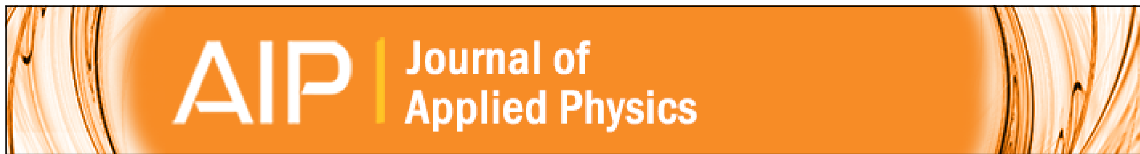


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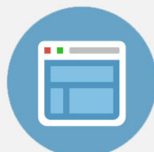

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# Effect of thermal annealing on Te precipitates in CdTe wafers studied by Raman scattering and cathodoluminescence

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A combination of Raman scattering and cathodoluminescence techniques has been used to study the spatial distribution of Te precipitates in the volume of CdTe wafers. Starting with the as-grown crystals with random distribution of precipitates over the whole volume, improvement at different stages of thermal annealing is demonstrated. As-grown *p*-CdTe wafers were annealed at 500–600 °C either in Ga melt or in Cd vapor for 2 or 22 h. The kinetics of dissolution of Te precipitates was found to be similar for both the Ga melt and Cd vapor annealing processes. Short-time annealing causes the disappearance of small Te precipitates, while the larger ones, 5–10 $\mu$m in size which decorate the extended structural defects, still remain. After a long-time annealing, the complete disappearance of Te precipitates occurs in the wafers volume. Interestingly, it was observed that the disappearance of Te precipitates during annealing starts in the central part of the bulk wafer and is followed by a precipitate gettering at the wafer surface. This implies that it is possible to obtain precipitate-free CdTe wafers by postgrowth annealing. © *1995 American Institute of Physics.*

CdTe is a well-known II-VI semiconductor that is currently employed as a substrate for HgTe-based epitaxy in layers for infrared array technology,[1,2] for the fabrication of nuclear radiation detectors,[3,4] and for high-efficiency solar cells.[5,6] Moreover, recently an additional interest has been stimulated by the discovery of infrared photorefractivity in CdTe.[7,8] It is known that one can get CdTe wafers with desirable properties by different kinds of thermal annealing. We have recently investigated the problem of out-diffusion of residual impurities from CdTe substrates during the growth of $Hg_{1-x}Cd_xTe$ layers by liquid-phase epitaxy,[2] the in-diffusion of Ga as a shallow donor in the *p*-CdTe wafers,[9,10] and the deposition of $Hg_{1-x}Cd_xTe$ ohmic contact layers on *p*-CdTe samples by vapor-phase epitaxy.[11,12]

Because of the known peculiarities of the CdTe phase diagram,[13] CdTe bulk crystals grown by different techniques have excess Te than the stoichiometric composition which aggregates as Te precipitates. It was also shown in numerous studies that it is not possible to avoid completely the presence of Te precipitates in CdTe crystals by a modification of growth process and a postgrowth annealing of the boule, as in Cd vapor, due to the low thermal conductivity of CdTe.[10,14–16] It has been found[17] that some reduction in the concentration of Te precipitates can be obtained by annealing the as-grown CdTe wafers in a Cd vapor atmosphere.

Recently, Jayathirtha *et al.*[18] have carried out studies on Te precipitate in CdTe. While there is an obvious disagreement on the elimination of Te precipitates by Cl doping during growth as reported earlier,[14–16] this study points out the necessity of extending the number of characterization techniques needed to study the Te precipitates in CdTe. Besides infrared microscopy, it was shown by Shin *et al.*[17] that there are other techniques for the Te precipitate study among which Raman microprobe spectroscopy was demonstrated to be a direct method.

In the present communication we present the results of the kinetics of Te precipitates transformation during thermal annealing of CdTe wafer and demonstrate the capabilities of the combined Raman scattering (RS) and cathodoluminescence (CL) techniques for the studies of Te precipitates in the volume of CdTe wafers. It is also worth mentioning that the data presented provide the interesting possibility of comparing the Te precipitates in CdTe with the As precipitates in GaAs; the latter is the current subject of numerous studies.[19,20]

The CdTe(111) single-crystalline wafers of about $20\times20\times1.0$ mm$^3$ in size were used for our studies. The wafers were cut from the as-grown undoped *p*-CdTe bulk crystals grown by the Bridgman method.[10]

Samples were annealed either in liquid Ga or in Cd vapor for 2 h (short-time annealing) or for 22 h (long-time annealing). All the annealing processes were carried out in evacuated quartz ampoules at temperatures in the range of 500–600 °C. For the annealing in Cd vapor, a piece of Cd was introduced into the ampoule. For the Ga annealing, a layer of pure Ga (6N) of 0.5–1 mm thickness was deposited at room temperature (RT) on one or both sides of a wafer.

