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STUDY OF THE DEFECT LEVELS, ELECTROOPTICS, AND INTERFACE PROPERTIES OF POLYCRYSTALLINE CdTe AND CdS THIN FILMS AND THEIR JUNCTION

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ABSTRACT

In this study, the electrical behavior of CdS/CdTe junctions was investigated using deep-level transient spectroscopy (DLTS) and capacitance-voltage (c-v) measurements. The results were then correlated to chemical composition and optical properties (measured by wavelength-scanning ellipsometery) of the CdTe film and the dominant defect states were determined by photoluminescence (PL) emission measured before and after post-deposition $CdCl_2$ treatments. CdTe films used in this study were prepared by electrochemical deposition (ED), close-spaced sublimation (CSS), and physical vapor deposition (PVD). The chemical and heat treatments are shown to decrease Cd-vacancy levels (PL measurements) and quench majority-carrier deep traps. These treatments, which determine various parameters crucial to the device performance such as the type and concentration of the dominant defects and deep levels, greatly affect the device performance by controlling open-circuit voltage.

INTRODUCTION

CdTe technology has been established for a large number of applications, including solar cells, optical [1] and nuclear [2] detectors, and thermal- and radiation-imaging devices [3]. CdS/CdTe polycrystalline heterojunction cells of efficiencies close to 16% have been reported recently [4]. Most of the problems associated with the use of polycrystalline CdTe films are attributed to inhomogeneity, self-compensation, and the difficulty of forming a stable and low-resistivity ohmic contact.

EXPERIMENTAL METHODS

Samples of polycrystalline CdTe thin films prepared by CSS, PVD, and ED methods were investigated in this study. Heat treatments were carried out by depositing a thin layer of CdCl from CdCl-saturated solution in methanol, on the CdTe film; the structures were then heat treated for 20-30 minutes at 350°-450°C in a tube furnace. The optical properties of the CdTe films were measured using a wavelength-scanning ellipsometer (WSE) in the wavelength range 300-800 nm. High-resolution PL emission spectra were obtained at different temperatures (5-300 K) using the 633-nm line from a He Ne laser at different excitation powers (1-30 mW, unfocused). The DLTS technique has been used to determine both the trap levels and densities dominating each material.

RESULTS

Defect Levels in CdTe

The transitions dominating the PL emission from various untreated CdTe films are 1.53 eV for CSS, 1.47 eV for PVD, and 1.425 eV for ED samples. After the $CdCl_2$ treatments of these samples, not only did the defect states dominating each sample change, but their relative concentrations also varied according to the condition of the treatment and the deposition process of the CdTe film. The PL emission from all polycrystalline CdTe thin films consists of two groups of peaks in addition to the peak resulting from band-to-band (B-B) recombination at 1.587 eV. The first group consists of four peaks, at 1.55, 1.53-1.515, 1.491-1.475, and 1.45 eV which are labeled as A, B, C, and D, respectively. Note that the location of the two peaks B and C may shift according to the method of preparation and the $CdCl_2$ treatment and, consequently, the type of impurities that may exist. The second group consists of two well-resolved emission lines (1 and 2), which appear at 1.435 and 1.41 eV, and two additional (less resolved) lines, labeled 3 and 4, at energies 1.39 and 1.37 eV. From the changes in the PL emission-peak location and intensity due to changing the excitation power and measuring temperature, the origin of most of the PL peaks are identified using the chemical composition of CdTe films as a guideline. The first group is attributed to band-related recombination, where A and B are caused by bound exciton recombination involving two shallow donors d1 and d2 at 40 and 60-80 meV below the conduction band (CB). The respective sources of these donor levels are probably Te vacancies and Cd atoms substituting for Te. The peaks C and D, on the other hand, are attributed to CB-acceptor recombination involving two acceptors, a1 and a2, at 95-115 and 140 meV above the valance band (VB). The possible sources of the two acceptors are Cd vacancies [5] and some anti-site Cd_{Te} defect forming complex defects involving CdTe impurities, possibly Cu (Cl in treated films). The 1-4 emission peaks are attributed to donor-acceptor (D-A) recombination. Peaks 1 and 2 involve a common donor, d1, and the two acceptor levels, a1 and a2. The two peaks 3 and 4 also

involve d2 as a common donor level, but they would end at level a2 and level a3 at approximately 160 meV above VB. Fig. 1 demonstrates the PL-emission spectrum measured at 5K, from the surface of three CdTe samples S1, S2, and S3 deposited by the CSS method using the same source temperature of 650°C and different substrate
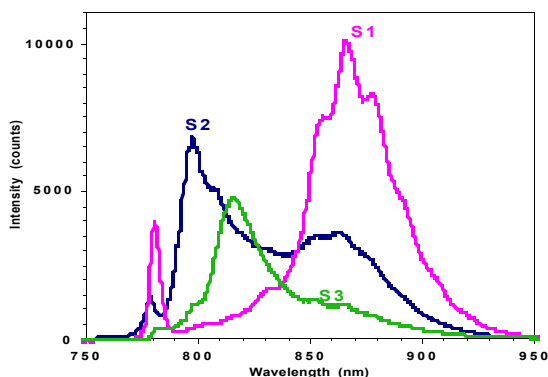

