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CATHODOLUMINESCENCE STUDIES OF THE 1.4 eV BANDS IN VAPOR-PHASE-GROWN CdTe

C. B. Norris

Sandia Laboratories
Albuquerque, New Mexico 87185

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Vapor-phase-grown CdTe is interesting in that it represents an alternate growth technology for CdTe and in addition provides an alternate setting in which to observe the poorly-understood 1.4 eV luminescence that has received much attention in liquid-phase-grown material. In this paper we present the first cathodoluminescence measurements in vapor-phase-grown CdTe. We describe the injection level dependence, temperature dependence, and frequency response of the luminescence of vapor-phase-grown CdTe and compare the results to those reported previously on liquid-phase-grown CdTe.

Key Words: cadmium telluride, luminescence

Introduction

CdTe is a technologically-important compound semiconductor with definite applications in radiation detection systems and possible usefulness in optoelectronic systems. CdTe is particularly suitable as a solid-state radiation detector because of its combination of high average Z-number, moderate band-gap, fair transport properties, and useful p- and n-type conduction. However, virtually all the performance results reported to date on CdTe detectors

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are dominated by extrinsic properties of currently-available materials. Thus, there is strong motivation for fundamental studies relating to defect energy levels and recombination and trapping processes in CdTe, and also for the exploration of different growth methods for the production of CdTe.

Previously, we have reported luminescence studies (1,2) which were directed toward understanding the nature of the defects responsible for the commonly-observed 1.4 ev extrinsic luminescence in CdTe and also toward establishing the nature of the electronic transition involved. This work, as most of the reported experimental work in CdTe, was performed on liquid-phase-grown material. However, it has been noted (3) that vapor-phase-growth may hold promise for improving the quality of CdTe. Furthermore, radiation detectors have been fabricated from vapor-phase-grown material. (4,5) Although its potential device advantages have yet to be demonstrated, vapor-phase-grown (VPG) CdTe provides an interesting comparison to the liquid-phase-grown (LPG) material. In this paper, we extend our earlier luminescence research on CdTe to studies of the injection level dependence, frequency response, and temperature dependence of cathodoluminescence in VPG CdTe and compare the results to those reported previously for LPG CdTe.

Experiment

Both the experimental apparatus and methods used in the present work are identical to those used in previous studies on CdTe. (1,2,6) In brief, cathodoluminescence measurements were performed with uniform excitation of an accurately known sample area (0.0955 cm^2) by a 20-keV electron beam. The range of 20 keV electrons in CdTe is approximately 1.4 μm. (7) The electron beam was sinusoidally current-modulated and the modulation frequency signal in the photomultiplier output was detected and digitized. A computer data acquisition system was employed to simultaneously record the digitized luminescence signal and monochromator wavelength.

The effects of different electron-hole pair injection levels on the luminescence spectra were determined in a routine manner by recording spectra excited using different electron beam currents at constant beam potential. The luminescence kinetics were investigated by changing the electron beam modulation frequency while keeping the electron beam voltage and both the DC and AC components of the beam current constant. Reproducible electron beam excitation conditions were ensured through energy analysis of the incident electron beam together with use of a Faraday cage surrounding the copper cryostat block on which the CdTe samples were bonded.

Luminescence spectra were recorded over a photon energy range of 1.0-1.6 eV. In the spectra to be displayed, the lowest 0.1-0.2 eV of recorded data are suppressed owing to the absence of meaningful luminescence and the comparatively poor signal-to-noise ratio in that region. All displayed spectra were computer-plotted and have been accurately corrected for the wavelength-dependent response of the complete optical detection system. The monochromator slit openings used gave a 24 Å FWHM system resolution, which corresponds to a worst-case photon energy resolution of 5 meV at energies near 1.6 eV.

The VPG CdTe used in the present studies was nominally undoped material grown by L. R. Shiozawa at Cleveland Crystals, Inc. The growth occurred within a closed silica tube approximately 30 cm in length which was inserted in a short horizontal tube furnace. The tube was intentionally subjected to a bell-shaped temperature profile which peaked at 1065°C near the center of the tube. Self-nucleated crystal growth occurred at the cooler ends of the tube through sublimation of a sintered CdTe powder slug placed centrally within the tube. Exhaustion of the source occurred after a period of 4-5 days, but the furnace temperature was maintained for several days more in order to increase the dimensions of the single-crystal regions in the sublimed material. A N_2 overpressure slightly above 1 atm was maintained in the silica tube during the growth and stabilization processes.

