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Annealing Effect on the Photoluminescence of CdTe/CdSe Thin Film Photovoltaic Devices

The depth dependence of photoluminescence from as grown and CdCl₂ treated polycrystalline CdSe/CdTe solar cells has been compared using a bevel etch technique. It has been found that the three emission bands observed at 1.59eV, 1.55eV and 1.45eV all became more intense after the treatment, with the emission at 1.55eV near the CdSe/CdTe interface being the most affected.

Keywords: Thin films, CdTe solar cells, CdSe-based devices, photoluminescence

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1. Introduction

There is a great deal of interest in the production of a large area low cost thin film photovoltaic device with efficiency great enough to allow commercial development. One of the most promising contenders for this is the CdTe/CdSe material system. These layers can be grown by the low cost close space sublimation (CSS) technique, which produces polycrystalline structures. Theoretical calculations indicate this material system may have conversion efficiency greater than 29% [1-4].

Post growth treatment is known to affect the cell by increasing the grain size, converting the material from p-type to n-type [5], increasing the heterojunction uniformity [6] and changing the current transport mechanism from tunnelling to thermally activated [7]. As a result, the open-circuit voltage (V_{OC}), short circuit current density (J_{SC}) and fill-factor all increase for the cell while the series resistance (R_S) decreases.

Photoluminescence (PL) is a useful tool for the analysis of these samples since it is in principle capable of detecting energy levels resulting from the CdCl₂ treatment, the annealing, extended defects or out-diffusion from the substrate. Also, the relative intensity of PL lines can give an indication to the extent to which non-radiative recombination is important in a given sample. In this study the PL technique has been combined with bevel etching, which has enabled depth dependent information to be obtained from the CdTe layer.

2. Experimental Details

The two devices studied were made in the same run and consist of 6 μ m of polycrystalline CdTe on a thin (100nm) layer of CdSe, both layers being deposited by close space sublimation (CSS) onto ITO coated glass. Half of the sample was then coated with CdCl₂ and annealed in air for 30 minutes at 400°C. Bevel etching was achieved by slow immersion into a bromine, methanol and ethylene glycol etchant through a liquid methanol/etchant interface. The bevel etch gave a varying thickness of CdTe on the CdSe layer. The depth profile of the CdTe along the device was measured using an Alpha Step 200. The structures were placed in a closed cycle helium cryostat mounted on a translation stage and the PL measured at 10K.

3. Results and Discussion

Three luminescence bands were observed in both samples as shown in figure 1. The one at 1.59eV results from donor or acceptor bound excitons. The 1.55eV band has been variously ascribed to either oxygen O_{Te} acceptors [8] or cadmium vacancy V_{Cd} complex based acceptors [9] participating in a donor-acceptor pair (DAP) recombination. A further band at 1.45eV is characteristic of a further complex DAP emission often seen in CdTe. There were some important differences between the spectra of the two samples. The CdCl₂ treatment causes a general increase in luminescent intensity indicating either an increase in the concentration of the active centers or a decrease in the non-radiative

recombination sites. The latter is certainly important since the treatment is known to suppress recombination in the device and is associated with grain growth and a reduction in dislocation stacking fault density [10].

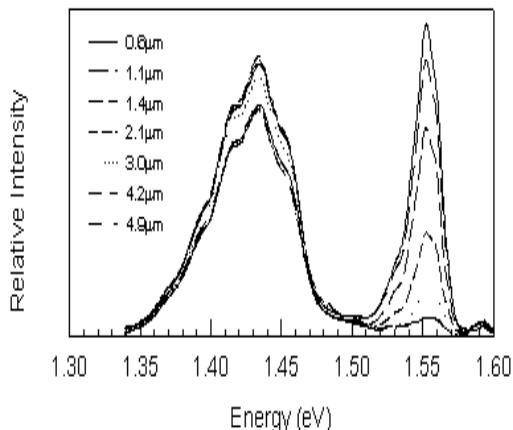


Fig. (1): PL spectra of CdCl₂ treated sample from the CdTe layer at different depths from the junction

