have been grown using the horizontal gradient freeze (HGF) technique [1–4]. Efficient frequency doubling of high-power CO_2 lasers has been demonstrated [5] and tunable infrared output using $CdGeAs_2$ crystals has also

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been reported [6, 7]. To further improve the infrared conversion efficiency of $CdGeAs_2$, a defect-induced absorption band peaking near 5.5 μm at 300 K needs to be eliminated from the as-grown crystals. Reducing the absorption losses will allow the nonlinear optical devices to operate at higher input and output powers.

$CdGeAs_2$ is a direct-gap semiconductor which crystallizes in the chalcopyrite structure. Its bandgap energy is approximately 0.57 eV at 300 K and approaches 0.7 eV at 5 K. This material has three closely spaced valence bands due to the spin–orbit and crystal field splitting [8]. The absorption band commonly seen near 5.5 μm (about 0.22 eV) in p-type material increases in intensity with temperature and with hole concentration, and is attributed to transitions from the second-highest valence band to the highest valence band. In general, this intervalence band absorption is enhanced in samples when holes in the highest valence band are produced through the thermal ionization of acceptor states [9]. The energy difference between the top two valence bands (at $k = 0$) is approximately 0.16 eV. Theoretical models that include the transition probabilities for nonzero k have predicted the absorption band to be centred near 0.22 eV [10, 11] and this agrees with experimental data. The absorption band at 5.5 μm is highly polarized, with the intensity measured with $\boldsymbol{E} \parallel c$ being about 3 times larger than that measured with $\boldsymbol{E} \perp c$ [12]. Recently, the Ge_{As} antisite defect was proposed as a possible model for the primary shallow acceptor that causes this absorption in bulk p-type $CdGeAs_2$ crystals grown by the HGF technique [12]. It has been shown in separate experiments that electron irradiation of as-grown p-type bulk crystals provides appreciable compensation of acceptor defects and thus reduces the 5.5 μm absorption [13].

Bulk $CdGeAs_2$ crystals generally exhibit two photoluminescence (PL) bands. A broad band near 0.35 eV has been assigned to donor–acceptor-pair (DAP) recombination by one group [14] and to an (e, A^0) transition by another group [15]. In these earlier studies, the deep acceptor was not identified. A second PL band peaks near 0.55 eV and shifts to higher energies with increasing excitation intensity. This second band was suggested to be a DAP transition involving a shallower acceptor [14, 15] and has been observed to shift in peak position by tens of millielectronvolts just by moving the excitation location several mm across a sample surface. This behaviour of the 0.55 eV emission can be explained by DAP recombination in the presence of potential fluctuations [16]. In the present study, sets of data taken from a large number of $CdGeAs_2$ samples grown at two different locations are used to establish a correlation between the room-temperature absorption band at 5.5 μm and the PL band peaking near 0.55 eV.

2. Experimental methods

The $CdGeAs_2$ samples used in this investigation were grown by the HGF technique at BAE Systems (formerly Sanders, a Lockheed Martin Company) and at Stanford University. Absorption and PL experiments were performed on 51 bulk single-crystal $CdGeAs_2$ samples cut from 17 different boules. Sample surfaces were mechanically polished using diamond paste with granulation down to 0.1 μm. The effects of additional chemical etching with three different mixtures of HNO_3:HF:H_2O were evaluated. Specifically, PL data were obtained from sample surfaces before and after etching treatments to determine whether changes in the PL spectra could be introduced by modifying the surfaces. This general etch solution has been used previously in a 3:1:2 ratio for preparation of $CdGeAs_2$ surfaces for absorption and photoconductivity studies [17] and in a 1:1:2 ratio for etch-pit density studies [18].

The amount of surface roughness on mechanically polished and chemically etched surfaces was measured with a scanning probe microscope (JEOL SPM-4210) at atmospheric pressure. The instrument was operated in the contact-atomic force microscopy (AFM) mode.

