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In-doped CdTe films by CSVT combined with free evaporation: morphological, stoichiometric and electrical studies

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ABSTRACT. We report the morphological, stoichiometric and electrical properties of polycrystalline films of CdTe doped with metallic indium, using a new fabrication process of close-spaced vapor transport (CSVT) combined with free evaporation (CSVT-FE). All the samples were prepared using 500 °C and 600 °C as substrate temperature and CdTe source temperature, respectively. Indium (In) was introduced as doping by evaporation during films preparation. In order to obtain different concentrations the In source temperature ranged from 500 °C to 800 °C. The films were studied by scanning electron microscopy (SEM), Auger electron spectroscopy (AES), conductivity and Hall effect measurements. The mean grain size, the stoichiometry and the dark conductivity were found to depend on the In source temperature and its relation is discussed using two models: self-compensation due to the formation of compensating complexes and charge trapping in grain boundaries.

RESUMEN. Reportamos las propiedades morfológicas, estequiométricas y eléctricas de películas policristalinas de CdTe dopadas con indio, usando un nuevo proceso de fabricación: transporte de vapor en espacio reducido combinado con evaporación libre (CSVT-FE). Todas las muestras fueron preparadas usando 500 °C y 600 °C como temperaturas de substrato y fuente de evaporación de CdTe respectivamente. El indio fué introducido como dopante por evaporación durante la prepación de las películas. La temperatura de la fuente del indio fue variada desde 500 °C a 800 °C con el propósito de obtener diferentes concentraciones de indio en las películas. Las películas fueron estudiadas por microscopía electrónica de barrido (SEM), espectroscopía de electrones Auger (AES), mediciones de conductividad y efecto Hall. El tamaño de los granos, la estequiometría y la conductividad dependen de la temperatura de la fuente de indio y sus relaciones son discutidas usando dos modelos: autocompensación debido a la formación de complejos compensatorios y atrapamiento de carga en fronteras de grano.

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1. INTRODUCTION

The II–VI compounds are materials which exhibit many interesting solid state phenomena of considerable practical importance [1]. The compound CdTe can be considered as quite

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representative of this group. CdTe has a direct band gap of 1.5 eV at room temperature [2] and is a suitable material for application to solar cells and photovoltaic cells [3]. 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. In order to improve their electrical properties, the film needs to be doped with some material to have n-type or p-type semiconductors. The doping of CdTe films is a continuing problem, in which research groups such as Fortmann *et al.* [4] and Anthony *et al.* [5] reported dopant incorporation in CdTe using Hot-Wall Vacuum Evaporation (HWVE) and CSVT. Also, Suzuki *et al.* [6] has reported indium incorporation in CdTe films by coevaporation of CdTe and metallic indium. Reproducible control of the doping and high conductivity are urgently needed for thin film device applications.

A general problem for II–VI compounds is that intentional doping leads to the formation of compensating complexes. Due to this self-compensation, either p- or n-type doping of a given II–VI semiconductor is hard to achieve. Progress in this direction has recently been achieved by means of the photoassisted molecular beam (PAMBE) technique which enhances the substitutional incorporation of the dopants and the structural perfection of the CdTe epilayers. For n-type doping, indium is commonly used, which gives high doping free-carrier concentration at room temperature of $(2\text{–}6) \times 10^{17}$ cm^{-3} [7]. However, using CSVT-FE technique we have obtained free-carrier concentration approaching values obtained with the PAMBE technique.

Nevertheless, the tendency for In-doped films towards self-compensation is rather strong. This effect can interfere with the desired result of obtaining high densities of indium donor, and can produce chemical reactions of indium with tellurium, decreasing the fraction of indium which can form neutral donors ($\text{In}^{\circ}_{\text{Cd}}$).

The role of grain size on electrical properties has been studied by several authors in II–VI compounds as well as in other semiconductor thin films [5,8,9]. It is clear that a morphological study of thin films is necessary to try to improve their quality for technological applications. Since a study of the effect of doping on the grain size of CdTe films is lacking (in particular of indium doping) then, the aim of this paper is to present a study on the morphological, stoichiometric and electrical properties of indium doping in CdTe films by a novel deposition technique involving the combined use of free evaporation and CSVT. The main goal for our study was to use the indium source temperature as a pertinent growth parameter for growing quality In-doped CdTe films.

