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Photoluminescence studies of CdTe polycrystalline films

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Abstract. Photoluminescence (PL) studies of CdTe polycrystalline films are reported. The films were grown using the modified close space sublimation technique on sapphire substrates. The mean grain size in the investigated films was ranged from 10 up to 360 μm. The distinct spectral bands around 1.580 and 1.440 eV were observed at 77 K. These bands are attributed to shallow bound excitons at dislocations and deep defects, respectively. The intensity of luminescence related to dislocation defects is found to be proportional to the density of grain boundaries. The nature of grain boundaries in the investigated films has been briefly discussed.

Keywords: CdTe, polycrystalline film, photoluminescence, dislocations, defects.

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1. Introduction

Polycrystalline CdTe thin films are intensively investigated as potential candidates for high efficiency photovoltaic applications [1]. Due to its almost ideal bandgap and high optical absorption coefficient, the conversion efficiency of 29% was theoretically predicted for single-junction devices [2]. Aramoto *et al.* reported 16% efficiency for CdTe/CdS solar cells, which seems to be the highest efficiency for CdTe-based solar cells [3]. The performance of solar cells on CdTe polycrystalline films depends on nature of defect states. The goal of this study is to investigate defect-related photoluminescence (PL) in CdTe polycrystalline films in order to understand better their impact on the solar cell performance.

2. Experimental details

Preparation of CdTe polycrystalline films with stable and predictable characteristics still to be a topical task for device applications. Different kinds of vapor deposition techniques have been used for growing CdTe polycrystalline films on semiconductor and dielectric substrates [1]. Among them, the close-spaced vapor transport technique possesses several advantages. Since the as-grown films have poor electrical properties, they are annealed in $CdCl_2$ atmosphere. In this study, CdTe polycrystalline films were prepared using the close-spaced vapor transport technique modified in our laboratory. Samples of mechanically polished sapphire were used as substrates. These substrates have such advantages as manufacturability, high transparency in a wide spectral range, high thermal conductivity, thermal and chemical stability. The substrates were etched in aqueous solution of hydrofluoric acid and washed in distilled water. For deposition, polycrystalline CdTe of *n*-type conductivity doped with indium was used as a source. The substrate holder and source container were made from a high-density graphite block. Both of them have individual heaters that allow one to regulate their temperatures with the accuracy ±3 ºC. The distance *h* between the substrate and surface of CdTe source was chosen within one to three millimeters. The developed technological module was placed in a silica ampoule and mounted in a vacuum chamber ($P = 10^{-4}$ Pa) by using vertical arrangement.

The source and substrate temperatures (T_{so}, T_{sub}) and the distance *h* were varied in order to find optimal deposition conditions. Immediately before deposition, the substrate was heated to approximately 600 ºC and maintained at this temperature for half an hour. After

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that, the substrate temperature was gradually decreased to the required value 350-400 ºC. Simultaneously, the source temperature was increased up to 500-600 ºC. The films investigated in this study had the mean grain size ranged from 10 up to 360 μm. The freshly prepared films were of *n*-type conductivity. The type of conductivity was checked by measuring the photoresponse signal polarity in Schottky contacts deposited on the films. Previously, the polarity of photoresponse signal was calibrated using a sample of CdTe film with known type of conductivity. The contacts were prepared by electrolytic deposition of Au. Ohmic contacts were deposited by thermal vacuum evaporation of indium.

It is necessary to note that the investigated films were not annealed. They exhibited high photosensitivity and stable values of resistance after repeated temperature cycling within the range T = 77-300 K. Moreover, comparatively small changes in electrical and photoelectrical characteristics were observed in the investigated films after storage for five years under ambient laboratory conditions. The deposition method used in this investigation is also characterized by high transfer efficiency of the starting material in the growth chamber (losses were less than 5%).

Photoluminescence measurements were performed at the temperature 77 K under CW excitation using the 630 nm line of a He-Ne laser. The luminescence emission passed through a grating spectrometer and was detected at the exit slit by using a non-cooled Ge photodetector and photomultiplier tube. The signal was subsequently processed by a lock-in amplifier. The investigated films were illuminated from the free surface side. The back-side illumination was also used, but experimental results for this excitation geometry will be analyzed elsewhere.

