

Heavily doped CdTe films grown by close-spaced vapor transport technique combined with free evaporation

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Very heavily doped *n*-type polycrystalline CdTe films doped with metallic cadmium were prepared by using close-spaced vapor transport technique combined with free evaporation and the electrical, structural, and morphological properties were investigated. Cadmium was introduced as a dopant by evaporation during films preparation. The highest dark conductivity at room temperature of the films obtained was $1.18 \times 10^4 \text{ S cm}^{-1}$. The dark conductivity decreased with the increase of the ambient temperature. The highest dark electron concentration obtained was $1.59 \times 10^{22} \text{ cm}^{-3}$ and increased with the temperature. The mobility decreased with the temperature. The film was a polycrystalline cubic phase. We show the surface topography of the film using scanning electron microscope and scanning tunneling microscopy techniques, in order to see the growth patterns. The crystallite size was very uniform of a few μm , and the growth patterns on the grain surface were in form of terraces. © 1996 American Institute of Physics. [S0021-8979(95)04324-9]

I. INTRODUCTION

Reproducible and well-controlled doping is one of the major requirements for semiconductor material applications. In particular, most electronic devices require preparation of very heavily doped. It had been recognized since the early stage of semiconductor research that, unlike elemental semiconductors which can be doped to very high levels, compound semiconductors in general exhibit lower dopant activation efficiency at least for one dopant type (*n* or *p* type).¹ Understanding of the basic mechanisms leading to the saturation of free-carrier concentration in compound semiconductors is an issue of great fundamental and practical importance. The II–VI compounds are materials which exhibit many interesting solid-state phenomena of considerable practical importance.² The compound CdTe can be considered as quite representative of this group. CdTe has a direct band gap of 1.5 eV at room temperature³ and is a suitable material for application to solar cells and photovoltaic cells.⁴ To be economical, a cell should be prepared in the form of a thin film. Thin-film structure is proper for electronic applications, but high film conductivity is necessary for thin-film device application. The doping of CdTe films is a continuing problem, in which research groups such as Fortmann, Fahrenbruch, and Bube⁵ and Anthony *et al.*⁶ reported dopant incorporation in CdTe using hot-wall vacuum evaporation (HWVE) and close-spaced vapor transport (CSV T). Also, Suzuki, Ema, and Hayashi⁷ have reported cadmium incorporation in CdTe films by coevaporation of CdTe and metallic cadmium. Afterward, using CSV T technique combined with free evaporation (CSV T FE) and raising the substrate temperature to 130 °C, we succeeded in preparing a heavily doped (with a very high conductivity) film with a crystallite size of a few μm . This film showed interesting electrical characteristics. In this article the preparation method and the interesting properties found in the films are described.

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II. SAMPLE PREPARATION

All films were prepared in a conventional vacuum evaporation system evacuated by an oil-diffusion pump with a liquid-nitrogen trap, capable of obtaining a background pressure of 10^{-6} Torr. The pressure during evaporation was below 10^{-5} Torr. To obtain Cd-doped films we used a novel deposition technique previously reported by two of the authors⁸ consisting of CSV T combined with free evaporation. Figure 1 shows a schematic view of the system. In our experiments we used high-purity Balzers metallic cadmium (99.999 at.% pure). The CdTe (99.999 at.% pure Balzers) sublimates at a temperature (T_2) of 600 °C and is deposited on substrates of 7059 Corning glass, at a temperature (T_1) of 130 °C. The control gas used during the film growth was Matheson argon 99.999 at.% pure. Chromel–Alumel thermocouples were used to monitor the temperature. The time of the films growth was 10 min. The graphite wall used as container (5 mm high) and the two blocks were made from a high-density graphite. A ceramic ring 6 mm in diameter was introduced into the graphite block of the CdTe source. The function of the ceramic ring was to guide the atoms of the evaporated Cd and to introduce them into the container. The distance between the Cd source to the substrate was 8 mm. The temperature of the Cd source (T_3) was set to 230 °C (sample M1) and 250 °C (sample M2). The evaporation rate of CdTe must be low to prevent generation of native acceptors.⁹ In this study, the rate was 85 \AA s^{-1} . About five samples identical to M1 and M2 were fabricated with similar characteristics that are discussed now.

