IMPROVEMENT OF CdS CRYSTALLINITY BY Nd:YAG LASER RADIATION

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Abstract

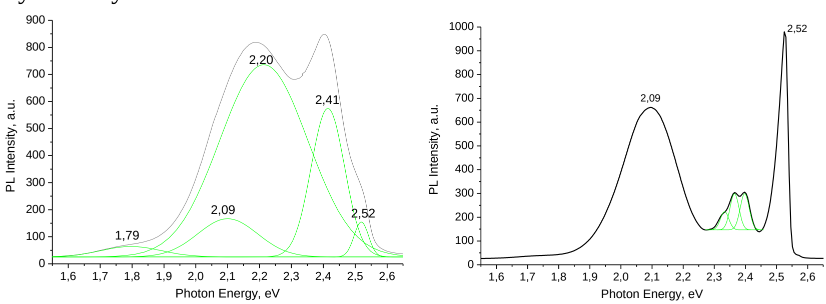
A possibility to improve the quality of polycrystalline CdS thin film by Nd:YAG laser irradiation was shown. The CdS thin film was prepared by closed space sublimation method on ITO/glass structure and irradiated by the 532 nm wavelength laser radiation with intensity up to 15 MW/cm^2. Several evidences demonstrated the improvement of the cryatallinity of the CdS thin film after the laser radiation. The improvement was proved by optical methods: the appearance of photoluminescence band at ~2.520 eV, which is attributed to free exciton emission; the appearance of “spike” in the reflection spectrum at ~2.573 eV between upper and lower polariton branches and the increase of the intensity of LO phonon line at 305 cm^{-1} about 3 times in Raman back scattering spectra. Moreover, the increase by 20% of the size of CdS crystals after laser radiation takes place, which was proved by X-Ray diffraction pattern and using the Scherrer equation.

Key words: *CdS; Closed space sublimation method, Nd:YAG laser;*

Laser processing of semiconductor materials is known to be a relatively simple and effective process in steps of formation of opto- and microelectronic devices. The CdS layer in CdTe-based solar cells (SC) plays an important role for its efficiency [1]. However, this film has a lot of electrical and optical active intrinsic point defects. The quality of CdS layer depends on growth conditions and post-growth annealing as crucial factors influencing photo-electrical properties of CdS [1]. Usually to reduce the concentration of lattice defects in CdS films an annealing process in $CdCl_2$ is used, that improves the film quality only partially. Furthermore, the investigations of excitonic states in CdS single crystals irradiated by N_2 laser by means of photoluminescence and reflectance methods have shown a generating of point defects - shallow donors and acceptors. It is supposed that these defects from irradiated surface of the crystal are connected with Si and V_S, respectively that is explained by evaporation of sulphur atoms under action of the laser radiation [2]. In this case, the formation of donors - V_S is dominating effect at the irradiated surface of the crystal. This effect was proved by the increase of dark current. Irradiation of CdS single crystal by ruby laser using two photon absorption has shown the same point defects generation [3]. Moreover, irradiation of polycrystalline CdS film on glass by Nd:YAG laser at intensities of 0.2-2.5 MW/cm^2 causes the improvement of their structural and electrical properties due to the recrystallization of the CdS film [4]. The irradiation with laser pulses reduces the number of defects present in the films, thereby increasing the electrons mobility. The authors explained the possible reason of these changes by the presence of V_S levels. Optical properties of the polycrystalline CdS thin film after laser radiation have not been investigated. Therefore, this work is mostly aimed to improve the polycrystalline CdS thin film by Nd:YAG laser radiation.

The polycrystalline CdS thin film was deposited on commercially available ITO/glass substrate at source temperature 850 °C by using closed space sublimation method (CSS) (pressure in the chamber: 1 mbar, deposition time: 30 min, distance between source and substrate: 1 mm). Afterwards (Then) CdS thin film was annealed in $CdCl_2$ atmosphere to reduce the concentration of lattice defects. Nanosecond Nd:YAG laser with intensity up to $I=15.0\ MW/cm^2$ was used for improvement of the quality of polycrystalline CdS thin film (pulse repetition rate at 10 Hz, wavelength $\lambda=532\ nm$, pulse duration $\tau=4\ ns$).

