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RECrysTALLIZATION OF CdTe UNDER CONDITIONS OF HIGH TEMPERATURE AND PRESSURE

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1. Introduction

The low efficiency and reliability of polycrystalline thin film CdTe solar cells are mainly caused by imperfections in the structure of absorber layer. Large amounts of generated carriers are absorbed by defects like grain boundaries, dislocations, impurities and inclusions of residual phases as oxides and elemental tellurium [1]. To improve the quality of such cells, various chemical and physical treatment methods have been developed. The tradition in the sintering of II –VI type crystalline films is to use a liquid phase [2] (usually chlorides like CdCl₂ for Cd compounds) for acceleration of mass transfer at low temperatures, around 400°C. Heating of the heterostructure of CdTe/CdS at 400°C for 30 min in air in the presence of CdCl₂ increases the grain size of a CdTe film from 0.05 to 0.5 µm, and the end product (solar cell) efficiency from 3 to 12.4% [3].

Figure 1. Hot-pressed (200 MPa) bromide sodalite structure obtained via solid phase recrystallization; a - 950°C (0.6 Tₛ), b - 1150°C (0.75 Tₛ), c - 1250°C (0.8 Tₛ) [4].

The high temperature (near to the melting point) solid phase recrystallization (SPRC) of optoelectronic thin films has not previously been studied (Figure 1). The disadvantage of liquide-phase sintering is the formation of undesirable residuals like oxychloride of cadmium in the grain boundaries of

the recrystallized film [1]. In the case of the deformation aided SPRC process, crystal grains of the matter are exchanged with the crystals, which are more perfect (without defects), have the same phase and a lower total energy. An increase in crystal size of 10-100 times can be achieved [4]. The present study is devoted to obtaining dense polycrystalline CdTe films with large (> 5 μm) grains with a honeycomb-like structure, which is recrystallized under the SPRC crystal-growth conditions (Figure 1b). There is a considerable previous experience in the preparation of CdTe crystals and films. CdTe is the optimal material for solar cell applications, since the theoretical limit of a CdTe based solar cell efficiency is 40.7% [5], whereas only 16.5% has been achieved; CdTe is a simple chemical compound (the unknown phases will not form during high temperature treatment). This means that the results are more easily interpretable. In comparison with other solar cell materials, CdTe is relatively cheap and is stable over long-time use.

2. Materials and methods

![Figure 2. Schematic illustration of the hot-pressing experimental device.](image)

Our experiment was carried out with high purity CdTe powder and 100 μm thick Mo plates. The CdTe powder was mechanically refined and compressed into thin (50 μm) tablet form. Figure 2 shows a schematic illustration of the hot-pressing experimental device built up from a VUB-5 high vacuum system. Temperature was generated by a resistance-heating plate and measured from both sides of the sample with Pt-Pt(Rh) thermocouples. A temperature of 800°C was applied (bottom side) and 400°C was measured from the top side of the sample (the melting temperature of CdTe is 1050°C). A mechanical pressure of 5 N/cm² and a heating time 1 hour were used. Figure 2 shows the possibility
for using a spring instead of the weights. This allows adjustment of the load pressure on a large scale, but is not used in the current experiment.

The structures of the CdTe films were examined using a Jeol JSM-840A scanning electron microscope. The chemical composition and possible phase changes in the CdTe films were evaluated by a point EDS analysis method, using a Link Analytical AN10000 analyser. Electrical resistivity and I-V characteristics of the Mo/CdTe interface were measured with a Keithley 2400 SourceMeter. Indium dot contacts \(1\text{mm}^2\) area were applied to the CdTe surface.

3. Results and Discussion

As shown in Figure 2, the CdTe sample is situated in a high temperature gradient, which is caused by heat conduction from the hot plate through the Mo plates and CdTe tablet into the bulk, which has high radiation losses from its surface. By use of a temperature gradient in CdTe film preparation, two critical problems in high temperature treatment has been resolved: 1. the recrystallized film is joined to the surface of the upper low-temperature (400 °C) Mo disk, which reduces the problem of adhesion between the film and substrate; 2. the temperature gradient enables use of traditional and cheap substrate materials like Mo or ITO coated glass in high temperature processing. Figure 3 shows the results obtained from the hot-pressing SPRC treatment of a CdTe film. The shortcomings of this experiment were inhomogeneities in the particle size of the

![Figure 3](image-url)
initial CdTe powder (Figure 3a) and variations in thicknesses over the compressed tablet, but also to too low a mechanical pressure. As the result, areas with different recrystallization structures appeared in the film (areas 1 and 2 in Figure 3b, which correspond to Figures 3c and d respectively).

Freely (without pressure) grown grains had sizes up to 30 μm (Figure 3c), but this process is not verifiable over large areas. Structures obtained under hot-pressing conditions had grain sizes of 1-5 μm (Figure 3d). Due to the low mechanical pressure and imperfections in the initial material, the obtained structure was porous, and the recrystallized grains were defective. It is characteristic for all areas of the tablet that CdTe crystals and compressed regions are firmly joined (stuck) to the upper low-temperature Mo plate. This results from the high temperature gradient across the sample. Linear ohmic contacts were seen on the Mo/CdTe back contact interface for the hot-pressed regions of CdTe specimens. The resistivities of the layers varied between $10^6$ and $10^7$ Ohm-cm. Freely grown regions had symmetrical nonlinearities of their I-V curves, indicating the porous polycrystalline character of the material.

It should be noted that this was a first step in this kind of CdTe film processing, and more accurate powder compacting could be achieved at higher mechanical pressures, for a finer and more homogeneous particle size in the initial powder.

4. Conclusions

The method of high temperature gradient in CdTe film preparation enabled us to join the recrystallized film to the upper low-temperature (400°C) surface of a Mo disk, and to achieve an ohmic linear contact between the Mo and CdTe, enabling one to use cheap substrates of Mo- or ITO-glass in high temperature vacuum hot-pressing.

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