2. EXPERIMENTAL DETAILS

2.1. 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 In-doped films we used a novel deposition technique previously reported by Castro *et al.* [10] consisting of CSVT combined with free evaporation. Figure 1.a shows a schematic view of the system. In our experiments we used high purity Balzers metallic indium (99.999% at.

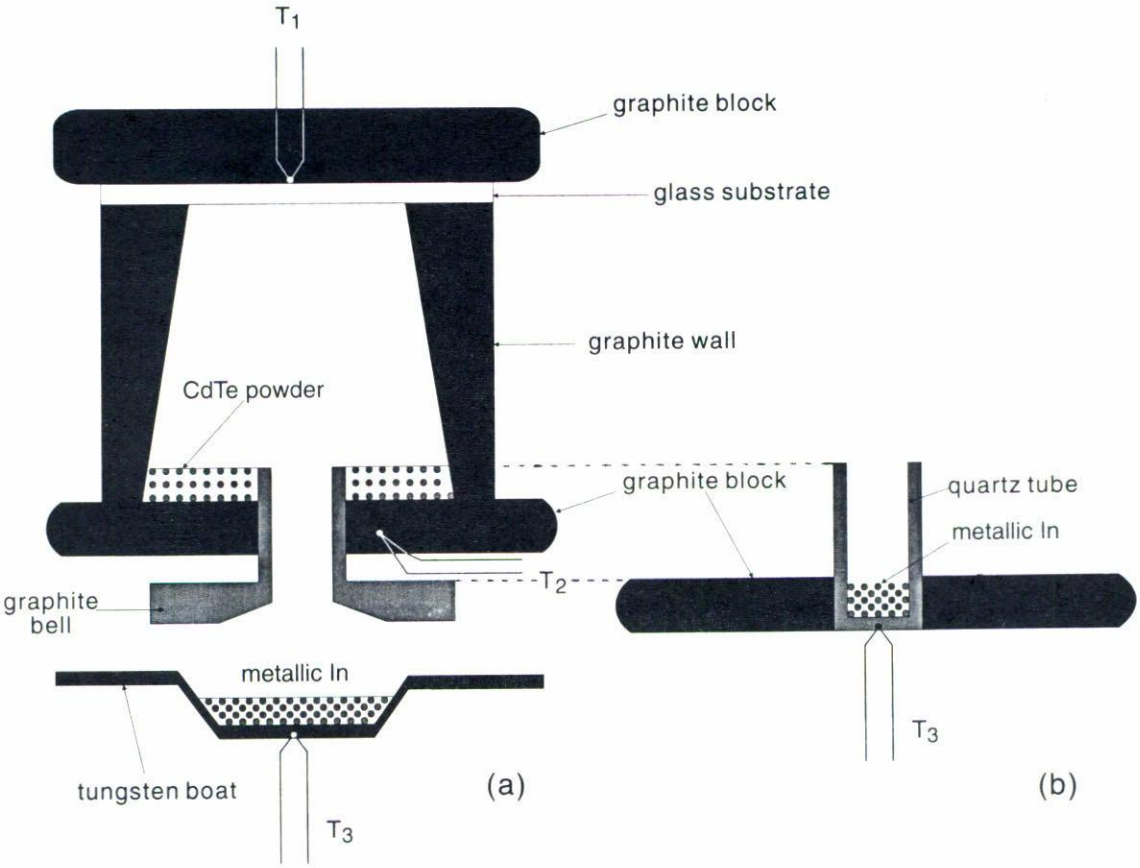

FIGURE 1. Artist's rendition of the chamber used for CSVT combined with free evaporation: a) CSVT-FE with external indium source, b) CSVT-FE with internal indium source.

pure). The CdTe (99.999% at. pure Balzers) sublimes at a temperature (T_2) of 600 °C, and is deposited on substrates of 7059 Corning glass, at a temperature (T_1) of 500 °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 film growth was 5 minutes. The graphite wall used as container (8 mm high) and the two blocks were made from a high-density graphite. A graphite bell 3 mm in diameter was screwed into the graphite block of the CdTe source. The function of the graphite bell is to guide the atoms of the evaporated indium and to introduce these atoms into the container. The distance between the metallic indium source to the substrate was 21 mm. This system is called "CSVT-FE with external indium source". The thickness of the films ranged from 10 to 60 μm. The temperature of the In source (T_3) was selected to have a value between 500 °C and 800 °C. The indium pieces were chipped off of a larger piece and etched in dilute HNO_3 immediately before experiment.

