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PULSED LASER ANNEALING OF CdTe SINGLE CRYSTALS

P. Fernández, J. Solis[a], J. Piqueras

Deptartamento Física de Materiales, Fac. Físicas, Universidad Complutense,
Ciudad Universitaria, 28040 Madrid, Spain
[a]Instituto Optica “Daza de Valdés”, Centro de Física “Miguel Catalán”, C.S.I.C.,
Serrano 121, 28006 Madrid, Spain

Pulsed laser treatments in air and in vacuum have been performed in CdTe wafers. The laser induced changes have been monitored by emissive mode and cathodoluminescence (CL) in a scanning electron microscope. Remarkable differences between the effects of both types of treatment have been found. In particular, while the irradiation in vacuum appears as a suitable technique for rapid annealing, irradiations in air can be accompanied by strong degradation of the sample surface.

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1. Introduction

CdTe is a wide band gap semiconductor which has been extensively studied due to its applicability as X- and γ-ray detector [1, 2] and for high efficiency solar cells [3, 4]. Also an important field of application is the fabrication of suitable substrates for HgTe and CdTe based epitaxial layers to be used in the infrared technology. Metalorganic vapor phase epitaxy (MOVPE) has been often used to grow CdTe layers over different substrates as GaAs, Si, sapphire etc. These epilayers can then be used as substrates for the deposition of HgCdTe alloys for infrared applications [5, 6, 7]. As in many other cases of epitaxial growth, one of the main problems encountered is the lack of good quality substrates to grow unstrained and defect-free layers. Indeed the substrates mentioned above render strained epilayers due to their high lattice mismatch with CdTe.

In a previous work [8] we have used cathodoluminescence (CL) microscopy to study laser induced recrystallization of CdTe layers grown on different substrates. It was shown that the properties and the defect structure of the recrystallized layer were strongly dependent on the nature of the substrate. The results of this work suggest that laser induced modification of the defect structure of CdTe wafers would enable to obtain substrates able to support high quality unstrained epilayers. Laser treatments of CdTe crystals have been previously reported [9, 10].

In this work we investigate the possibility to improve the quality of the CdTe substrates by pulsed laser treatments and to monitor the structural changes by CL.

2. Experimental method

The results from X ray analysis do not show any difference between unirradiated and either air or vacuum irradiated samples.

The samples investigated have been grown by the Travelling Heater Method (THM). They are undoped and show a p-type conductivity ($\rho \approx 30\ \Omega$cm) approximately. The samples were irradiated either in air or in vacuum (10^{-6} torr) with 12 ns ArF excimer laser pulses at 193 nm. The use of a beam homogeneizer allows to obtain a flat irradiance profile with a maximum deviation of 5% over a surface of 4×4 mm^2 at the sample site. The pulse repetition rate used was 1Hz and the pulse to pulse energy fluctuation was lower than 5%. In each case four different series of irradiations were performed, the corresponding number of pulses and energy were 20 pulses with an energy of 30 mJ/cm^2, 20 pulses with an energy of 60 mJ/cm^2, 20 pulses at 60 mJ/cm^2 followed by 20 pulses at 30 mJ/cm^2 and 20 pulses at 60 mJ/cm^2 followed by 80 pulses at 30 mJ/cm^2. The regions corresponding to the four different irradiation series could be done in the same wafer by shifting the sample, thus allowing the CL measurements to be performed under exactly the same conditions. Before and after irradiation the samples were investigated in the secondary electron and CL modes of a scanning electron microscope (SEM) by using a Hitachi S-2500 microscope with an electron beam energy of 25-30 keV. CL measurements were performed at liquid nitrogen temperature. For light detection in the near infrared range an ADC Ge detector has been used. A light guide feeding the light into an Oriel 78215 computer controlled monochromator was used to record the spectra.

To check structural or stoichiometric changes occurred as a consequence of the irradiations, Wavelength Dispersive X ray (WDX) mappings and X ray diffraction have been also performed.

3. Results and discussion

The CL images from the unirradiated sample are rather typical for single crystals of this material and other semiconductors (Fig. 1a). The emission is rather homogeneous and only some dislocation related features are observed.

As shown in Fig. 1b irradiation in air induces important variations in the CL images. The most striking change observed in the CL images is the apparition of some round-shaped dark spots with sizes between 50 and 200 μm depending on the irradiation conditions of the region considered. The smallest spots are observed in the area irradiated with 20 pulses at 30 mJ/cm^2, i.e. the more slightly irradiated zone. By increasing the energy of the pulses the size of the dark regions increases considerably as observed in region 2, (20 pulses at 60 mJ/cm^2). The images obtained from the regions irradiated with 20 pulses at 60 mJ/cm^2 plus 20 pulses at 30 mJ/cm^2 are very similar to those described for region 2. Finally the dark spots from the region irradiated with 20 pulses at 60 mJ/cm^2 followed by 80 pulses at 30 mJ/cm^2 show a wider size distribution. The regular rounded form of these dark features suggests the formation of drops, which would result from the local melting of the material and subsequent resolidification. A local decrease of the melting point has been observed in several materials at defective sites and stressed regions, like grain boundaries, thin film interfaces or dislocations [11, 12]. The drop-like features would thus correspond to local molten and resolidified regions whose thickness, considering the wavelength and pulse duration of the laser used [13], would be of the order of several tens of nanometer. This latter assumption is confirmed by the absence of contrast associated to these features in the emissive mode of the SEM. Since the laser pulses are very short, a rapid resolidification process is expected, and consequently the formation of material either amorphous or with low crystalinity regions could take place. As the pulse energy increases bigger areas are melted giving rise to the bigger resolidified regions.