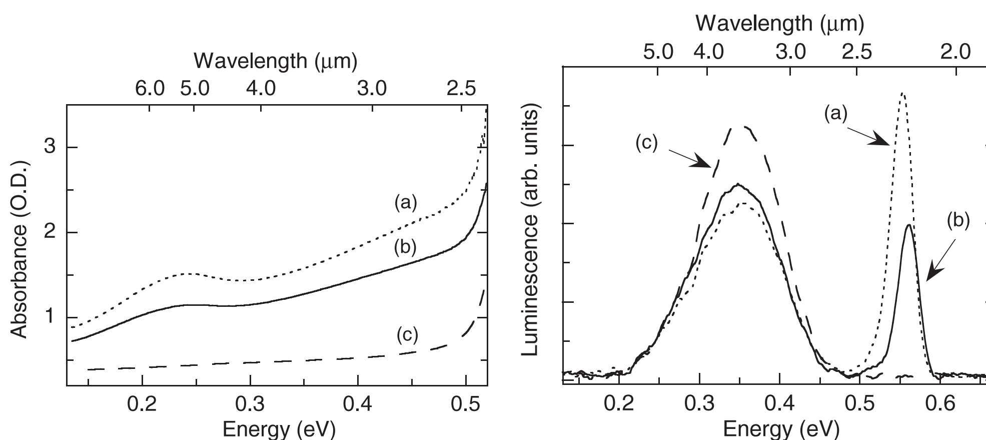

Figure 1. Absorption spectra taken at three positions on a cross-section slice of a $CdGeAs_2$ boule. Data were taken at room temperature from (a) the edge or 'dark' region, (b) the boundary between the two regions and (c) the centre or 'light' region of the slice.

Figure 2. PL spectra taken at the three positions used to obtain the absorption data shown in figure 1. The measurement temperature was 10 K and the excitation power density was 2.5 W cm^{-2}. The (a), (b) and (c) labelling is correlated with figure 1.

Topographic surface images were calibrated using a set of micromesh silicon gratings obtained from K-Tek International. The Olympus cantilevers used in the analysis were from Asylum Research.

Infrared absorption and PL data were taken using a nitrogen-purged Fourier-transform infrared (FTIR) spectrometer (ThermoNicolet Nexus 870). Absorption data were taken with $\boldsymbol{E} \perp c$ at room temperature using a KBr beamsplitter and a HgCdTe detector cooled to 77 K. Reflective losses, scattering and other contributions (tails of partially overlapping bands) to the absorption at 5.5 μm were subtracted out, thus giving the absorption coefficient (α) due to the discrete intervalence band transition only.

The PL spectra were acquired using a CaF_2 beamsplitter and the cooled HgCdTe detector. Samples were mounted in an Oxford Instruments cryostat (helium-gas flow system) positioned outside the FTIR. This allowed the sample temperature to be maintained near 10 K during the measurements. A Nd:YAG laser operating at 1.064 μm (1.17 eV) was used as an above-bandgap cw excitation source. The incident power density of the laser beam on the sample was about 2.5 W cm^{-2} unless indicated otherwise. Emitted light was collected by a CaF_2 lens and directed into the FTIR spectrometer through an external port. Scattered laser light was blocked by a polished Ge wafer placed in the optical path and used as a long-pass filter. An optical chopper and lock-in amplifier allowed detection of the PL signal portion of the interferogram provided by the internal HgCdTe detector of the FTIR system.

3. Results and discussion

Achieving uniformly low absorption throughout a boule is a major challenge in the growth of $CdGeAs_2$ crystals. Optical absorption spectra measured at different locations within a boule often provide evidence that significant variations are present. Figure 1 shows room-temperature absorption spectra taken at three different positions on a large cross-section slice cut from a $CdGeAs_2$ boule. This cross-section slice has dark regions toward the edges (i.e. high absorption) and light regions in the middle (i.e. low absorption) [4]. Curve (a) was taken from the dark region near one edge of the slice. Curve (b) was taken from an intermediate position

bordering the dark and light regions of the slice. Curve (c) was taken from the light region in the centre of the slice. The absorption band at 5.5 μm is large in the dark region near the edge and is too small to observe in the light region near the centre.