In a second experiment we changed the graphite bell by a quartz tube with 10 mm inner diameter which was introduced into the graphite block of the CdTe source as show in Fig. 1.b, this other system is called "CSVT-FE with internal indium source".

Three serials of films, RC1, RC2 and RC3 were prepared. The serial RC1 and RC2 were prepared using the "CSVT-FE with external indium source", the difference between serial RC1 and RC2 was that all the films of serial RC2 were heat-treated at 200 °C for at least 2 hr under inert atmosphere before application of the electrical contacts. The serial RC3 were prepared using the "CSVT-FE with internal indium source".

2.2. Measurement equipment

The SEM equipment used in this work is a HITACHI S-2700 with a fourquadrant solid state BSE detector installed. This equipment has a system for SEM control, scanning and data acquisition based on an IBM PS/2 system. The SEM images were obtained using energy at 20 kV.

The stoichiometry of the films was analyzed by AES using a Perkin-Elmer PHI-560, an ESCA-SAM system. Before analysis, samples were cleaned by immersion for 30 sec. in a methanol–3% bromine solution. The X-ray anode used was magnesium. Auger measurements of elemental composition were obtained for several points on the film after 20 minutes of argon ion sputtering. For this work we used a 3 keV electron beam, and the detection of Auger electrons was carried out with a double pass cylindrical mirror analyzer. The SEM and AES measurements were made before putting on the electric contacts.

The contacts were made with metallic indium previously evaporated on the film, and by heating 50 °C over the melting point of indium for 10 min under inert atmosphere. The Van der Pauw-Hall technique was used to study the dark conductivity and the dark carrier density at room temperature.

3. SEM MEASUREMENTS

Every one of the serial RC1 was observed by SEM. Images were obtained in different scales in order to measure the grain size and other morphological parameters. We tried to find out a relationship between the indium concentration —as measured by electrical conductivity— and the grain size. Figure 2 shows a group of 6 SEM images obtained from the center of the films. All images have 24 μm × 24 μm size for easy comparison. By measuring grain size on these images we obtained the mean grain size for each case. Figure 3 shows the mean grain size obtained as a function of the indium source temperature. The error bar for each point in the figure means the range of grain sizes observed around the center.

4. AES MEASUREMENTS

The Auger analysis corresponding to the films of the serial RC1 showed a maximum indium concentration of 7.5 % at., and near stoichiometric concentration between Cd and Te. Figure 4 shows these concentrations as a function of the indium source temperature. The Auger analysis corresponding to the serial RC3 is shown in Fig. 5. It can be observed