3. Results and discussion

The photoluminescence spectra measured at 77 K are shown in Figs 1 and 2. The most intensive luminescent lines were found to be centered at 1.580 and 1.440 eV. The spectral lines at a higher energy are near the bandgap of CdTe (1.590 eV at 77 K [4]). These lines are usually ascribed to excitons localized at shallow donors or acceptors [5-7]. As in single crystals the excitonic luminescence lines are often used for characterization of their quality, the emission from a single crystal of high quality was also measured for comparison, Fig. 1.

PL emission in a polycrystalline system may be significantly influenced by grain boundaries (GBs). One effect of GBs is that the photoluminescence bands are broadened by the variety of recombination centers that can exist in a polycrystalline film. Also, as GBs can provide an effective channel for non-radiative recombination, in polycrystalline material radiative transitions are expected to be less effective as compared to those in single crystals. As shown in Fig. 1, in the investigated films the amplitude and the half-width (FWHM) of the excitonic lines depend on grain sizes. The FWHM is decreased from 25 meV in the film with the smallest grain size of 10 μm up to 10 meV in that one with the grain size of 360 μm. The value of 10 meV was also observed in a sample of single crystal. At the same time, as seen from Fig. 1, the most intensive excitonic line is observed in the film composed of the smallest grains. With increase in the grain size the intensity of the excitonic lines is monotonically decreased.

Variation in the PL intensity versus laser power for the PL lines at 1.580 eV measured in two films with different sizes of grains is shown in Fig. 2. The dependence of the PL emission on the laser power can be fitted using the relationship $I_{PL} \sim I^k$, where I_{PL} and I are the luminescence and laser intensities, respectively. Values of the exponent k between one and two are usually observed in CdTe. In the investigated films, k was within the range from 1.5 up to 2.0. In order to explain the observed values, two models have been proposed by Taguchi *et al.* [8] and Cooper *et al.* [9]. Taguchi *et al.* predicted that $k = 1$ for free excitons and $k = 1.5$ for bound excitons. However, if the laser excitation is resonant with the bound-exciton energy, it is found that $k = 1$. Cooper *et al.* suggested that since the rate of excitons should be proportional to the product of the electron concentration and that of holes, the exponent k should be equal to 2. The measured values of k support the suggestion that the PL emission peaks at 1.580 eV have exciton nature.

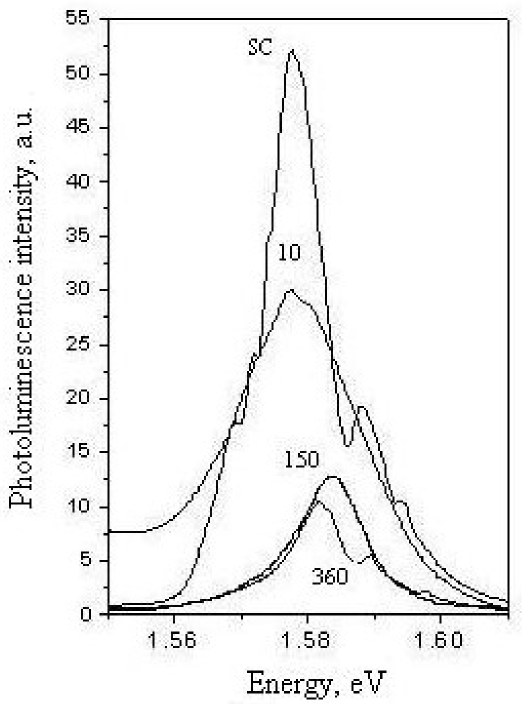

Fig. 1. PL spectra measured at 77 K in CdTe polycrystalline films with the average crystallite size 10, 150 and 360 μm as well as in a bulk crystal (sc).