III. MEASUREMENT EQUIPMENT

The Van der Pauw–Hall technique was used to study the dark conductivity, dark carrier density, and the mobility of the sample. The x-ray-diffraction equipment used was a SIEMENS D-5000. The scanning electron microscopy (SEM) and scanning tunneling microscopy (STM) techniques were used for determining the surface morphology of

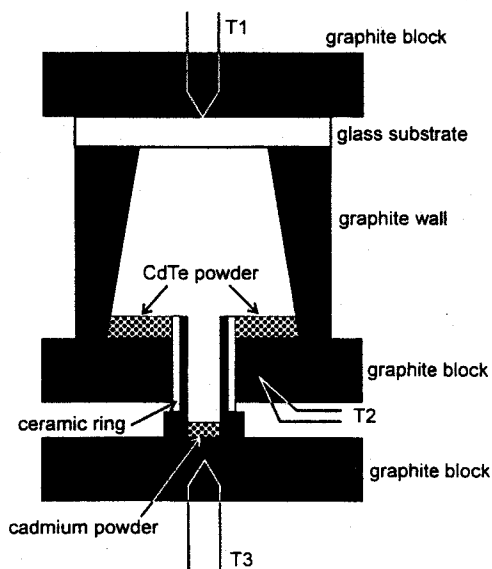


FIG. 1. Schematic of the chamber used for CSVT technique combined with free evaporation.

the films. The SEM equipment used in this work is a JEOL JSM-35C and the STM measurements were performed using a homemade equipment. The electrical contacts were made with metallic indium previously evaporated on the film, and by heating 50 °C over the melting point of indium for 5 min under inert atmosphere.

IV. RESULTS AND DISCUSSION

Figure 2 shows dark conductivity versus reciprocal temperature characteristic of samples M1 and M2. The dark conductivity of sample M2 at room temperature is higher, $1.18 \times 10^4 \text{ S cm}^{-1}$, than that the sample M1. It should be noted from Fig. 2 that the dark conductivity in all samples decreased with the increase of the temperature. Slow dark conductivity of sample M1 was due to the low temperature used for Cd evaporation. To investigate the transport mechanism of sample M2, the temperature characteristic of the

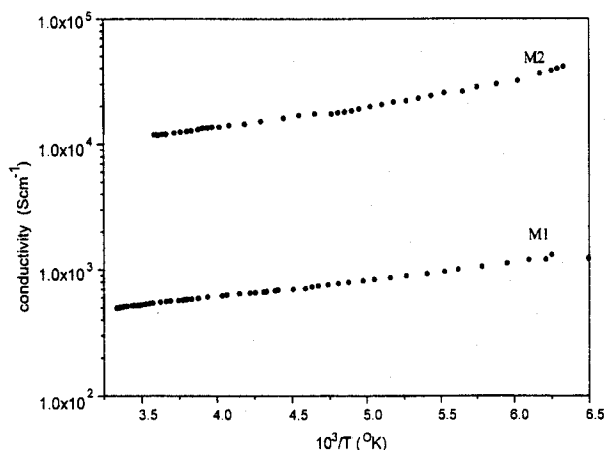


FIG. 2. Dark conductivity of film vs reciprocal temperature characteristic of samples M1 and M2.