Fig. 1. PL emission from untreated CdTe films.

temperatures of 625°, 550°, and 500 °C, respectively. The conversion efficiencies of the devices made of the three samples after receiving CdCl treatment are 12%, 9%, and 5%, respectively. It is clear that emission from S1 has strong band-to-band recombination and is dominated by peak 1 before receiving CdCl treatment. The A, B, and C peaks of this spectrum are extremely weak. The emission spectrum of sample S2, on the other hand, is dominated by transition A and demonstrates peaks 1-4 at much lower intensity. The emission from sample S3 is dominated by peak B. Peaks 1-4 of this sample are relatively weaker than those of sample S2. The emission from the surface of these samples after receiving the $CdCl_2$ treatment is demonstrated in Fig. 2, which indicates that S1 and S2 are dominated by the B-B transition. Fig. 2 also shows a very weak emission from sample S1 in both energy regions. However, sample S2 showed very strong emission in the
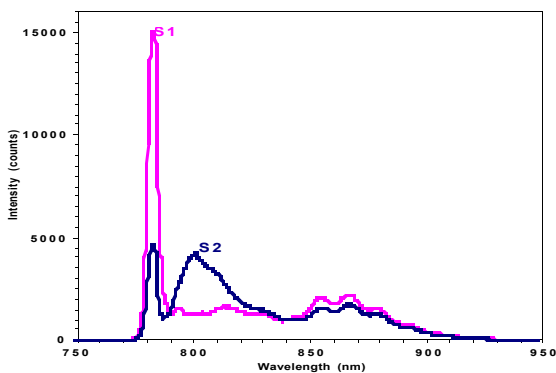

Fig. 2. PL emission from the surface of S1 and S2 after the CdCl treatment.

first region and maintained the same relative intensity in the second region. The PL emission from the treated

samples was also measured at the junction of the device through the CdS film, and the results are shown in Fig. 3. The PL spectra of the three samples show qualitative similarities where the emissions from all samples are dominated by the first region (peak C for S1 and peak B for S2 and S3) and showed weaker emission in the second region.
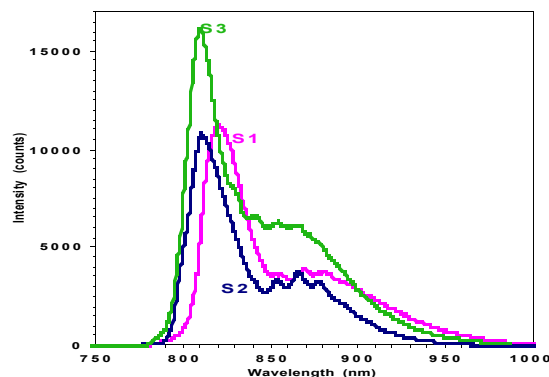

Fig. 3. PL emission from the junction of S1, S2, and S3 devices.

The main difference is the lower relative intensity of the second-region emission of samples S1 and S2 as compared to S3. It is apparent that the degree of compensation of the CdTe layer near the junction of S2 and S3 is higher than in S1, which resulted in a poorer performance of these two devices.

Optical Properties

The surface roughness of CdTe polycrystalline thin films varies with the method of film deposition, as well as the preparation condition. ED films were so rough that ellipsometric measurements were only carried out after polishing the film surface. On the other hand, PVD films were specular and gave the most accurate values of n and k without polishing (as compared to those obtained from a polished CdTe single-crystal surface). The CdCl treatment followed by thermal annealing is found to increase the surface roughness. Fig. 4 demonstrates the absorption coefficients (obtained from WSE measurements) of untreated ED, CSS, and PVD samples. The data showed that the optical absorption of the PVD CdTe film is the highest, followed by CSS film, with ED film being the least-absorbing film. The optical constants of the three types of CdTe films have shown a substantial improvement in the optical properties resulting from the CdCl treatment. Fig. 5 shows the optical parameters of three untreated CSS films deposited at different substrate temperatures. It is noteworthy that as-deposited films, which initially have better optical parameters n and k, have produced the most efficient (10%-12%) devices after the CdCl treatment. Devices made of films that demonstrated poor optical properties as-deposited have also shown lower conversion efficiencies after receiving the same $CdCl_2$ treatment. From PL and WSE, we concluded that the initial