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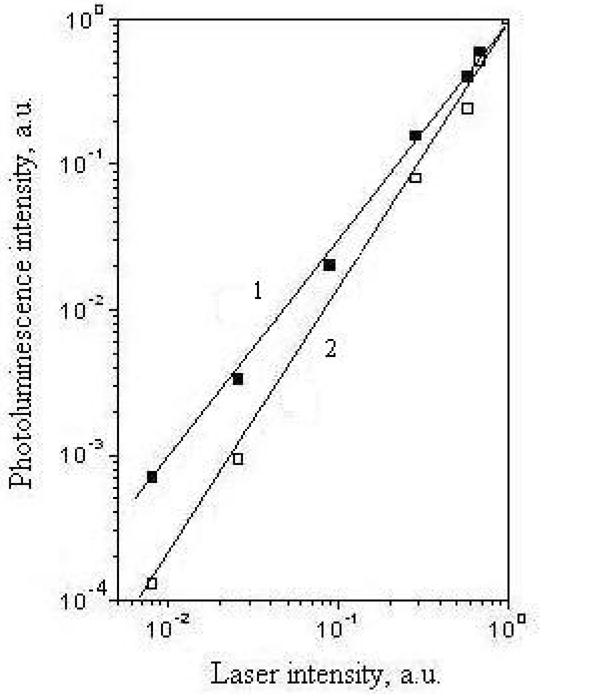

Fig. 2. PL intensity of excitonic lines in CdTe polycrystalline films with the average sizes of crystallites 10(*1*) and 360(*2*) μm. The intensity of PL has been calculated as the total area under the lines shown in Fig. 1.

However, the most intensive emission was observed at the energies around 1.44 eV, Fig. 3. The broad spectral bands centered at 1.44 eV had the FWHM of the order of ~100 meV, which is independent of the grain size. The amplitude of these bands is increased by three orders of magnitude with decreasing the grain sizes from 360 down to 10 μm.

The emission between 1.40 and 1.49 eV, also known as the Y-band, was observed in single crystals, epitaxial and polycrystalline films of CdTe by many authors (see e.g. [10] and citations therein).The peak wavelength was found to depend on temperature and growth conditions. For the first time, the relatively broad spectral band peaking at 1.476 eV was observed by Dean *et al.* [11]. A number of recombination mechanisms with participation of bulk and surface defects have been proposed to explain this emission [12–19].

Despite the fact that exact nature of defects involved in this emission is not finally ascertained, weak phonon coupling and a relatively broad zero-phonon line clearly indicate that this emission is related to extended defects. A strong correlation between the 1.47 eV emission band and dislocation density in bulk CdTe has been observed by Seto *et al.* [20]. Also, it was shown that the Y-band may be related not only to dislocations, but also to point defects such as the Frenkel ones. The strain field induced in the vicinity of these defects is responsible for recombination centers providing the 1.47 eV band [20]. As shown by Babentsov [21], the intensity of this photoluminescence band is increased in CdTe single crystals with mechanically polished surfaces. In the cathodoluminescence studies performed by Leipner *et al.* [22], generation of point defects by moving dislocations was observed. These authors argued that the emission at 1.48 eV is caused by point defects that are probably vacancies. These defects are generated near dislocations by a jog dragging mechanism. The correlation between the Y-band and the dislocation-induced defects generated by moving dislocation was observed by Babentsov *et al.* [23].

Bubulac *et al.* [24] investigated the spatial origin of the exciton and defect PL lines in CdTe at 77 K. It was concluded that the exciton and defect luminescence lines in CdTe can originate from the different spatial locations in the sample. The excitonic emission appears to originate from the clustered dislocations associated with grain boundaries, and the deep-level emission originates from the internal parts of the grains [24]. The results obtained in this study are in some contradiction with those obtained by Bubulac *et al.* As seen from Figs 1 and 3, both excitonic and defect-related emissions are increased with decreasing the grain sizes. However, the intensity of the 1.44 eV PL band is proportional to the density of the GBs, whereas such propotionality is not observed for the excitonic lines. This result seems to be observed for the first time in polycrystalline films of CdTe.