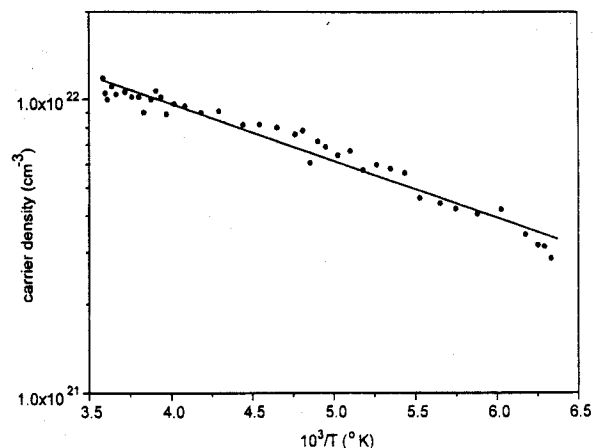


FIG. 3. Electron concentration vs reciprocal temperature characteristic of sample M2.

electron concentration and Hall mobility were measured. Figure 3 shows the electron concentration versus the reciprocal temperature characteristic of sample M2. The electronic concentration increases with temperature. This shows that sample M2 has a semiconductor characteristic. The electron concentration of sample M2 at room temperature is very high, $1.59 \times 10^{22} \text{ cm}^{-3}$. A Hall mobility versus the reciprocal temperature characteristic of sample M2 is shown in Fig. 4. The mobility decreases with temperature. This shows the lattice scattering characteristic. This interesting characteristic is discussed later.

All surfaces of the films were smooth, and adhered firmly to the substrate. The color of the film surface of the samples was rough and gray. The structures were analyzed by x-ray diffraction ($\text{Cu K}\alpha$). Figure 5 show the x-ray-diffraction patterns of sample M2. The experimental x-ray-diffraction pattern of the samples M2 are similar to the x-ray patterns of CdTe powder with cubic structure. The peak positions show a markedly preferential growth of film crystallites toward the (111) plane parallel to the substrate. The crystallinity size of sample M2 was between 3 and 6 m. This was estimated by a SEM image of the film surface shown in

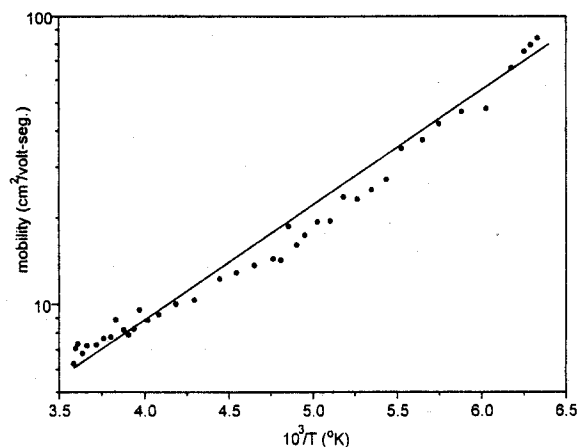


FIG. 4. Electron mobility vs reciprocal temperature characteristic of sample M2.

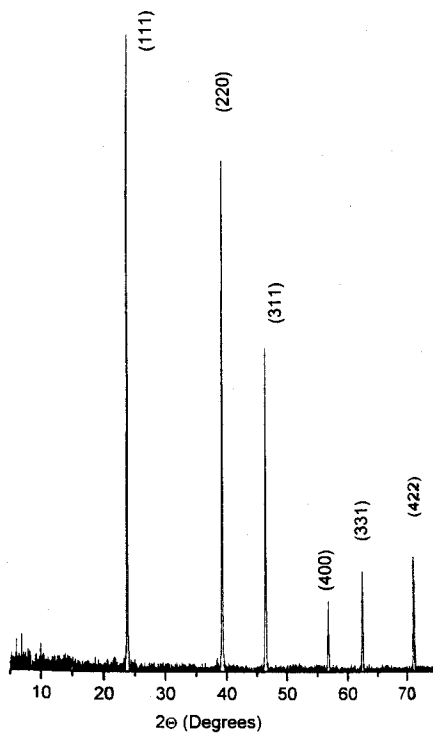


FIG. 5. X-ray-diffraction patterns characteristic of sample M2.

