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Cathodoluminescence study of the effect of annealing in HgI_2 vapor on the defect structure of CdTe

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Abstract

The origin and spatial distribution of radiative defects in undoped and Ge-doped CdTe wafers have been studied by CL spectroscopy and imaging techniques in the scanning electron microscope (SEM) before and after the wafer annealing in HgI_2 vapor. The annealing procedure has been carried out under isothermal conditions at 250°C for 24 h for or for 48 h. It has been shown that the annealing results in the growth of α-HgI_2 polycrystalline layer on the wafer surface, and this layer acts as a getter for Te precipitates distributed randomly over the whole volume of the as-grown CdTe wafers. The annealing affects mainly the CL bands related with Te vacancies (band at about 1.00 eV) and Ge dopant (0.82 and 0.89 eV bands). The contribution of the latter to the total luminescence emission of CdTe wafers decreases after the annealing. The quality improvement of CdTe wafers, revealed by the elimination of Te precipitates from the wafer bulk, has been shown to be an important result of the annealing procedure.

Keywords: Cathodoluminescence; Spectroscopy; Wafer annealing

1. Introduction

There has been considerable progress in manufacturing CdTe crystals for infrared and nuclear detector applications by a number of commercially important growth techniques like the Bridgman method, travelling heater method and gradient freeze method [1]. Although a large size and good crystalline quality of the crystals have been achieved, the control of crystal bulk uniformity in terms of the distribution of native structural defects, residual impurities and dopants still remains a problem in all growth techniques [1–3].

Recently, it has been shown that further progress in controlling CdTe crystal properties can be achieved by post-growth thermal annealing of CdTe wafers in an appropriate ambient [4]. Depending on concrete technological goals, different ambients such as a vacuum,

vapors of Cd, Hg, HgTe, $CdCl_2$, $CdBr_2$ or CdI_2 and a melt of Hg, Bi or Ga have been used at a wide range of annealing conditions, and the influence of the ambient has been demonstrated [4–12]. For example, we have recently shown that the annealing in Ga melt at 600°C for 24 h causes the elimination of Te precipitates from CdTe wafers, while the annealing in a vacuum with the same time–temperature conditions is simply followed by a weak-pronounced redistribution of the precipitates in the wafer volume [12]. It has also been revealed that the annealing procedures can affect some properties of CdTe wafers because of the impurity indiffusion both from the ambient and from the internal sources of residual impurities like precipitates or extended structural defects, e.g. the indiffusion of Ga atoms and the group I residual impurities during the annealing in Ga melt [9–12]. For these reasons it is a subject of interest the study of the mechanisms enabling the post-growth control of CdTe wafer properties as well as to search for new annealing procedures.

In this paper we present the experimental results on the annealing of undoped and Ge-doped CdTe wafers in HgI_2 vapor. Cathodoluminescence (CL) microscopic techniques were employed to investigate the effect of

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the annealing procedure on the spatial distribution of structural defects in the wafer volume. In essence, we were interested in making a comparison of the annealing impact on the CL properties of the undoped and Ge-doped CdTe, which are substantially different in the as-grown wafers [12,13]. Additionally, it seemed important to check for a role of the complex doping with mercury and iodine (Hg is an isoelectronic impurity in Cd-sublattice [6–8] and I is a perspective doner-type dopant in the Te-sublattice [5,14–16]). The data obtained provided some new information on the behaviour of radiative defects in CdTe crystals and enabled us to make conclusions concerning the efficiency of the annealing in HgI_2 vapor.