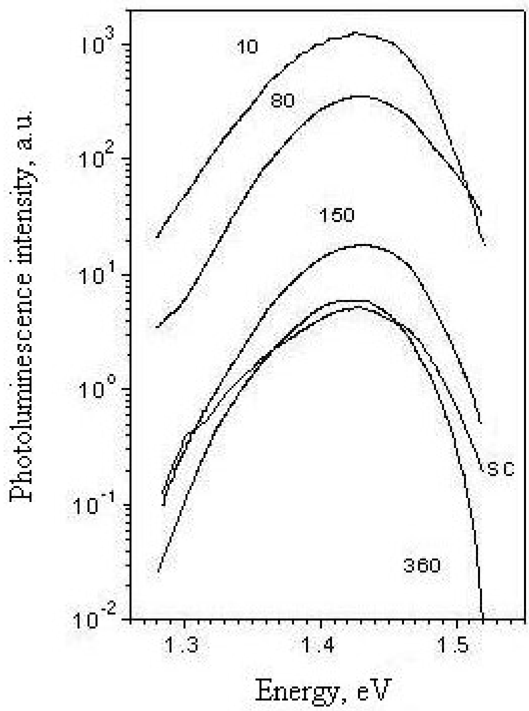

Fig. 3. Y-emission bands in CdTe polycrystalline films with different sizes of crystallites and in a bulk crystal (sc).

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The GBs in polycrystalline films are known to consist of various kinds of dislocation arrangements [25-27]. When the misorientation between two grains is small, the grain boundary can be described by a relatively simple configuration of dislocations (e.g., an edge dislocation line). In the case when misorientation is large (high-angle grain boundary), more complicated structures arise. Interaction of point defects with dislocations results in formation of point defect clouds also known as Cottrell's atmospheres [25-27]. This may be the reason for the observed correlation between the intensity of the 1.44 eV PL band and the density of the GBs. A very high defect states density (> 10^{18} cm^{-3}) at the GBs in CdTe polycrystalline films was observed experimentally [28].

4. Conclusions

Photoluminescence spectra have been investigated in CdTe polycrystalline films grown using the modified close space sublimation technique on sapphire substrates. Correlation between the intensity of the 1.44 eV photoluminescence spectral band and the density of grain boundaries have been observed in the polycrystalline films with the mean grain sizes ranged from 10 up to 360 μm. It has been supposed that the 1.44 eV band is related to defects localized around dislocations.

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References

1. T.M. Razykov, C.S. Ferekides, D. Morel, E. Stefanakos, H.S. Ullal, H.M. Upadhyaya, Solar photovoltaic electricity: Current status and future prospects // *Solar Energy*, **85**(8), p. 1580-1608 (2011).
2. A. De Vos, J.E. Parrott, P. Baruch, P.T. Landsberg, *12th European Photovoltaic Solar Energy Conf.,* Amsterdam, The Netherlands, p. 1315 (1994).
3. T. Aramoto, S. Kumazawa, H. Higuchi et al., 16.0% efficient thin-film CdS/CdTe solar cells // *Jpn. J. Appl. Phys*., **36**(10), p. 6304-6305 (1997).
4. M. Hage-Ali and P. Siffert, Semiconductors for room temperature nuclear detector applications // *Semiconductor and Semimetals*, **43**, Eds. T.E. Schlesinger, and R.B. James, Academic Press, San Diego, 1995.
5. Z.C. Feng, M.J. Bevan, S.V. Krishnaswamy, and W.J. Choyke, A photoluminescence comparison of CdTe thin films grown by molecular-beam epitaxy, metalorganic chemical vapor deposition, and sputtering in ultrahigh vacuum // *J. Appl. Phys*., **64(**5), p. 2595-2600 (1988).
6. D.P. Halliday, J.M. Eggleston, K. Durose, A photoluminescence study of polycrystalline thin-film CdTe/CdS solar cells // *J. Crystal Growth*, **186**, p. 543-549 (1998).
7. N.V. Agrinskaya, N.N. Zinovyev, O.A. Matveev, I.D. Yaroshetskii, Spectra of excitonic luminescence and their relation with concentration of shallow impurities in cadmium telluride // *Fizika tekhnika poluprovodnikov*, **15**(1), p. 172-174 (1980), in Russian.
8. T. Taguchi, J. Shirfuji, Y. Inuishi, Excitonic emission in cadmium telluride // *Phys. status solidi* (*b*), **68**(2), p. 727-738 (1975).
9. D.E. Cooper, J. Bajaj, P.R. Newman, Photoluminescence spectroscopy of excitons for evaluation of high-quality CdTe crystals // *J. Crystal Growth*, **86**(1-4), p. 544-551 (1988).
10. D.P. Halliday, M.D.G. Potter, J.T. Mullins, A.W. Brinkman, Photoluminescence study of a bulk vapour grown CdTe crystal // *J. Crystal Growth* **220**(1), p. 30-38 (2000).
11. P.J. Dean, G.M. Williams, G. Blackmore, Novel type of optical transition observed in mbe grown CdTe // *J. Phys. D.: Appl. Phys*. p. 2291-2300 (1984).
12. H.L. Cotal, A.C. Lewandowski, B.G. Markey, S.W.S. McKeever, E. Cantwell, and J. Aldridge, 1.4-eV photoluminescence and thermally stimulated conductivity in cadmium telluride // *J. Appl. Phys*. **67**(2), p. 975-982 (1990).
13. T. Taguchi, J. Shirafuji and Y. Inuishi, Edge and donor-acceptor pair emissions in cadmium telluride // *Jpn. J. Appl. Phys*. **12**(10), p. 1558-1660 (1973).
14. D.M. Hofmann, P. Omling, H.G. Grimmeiss, B.K. Meyer, K.W. Benz and D. Sinerius, Identification of the chlorine *A* center in CdTe // *Phys. Rev. B,* **45**(11), p. 6247-6250 (1992).
15. J. Krustok, J. Madasson, K. Hjelt and H. Collan, 1.4 eV photoluminescence in CdTe with a high density of defects // *J. Mater. Sci.* **32**, p**.** 1545-1550 (1997).
16. N.C. Giles-Taylor, R.N. Bicknell, D.K. Blanka, T.H. Myers, and J.F. Schetzina, Photoluminescence of CdTe: A comparison of bulk and epitaxial materials // *J. Vac. Sci. Technol.* **A3**(1), p. 76-82 (1985).
17. C.B. Norris and K.R. Zanio, Effects of Cd-vapor and Te-vapor heat treatments on the luminescence of solution-grown CdTe // *J. Appl. Phys*., **53**(9), p. 6347-6359 (1982).
18. J.L. Pautrat, J.M. Francou, N. Magnea, E. Molva, K. Saminadayar, Donors and acceptors in tellurium compounds; The problem of doping and self-compensation // *J. Crystal Growth*, **72**(1-2), p. 194-204 (1985).