The PL spectra shown in figure 2 were taken from the same three sample locations used to obtain the absorption data shown in figure 1. These PL data were taken at 10 K. There are two emission bands at about 0.35 and 0.55 eV. The broad emission centred near 0.35 eV is present in all three sets of data. Comparing figures 1 and 2, the sample region with large absorption at 5.5 μm (curve (a) in both figures) has the brightest PL emission at 0.55 eV and the lowest PL emission at 0.35 eV. The intermediate absorption region (curve (b) in both figures) exhibits a weaker PL emission at 0.55 eV and a slightly stronger emission at 0.35 eV. In contrast, the low-absorption region (curve (c) in both figures) does not have the PL band at 0.55 eV and has the largest PL band at 0.35 eV.

The absorption and PL data in figures 1 and 2 suggest a direct correlation between the PL emission at 0.55 eV and the intervalence band absorption at 5.5 μm. These data were taken, however, on mechanically polished surfaces. Because the above-bandgap excitation used in our PL measurements is absorbed in the near-surface region of the sample, the intensity of the PL could be strongly dependent on surface treatment. Since the absence, or presence, of the 0.55 eV band is an important aspect of our study, a comparison of mechanically polished and chemically etched surfaces was performed in order to determine whether the ability to detect the PL bands would change as a function of surface treatment.

In many materials, PL emission from chemically etched surfaces will be much more intense than from mechanically polished surfaces. This is because surface states often provide nonradiative recombination sites. Figure 3(a) shows a three-dimensional AFM topographic image of a 20 μm $\times$ 20 μm area of a mechanically polished $CdGeAs_2$ sample. Scratches can be clearly seen along random directions on the surface. The mean surface roughness was 101 nm (with a rms value of 17.5 nm), which agrees with the 0.1 μm size of the finest diamond paste used in the mechanical polishing. Three different mixture ratios of HNO_3:HF:H_2O were then explored as a means of modifying/improving the sample surfaces. A representative etched surface using a 3:2:2 ratio for approximately 2 s at room temperature is shown in figure 3(b). About 15 μm was removed from the sample surface by this chemical etch. The resulting mean surface roughness was 64 nm (with a rms value of 10.5 nm), thus representing an improvement of about a factor of 1.6 compared to the mechanical polish.

Figure 4 illustrates the effects of three different chemical etching strengths on the PL emission from $CdGeAs_2$ surfaces. Data from three different 'dark' (high α) samples are shown, each etched with a particular ratio of HNO_3:HF:H_2O. PL data were taken before (full curves) and after (broken curves) the chemical etchings. In figure 4(a), the sample was etched in a weak 1:1:4 solution of HNO_3:HF:H_2O for 145 s. About 4 μm was removed from the surface. The intensity of both PL bands decreased after etching. The sample in figure 4(b) was etched in a 3:2:2 solution of HNO_3:HF:H_2O for 2 s. About 15 μm was removed during this etching process. The intensity of both PL bands increased and the higher energy band (near 0.55 eV) shifted slightly to lower energy. The sample shown in figure 4(c) was etched in a 3:1:2 ratio of HNO_3:HF:H_2O for 30 s. About 200 μm was removed from the sample surface. The intensity of the lower energy PL band did not significantly change and the intensity of the higher energy band decreased. This latter band shifted to higher energy.