2. Experiment

The CdTe bulk crystals, undoped and doped with Ge at the concentration level 10^{19} cm^{-3}, were grown by the vertical Bridgman method. The growth conditions and the crystal characteristics have been specified elsewhere [12,13]. CdTe (111)-oriented single-crystalline wafers of about $20 \times 20 \times 0.8$ and $10 \times 10 \times 3$ mm^3 were cut from the crystals. The wafers were chemomechanically polished using Br_2 (2 vol.%)-butanol solution and later washed with ethylene–glycol and isopropanol to remove the surface damage and contamination. Pieces of stoichiometric α-HgI_2 (red mercuric iodide) polycrystal, which was manufactured from high purity starting material (Johnson Matthey Electronics, 6N grade components) in a conventional way [17,18], were used as a source to create the ambient of HgI_2 vapor. The annealing procedures were carried out under isothermal conditions at 250°C for 24 h or for 48 h. CL measurements were performed in the spectral and panchromatic regimes with a Hitachi S-2500 scanning electron microscope (SEM) equipped with a liquid nitrogen cooled germanium detector. The CL experimental set-up has been reported elsewhere [19]. CL spectra were recorded at 80 K under different focusing conditions of the electron beam ($E_b = 25$ keV, $I_b = 10^{-8}$ A) on the sample surface to detect the different radiative centers (focused and defocused regimes). It has been previously observed [20–22] that by defocusing the microscope electron beam the intensity of the main deep level bands is enhanced relative to the background and to the near band edge emission. For this reason a defocused electron beam was used when recording the spectra presented. A number of the annealed wafers were also studied by energy dispersive analysis of X-rays (EDAX) in a Philips XL30 scanning electron microscope to investigate the effect of the annealing procedure on the distribution of the components (Cd, Te, Hg, I) over the wafer thickness.

3. Results and discussion

3.1. Wafer morphology

The surface morphology and cross section of a CdTe wafer after the annealing in HgI_2 vapor at 250°C for 48 h prove that the annealing procedure results in the growth of a polycrystalline layer with a thickness 60–70 μm on the wafer surface. A sharp interface between the polycrystalline layer and the wafer has been revealed without specific defects, like voids, that could be attributed to the annealing process.

The EDAX analysis has given the atomic concentrations of Cd, Te, Hg and I over the cross section. These concentration data and the tetragonal crystal shape indicate that the polycrystalline layer is mainly formed by α-HgI_2 platelets grown due to the transport of HgI_2 vapor from the source to the wafer surface. Near the interface, the polycrystalline layer is enriched with Te and has the complex composition Hg(17 at.%)–Te(37 at.%)–I(46 at.%). The latter could arise from the known peculiarity of the phase diagram of HgI_2–CdTe system, which is the formation of the different Te-based phases such as $Hg_3Te_2I_2$ and HgTe in the HgI_2-rich low-temperature region [23]. The composition of the annealed wafer was found to be homogeneous CdTe over the whole wafer cross section, and no remarkable quantity of Hg or of I appears in the wafer within the sensitivity of the EDAX technique. After the annealing in HgI_2 vapor at 250°C for 24 h, the surface morphology and cross section of CdTe wafer were found to be similar to those revealed after the long time annealing. The quantitative difference between the 24 and 48 h processes is that the first causes the growth of the α-HgI_2 polycrystalline layer with the thickness reduced to 40–50 μm and with the Te concentration near the interface reduced to about 20 at.%.

Finally, the α-HgI_2 polycrystalline layer and the interface region can be completely removed from the surface of the annealed wafers by washing with a KI-H_2O 20 vol.% solution followed by the chemomechanical polishing described above.
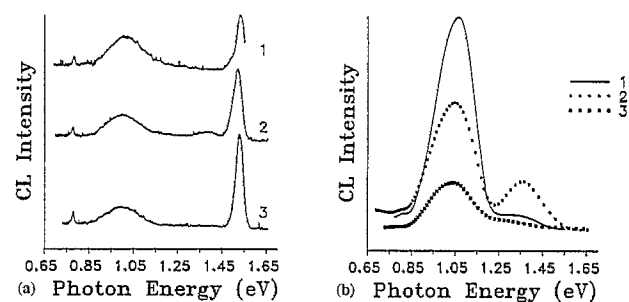

Fig. 1. CL spectra recorded with a focused (a) and defocused (b) electron beam from a cross section of undoped CdTe wafers: (1) the as-grown wafer, (2) the wafer annealed in HgI_2 vapor at 250°C for 24 h and (3) the wafer annealed in HgI_2 vapor at 250°C for 48 h.