defect states and optical parameters are crucial factors in determing final device parameters, despite the strong effects of the post-deposition $CdCl_2$ treatments on structural [6] and optical properties of the film.
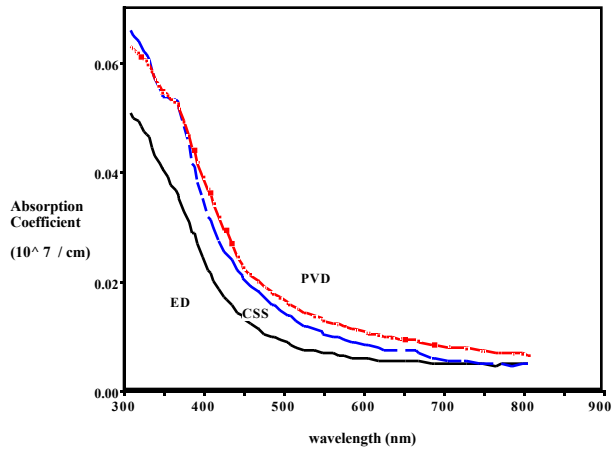

Fig. 4. Optical absorption coefficient of untreated PVD, CSS, and ED films
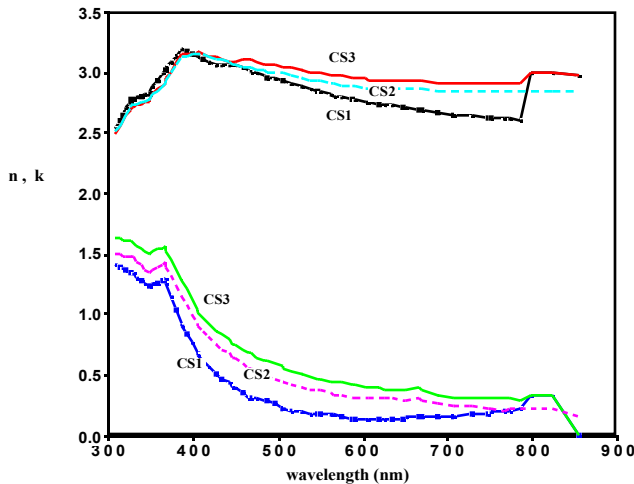

Fig. 5. n and k of CSS films deposited at different temperatures

Deep Levels in CdTe Devices

Devices fabricated from CdTe films without receiving the $CdCl_2$ treatment have shown at least one majority trap level. After receiving the $CdCl_2$ treatment, the deep trap level disappears and the device is dominated by a minority-carrier deep level. Fig. 6 demonstrates the DLTS spectra and Arrhenius plots of the minority-carrier level EDE and the majority-carrier trap EDH, detected in ED material that produced 8%-efficient device after exposing the film to CdCl vapor for 15 s and annealing it at 410°C for

45 min. The doping concentration in the ED devices varies between 4.1 x 10^{14} and 2.6 x 10^{15} cm^{-3}. The EDH trap (Ep= 0.38 eV $\pm$ 0.04) is attributed to the formation of Cd-vacancy (V_{cd}) related defects resulting from residual acceptor impurities in the solution (Ou, etal. [7]). The fact that the peak intensity decreases with the rate window confirms the nonuniform distribution of this defect level within the bandgap. The EDE level (En = 0.59 eV), on the other hand, is attributed to interface states in the depletion region. This conclusion is based on the fact that
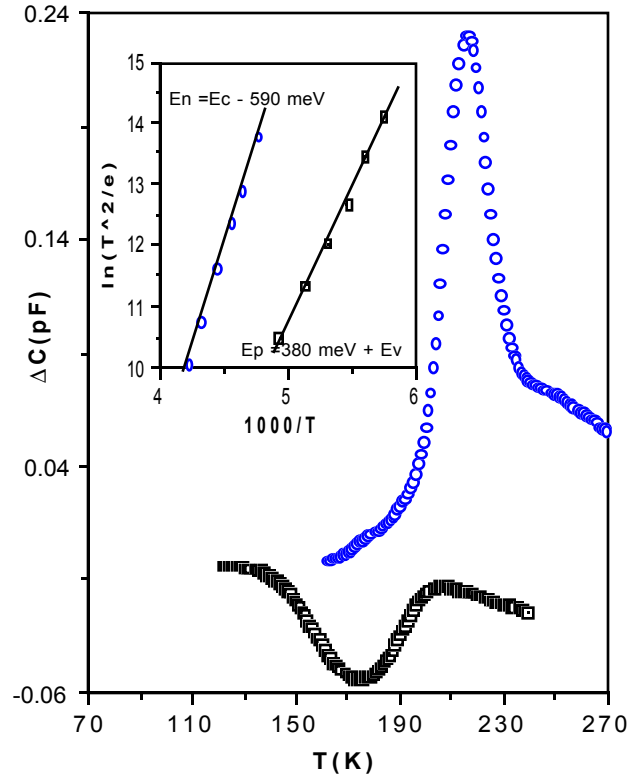

