Effect of laser annealing on the distribution of defect levels in CdSe films

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Abstract

Effects of laser treatment on the modification and/or distribution of defect levels in chemically-deposited CdSe thin films have been discussed. By annealing the CdSe films with laser in air, we could observe a drastic reduction of defect density and a redistribution of defect states in the low quality chemically deposited films. Increase of photoluminescence efficiency by laser treatment demonstrates the effect of recombination enhanced defect reactions at the annealed region. By manipulating the laser power and the time of annealing, we could obtain the films of better optoelectronic quality. The process might be useful for the control of defect levels in chalcogenide thin films for their applications in optoelectronic devices. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Cadmium selenide thin films have shown great promise for their applications as photoelectrochemical cells [1,2], thin film transistors [3,4], photoconductors [4,5], gamma ray detectors [6], etc. However, because of the inherent defects present in polycrystalline materials as compared to single crystals, a considerable portion of the photogenerated charge carriers is lost due to recombination in the intergrain regions. Several workers [7–10] have reported the existence of different structural or impurity-related defect states in CdSe films and dealt with several methods of post-deposition treatment for their modification, reduction or even elimination. Vacuum annealing [7,11], prolonged air exposition [11], air annealing [12], laser annealing [7] are the few among them.

In the present work we applied the laser annealing treatment on the low quality chemically deposited CdSe films in air. Photoluminescence (PL) measurements were done on the as-grown and laser treated samples at different temperatures. A drastic modification of PL emission is observed on laser treatment. The effect of laser annealing on the distribution of the defect levels and hence the modification of PL emission in CdSe films is discussed.

2. Experiments

CdSe thin films were grown by chemical bath deposition (CBD) technique following the sequence proposed

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by Kainthala et al. [13]. The process follows the formation of CdSe films through the decomposition of selenourea $[CSe(NH_2)_2]$ in an alkaline solution of the corresponding salts of cation. The final working solution was prepared by mixing cadmium chloride $(CdCl_2)$, sodium hydroxide (NaOH), ammonium nitrate (NH_4NO_3) and selenourea, previously dissolved in deionized water. The films of approximately 0.35-μm thickness and 2×3 cm^2 area were prepared on glass substrates by holding them in the freshly prepared mixture of 18 ml of 0.0038 M $CdCl_2$, 14 ml of 0.01 M $CSe(NH_2)_2$, 7 ml of 0.10 M NaOH and 21 ml of 0.50 M NH_4NO_3 solutions at 70°C. X-Ray diffraction study of the as-grown films revealed that the films were polycrystalline in nature with average particle size of the order of 0.20 μm. An as-grown film was divided into several pieces for laser annealing treatments. Laser annealing was performed by fixing the as-grown films on a metallic support and irradiating them by an unfocused beam of argon laser (Spectra Physics 217) in its multimode, on a-0.35 mm^2 film area in air. Keeping the time of exposure fixed to 1 min, the films were annealed at different powers of the laser beam to obtain the different doses of irradiation on the film surface. Several samples (D1−D8) were prepared by successive application of different laser doses. For example, the dose D1 correspond to the application of a laser beam of 75.75 W/cm^2 intensity for 1 min; the dose D2 correspond to the application of the same dose as of D1, followed by another dose of 151.50 W/cm^2 for 1 min, and so on. Some parameters of laser annealing are summarized in Table 1. The rise of temperature in the samples was recorded by fixing a copper-constantan thermocouple on the film surface slightly away from the laser spot. The composition and the morphology of the films were studied using a JEOL, JSM 5400LV scanning electron microscope (SEM) with NORAN system. The photoluminescence (PL) spectra of the films were recorded by mounting them on a cold finger of a Displex system and keeping the temperature in between 20 and 300 K. The samples were excited by the 488 nm line of a cw Ar ion laser (Spectra Physics) and the spectra were analyzed through an automated, 1-m long SPEX 1000M monochromator.

3. Results and discussion

The as-grown films were more or less uniform (in thickness and in composition), gray in color, and with good adhesion with the substrates but non-stoichiometric. X-Ray diffraction revealed the hexagonal phase of the films with a preferential orientation of the (002) planes parallel to the substrate. In Fig. 1, the SEM micrographs of the typical as-grown and laser treated films are shown. Apart from a homogeneous grain structure, there appeared some scattered cauliflower-like structures on the films. There was no significant change in morphology between the as-grown samples and the laser-treated samples except the production of some micropores by laser treatments at higher doses. No appreciable change in grain size has been observed on laser treatment. However, on laser treatment, the composition of the films changed gradually (Table 1), increasing Cd/Se ratio with the increase of irradiation dose.