annealing are shown in Fig. 2. Two deep-level bands with maxima at about 0.82 and 0.89 eV, which have
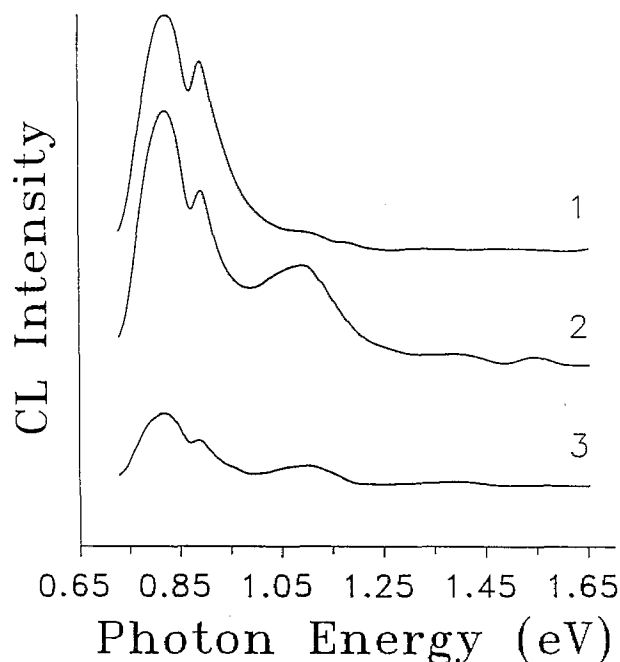

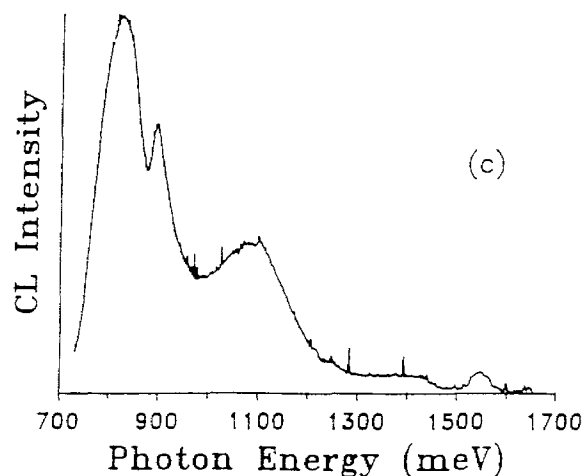Fig. 2. CL spectra recorded with a defocused electron beam from a cross section of Ge-doped CdTe wafers: (1) the as-grown wafer, (2) the 24 h annealed wafer and (3) the 48 h annealed wafer.

3.2. Cl spectra

Fig. 1 presents typical CL spectra recorded with a focused (a) and defocused (b) electron beam from a cross section of the undoped CdTe wafer before (curve 1) and after the annealing for 24 h (curve 2) or for 48 h (curve 3). Depending on the focusing conditions, four emission bands can be seen in the spectra. They are one sharp and two broad deep-level bands with maxima peaked at about 0.77, 1.00 and 1.39 eV and the sharp edge band with the maximum at 1.53 eV. All these bands have been previously observed and attributed to the different defects in CdTe crystals, such as Si residual impurities (0.77 eV band), Te vacancy–impurity complexes (1.00 eV band), Cd vacancy–impurity complexes (1.39 eV band) and donor–acceptor pairs (1.53 eV band) [12]. After the annealing procedure the intensity of the CL bands was found to change with a marked dependence on the annealing time. The annealing for 24 h results in a decrease of the 1.00 eV band relative to the near band edge emission as well as an increase of the 1.36 eV band observed under defocusing conditions (Fig. 1(b), curve 2). An increase of the annealing time causes a decrease of the bands relative to the edge band and an increase of the 0.77 eV band (Fig. 1(a), curve 3).