Single-crystal samples with dimensions of $6.3 \times 10 \times 1.5$ mm^3 were cut from the as-grown material for our experiments. The front surfaces of the samples were chem-mechanically polished prior to cathodoluminescence measurements using a dilute Br:CH_3OH solution in conjunction with a rotating felt polishing pad. The back surfaces of the samples were bonded to the copper cryostat block with In foil to ensure reliable thermal contact.

Results and Discussion

Fig. 1 shows 80K cathodoluminescence spectra from the VPG CdTe we studied together with the dependence of the luminescence spectra on injection level for a 189-fold variation in electron beam current. The major spectral features include a prominent edge emission band near 1.57 eV together with a broad extrinsic band centered near 1.42 eV and weaker extrinsic emission in the vicinity of 1.2 eV. The 1.42 eV luminescence appears to consist of a broad band together with a weaker and narrower band near 1.46 eV. A weak band also appears near 1.54 eV and is not distinctly resolved from the edge emission at 80K.

In Fig. 2, we compare the 1.42 eV band observed in VPG CdTe with a corresponding band seen in lightly In-doped LPG CdTe. The spectra shown in Fig. 2 were obtained under identical conditions of excitation and temperature and then computer normalized to the same ordinate at 1.425 eV. The LPG spectrum is believed not to involve overlapping bands and thus provides an interesting comparison to the 1.42 eV band observed in VPG CdTe. It should be noted that the "1.42 eV" band has been found to peak between 1.42 and 1.45 eV in LPG CdTe:In, and that the LPG sample characterized in Fig. 2 was chosen to yield an approximate match to the spectrum of the VPG material.

Injection Level Dependence.

As shown by the sequence of spectra in Fig. 1, increasing injection level causes both the 1.42 and 1.2 eV bands to diminish in prominence relative to the edge emission, which is the typical relative behavior of extrinsic and intrinsic emission bands. However, it is noteworthy that the 1.42 eV band and the edge emission show much less change in relative prominence with injection level in VPG CdTe as compared to LPG CdTe. For the range of injection levels used in Fig. 1, there is only about a two-fold change in prominence in the VPG material, whereas changes in prominence of 10-30 are typical of undoped or lightly In-doped LPG material under identical excitation conditions. Furthermore, the integrated luminescence intensity is considerably weaker in our VPG material as compared to typical samples of LPG material previously studied, with the intensities of the former typically 10-100x below intensities of

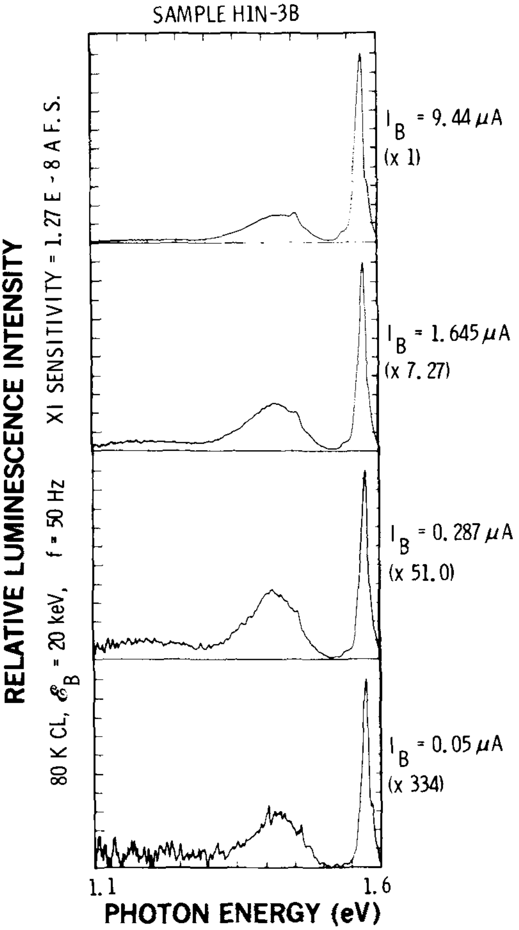

Fig. 1. Computer-normalized luminescense spectra from VPG CdTe recorded at four different injection levels.