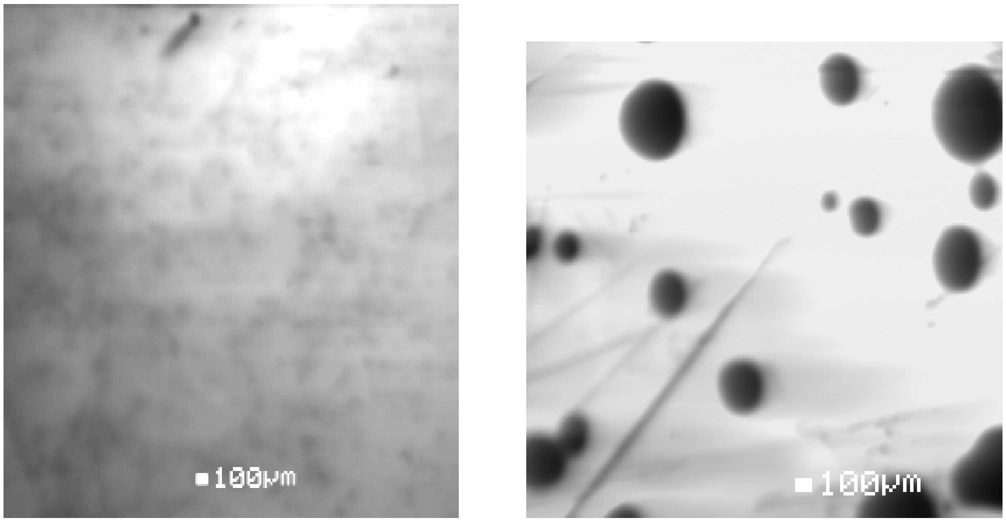

Fig. 1. Panchromatic cathodoluminescence image of a CdTe sample. a) Unirradiated; b) irradiated in air.

The emission spectrum from the unirradiated sample consists of two bands peaked at 1.52 eV and 0.78 eV (Fig. 2). The spectra remain practically unchanged upon laser irradiation in air. One representative spectrum of the irradiated samples is shown in Fig. 3. Only in some cases a slight shift of the near band edge peak is observed, from 1.52 to 1.56 eV, which could be attributed to differences in the relative intensity of the components of this band. The 0.78 eV band has been frequently observed in CdTe samples and attributted to different kinds of impurities in cadmium sites [14].

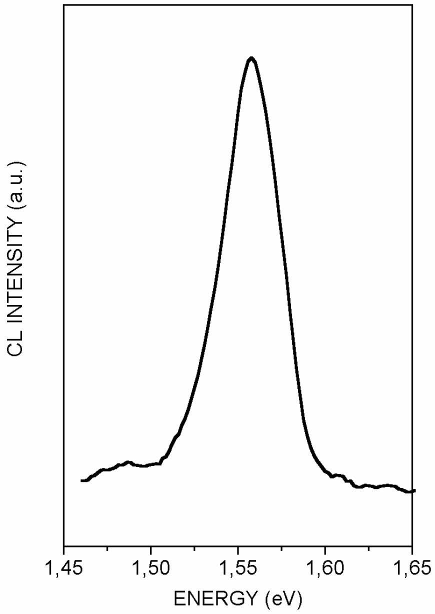

Fig. 2. Typical CL spectrum from unirradiated samples.

After irradiation in air all the laser irradiated areas are very sensitive to electron irradiation, which can even induce dramatic topography changes, along with strong quenching of the cathodoluminescent emission.

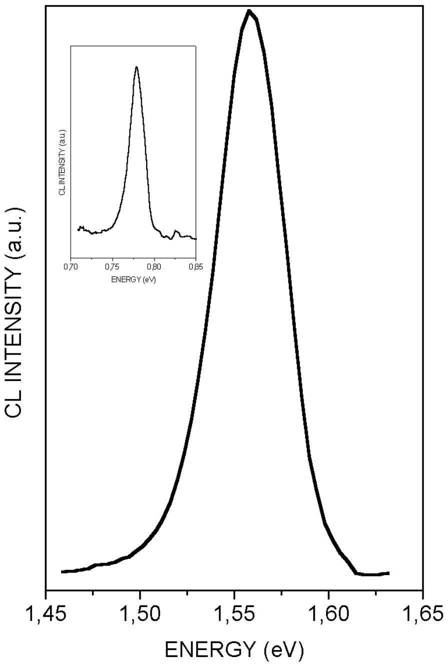

Fig. 3. CL spectrum obtained after irradiation in air. The inset shows the spectrum of low energy region obtained from samples irradiated in air.

