INFLUENCE OF SOURCE TEMPERATURE UPON THE CONTAMINATION WITH CU OF THIN-FILM CDTE SOLAR CELLS GROWN BY CLOSE SPACE SUBLIMATION TECHNIQUE

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Photoconversion efficiencies up to 16.5 % have been attained from CdTe/CdS solar cells. CdTe/CdS heterojunction can be deposited cheaply over large areas using the close space sublimation (CSS) technique. In a previous study of CdTe/CdS thin film solar cells [1] we have established that a post growth treatment involving deposition of CdCl₂ and annealing in air at 400 °C increases the photovoltaic efficiency of the junction by two orders of magnitude. The stability issues are now of prime importance for future implementation of thin-film CdTe solar cells. The diffusion of Cu from the back contact represents the most suspected source of instability for CdTe/CdS solar cells. Another source of contamination with Cu during the CSS process is the source material containing a residual Cu impurity.

Photoluminescence (PL) provides insight into the optical and electrical properties of II-VI compounds. Luminescence studies have been used to explore alloying effects, diffusion and cell degradation for CdTe-based solar cells [2,3].

In this work we investigate by means of photoluminescence the impact of source temperature during the CSS process upon the incorporation of Cu into CdTe/CdS heterojunction.

Thin film CdS/CdTe hetero-junction solar cells were fabricated on glass substrates covered by a SnO₂ layer with a sheet resistivity of about 10 Ω/\Box . SnO₂ layer served as a transparent front contact to CdS layer. Both CdS and CdTe layers were deposited by CSS method. The CdTe source contained Cu at a level of 1×10^{19} cm⁻³ as a main residual impurity. Different hetero-junctions were fabricated with various source temperatures from the interval of 530-560 °C. The substrate temperature was kept at 290 °C. After the CdTe layer was deposited, the structures were held in a CdCl₂:H₂O saturated solution and subsequently annealed in air at the temperature T = 400 °C during 30 min. More details on hetero-junction fabrication are presented elsewhere [1].

The photoluminescence (PL) was excited by the 514.5 nm line of an Ar⁺ SpectraPhysics laser and analyzed in a quasi-backscattering geometry through a double SDL-1 (LOMO) spectrometer. The signal from a FEU-62 photomultiplier amplified by a Unipan 232 lock-in nanovoltmeter was introduced in an IBM computer via the IEEE-488 interface. The samples were mounted on the cold station of a LTS-22-C-330 optical cryogenic system.

Fig. 1 presents PL spectra of different CdS/CdTe hetero-junctions grown with different source temperatures. The luminescence was excited through the glass substrates and the CdS layer and measured at T = 10 K in the backscattering geometry. One can see that all the spectra consist of a weak broad PL band in the spectral range of 1.6 - 2.0 eV and a stronger complex PL band in the spectral interval from 1.2 eV to 1.5 eV. The first one corresponds to photon energies higher than the bandgap of CdTe, and it is suggested to come from a transition layer at the CdS/CdTe interface. The broadness of this PL band is indicative of a gradual change in the composition of the transition layer resulting from the intermixing at the CdS/CdTe interface. It is known that treatment with CdCl₂ apart from increasing of grain size and lowering the concentration of structural defects promotes also S diffusion throughout CdTe film and Te diffusion into CdS.

The analysis of the second PL band through the deconvolution of the spectra shows that it consists of at least three PL bands. The central PL band centered at 1.35 eV increases in intensity with the increase of the source temperature in the CSS process. The other two bands located at 1.30 eV and 1.45 eV become resolved in samples with a low intensity of the 1.35 eV PL band (for instance samples 1).

At room temperature the PL spectra of all the samples are practically identical, and consist of a band at 1.27 eV with a shoulder at 1.39 eV (see Fig. 2). The practical coincidence of spectra for different samples at room temperature is explained by the quenching of the PL band at 1.35 eV with the temperature increase. The intensity of two other bands occurring at high temperatures is practically the same for all the samples. Therefore, the only difference between the samples is the intensity of the 1.35 eV PL band.

The PL band at 1.45 eV (at T = 10 K) is commonly believed to originate from an electron transition between the conduction band and a $V_{Cd}Cl_{Te}$ complex [4,5], or from radiative recombination of free carriers via donor-acceptor pairs (DAP) involving the $V_{Cd}Cl_{Te}$ acceptor and a shallow donor [3,5]. The independence of the position of this band upon the excitation power

density as illustrated in Fig. 3 is indicative of its connection with the transition between the conduction band and the acceptor complex.



Fig. 1. PL spectra measured at T = 10 K from CdS/CdTe hetero-junctions fabricated with different source temperatures: 1 - 530 °C, 2 - 540 °C, 3 - 550 °C, 4 - 560 °C.



Fig. 2. PL spectra measured at T = 300 K from CdS/CdTe hetero-junctions fabricated with different source temperatures: 1 - 530 °C, 2 - 540 °C, 3 - 550 °C, 4 - 560 °C.



Fig. 3. The normalized PL spectra of the sample grown with the source temperature of 530 °C measured at 10 K with different excitation power densities: 1 - 0.01; 2 - 0.1; 3 - 1 W/cm².

Fig. 4. Same as Fig. 3 but for the sample grown with the source temperature of $560 \,^{\circ}\text{C}$

By the contrary, the energy position of the PL band at 1.35 eV shifts to higher energies with increasing excitation power density (see Fig. 4), which is consistent with the saturation of distant

pairs under increasing excitation, as expected for DAP recombination. In a previous study, a luminescence band around 1.32 eV was observe in CdTe films containing Cu impurity, and this emission was suggested to be related to Cu substituting for Cd [2]. Grecu et al [3] assumed that another luminescence band at 1.45 eV is associated with Cu_{Cd} defects. One can assume that this scatter in the experimental data is related to different charge states of the Cu_{Cd} defect and (or) to the formation of complexes involving this defect. Since Cu is the main impurity in our samples we suggest that the PL band at 1.35 eV is related to a D - Cu_{Cd} complex, where Cu_i, Cl_{Te}, or other donor-type defects may play the role of the donor D. In such a case, one can use the intensity of this PL band for monitoring the incorporation of the impurity from the source into the CdTe layer. The intensity of luminescence increases with the increase of the source as low as possible to avoid the contamination of the film. However, low source temperature results in low deposition rates of the CdTe film. Therefore, one should find a compromise between the degree of contamination and the deposition rate.

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