Fig.1 shows photoluminescence (PL) spectra of CdS layer before and after irradiation by Nd:YAG laser up to $I=15.0\ MW/cm^2$. It is known, that the PL band at around 2.520 eV is attributed to free exciton in CdS [5]. It can be seen, that the band intensity after irradiation by Nd:YAG laser is dominating and increased by more than 5 times. This is an indicator of improvement of crystallinity of the material.



(a) (b)

Fig.1. PL spectra of CdS film measured at T=1.6 K temperature: (a) non-irradiated and (b) irradiated by Nd:YAG laser.

Raman back scattering spectra of non-irradiated and irradiated by Nd:YAG laser CdS thin films were studied as well. The band at about 305 cm^{-1} for non-irradiated and irradiated of CdS film, which is attributed to longitudinal optical (LO) phonon mode in CdS. Obtained value is in good agreement with the earlier reported peak position for defect-free crystalline CdS films [6]. Raman peak of CdS thin film prepared by chemical-bath-deposited method and vacuum evaporation after pulse laser deposition technique appears at about 300.3 cm^{-1} and 303 cm^{-1}, respectively [7]. The value of peak position for the CdS thin films prepared by CSS technique is comparable to the samples which have good crystalline quality. The intensity of this LO mode in the irradiated samples has increased about 3 times with respect to the non-irradiated CdS. It is evident that the crystallization of CdS film improves the quality after laser irradiation. The frequency of LO phonon mode for hexagonal phase is close to the LO phonon value in cubic phase of CdS in the Raman spectrum so it is very difficult to distinguish between these two modifications [8]. Raman frequencies of CdS thin films prepared by other techniques are falling in the range explained in the earlier report [9].

The reflection spectra of non-irradiated and irradiated by Nd:YAG laser CdS thin films at temperature *T=1.6 K* are shown in Fig.2 a and b, respectively. In the non-irradiated case two sharp bands have been revealed: A-free exciton at 2.551/2.54 eV (min/max) and B – free exciton at 2.579/2.569 eV (min/max). These features are assigned to hexagonal phase, but the feature around 2.47/2.44 (min/max) may be associated with the cubic phase. After irradiation of CdS film with laser of intensity of 15 MW/cm^2, the increase of the reflectivity peak intensity takes place. Moreover, the appearance of “spike” (at around 2.573 eV), which is usually interpreted as a result of interference in surface exciton dead layer and is strongly sensitive to surface modification [10] has been observed. These changes in the reflection spectra are explained by the improvement of quality of CdS thin film.

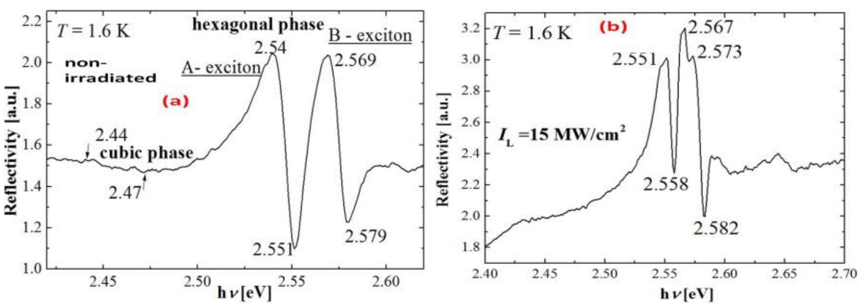


Fig.2. Reflectivity spectrum of CdS film: (a) non-irradiated and (b) irradiated.

Topography image of irradiated CdS thin film measured by SEM has shown micro-ripples formation at the surface. It indicates that CdS surface undergoes a partial melting. Afterwards, the recrystallization of the melted substance took place, with the formation of ripples and strings as several consequences of a partial heating.

The structure of the films before and after laser irradiation has also been analysed by using of GA-XRD. The GA-XRD pattern shows three main peaks, corresponding to (111), (220) and (331) directions. According to the Scherrer equation and XRD measurements the size of CdS crystals is increased by 20%.

Conclusions

The polycrystalline CdS thin film irradiated with the laser radiation up to 15 MW/cm^2 demonstrates several evidences of the improvement of the crystallinity of the film: sharp and intense exciton band; the increase of LO phonon band intensity by about 3 times with respect to the non-irradiated area in Raman spectrum. The formation of micro-ripples after CdS irradiation as shown by SEM image lets us deduce that melting of surface and later recrystallization of surface layer occurred.

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