In figure 4, the two cases where the PL intensity at 0.55 eV decreased after etching also show a shift of this band to higher energies. In figure 4(b), where the intensity increased after etching, the band shifts to slightly lower energy. This behaviour is consistent with the DAP transition model in the presence of potential fluctuations, where more participating defects (i.e. brighter PL) will shift the band to lower energies [19]. Before and after etching, the

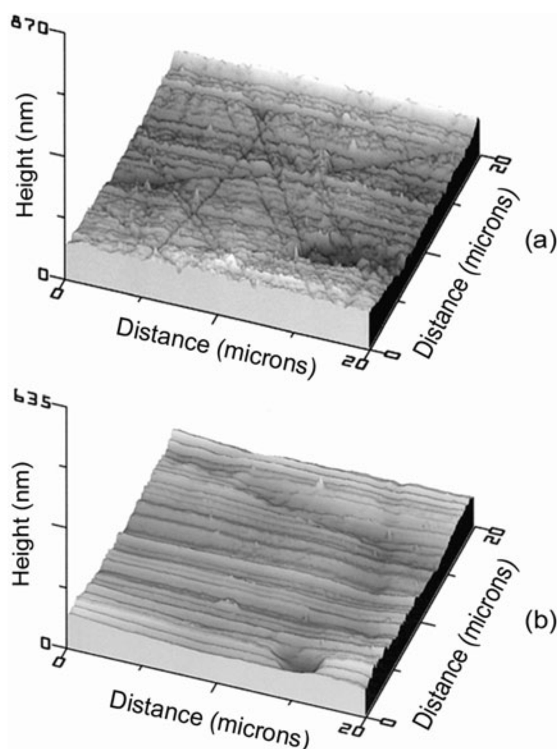

Figure 3. AFM topographic images of $CdGeAs_2$ surfaces after (a) a mechanical polish only and (b) a mechanical polish followed by an etch in a 3:2:2 ratio of HNO_3:HF:H_2O.

PL spectra from the three 'dark' $CdGeAs_2$ samples consistently show the 0.55 eV band as being more intense than the 0.35 eV band. In general, our etching study did not indicate major changes in the PL emission as a result of these surface treatments. Samples that initially had one primary PL band still have the one band after etching and samples that initially exhibited two emission bands still have these two bands after etching, with the higher energy band being dominant. We attribute the changes in peak intensity and in peak position observed during etching to the possibility that the samples are not uniform in depth. Although AFM measurements clearly indicated that the surface morphology of $CdGeAs_2$ was improved after etching for all these samples, our optical results suggest that mechanically polished surfaces have sufficient quality for PL measurements.

After verifying that the mechanically polished $CdGeAs_2$ surfaces were suitable for our PL and absorption correlation study, we then collected sets of data from 51 samples. These results are summarized in figure 5. The horizontal axis represents the energy of the observed PL bands at 10 K and the vertical axis is the room-temperature optical absorption coefficient measured at 5.5 μm for the intervalence band transition. Each sample has a specific absorption value and there are either one or two data points entered on the plot for that value of absorption, representing the one or two PL bands that were present in the sample. Information about the relative intensities of the PL bands is not included. This large sample set contained crystals with a wide variation in the absorption coefficient at 5.5 μm. The vertical axis in figure 5 is logarithmic and data spanned a range of over two orders of magnitude.

We see two types of behaviour in figure 5. When the absorption coefficient at 5.5 μm is above 3 cm^{-1}, both PL bands are always present. In contrast, when the absorption coefficient