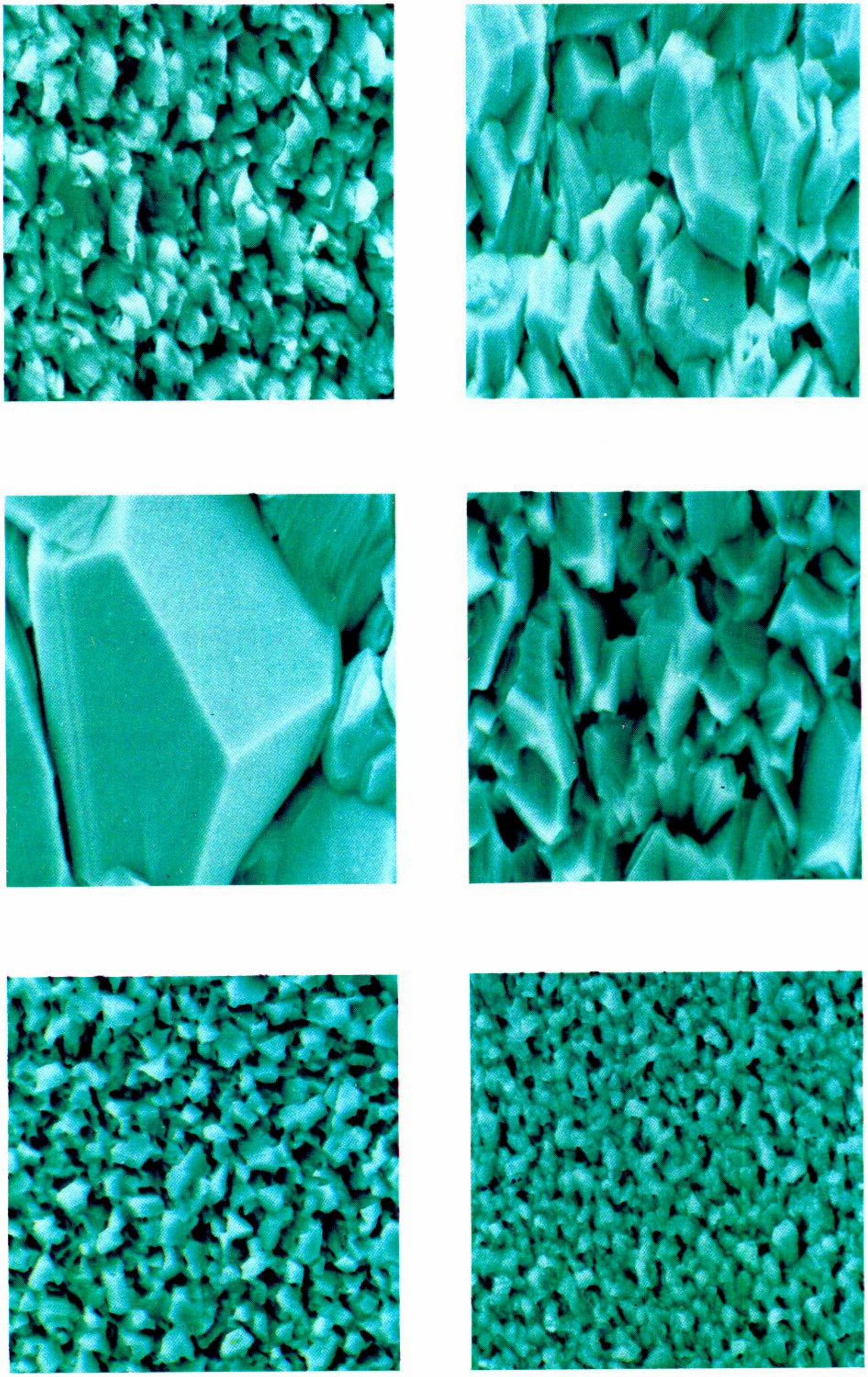

FIGURE 2. 24 μm × 24 μm SEM images of In-doped CdTe films at different temperature. CdTe source and substrata temperature used for all samples are 600 °C and 500 °C respectively. Indium source temperature in images are: a) 560 °C, b) 600 °C, c) 640 °C, d) 650 °C, e) 670 °C and f) 720 °C. Serial RC1.

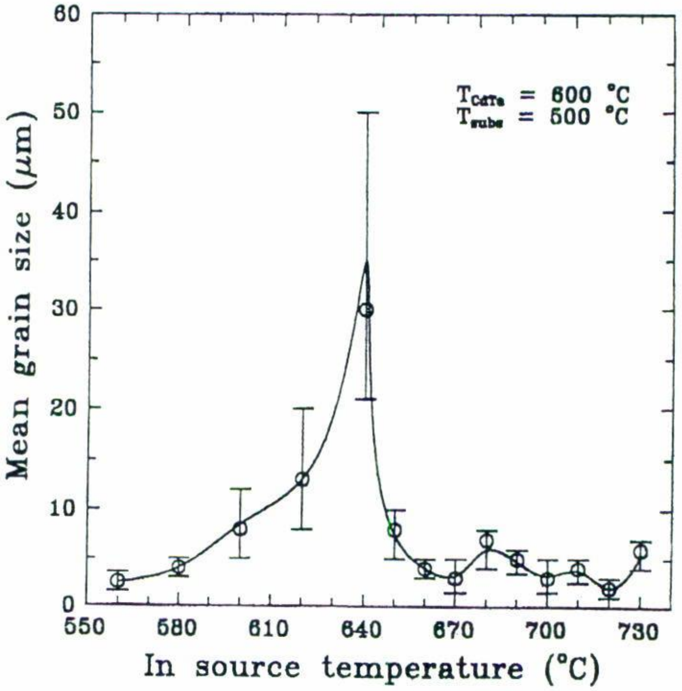

FIGURE 3. Mean grain size versus indium source temperature measured from In-doped CdTe films. The error bars shown the range of grain sizes found on films. Serial RC1.

that the indium concentration increased monotonically with the indium source temperature from 6.5% at. to 54% at., while the concentration of Cd decreased from 44.3% at. to 6.7% at., the concentration of Te is almost constant in all the range of indium source temperature studied.