To study the spatial distribution of Te precipitates, all over the wafer volume, the wafers were cleaved perpendicularly to the [111] direction just before the RS and CL measurements and the cleaved surfaces were investigated. Doing this, we have also eliminated the possible influence of the wafer surface treatment which could disable the use of RS

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for the Te precipitates study as it was shown by Amirtharaj and Pollak.[21]

RS spectra were excited with an Ar-ion laser and recorded with a Dilor XY spectrometer at RT. The laser wavelength was 514.4 nm and the spectral resolution was 5 $cm^{-1}$. The dimensions of the laser-beam spot on the sample surface were of a few microns in the microregime, or about 5 mm $\times 100$ $\mu m$ in the macroregime. The laser power was kept below 2 and 100 mW for micro- and macroregime, respectively, to avoid damage of the sample.

CL measurements were performed in a Hitachi S-2500 scanning electron microscope (SEM) at temperatures between 80 and 300 K with an accelerating voltage of 25 kV. The experimental setup has been previously described.[22]

Typical RS spectra of the as-grown and as-annealed CdTe wafers are presented in Fig. 1 for the microregime [Figs. 1(a)–1(c)] and the macroregime [Fig. 1(d)]. Figure 1(a) shows two peaks at 125 and 143 $cm^{-1}$ for an as-grown sample, which can be attributed to Te precipitates.[17,21] No CdTe-related peaks were seen in the microregime. After a short-time annealing the disappearance of Te-related peaks was observed in the central part of a wafer thickness all over the wafer area [Fig. 1(b)], while near the wafer surface the Te-related peaks were still present. Only after a long-time annealing did the Te-related peaks disappear all over the wafer volume [Fig. 1(c)]. In macroregime, the modification of the RS spectra was apparent after a long-time annealing [Fig. 1(d)]. While the Te-related peaks dominate the RS spectra of as-grown wafers, for the annealed samples the RS spectra have only the two CdTe related peaks, corresponding to the transversal-optical (TO) phonon at 142 $cm^{-1}$ and the longitudinal-optical (LO) phonon at 170 $cm^{-1}$. The RS spectra for both the Ga- and Cd-annealed samples were found to be similar.

Figure 2 shows the typical CL images of the (a) as-grown and (b), (c) annealed CdTe wafers. It was found that

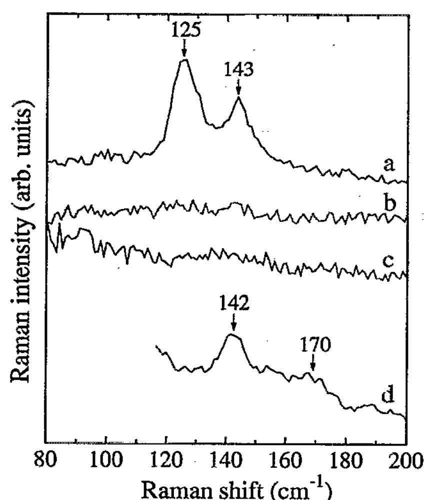
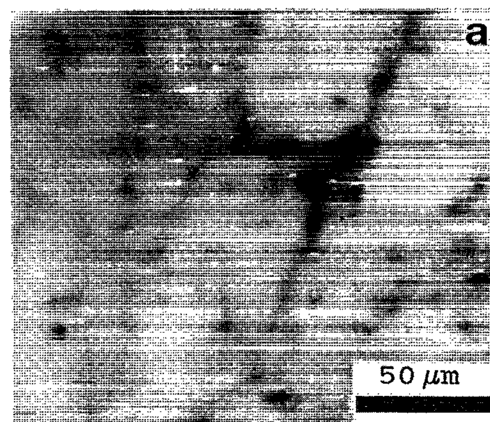
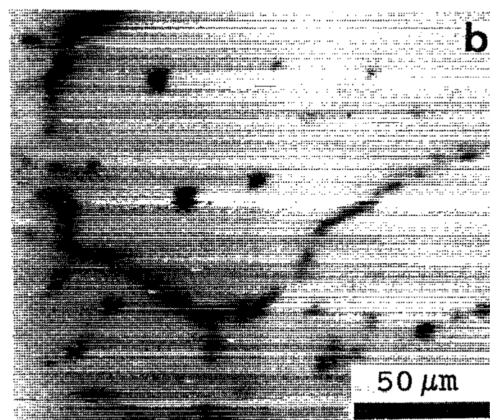


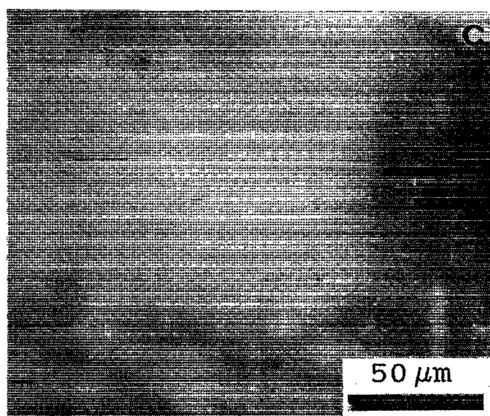

FIG. 1. Raman spectra of CdTe wafers in microregime: (a) as grown; (b) 2 h annealed (500 °C), and (c) 22 h annealed (500 °C); and in macroregime: (d) 22 h annealed (500 °C). All the spectra were recorded at the cross section at RT.