Fig. 6, and as can be seen the grain sizes are very uniform. A closer view was detected by using STM; this was possible because the films are heavily doped ($>10^{19}$ carrier density/cm³), sufficiently to obtain tunnel current and good stability function. An image of $85 \times 85 \text{ nm}^2$ is presented in Fig. 7. The image is formed by 200×200 pixels and is presented in solid graphic. Tunnel current was 1 nA and V_{bias} is +30 mV. We suppose that the STM image corresponds to a grain surface. The STM image was taken near the film edge and some terraces on the grain surface can be observed. A STM image with high magnification can be seen in Fig. 8 when these terraces are clearly seen. These terraces are formed during the film growth. Initial study of the growth conditions showed different growth patterns on the film center than in the film edge. Terraces were measured given 10 \AA

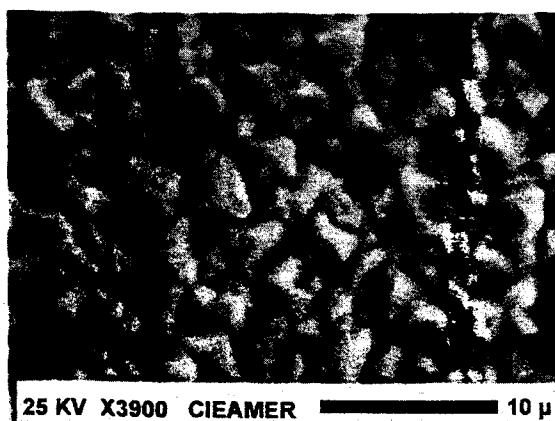


FIG. 6. Scanning electron microscope micrograph of the surface of sample M2. Image size: $22 \times 30 \text{ μm}^2$. Image was obtained with 25 kV, $3600 \times$.

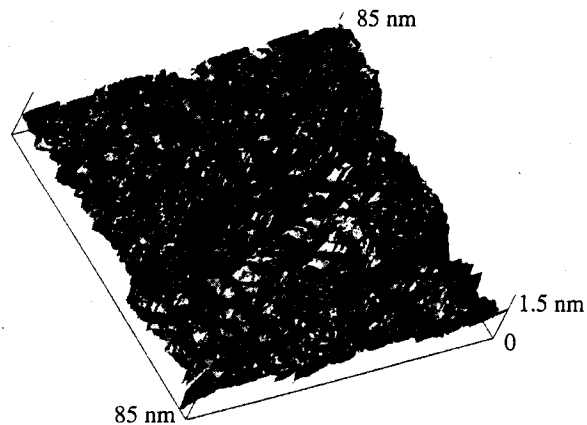
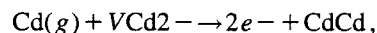


FIG. 7. Scanning tunneling microscopy image made on a grain surface, acquired at a bias voltage of +30 mV. The image extends laterally over an area of $85 \times 85 \text{ nm}^2$.

approximately. As we know, this are the first images obtained with a STM from these heavily doped CdTe films.

On the other hand, using a similar argument made previously by Suzuki and co-workers⁷ to explain the formation of very high-conductivity CdTe film, we considered the above results using the following next tentative model. The Cd overpressure effect during the formation of the CdTe films works by preventing vacancy formation. Formally, this is represented by



which shows clearly that the electron concentration increases and the vacancy concentration decreases when the cadmium pressure increasing. This can be explained as follows: First the Cd atoms fill Cd vacancies of CdTe crystallites substitutionally. After the Cd vacancies in CdTe evaporated films are completely compensated by Cd atoms, any additional Cd atoms then can be doped interstitially into the films. In our film, Cd atoms are present at almost all interstitially sites of the CdTe crystal. The interstitial Cd atoms may be considered to act as a donor. Therefore, the interstitial Cd atoms do not disturb the crystal periodicity. As a result, the electron