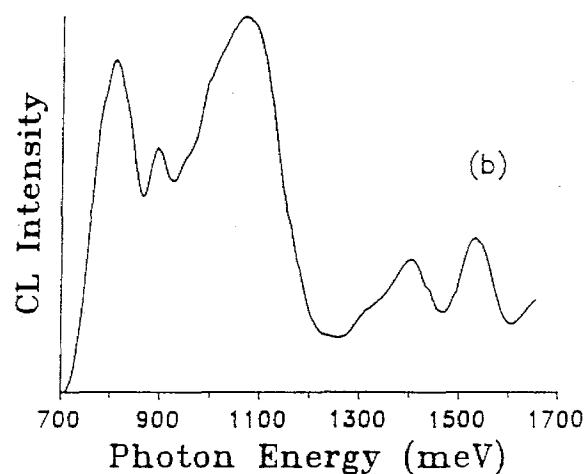The typical CL spectra of the Ge-doped CdTe wafers recorded before and after the 24 and 48 h
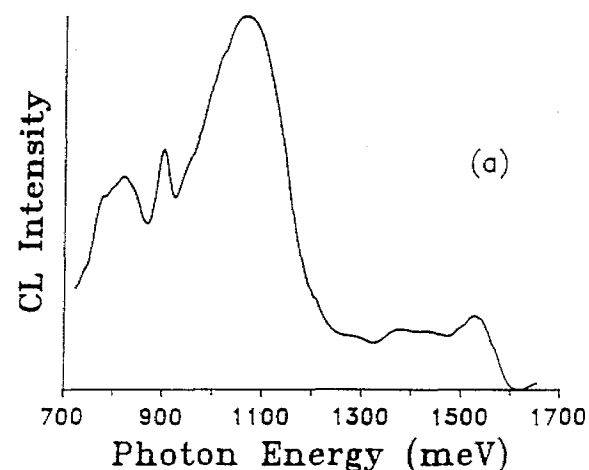

Fig. 3. CL spectra of the substrate recorded at different distances from the α-HgI₂/CdTe:Ge interface: 50 μm (a), 400 μm (b) and 500 μm (c).

been attributed to Ge dopant [13] are seen in the spectrum of the as-grown wafer (curve 1). As in the case of the undoped wafers the CL spectra were drastically modified by the annealing treatments. The 24 h annealing result in the appearance of bands peaked at 1.09 eV, and at about 1.4 and 1.54 eV (Fig. 2, curve 2). The latter is only revealed in annealed samples and it is more intense for focusing conditions. The 1.09 eV band has been previously observed in CL spectra of undoped CdTe wafers and it has been attributed to Te vacancy–impurity complexes [12], i.e. to the same type of defects that is referred to the 1.00 eV band. We suggest that the photon-energy shift of this band can be due to a variety in the distribution of residual impurities in CdTe crystals grown in different runs. The 48 h annealing results mainly in a decrease of the contribution of the Ge-related and 1.1 eV band emissions to the total luminescence intensity of the Ge-doped wafers (Fig. 2).

The behaviour of the CL bands of Figs. 1 and 2 can be explained by transformations of radiative centers during annealing. Annealing affects mainly the CL bands related with Te vacancies (1.00 or 1.09 eV bands) and with Ge dopant (0.82 and 0.89 eV bands). The decreased contribution of the Ge-related bands to the total luminescence emission shows that the annealing reduces the concentration of the related defects in the wafer. This effect is observed in a layer of the CdTe:Ge wafer surface covered by the HgI_2. As described in the next section, the extension of the layer affected by the treatment in CdTe:Ge is clearly revealed in CL images. For this reason it was possible to determine by recording spectra at different distances from the surface, that in the layer in which the Ge-related band decreases the luminescence band attributed to V_{Te} appears. Fig. 3 shows CL spectra recorded at different distances from the interface. The series of Fig. 3 shows the intense band at 1.07 eV in the modified layer and that the relative intensity of the three bands—1.07, 0.9 and 0.81 eV—depends on the distance to the interface. This observation does not provide information on the mechanism of V_{Te} generation during annealing which extends up to hundreds of micrometers from the surface (500 μm for 24 h annealing). However, the fact that the increase of the luminescence related to V_{Te} takes place only in the Ge doped sample and in the region in which Ge related luminescent centers anneal out, suggests that Ge impurities could influence the appearance of the 1.1 eV emission. Spectra of the modified region indicate that the luminescence increase near the interface is due to increase of intensity of bands at about 1.05 meV and