5. FILM DARK CONDUCTIVITY AND CARRIER DENSITY AT ROOM TEMPERATURE VERSUS INDIUM SOURCE TEMPERATURE

Figure 6 shows the relation between dark conductivity vs indium source temperature of the films for the serials RC1, RC2 and RC3 at room temperature. The conductivity of the serial RC1 increased with the indium source temperature and reached 10^{-5} Scm^{-1}, serial RC2 reached 8×10^{-5} Scm^{-1}, while the serial RC3 increased monotonically and reached 4.5×10^{-2} Scm^{-1}.

In order to evaluate the carrier density of the samples, van der Pauw-Hall effect was used. Figure 7 shows the carrier density vs indium source temperature at room temperature. Similar to the conductivity vs the indium source temperature characteristic, the carrier density of the serial RC1 increased and reached 6×10^{12} cm^{-3}, the serial RC2 reached 10^{13} cm^{-3}, while the serial RC3 increased monotonically and reached 6.8×10^{17} cm^{-3}.

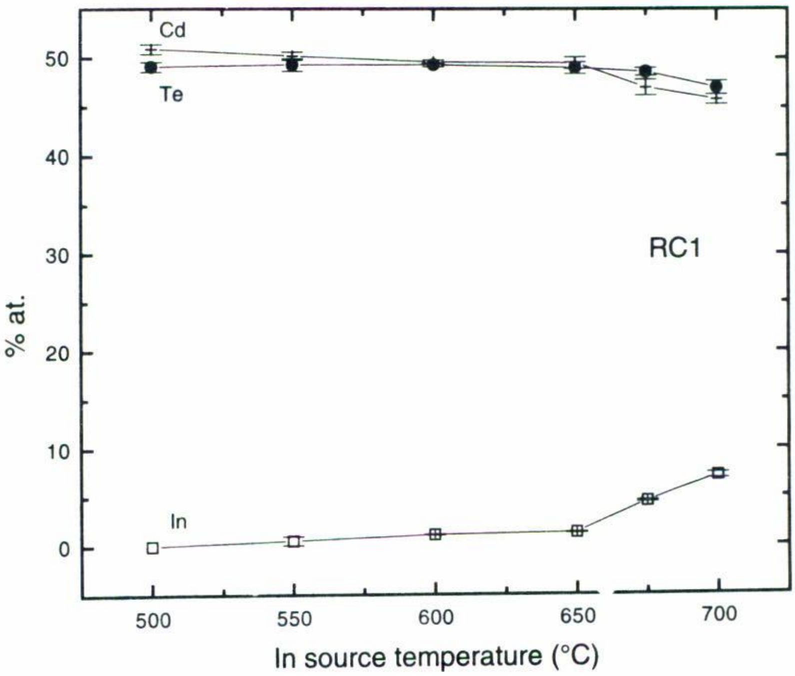

FIGURE 4. Atomic concentration in the In-doped CdTe films by AES, versus indium source temperature. Serial RC1.