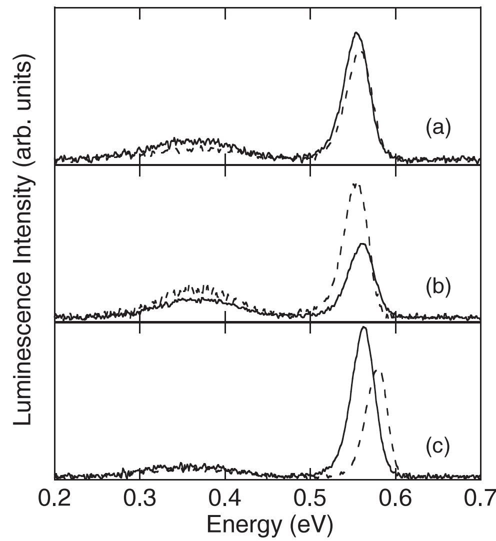

Figure 4. PL spectra before and after chemical etching for three 'dark' $CdGeAs_2$ samples. Full curves are data obtained from mechanically polished surfaces (i.e. before etching). Dotted curves are data taken after HNO_3:HF:H_2O etching with (a) a ratio of 1:1:4 for 145 s ($\sim$4 μm removed); (b) a 3:2:2 ratio for 2 s ($\sim$15 μm removed) and (c) a 3:1:2 ratio for 30 s ($\sim$200 μm removed).

is below 3 cm^{-1}, only a few samples have the high-energy PL band. Of the 51 samples included in this figure, only 6 out of the 32 with the absorption coefficient less than 3 cm^{-1} had both PL bands present, whereas all 19 samples with the absorption coefficient greater than 3 cm^{-1} had both PL bands present. These results lead us to conclude that the main decrease in intervalence band absorption is due to a reduction in the concentration of shallow acceptors involved in the DAP recombination, and not due to compensation. We note that there are a few samples (i.e. the six previously mentioned) with a low absorption coefficient at 5.5 μm which do display this higher energy PL band. In those cases, we believe the decrease in free hole concentration is due to compensation of acceptors with donors, and the DAP transition is still a radiative recombination path. Although not shown, there were three samples included in this large sample set which also displayed a very weak PL emission near 0.6 eV. We suggest that this band is the electron–acceptor (e, A^0) transition involving the same shallow acceptor that participates in the 0.55 eV DAP emission. From our prior study [16], we determined the energy of this acceptor to be 120 meV and this is in agreement with our assignment of the (e, A^0) transition to a peak near 0.6 eV. For samples with the PL band peaking near 0.55 eV, the data in figure 5 show that the energy position varied significantly from sample to sample. These large peak shifts are associated with the potential fluctuations [19] caused by variations in the concentration of ionized donors and acceptors.

In performing a sample-to-sample PL comparison, it is important to keep the same incident power density. The relative intensities of the two PL bands in $CdGeAs_2$ change significantly with power, as shown in figure 6 for a sample with an absorption coefficient at 5.5 μm of 5.8 cm^{-1}. The integrated intensities for the 0.35 eV band (triangles) and the 0.55 eV band (circles) are plotted as a function of incident power density. In our measurements, the power could only be varied by a factor of 40 (the upper limit was established by the maximum output intensity of our laser). At the lower powers, the 0.55 eV PL signal was difficult to detect. The straight lines are the curve-fitting results using a general power-law expression of the form $I \sim J^k$, where I is the PL intensity, J is the incident power density used for excitation and k is

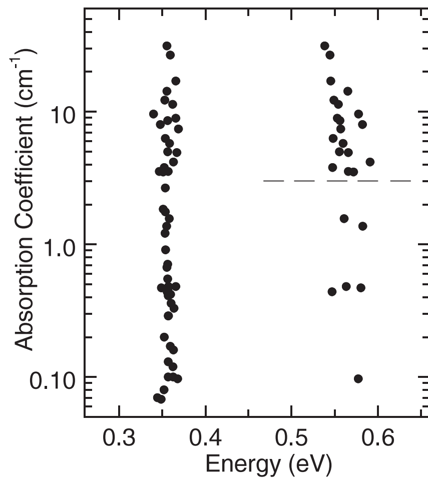

Figure 5. The absorption coefficient at 5.5 μm and the corresponding peak positions of the PL bands are shown for 51 $CdGeAs_2$ samples. For some samples, both the 0.35 and the 0.55 eV PL bands were present. Other samples had only the 0.35 eV PL band. The broken line indicates an absorption coefficient of 3 cm^{-1}.