(a)   100 μm

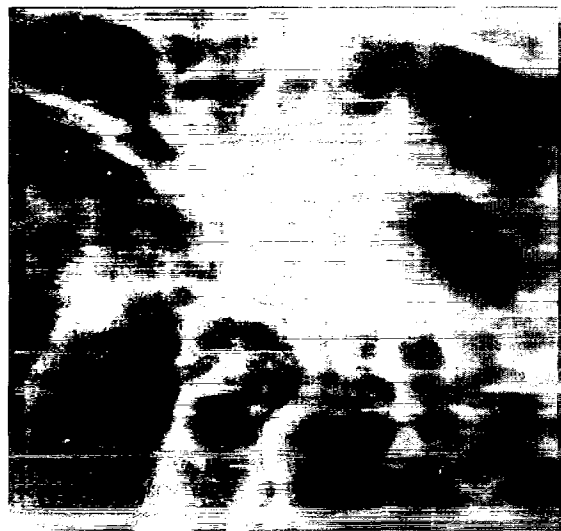

(b)   100 μm
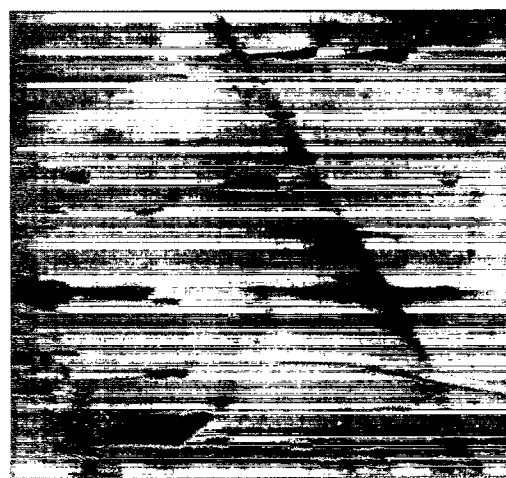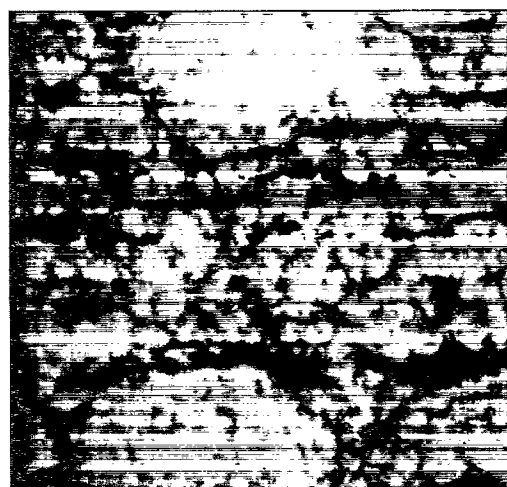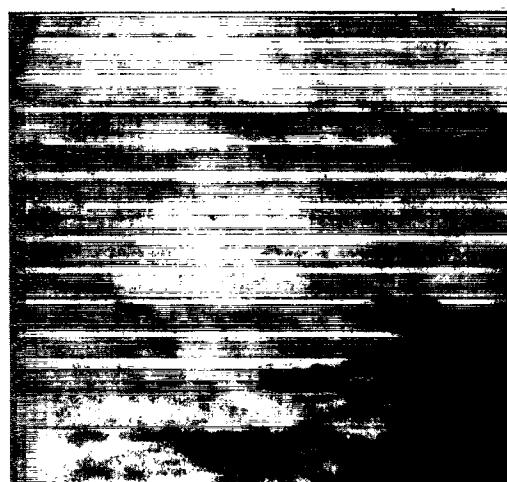
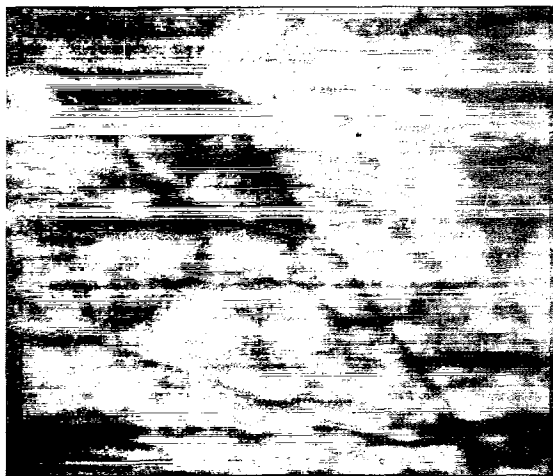(c)   100 μm