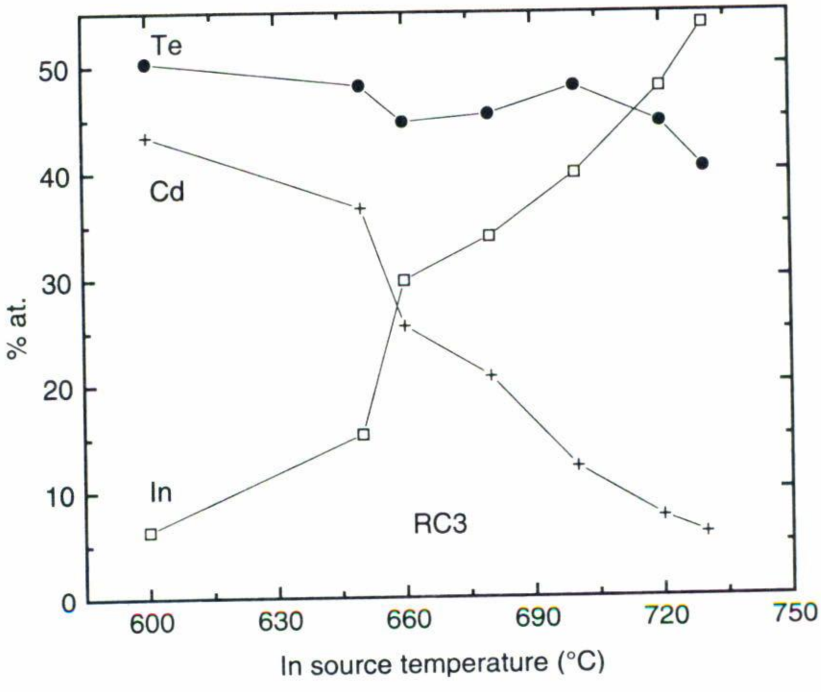

FIGURE 5. Atomic concentration in the In-doped CdTe films by AES, versus indium source temperature. Serial RC3.

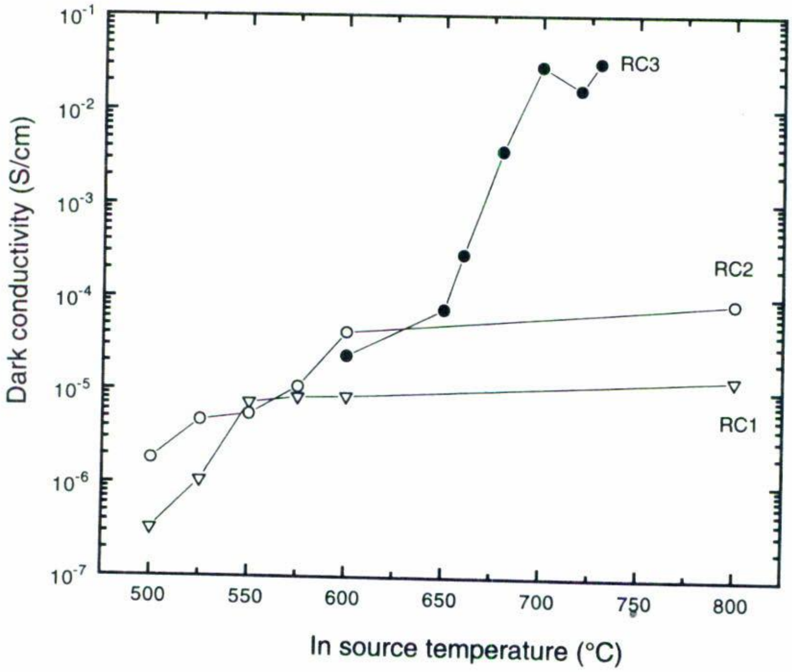

FIGURE 6. Dark conductivity of the In-doped CdTe films versus indium source temperature.

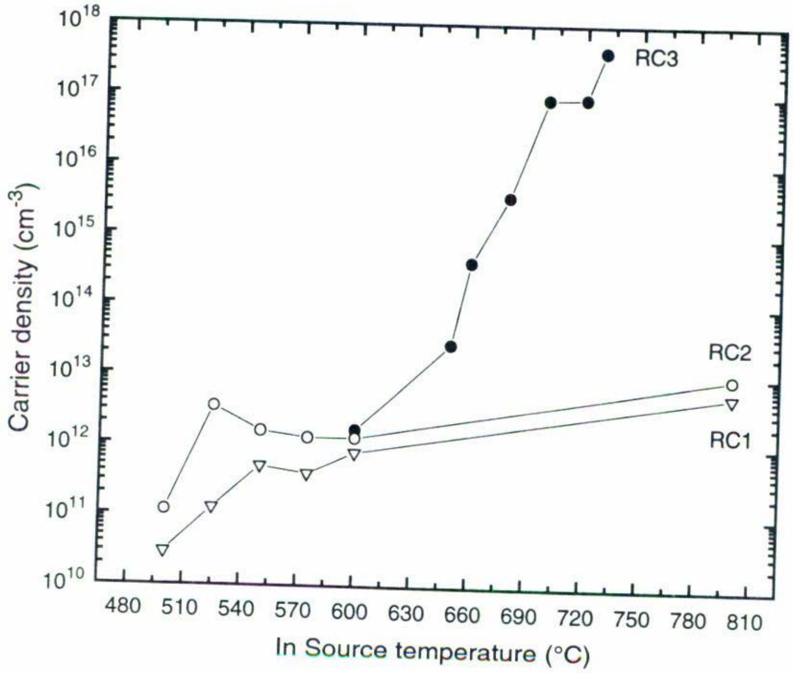

FIGURE 7. Carrier density of the In-doped CdTe films versus indium source temperature.