Bevel etching has enabled the depth dependence of the luminescence to be investigated as shown in figures 2 and 3. For both the as grown and CdCl₂ treated samples the 1.44eV band is most intense in the bulk of the layer with the broad maximum being slightly nearer the interface for the CdCl₂ treated sample. The origin of the DAP luminescence is known to be complicated and possible assignments such as (V_{Cd}-Cl_{Te}) as the acceptor and Cl_T as the donor are speculative.

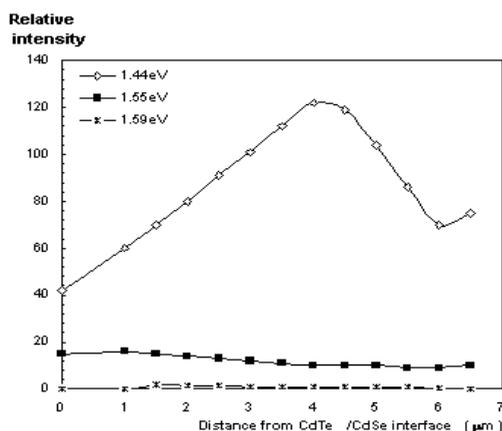


Fig. (2): Variation of emission intensities with the distance from CdTe/CdSe interface for as grown sample

We can only state that there is likely to be some variation in the concentration of active centers throughout the layers both before and after treatment. The excitonic luminescence is uniform in both samples. If the acceptor bound

excitonic luminescence is related to acceptors responsible for p-type conductivity at room temperature then it must be remarked that the surface application of CdCl₂ and air bake have been remarkably effective in producing homogenous doping in the polycrystalline material.

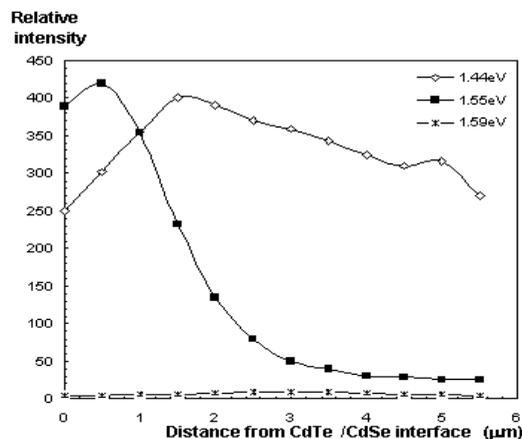


Fig. (3): Variation in emission intensities with the distance from CdTe/CdSe interface for CdCl₂ treated sample

The greatest variation in the spatial distribution of luminescence was seen for the 1.55eV peak which was changed by the CdCl₂ treatment from being weak and uniform in the as grown sample (figure 2) to being strong in the half of the film nearest the substrate (figure 3). Given the history of the sample the more likely of the two reported assignments in this case is V_{Cd} complexes rather than O_{Te}. This is further implicated by the supposition that if both added Cd and displaced Te are substitutional and Cl incorporates as Cl_{Te} then addition of each unit of CdCl₂ creates one cadmium vacancy in some form. However a contribution from the substrate possibly through Na, In, S or Sn out diffusion cannot be ruled out.

4. Conclusion

A PL/bevel etching technique has been shown to be valid for use in comparing the spatial distribution of luminescence throughout the thickness of the CdTe layer in these structures. The general enhancement of the luminescence by the treatment is thought to be associated with grain boundary passivation, which reduces competition with radiative routes. The large increase in the 1.55eV emission is interpreted as resulting from an increase in DAP emission involving V_{Cd} sites present forming complexes with Cl atoms on adjacent Te sites. Considering the large increase in the intensity of this emission, it would seem that it is important in the understanding of the increase in device efficiency.

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