In Fig. 2, the PL spectra of an as-grown sample, recorded at different temperatures are presented. At room temperature, the PL spectrum is broad, extending from 1.35 to 1.90 eV. Whereas, a relatively sharp maximum, followed by a long slowly falling saddle to a broader maximum is observed at low temperatures. The broadness of the 300 K PL spectrum, corresponds to the presence of closely neighboring donor−acceptor states in the sample, as has been observed by several workers [14−16] in CdS and CdSe samples. The broad band appeared at approximately 1.44 eV at low temperatures, is generally assigned to the impurity-assisted acceptor level [17,18]. In Fig. 3, the effect of laser dose on the PL emission has been shown. We can observe, that, with the increase of laser dose, the overall PL spectrum became sharper, the intensity of the 1.44 eV band increased initially and the peak position shifted towards higher energy up to 1.50 W laser power. On further increase of laser power, the main emission

Table 1
Parameters of laser treatments and the corresponding variation of composition and PL intensity in CdSe films

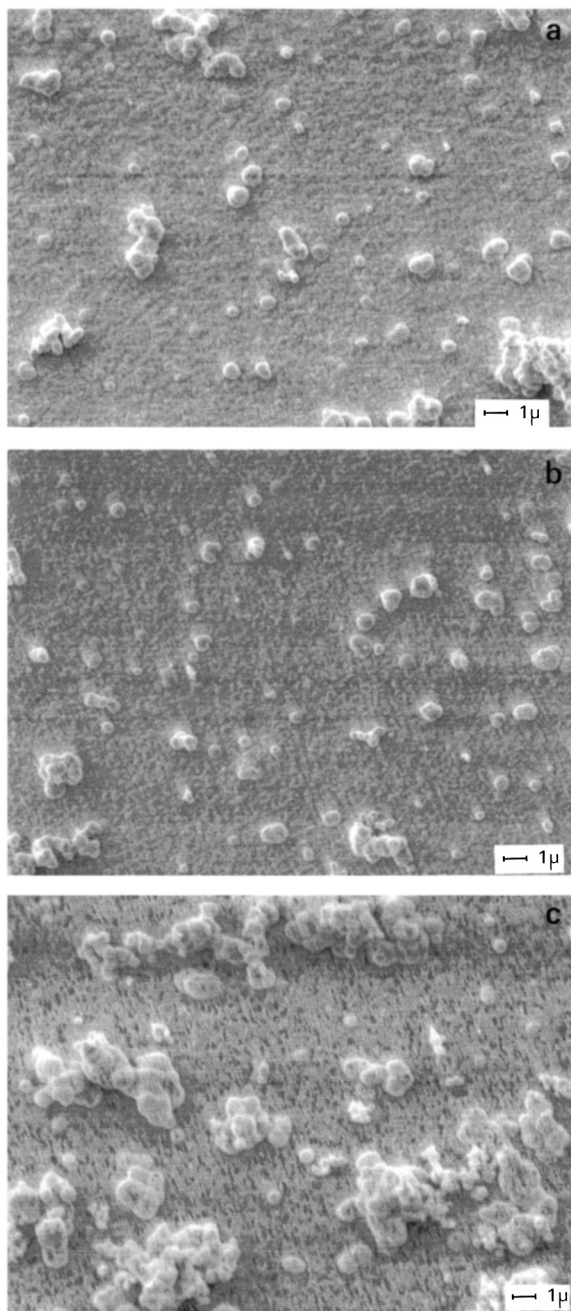| Treatment	Laser power (W)	Dose (W/cm^2)	Final temperature (K)	Cd/Se (Atomic ratio)	PL intensity (a.u.)
Untreated	−	−	300	1.18	13.0
D1	0.25	75.75	326	1.18	13.2
D2	0.50	151.50	364	1.19	13.5
D3	0.75	227.25	377	1.21	14.0
D4	1.00	303.30	404	1.22	18.5
D5	1.25	378.75	427	1.23	20.4
D6	1.50	454.50	449	1.24	21.5
D7	1.75	530.50	475	1.26	26.8
D8	1.92	581.80	485	1.28	33.0

Fig. 1. Scanning electron micrographs of the: (a) as-grown; (b) laser treated with dose D4; and (c) laser treated with dose D8, CdSe films.
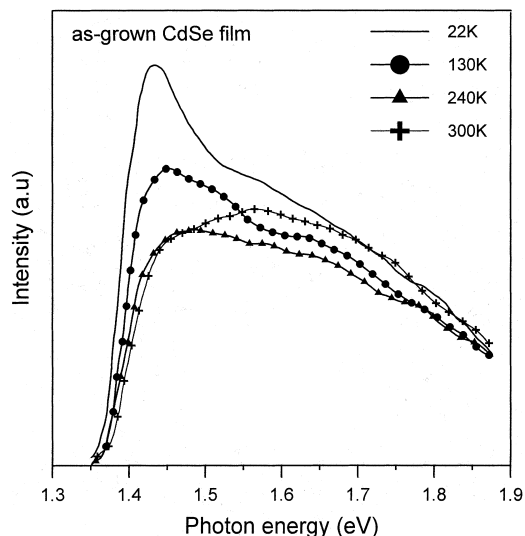