6. DISCUSSION

In Fig. 3, we can see a maximum in the mean grain size at indium source temperatures around 640 °C. We will use this point as a reference for discussion. We can divide the graph into two parts: before the peak and after the peak. We must remember that the CdTe source temperature and the substrate temperature were maintained constant during the preparation of all samples and that the indium source temperature is the only changing variable.

We first will discuss the low temperature part of the graph shown in Fig. 3, (*i.e.*, from 560 °C to 640 °C). The conductivity values of the serial RC1 in this region do not show important changes (Fig. 6), *i.e.*, they have similar values. In this first part of grain size curve, we observe an increase in the grain size with the indium source temperature until the maximum value is reached.

We have two possible explanations for this result: either i) indium concentration increases but there is not an increase in conductivity due to the changes in grain morphology induced by the indium, or ii) indium concentration is essentially constant and morphological changes are due to an experimental artifact: the close indium source induces local temperature increasing of the CdTe source temperature by thermal radiation which, in turn, increases the evaporation and deposition rates of CdTe. This is a very reasonable explanation because in Fig. 3, we observe that the increase in the grain size occurs just when indium source temperature and CdTe source temperature are just similar (600 °C). To elucidate between both possibilities a film was grown under the same conditions with indium source temperature at 640 °C but without indium in the oven. The result obtained for this sample is that the morphology of the CdTe film changes but we do not observe the large microcrystals. Thus, although there is an experimental error in the evaporation rate, it cannot explain the large increase in microcrystal size.

A change in the slope of the curve can be seen in Fig. 3 at 20 °C above the threshold of 600 °C, until maximum grain size is reached at about 640 °C. At this temperature the grain size is the largest one (30–50 μm) found. After the peak, *i.e.*, above 640 °C, grain size decreases and the shape of the grains change. In fact, morphological changes can be seen in Fig. 2, images from a to f, that shows a zoom (24 μm × 24 μm) of the samples shown in Fig. 3. At low indium source temperature (below 580 °C) formless grains are observed (image a), in the peak region (images b, c, d) grains with clear hexagonal faces are observed. At high indium source temperature (images e, f) we can observe microcrystals with only rectangular faces (not observed at lower temperatures) and a small amount of hexagonal faces. Thus, from 580 °C indium source temperature grains are nearly perfect microcrystal with well characterized faces, edges and growth terraces forming idiomorphous crystals. Moreover, the whole film is a macle polycrystal, *i.e.*, grain boundaries are observable and a microcrystal becomes in a continuous way in the next microcrystal. On the other hand, above 580 °C grains are formless without well determined faces and edges: they are rounded grains with glue-like connections between then and grain boundaries are defined (oolitic aggregates).

On the other hand, we can write the indium doping process as

$$2\,\mathrm{In(g)} + \mathrm{Te_2(g)} \rightarrow 2\,\mathrm{In}_{\mathrm{Cd}}^{+} + 2\,e^{-} + 2\,\mathrm{Te}_{\mathrm{Te}}, \qquad (1)$$

where (g) designates gas phase species and subscripts Cd, Te designate lattice sites. As stated, the yield of electrons from process (1) is low without cadmium overpressure [11]. Also, spectroscopic evidence is accumulating that links low activation of the donors to the presence of cadmium vacancies. This suggests that, in competition with process (1), there is a second incorporation process,

$$2\,\mathrm{In(g)} + \tfrac{3}{2}\,\mathrm{Te_2(g)} \rightarrow 2\,\mathrm{In}^{+}_{\mathrm{Cd}} + V^{2-}_{\mathrm{Cd}} + 3\,\mathrm{Te}_{\mathrm{Te}}, \tag{2}$$

where the In^{+} are compensated by cation vacancies V^{2-}_{Cd}.