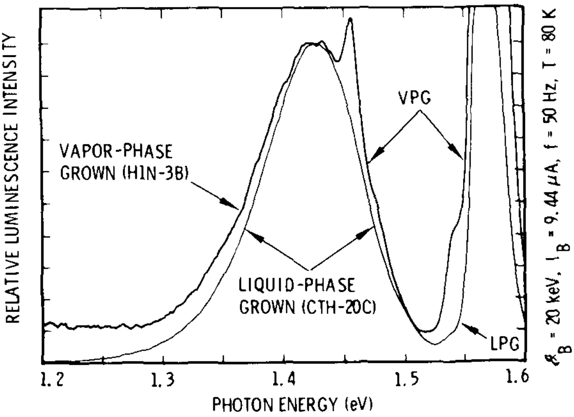

Fig. 2. Normalized spectra comparing the 1.4 eV band in VPG CdTe with that observed in an LPG sample. The VPG material is nominally undoped and the LPG material is lightly In-doped.

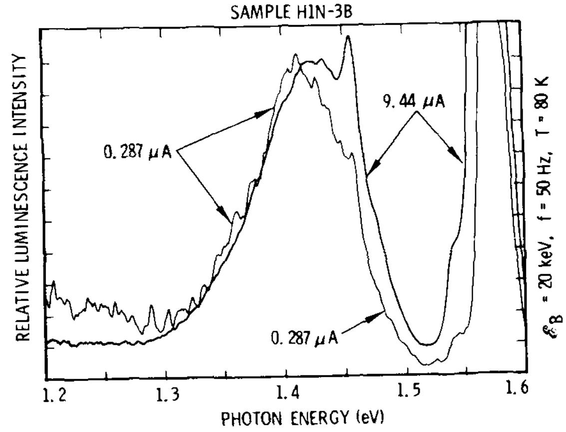

Fig. 3. Normalized spectra showing injection level effects on the shape and energy of the 1.4 eV band in VPG CdTe.

the latter under identical excitation conditions. Both these results indicate that nonradiative shunt paths for carrier recombination are significantly more effective in our present samples of VPG CdTe than in typical samples of LPG CdTe.

Fig. 3 shows the behavior of the 1.42 eV band in VPG CdTe at low and high injection levels with an intensity normalization that permits direct comparison of the superimposed spectra. Despite the interfering effects of the 1.46 eV band, it appears that the 1.42 eV band is injection level dependent and moves toward higher energy with increasing injection level. However, it is not clear that the observed 1.42 eV band is itself a single band rather than a broad band with unresolved contributions from different mechanisms, as has been observed previously (1) in some samples of undoped or lightly doped LPG CdTe.

Frequency Response.

Fig. 4 shows the effect of changing the electron beam modulation frequency from 50 Hz to 50 MHz on the luminescence spectra of VPG CdTe. These spectra are all normalized with respect to the edge emission peak and are not intended to indicate that the edge emission intensity is independent of frequency. However, it is apparent that the 1.42 and 1.2 eV bands have comparatively slow kinetics since their luminescence signals cannot follow the electron beam modulation at higher frequencies. The frequency dependences of the luminescence intensities of the 1.42 eV band and the edge emission are shown quantitatively in Fig. 5. Also shown in the figure are corresponding data (1) for a sample of nominally-undoped LPG CdTe for purposes of comparison. There are some similarities in the frequency dependences of the 1.4 eV luminescence in the two materials but in detail the agreement is poor. It is interesting that the frequency response of the 1.42 eV band in the VPG material indicates that the kinetics are dominated by a single, simple exponential process with a time constant of 0.1 μsec. In contrast, the kinetics of the 1.4 eV band in the LPG material are slower and depart significantly from simple exponential behavior. However, it is important to note in regard to the VPG material that the 50 MHz spectrum in Fig. 4 contains a significant contribution from the 1.46 eV band which is apparently less frequency-dependent than the 1.42 eV band.

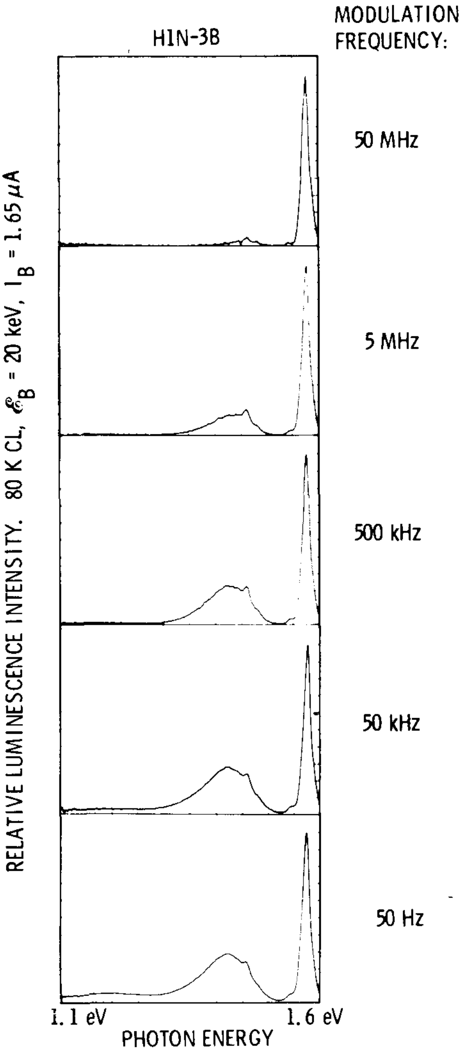

Fig. 4. Luminescence spectra as a function of electron beam modulation frequency in VPG CdTe.