Fig. 2. PL spectra of an as-grown CdSe film at different temperatures.

the recombination-enhanced defect annealing phenomenon observed during aging studies in III–V laser diodes grown by MBE and MOCVD [20]. A similar increase of PL intensity by laser treatments has been reported by Jordan et al. [21] for their II–VI laser diode structures and attributed to the removal of intrinsic point defects by optical annealing. The shift of the main PL band on laser treatment might be due to that a specific band of donors and/or acceptors has been chemically replaced due to the annealing process.

Generally, a lot of defect levels have been detected in CdSe crystals and thin films throughout its band gap by several workers [17,18,22–26]. They are either impurity-assisted or related to stoichiometry variation. For

band shifted further towards higher energy and the band close to 1.44 eV reappeared. The increase of laser power beyond 1.5 W also caused a drastic broadening of the main band. The PL spectrum for the film treated with 1.92 W laser power became as broad as untreated sample but with some sharper structures towards high energy. The overall intensity of the PL spectrum increased with the increase of laser dose. In Table 1 the integral PL intensities for different laser doses are given. The increase in PL intensity is an intrinsic property of the II–VI materials [19] and is similar to
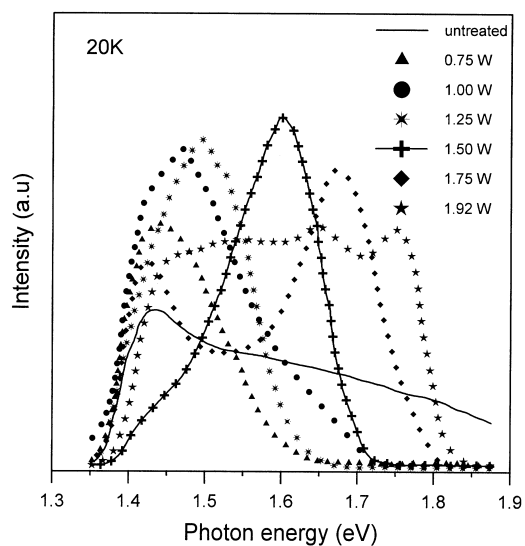

Fig. 3. 20 K PL spectra of the untreated and laser-treated CdSe films. The final laser powers used for the treatments are shown as the legends.

example, the 1.44 eV emission is very often correlated to the V_{Se} or Cl impurity [7,22,23]. A great deal of absorption structure in between 600 and 2500 nm was observed in Cd-annealed CdSe crystals at low temperature by Robinson and Bube [11]. Several emissions in between 1.70–1.82 eV in p-CdSe have been assigned to the impurity-assisted donor–acceptor pairs (DAP) and excitonic emissions [7,16]. Jäger-Waldau et al. [16] could reveal several emissions extending from 1.55 to 1.76 eV in evaporated CdSe films and assigned them to the donor–acceptor pairs. In the present case, as the samples were annealed in air, a reduction of V_{Se} by the incorporation of ambiental oxygen which acts as acceptor impurity in CdSe cannot be ruled out. However, at lower laser doses, we could observe a substantial increase of the 1.44 eV emission intensity, which might be due to the increase of selenium vacancy in the films on laser treatment. By increasing the laser dose, as the annealing temperature increased, incorporation of oxygen in the films became more probable and hence the disappearance of 1.44 eV peak is expected. Apart from the oxygen incorporation, the subsequent annealing process caused a reduction and redistribution of defect states causing the emission sharper and shifting towards higher energy. On annealing the films with a laser beam intensity higher than 1.5 W/cm², the 1.44 eV emission reappeared and the intensity of the main emission at high energy side reduced. These two phenomena can be explained through the following arguments: as by increasing the laser power, the Cd/Se ratio increased, the concentration of V_{Se} in the samples increased. The decrease of the intensity of the main peak at the higher energy side might be due to a rapid quenching of the samples after annealing with higher laser powers. The broad spectral distribution in the sample treated with 1.92 W/cm² laser power, is due to a sharp deviation of stoichiometry (Table 1). Due to the sharp deviation of stoichiometry a quasi-continuous high density distribution of donor states was created [11].