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19. T.H. Myers, J.F. Schetzina, S.T. Edwards and A.F. Schreiner, Effect of surface preparation on the 77 K photoluminescence of CdTe // *J. Appl. Phys*. **54**(7), p. 4232-4234 (1983).
20. S. Seto, A. Tanaka, F. Takeda, K. Matsuura, Defect-induced emission band in CdTe // *J. Crystal Growth*, **138**(1-4), p. 346-351 (1994).
21. V.N. Babentsov, Radiative recombination of a mechanically disordered undoped p-CdTe // *Semiconductors*, **30**(8), p. 1425-1433 (1996).
22. H.S. Leipner, J. Schreiber, H. Uniewski, and S. Hilderbrant, Dislocation luminescence in cadmium telluride // *Scanning Microscopy,* **12**(1), p. 149-160 (1998).
23. V. Babentsov, V. Boiko, G.A. Shepelskii, R.B. James, J. Franc, J. Procházka, P. Hlidek, Photoluminescence and electric spectroscopy of dislocation-induced electronic levels in semi-insulated CdTe and CdZnTe // *J. Luminescence*, **130**(8), p. 1425-1430 (2010).
24. L.O. Bubulac, J. Bajaj, W.E. Tennant, P.R. Newman, D.S. Lo, Spatial origin of various PL lines in CdTe at 77 K // *J. Crystal Growth,* **86**(1-4), p. 536-543 (1990).
25. D.B. Holt and B.G. Yacobi, *Extended Defects in Semiconductors. Electronic Properties, Device Effects and Structures*. Cambridge University Press, 2007.
26. H. Gleiter and B. Chalmers, High-Angle Grain Boundaries, in: *Progress in Materials Science*, **16**, Pergamon Press, 1972.
27. G. Harbeke (Ed.), *Polycrystalline Semiconductors. Physical Properties and Applications*. Springer, 1985.
28. A.S. Gilmore, V. Kaydanov, T.R. Ohno, D. Grecu, and D. Rose, Impedance Spectroscopy and Hall Measurements on CdTe Thin Polycrystalline Films, in: *II-VI Compound Semiconductor Photovoltaic Materials, MRS Proc.*, **668** (2001).

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