We have attempted to separate the contributions of the 1.42 and 1.46 eV bands in plotting the response data in Fig. 5 but any conclusions drawn from the apparent exponential behavior of the 1.42 eV band kinetics in the VPG material must be regarded with caution until better data become available.

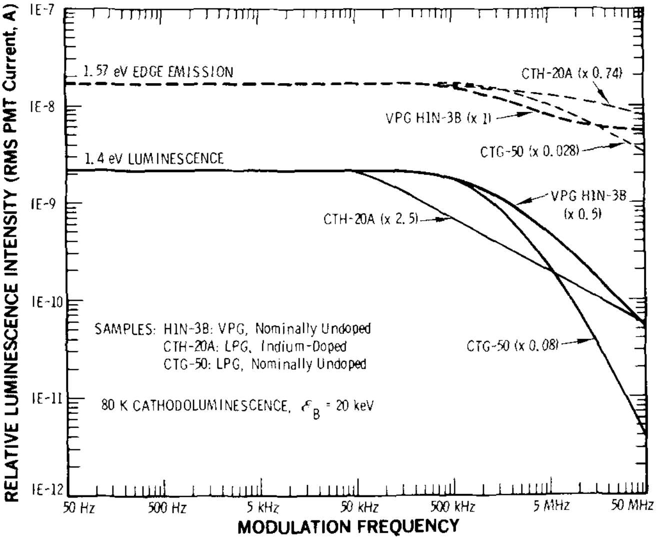

Fig. 5. Variation of extrinsic and intrinsic luminescence intensity with electron beam modulation frequency for VPG and LPG CdTe.

Temperature Dependence.

Fig. 6 shows the effect of temperature on the luminescence spectra from VPG CdTe. Both the 1.2 eV and 1.42 eV bands diminish rapidly with increasing temperature in comparison to the intensity of the edge emission, which shows the usual comparatively weak temperature dependence. The quality of the spectra from VPG CdTe is not sufficient to determine whether the 1.42 eV emission band broadens or shifts in energy with increasing temperature. However, the intensity vs temperature can be accurately measured over a modest temperature range, and the corresponding data are shown in Fig. 7. Thermal quenching of the 1.42 eV

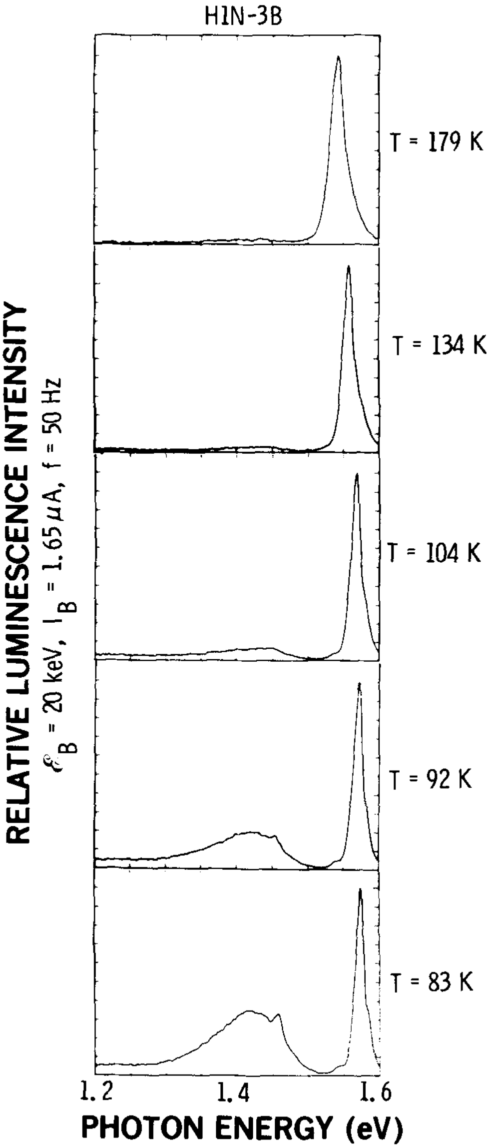

Fig. 6. Temperature dependence of the luminescence spectra from VPG CdTe.

luminescence occurs with an activation energy of 0.09 eV over approximately a 30-fold range of intensity. At high temperatures, the data in Fig. 7 must be discounted because the 1.42 eV band begins to disappear into a faint continuum emission that is only weakly temperature dependent.