Fig. 6. DLTS signal and Arrhenius plots of the two deep levels EDE and EDH.

the DLTS peak intensity is reduced by increasing the reverse bias voltage. The CSS device of the same conversion efficiency as the ED device also showed one minority-carrier level CSE, with En = 0.42 eV. Two majority carriers have been also detected in the energy range 0.320-0.665 eV. The doping concentration of the various CSS devices used in these measurements varied between 5.5 x 10^{13} and 2.4 x 10^{15} cm^{-3}. Fig. 7 demonstrates plots of the open-circuit voltage V_{oc} and short-circuit current density J_{sc} versus the concentration of the trap CSE. It is clear that V_{oc} increases as the trap density decreases, which suggests a reduction in the recombination current. On the other hand, no direct correlation was observed between J_{sc} and the trap density. We observed an increase in the activation energy of deep levels in devices that have higher efficiencies; however, the density goes down appreciably. We also noted that samples deposited

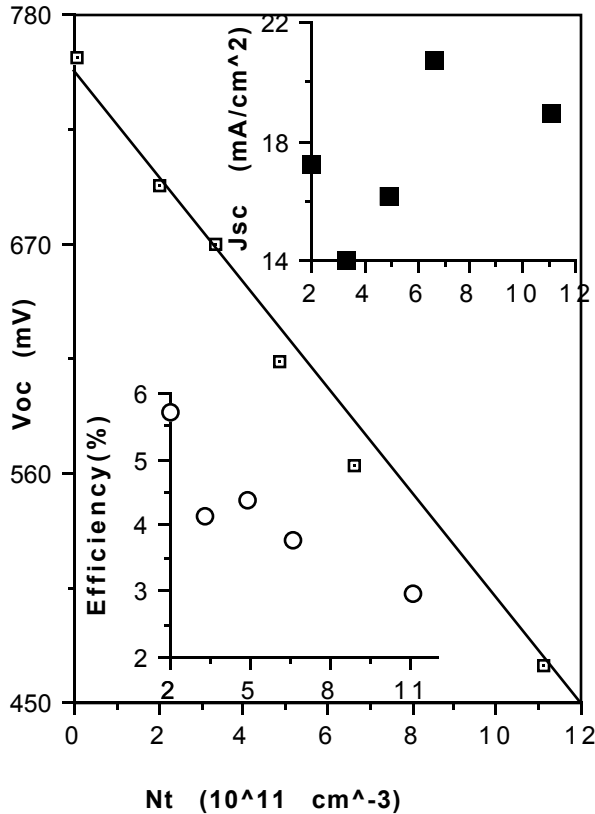at lower T_{sb} have much higher trap density unless they receive $CdCl_2$ treatment at higher temperature.

Fig. 7 Change in efficiency, V_{oc} , and J_{sc} with the density of deep levels.

CONCLUSIONS

PL measurements have shown that as-deposited CdTe films can be dominated by either D-VB or CB-A recombination, according to the degree of compensation of the as-deposited film (which can be controlled by the preparation method and conditions). Higher degrees of compensation are usually observed in CdTe films dominated by the D-VB recombination. After receiving the CdCl treatment, the degree of compensation is reduced dramatically. The most efficient devices are obtained from samples that are originally less compensated and dominated by the CB-A. This means that the improvement in the CdTe film properties induced by $CdCl_2$ treatment is limited by the original defects dominating the film. We also noted that the defect states dominating the surface of the CdTe film after receiving the CdCl treatment are different from those dominating the CdTe layer at the junction, where deeper states are more concentrated. It is apparent that the composition of this layer is different from the CdTe surface. The optical properties of CdTe films have shown a substantial improvement after receiving the $CdCl_2$ treatment, which is also limited by the properties of the original as-deposited film and changes with depth from the surface. DLTS measurements showed that each is characterized by at least one (sometimes two) minority-carrier interface states and one or two majority-carrier trap levels. The activation energies of all deep levels detected in all films were detected within the same energy range. Correlation between V_{oc} and the density of interface states was confirmed by DLTS measurements.

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