On this basis, one can conclude that Cd overpressure works by preventing vacancy formation. Formally, this is represented by

$$\mathrm{Cd(g)} + V^{2-}_{\mathrm{Cd}} \rightarrow 2\,e^{-} + \mathrm{Cd}_{\mathrm{Cd}}, \tag{3}$$

which shows clearly that the electron concentration increases and the vacancy concentration decreases with increasing cadmium pressure.

To relate our results to those obtained using CSVT-FE, we recall that the samples described in this work were not grown under cadmium overpressure. Then, the migration and cadmium vacancy formation considerably reduces the effective number of indium atoms that can contribute to the carrier concentration.

In samples RC1 and RC2, the low values of carrier concentration n with respect to the atomic indium concentration can be understood assuming a high degree of compensation of indium donors by Cd vacancies and other defects. Thermal treatment to sample RC2 is expected to decrease the concentration of Cd vacancies and segregated impurities. This could explain the rise in carrier concentration and conductivity with respect to samples RC1. Since thermal treatment has been done without Cd overpressure the increase in conductivity is not very high.

Carrier concentrations in samples RC1 and RC2 are very low ($n < 10^{13}$ cm^{-3}). Assuming a typical trap density $N_T \sim 10^{12}$ cm^{-2} at grain boundaries, even the larger (50 μm) grains must be depleted of carriers. In this situation the conductivity σ and the carrier concentration n are very sensitive to the grain size L and increase with it [9]. Then we may write

$$\frac{d\sigma}{dT_{\mathrm{i}}} = \left(\frac{\partial\sigma}{\partial N}\right)\left(\frac{\partial N}{\partial T_{\mathrm{i}}}\right) + \left(\frac{\partial\sigma}{\partial L}\right)\left(\frac{\partial L}{\partial T_{\mathrm{i}}}\right), \tag{4}$$

and

$$\frac{dn}{dT_{\mathrm{i}}} = \left(\frac{\partial n}{\partial N}\right)\left(\frac{\partial N}{\partial T_{\mathrm{i}}}\right) + \left(\frac{\partial n}{\partial L}\right)\left(\frac{\partial L}{\partial T_{\mathrm{i}}}\right), \tag{5}$$

where T_{i} is the indium source temperature and N is the concentration of active (non compensated) indium donors.

Since grain boundary traps are not completely filled $\partial\sigma/\partial N$ and $\partial n/\partial N$ are small positive quantities and $\partial\sigma/\partial L$, $\partial n/\partial L$, are positive. As T_{i} increases N is expected to increase, first slowly (from 500 °C to 650 °C) and then faster (Fig. 4), on the other hand $\partial L/\partial T_{\mathrm{i}}$ is high and positive up to 650 °C, then decreases abruptly and finally remains approximately constant (Fig. 3). This could explain why σ and n increase faster than the atomic indium concentration up to $T_{\mathrm{i}} = 650$ °C and then grow very slowly as the latter increase from 1% to 7% (Figs. 6 and 7).

As for samples RC3, the simplest hypothesis is that we have, as in Suzuki *et al.* [6] the system $\mathrm{Cd}_{1-x}\mathrm{In}_{\mathrm{Cd}\,x}\mathrm{In}_{\mathrm{i}\,y}\mathrm{Te}$ with $0.14 \leq x < 0.85$, $0 \leq y < 0.5$ and where In_{i} means indium atoms in interstitial sites. Relatively high carrier concentration ($n \sim 10^{17}$ cm^{-3}) but comparatively low mobilities ($\mu = 0.4$ cm^2 V^{-1} s^{-1}) are obtained.

To understand the electrical properties of these samples more detailed information about their temperature dependence and the location of indium atoms is required.

7. CONCLUSIONS

We have reported the deposition of In-doped CdTe films using a new technique; CSVT-FE. In comparison with modern epitaxy techniques as PAMBE, CSVT-FE is relatively simple and inexpensive. To recognize growth conditions exactly, further investigations are necessary, which are being carried out at present.

On the other hand, we presented a SEM study of the grain size and morphology of the films. We found a strong dependence between the grain size and the indium concentration combined with the indium source temperature.

The combination of these results with the interpretation of the electrical conduction in the films, can be summarized as follows:

i) The migration and cadmium vacancy formation considerably reduce the effective number of indium atoms that can contribute to the carrier concentration.

ii) The indium is affecting the density of the grain boundaries states, due to this, the electrical conductivity can decrease.

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