Fig. 4. Panchromatic CL images of a cross section of undoped CdTe wafers: (a) the as-grown wafer, (b) the 24 h annealed wafer and (c) the 48 h annealed wafer.

1.54 eV. The former has been attributed to the presence of Te vacancies [24,25] and the latter is not observed in Ge-doped crystals [13]. Its appearance would be a consequence of the decrease of the active Ge-center concentration in the modified layer. These results suggest a gettering of Ge-defects at the α-HgI$_2$/CdTe interface during the α-HgI$_2$ epitaxial growth. The small shifts of the deep-level band peaks as a function of the distance to the interface and the excitation conditions (Fig. 3) indicate that the defects contributing to these complex bands have a concentration gradient relative to the interface or appear in different charge states.

(a)

100 μm

(b)

100 μm

Fig. 5. Panchromatic CL images of a cross section of Ge-doped wafers: (a) the as-grown wafer, (b) the 24 h annealed wafer.

Defects involved in the 1.05 eV band peak shift are V_{Te} and/or residual impurities. It should be noted that the known thermal diffusion coefficients of iodine and mercury as well as of germanium in CdTe [26,27] at the time–temperature conditions of α-HgI$_2$ growth cannot explain the observed point defect effects in an extended—up to 500 μm—layer of the substrate.

In undoped samples annealing causes the reduction of the V_{Te} luminescence (Fig. 1(b)). This is probably due to an outdiffusion of Te excess from the wafer bulk to the α-HgI$_2$ polycrystalline layer on the wafer surface and to an indiffusion of iodine to the wafer. Both processes could result in a decrease of Te vacancy concentration. The effect of annealing on the bands at about 1.4 and 1.53 eV is lower that on the bands at lower energy. The only clear effect observed in the spectra is the increase of the 1.4 eV in the undoped samples annealed for 24 h. Since one of the components of this complex band is related to Cd vacancies, the observation can be explained by the evaporation of some amount of Cd from the wafer surface at the beginning of the annealing process.

3.3. CL images

CL images provide information on the spatial distribution of radiative defects contributing to CL spectra. Fig. 4 presents the typical CL images recorded from a cross section of the undoped CdTe wafer before (a) and after annealing for 24 h (b) or for 48 h (c). The image of the as-grown wafer exhibits a bright background in which dark defects are seen (Fig. 4(a)). According to our previous data [11,12], these spot-like defects are Te precipitates whose average size was estimated at higher magnification to be in the range of 5–15 μm. After the 24 h annealing, a decoration effect along the extended structural defects is seen over the whole wafer cross section (Fig. 4(b)). The 48 h annealing causes a disappearance of the decoration effect revealed by a general reduction of CL contrast of the defects, which can indicate a quality improvement of the wafer due to Te precipitate dissolution.