The PL spectra of donor-acceptor like transitions were found to be broad for polycrystalline CdSe films [16,24] due to their random and preferential pairing apart from their energetically closeness. The donor states in CdSe are believed to be Na_i and K_i while the acceptor states are Na_{Cd} and K_{Cd} [25,26]. The diffusion of these impurities through the lattice is very fast due to their small ionic radii [25]. Furthermore, the donors and acceptors feel Coulombic attraction. Consequently, such impurities tend to form hydrogenic pairs. Such pairs exhibit very weak coupling with phonons. These states produce the PL emissions which are energetically intermediate between the bound excitons and the low energy donor–acceptor transitions. In our samples, though the presence of K is not so probable, use of NaOH as a reagent, might have incorporated adequate

Na impurity in the films. From the EDX study we could not detect the presence of Na in the as-grown films which indicates that the Na content in the films was below the detection limit (< 0.1 at.%) of EDX analysis. The laser annealing might have caused the migration of Na ions to form different donor–acceptor pairs (DAP) at different energies depending on the laser dose. The modifications in PL emissions have also been observed by vacuum annealing by Henry et al. [25].

By applying a computer-simulated decomposition process we could observe that, most of the PL spectra consist of five component peaks located at approximately 1.40, 1.44, 1,53, 1.63 and 1.77 eV. With the increase of laser dose, the intensity and broadness of the peaks change drastically, indicating a redistribution of defect density in the films. In Fig. 4, the PL spectra of the untreated film and the films prepared with D5, D6 and D8 doses along with their computer-decomposed bands are shown. It is to be noted that the PL spectra of the samples prepared by applying doses D5 and D6 revealed only three component peaks. For the sample annealed with dose D5, the intensity of the 1.40 eV peak reduced drastically and the peaks of approximately 1.63 and 1.77 eV disappeared. The film prepared with dose D6 did not reveal the 1.40 and 1.77 eV peaks. However, for the film prepared with dose D8, there appeared two extra peaks at approximately 1.57 and 1.72 eV in excess of the previously mentioned five peaks. The peak appeared at approximately 1.72 eV is
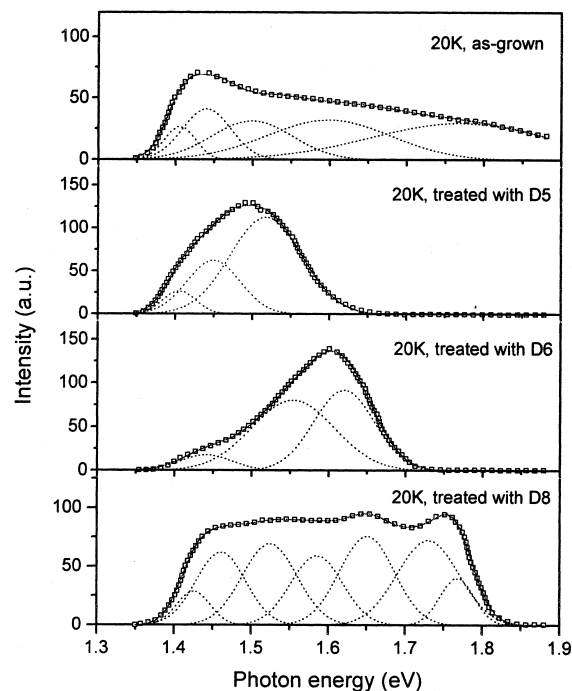

Fig. 4. The computer-simulated decomposition of PL peaks for the samples treated with different laser doses. The empty squares represent the experimental data points and the line connecting them represent their computer fitting.

generally assigned to the selenium-vacancy complexes with impurities or donors [24] and the peak at approximately 1.77 eV arises from the free (electron) to bound (hole to an acceptor state) transition [15,28]. The drastic broadening and appearance of extra peaks in the sample prepared with dose D8 is due to the sharp deviation of stoichiometry. Similar broad distribution of donor defects causing the broadening of PL bands has been observed by several workers [11,27] and attributed to a quasi-continuous high-density distribution of donor states related to composition inhomogeneities. From our results it seems that the doses like D5 and D6 are more effective for the reduction of defect density in CdSe films.

4. Conclusions

The PL emissions in the low quality chemically deposited CdSe films can be modified drastically by laser annealing treatment in air. The overall PL intensity increases with the increase of annealing dose due to recombination-enhanced defect reaction in the vicinity of point defects. Evolution of different component peaks in the PL band depends strongly on the laser power. By manipulating the laser dose and the time of laser treatment, CdSe films of better optoelectronic quality can be obtained. A further study is needed to optimize the conditions of laser treatment for obtaining the CdSe films of lowest defect density.

Acknowledgements

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