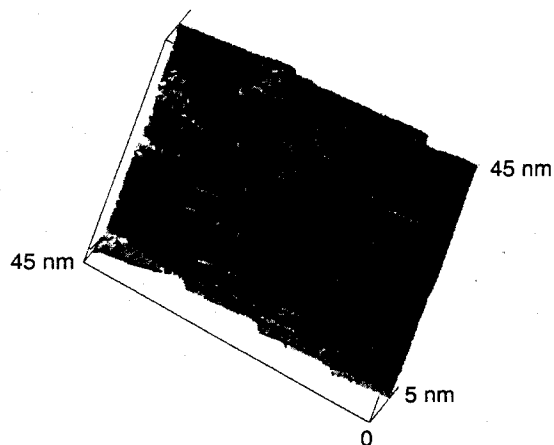


FIG. 8. Scanning tunneling microscopy image with higher magnification. The image extends laterally over an area of $45 \times 45 \text{ nm}^2$, with a vertical height of 5 nm.

transport is not limited by the impurity scattering but the lattice scattering. It should be noted here that the fabrication reproducibility of samples M1 and M2 was very high.

The carrier density as a function of the temperature for the sample M2 showed in Fig. 3 produces a linear relationship in an Arrhenius type plot showing a single well-defined activation energy E_a ; this is evidence of a thermally activation process for the electrical conduction in the polycrystalline sample. The activation energy value for CdTe film grown without Cd overpressure ($E_a=0.67$ eV)³ is an indication of an intrinsic conduction process. The activation energy 0.0342 eV obtained from sample M2 is very similar to the activation energy of the interstitial Cd atom in CdTe crystal.³ This shows that Cd is doped interstitially into the CdTe grain. The radius of Cd²⁺ is 0.97 Å. Therefore, the Cd ion may be doped interstitially into the CdTe crystal without any change of the lattice constant.

In addition to the above model, another model may be considered. That is, many Cd atoms may deposit at grain boundaries or upon the surface of the film after the growth; however, if this is true, the larger peaks corresponding to Cd should appear in the x-ray-diffraction pattern shown in Fig. 5, and these peaks were not detected in our films as can be seen in Fig. 5.

V. CONCLUSIONS

Very high conductivity of heavily doped *n*-type polycrystalline CdTe films doped with metallic cadmium, using CSVF FE, were prepared. Cd was introduced as doping by evaporation during the film preparation. The highest dark

conductivity at room temperature of the film obtained was 1.18×10^4 S cm⁻¹. The dark conductivity decreased with the increase of the ambient temperature. The highest dark electron concentration was 1.59×10^{22} cm⁻³ and increased with the temperature. The mobility decreased with the temperature. This interesting characteristic was explained by the lattice-scattering transport using a tentative CdTe crystalline model. The films were polycrystalline cubic phase with grain size between 3 and 6 Å. The surface topography made on a grain showed forms of terraces with sizes of 10 Å approximately. Topography by SEM and STM was obtained on a grain showing some terraces formed during evaporation.

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¹W. Walukiewics, *J. Vac. Sci. Technol. B* **6**, 1357 (1988).

²*Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1976).

³D. de Nobel, *Philips Res. Rep.* **14**, 361 (1959).

⁴J. J. Lofersky, *J. Appl. Phys.* **27**, 777 (1956).

⁵C. M. Fortmann, A. L. Fahrenbruch, and R. H. Bube, *J. Appl. Phys.* **61**, 2038 (1987).

⁶T. C. Anthony, A. L. Fahrenbruch, M. G. Peters, and R. H. Bube, *J. Appl. Phys.* **57**, 400 (1985).

⁷K. Suzuki, Y. Ema, and T. Hayashi, *J. Appl. Phys.* **60**, 4215 (1986).

⁸R. Castro-Rodriguez and J. L. Peña, *J. Vac. Sci. Technol. A* **11**, 3 (1993).

⁹Y. Kawai, Y. Ema, and T. Hayashi, *Jpn. J. Appl. Phys.* **22**, 803 (1983).