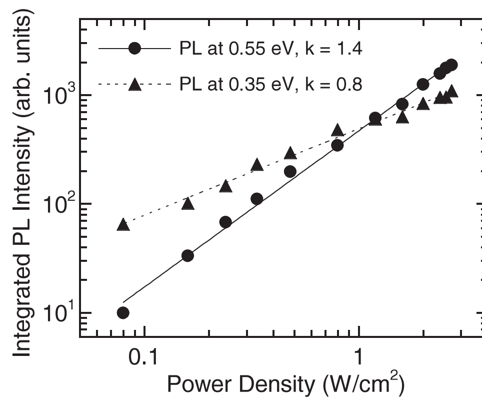

Figure 6. Integrated PL intensity versus incident power density (J) for the PL at 0.35 eV (triangles) and the PL at 0.55 eV (circles). The straight lines are the 'best-fit' results obtained using the power-law expression, $I \sim J^k$.

an exponent which can vary from much less than 1 to as high as 2 for different recombination processes [20]. From the data in figure 6, the exponent describing the lower energy PL band was $k = 0.8$. The exponent describing the 0.55 eV band was $k = 1.4$. Aufgang *et al* [15] reported similar values of $k = 0.85$ for PL near 0.35 eV and $k = 1.2$ for PL in the 0.5–0.6 eV range. We performed the same analysis on five additional high-absorption samples from our set. In general, k varied from about 0.7 to 0.9 for the 0.35 eV PL band. The exponent k for the 0.55 eV band varied from 1.2 to 1.7. Also, when the sum of the two integrated intensities was considered, the power dependence of the total integrated PL emission could be described by $k \sim 1$. Since the PL near 0.55 eV has already been assigned to DAP recombination, we suggest that the 0.35 eV PL is another DAP recombination involving the same donor but a different deeper acceptor, in agreement with McCrae *et al* [14]. Thus, the two PL bands represent two separate recombination paths, both involving shallow donors, that compete with each other in a particular sample. Typically, if one can vary the excitation power by many orders of magnitude, then the intensity of DAP emission will not be described by a power law expression with a single exponent and the saturation in intensity is due to the limiting number of defects in the sample volume being probed. Within our relatively small excitation range, we did not observe this saturation in DAP intensity. However, we did observe different behaviours for the two PL bands in the $CdGeAs_2$ crystals. The $k < 1$ value for the 0.35 eV band is consistent with a smaller overall concentration of the deeper acceptor centre, while the $k > 1$ value for the 0.55 eV band results from having a larger concentration of the shallow acceptor, which is the dominant cause of the p-type behaviour in high-absorption $CdGeAs_2$ crystals grown by the HGF technique.

4. Summary

In conclusion, we found that the PL spectra obtained from mechanically polished $CdGeAs_2$ surfaces was very similar to chemically etched surfaces, although etching clearly produced

improvements in surface morphology. There are two primary PL emission bands observed from $CdGeAs_2$ grown by the HGF technique. These bands occur near 0.55 and 0.35 eV. The PL band peaking near 0.55 eV is DAP recombination related to a shallow acceptor and is observed in all samples with enhanced intervalence-band absorption at 5.5 μm. The PL near 0.55 eV was also seen in a few low-absorption samples, indicating that the shallow acceptor defects are still present in these cases but are compensated by donors so that the free hole concentration is significantly reduced. Most low-absorption samples did not exhibit the 0.55 eV emission or it was too weak to detect. Thus it is possible to significantly reduce or completely eliminate this shallow acceptor defect during growth. The PL band near 0.35 eV was observed in all of our samples and is believed to be DAP recombination related to a deeper acceptor. Thus, our PL measurements indicate that the deeper acceptor is a common feature for all these bulk p-type $CdGeAs_2$ samples grown by the HGF technique.

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