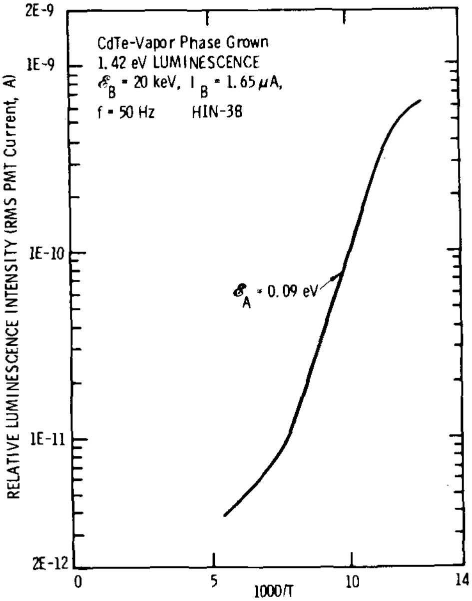

Fig. 7. Temperature dependence of the 1.4 eV band intensity in VPG CdTe.

Conclusion

In comparison to typical LPG CdTe, the shape and energy of the 1.4 eV band in the VPG material that we studied shows a much stronger injection level dependence. In the same comparison, the intensity of the 1.4 eV band in the VPG materials shows a less severe frequency dependence. However, the thermal quenching activation energy of the 1.4 eV luminescence in the VPG CdTe is comparable to the 0.09-0.1 eV values observed in LPG material which is nominally undoped or moderately In-doped. (1) And, except for the uncertainty introduced by the 1.46 eV peak, it appears that the 1.42 eV band in VPG material has a width and shape comparable to that typically seen in LPG material. In summary, then, the 1.42 eV band we have studied in VPG material is similar to the corresponding band in LPG material except that the kinetics are faster and the band moves toward higher energy with increasing injection level.

It is important to point out that the VPG CdTe we studied was grown at a temperature some 600°C higher than typical of the solution-grown LPG material to which we have been making comparisons in this paper. From this perspective, and noting also that the integrated luminescence is 10-100x stronger in the LPG material for typical excitation conditions, it is remarkable that the two materials exhibit extrinsic bands with any similarities. One possible explanation is that both the VPG and LPG materials have become similarly contaminated during growth as a result of impurities consistently present in starting materials. Alternatively, similar contamination could occur from impurities leached out of the quartzware in contact with the CdTe during growth. However, it should be noted that the LPG material is intentionally In-doped, and also that In has been definitely implicated in the 1.4 eV center in this material. (1) There is a remote possibility that our VPG material is unintentionally In-doped. However, it is more likely that the 1.4 eV luminescence involves defect-impurity complexes whose energy levels are determined primarily by the characteristics of the associated native defect, and depend only weakly on the chemical identity or even the sublattice location of the impurity. Such a situation is well established for the Donor-V_{Zn} deep-center blue complex in ZnS. (8)

Elsewhere, it has been observed that the characteristics of the 1.4 eV luminescence in LPG CdTe are remarkably insensitive to such strong perturbations as neutron irradiation, (9-11) ion implantation damage introduction, (6) and heat treatments at temperatures near 800°C in Cd vapor or Te vapor that strongly affect the edge emission. (9) The picture one gets from these results is that the 1.4 eV luminescence transition must be occurring in a spatially-localized region; perhaps it occurs between energy levels associated with a complex. However, the appearance of strong impurity banding in our cathodoluminescence study (2) of the 1.4 eV band in LPG CdTe:In, which was doped only to a concentration of 1 ppm In, argues that the wavefunctions associated with the acceptor-like recombination level have a significant extent in space.

Thus, we speculate that VPG CdTe contains 1.4 eV centers which are of the same nature as those in LPG material, but perturbed by the much larger concentration of non-radiative centers in the VPG material. Also, competing transitions may be possible from nearby trapping levels with energies near the conduction band edge to the acceptor-like levels of the 1.4 eV complexes. These factors may be responsible for the injection level dependence and the faster kinetics of the 1.4 eV band in VPG CdTe.

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