(a)




(b)




(c)

FIG. 2. Panchromatic CL image of a CdTe wafer: (a) as grown; (b) 2 h annealed (500 °C); and (c) 22 h annealed (500 °C). All the images were taken at the cross section at 80 K.

the CL image of an as-grown wafer exhibits a random spatial distribution of Te precipitates all over the wafer volume [Fig. 2(a)]. After a short-time annealing [Fig. 2(b)], a significant improvement of the CL image contrast was usually observed with the disappearance of small Te precipitates and a general reduction of the structural defects density. Large Te precipi-



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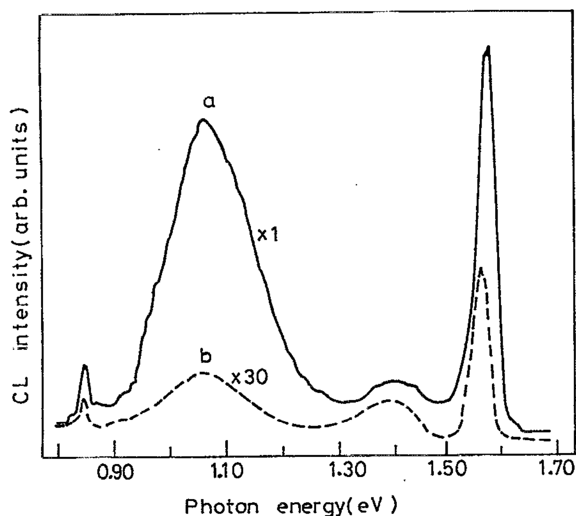


FIG. 3. CL spectra (80 K) of a CdTe wafer: (a) as grown; (b) 22 h Ga annealed (500 °C) in the middle of cross section.

tates of about 5–10 $\mu$m in size were still present and a decoration effect along the extended defects such as low-angle boundaries and dislocations can be seen. After a long-time annealing, the complete disappearance of Te precipitates took place in the wafer volume. Within a distance of about 100 $\mu$m from the wafer surface some residual defects were present [Fig. 2(c)]. A calibrated energy-dispersive analysis of x-rays in SEM (Philips XL30) has been done in order to determine the component composition of the 100 $\mu$m region away from the wafer surface. Strong enrichment with Te was found, which was of 70 at. % of Te and 30 at. % of Cd for the case of the long-time annealing in Ga melt.

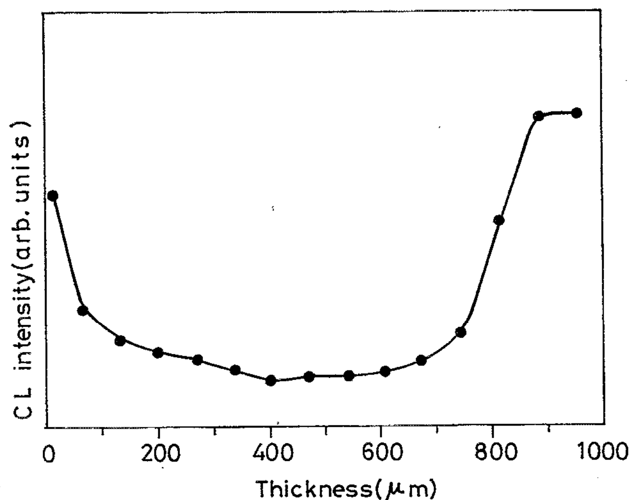


FIG. 4. Distribution of CL intensity of 1.4 eV band (80 K) across the cross section of the wafer annealed in Ga melt at 500 °C for 22 h.

Typical CL spectra of as-grown and annealed wafers show emission bands peaked at 1.54, 1.4, and 1.1 eV, respectively (Fig. 3). After a long-time annealing, the intensities of the CL bands decreased by a factor of 10–100 of the initial value. The 1.4 eV band, which is related to different defects as cadmium vacancies or tellurium excess,[23] is more relevant to the present discussion. Figure 4 shows the intensity profile of the 1.4 eV band along the wafer thickness after the long-time annealing in Ga melt. The high intensity at both sides corresponds to the region in which residual defects were observed in the CL image. By a chemomechanical polishing, the defect region has been completely removed from the surface of the annealed wafers.

In conclusion, combined RS and CL measurements have been employed to study Te precipitates in the volume of CdTe wafers. The dissolution of Te precipitates has been found to be similar during annealing in Ga melt and in Cd vapor. The disappearance of Te precipitates during annealing starts in the central part of wafer volume and is followed by the precipitate gettering at the wafer surface. This shows the possibility of obtaining precipitate-free CdTe wafers by thermal annealing.

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