The typical CL images recorded from a cross section of the Ge-doped CdTe wafer before and after the annealing procedure are shown in Fig. 5. Bright subboundaries and precipitate-like defects in the as-grown wafer are observed (Fig. 5(a)). After 24 h annealing, CL images show subboundaries and point-like defects as dark features in a bright background (Fig. 5(b)). This effect extends up to a distance of about 500 μm from the surface covered with the HgI$_2$ layer (Fig. 6). As described above, spectra show that in this modified region there is a decrease of the active Ge-center concentration which suggests a gettering of Ge-defects at the interface during the epitaxial growth.
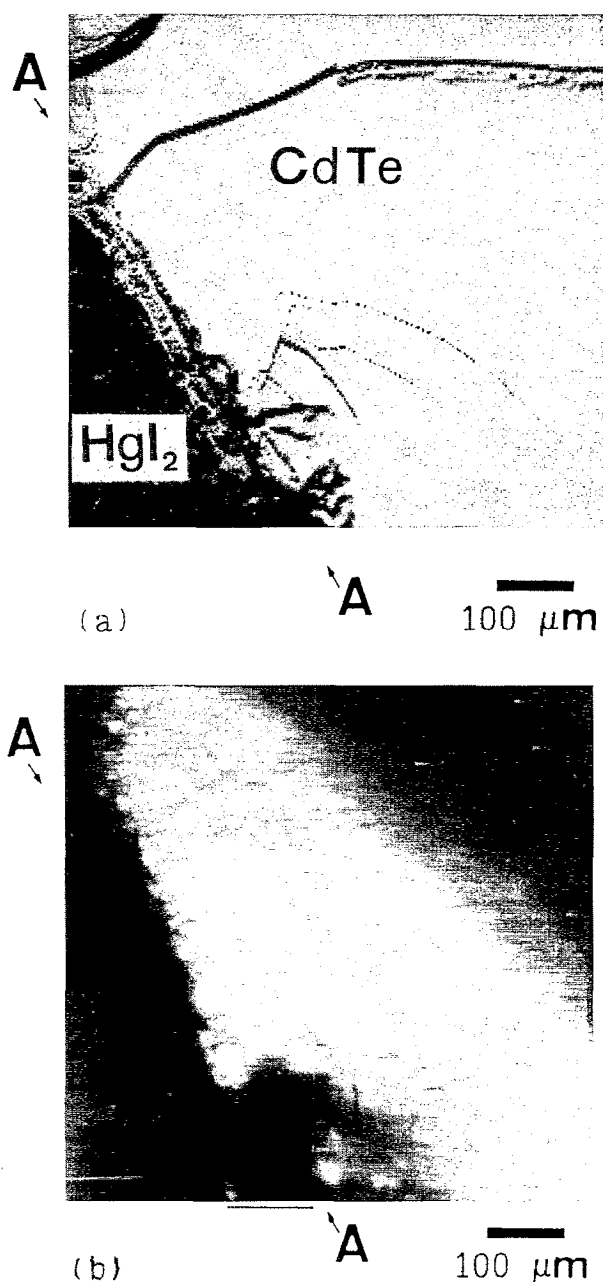
the growth of α-HgI_2 polycrystalline layer on the wafer surface, and this layer acts as a getter for defects distributed in the wafer. The annealing affects mainly the CL bands related with Te vacancies and with defects involving Ge. In particular, the emission related to Ge defects has been found to decrease in a region extending hundreds of microns from the wafer surface. In addition, during annealing of the crystals dissolution of Te precipitates and decoration effect take place.

Acknowledgements

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Fig. 6. (a) SE image of cleaved α-HgI_2/CdTe:Ge structure and (b) CL image of the same region. Line A–A marks α-HgI_2/CdTe:Ge interface.

4. Conclusions

The undoped and Ge-doped CdTe wafers have been annealed in HgI_2 vapor under isothermal conditions at 250°C for 24 h or for 48 h. The effect of the annealing procedure on the spatial distribution of structural defects in the wafer volume has been studied by CL spectroscopy and imaging techniques in SEM.

It has been shown that the annealing is followed by

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