Laser irradiation in vacuum were performed with the same pulse parameters. The results obtained are considerably different from those observed in the samples irradiated in air. No drop-like features are observed in these samples and, contrary to the observations described above, CL images before and after irradiation are practically identical although some changes occur in the spectra. After irradiation the spectra obtained from all the regions are very similar and consist mainly of three bands peaked at 0.85, 0.93 and 1.1 eV (Fig. 4). This behaviour is very similar to that previously observed CdTe samples annealed in inert atmosphere [15]. The 1.1 eV band is usually ascribed to V_{Te} centers [16, 17] while the other two bands are thought to be related to impurities in the cadmium sublattice [14]. Hence the laser treatment seems to enhance the migration of some impurities towards Cd lattice sites. As mentioned above all the vacuum irradiated samples show the same bands. However, the relative intensity of each of these bands depends on the irradiation conditions. In all regions except the most severely irradiated, the most intense band is that peaked at 1.1 eV associated to V_{Te} [16, 17]. The peaks at 0.85 and 0.93 eV appear as a bump in the low energy tail of the 1.1eV, though the intensity of these emissions relative to the 1.1 eV band intensity increases with the severity of the irradiation conditions. Fig. 4 shows representative spectra of the irradiated regions. The insets show with more detail this low energy tail where the evolution of the relative intensity of both bands 0.85 and 0.93 eV can be clearly observed. For the regions irradiated with low energy pulses the 0.93 eV band is more intense than the 0.85 eV one, while in the regions irradiated first with high energy pulses, the 0.85 eV peak has a higher relative intensity. The CL spectra indicate thus that the effect of irradiation in vacuum can be considered equivalent to a conventional annealing [15]. The absence of the drop-like features in the vacuum irradiated samples can be explained by a rapid vaporization of the very thin molten layer, due to the higher partial pressure of the molten constituents in vacuum.

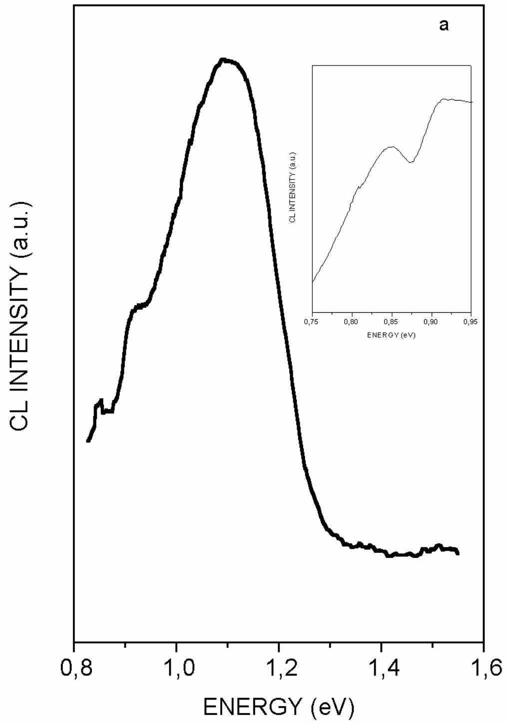

Fig. 4. CL spectra of two regions irradiated in vacuum with irradiation conditions: a) 20 pulses 30 mJ/cm^2; b) 20 pulses 60 mJ/cm^2 + 80 pulses 30 mJ/cm^2. The inset shows a detail of the low energy part of the spectra.

Some other processes can be considered as alternatives to explain these results. In particular, it has been suggested by other authors that upon laser irradiation in air an oxide phase is formed [18, 19]. The X ray measurements performed in this work do not reveal the existence of such oxidized regions. Nevertheless, this possibility cannot be discarded, since the expected thickness of these local molten regions would be far too thin to induce appreciable changes to be detected by X-ray microanalysis or diffraction.

Also the possibility that voids or precipitates of any of the elements are formed would deserve some consideration. In this case some stoichiometry changes should occur, but as explained before, the extremely small thickness of transformed material would be a handicap to the detection of changes in the X-ray microanalysis or diffractograms. However under this assumption the different behaviour found after irradiations in air or in vacuum is more difficult to explain. In particular since the Cd vapour pressure is higher, under vacuum conditions the formation of Te precipitates should be easier, but such precipitates have not been observed in our X-ray micrographs.

4. Conclusions

The results of this work shows that pulsed laser irradiation in vacuum is a suitable technique to perform thermal treatments of the CdTe substrates. However, care must be taken to avoid undesirable degradation effects associated to the presence of a non inert environment as has been described in the case of the irradiations performed in air.

Acknowledgements

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