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A modification of close-space vapor transport combined with free evaporation technique for doping semiconductor films and production of interfaces

A. Martel[1,2,3], R. Castro-Rodríguez[1], E. Purón[2], M. Zapata-Torres[1], and J.L. Peña[1]
[1] *Centro de Investigación y Estudios Avanzados del I.P.N. Unidad Mérida*
97310 Mérida, Yucatán, Mexico
[2] *Facultad de Física, Universidad de La Habana, San Lázaro y L. Vedado*
10400, La Habana, Cuba
[3] *e-mail: amartel@ff.oc.uh.cu*

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In this work a new method of double process close-space vapor transport technique (DCSVT) is presented. This new process can be divided in two steps: In the first step a graphite source, with CdTe powder as the CdTe source is used together with an other graphite block with or without Corning glass slide as substrate. In the second step the film deposited in the first step over the graphite block or Corning glass is used as packet CdTe source. Different substrates are used to obtain non-doped polycrystalline CdTe films. Metallic indium is used as impurity to obtain doped films. We describe the structural and morphological characteristics and properties of the films deposited using this new process.

Keywords: CdTe; polycrystalline films; CSVT

En este trabajo se presenta la nueva técnica de crecimiento de transporte de vapor en espacio reducido con doble proceso (DCSVT). El nuevo proceso puede ser dividido en dos pasos: en el primero, un bote de grafito cargado con polvo de CdTe actúa como fuente de CdTe, usándose un bloque de grafito cubierto o no con un vidrio Corning como substrato auxiliar. En el segundo paso, la película depositada en el primer paso sobre el bloque de grafito o sobre el substrato auxiliar, se usa como fuente de CdTe. Se utilizan diferentes substratos para obtener películas policristalinas de CdTe sin impurificar así como películas impurificadas con indio. Se describen las características estructurales y morfológicas de las películas depositadas por esta nueva técnica.

Descriptores: CdTe; películas policristalinas; CSVT

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1. Introduction

The close-spaced vapor transport (CSVT) technique is practically well suited to such a project because, theoretically [1–5], the flux of materials from the source to the substrate depends only on the temperature difference and the distance between the source and the substrate, as well as the diffusion of species transporting the materials (Ga_2O, As_2, and As_4 in the case of GaAs, and Cd, Te_2 in the case of CdTe). The dimensions of the substrate do not influence this mass transport, which means that CSVT may be easily scaled up. Furthermore, this technique is cost-efficient and does not require the storage of toxic precursor gases, since the sources of the materials are GaAs and CdTe themselves.

CSVT has already been used for the heteroepitaxial growth of GaAs on Ge [6] and for the production of CdTe / CdS solar cells [7–10]. Typically, the short distance between the source and the substrate are less than 5 mm, and the reaction chamber, consisting of the source and the substrate separated by a spacer, is held between two graphite blocks. A hot wall deposition chamber is inserted between the two graphite blocks. Heating is usually provided by the Joule effect, using both graphite blocks as resistance. In most cases, there is a temperature difference of approximately 100°C between the source and the substrate. The dimensions of the graphite blocks are usually of about $60 \times 20 \times 20$ mm^3.

In a previous work [11] we reported a novel deposition technique involving the combined use of free evaporation and CSVT, (called CSVT-FE), for the doping of semiconductor thin films. This technique was applied to grow M-doped CdTe films (M = indium, cadmium) with good electrical, stoichiometric, structural, and morphological properties [12–15]. In this case, a hole of 6-mm diameter is made in the center of the graphite source block to introduce a hollowed cylindrical graphite dopant source, with the purpose of introducing the atoms of the evaporated dopant into the CSVT deposition chamber.

However, during the use of these techniques (CSVT or CSVT-FE), the semiconductor source, the dopant source, and the graphite substrate heater are normally fixed, limiting the production of one film for each experimental process. Thus, only one doped or non-doped film can be deposited. On the other hand, the interfaces, (such as CdTe / CdS), are obtained *ex-situ* at the first deposition film or when one is used as substrate.

Here, we report a modification of CSVT-FE technique for doping semiconductor films and for the production of interfaces, obtaining, *in-situ*, three films for each experimental process. We have applied this technique to grow indium-doped CdTe and to grow non-doped-CdTe films on different substrates and interfaces with good structural and morphological properties.

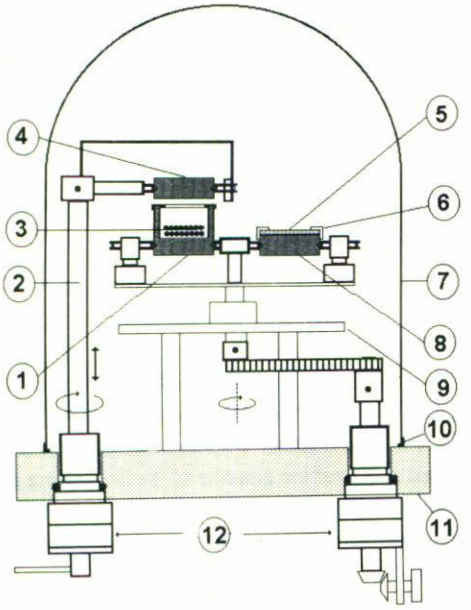


FIGURE 1. Scheme of the DCSVT technique with: (1) graphite source block, (2) mobile arm, (3) CdTe powder, (4) substrate block, (5) glass substrate, (6) ceramic spacer, (7) glass bell jar, (8) substrate heather, (9) revolving plate, (10) rubber gasket, (11) metallic plate, (12) vacuum passes.

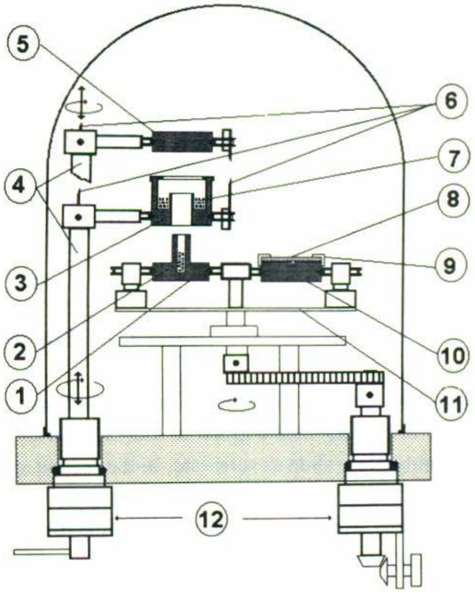


FIGURE 2. Scheme of the DCSVT-FE technique with: (1) dopant source, (2) metallic indium, (3) graphite source block, (4) mobile arms, (5) graphite block, (6) current carrier wire, (7) CdTe powder, (8) substrate, (9) ceramic spacer, (10) substrate heather, (11) revolving plate, (12) vacuum passes.

2. Construction and operation

The first modification process can be divided in two *in-situ* steps: First, using a graphite source with the shape of a hollowed cylinder with dimensions of 19 mm o.d, 13 mm i.d, 15 mm height and a hole of 7 mm depth, with semiconductor powder as the semiconductor source in the inner cavity of this source. The volatile semiconductor compound migrates to the substrate. Other graphite block is used as substrate to obtain a packed semiconductor film. The dimensions of this block are $25 \times 23 \times 9$ mm^3. Second, using the above graphite block with the packed semiconductor film deposited in the first steep as source of semiconductor and a Corning glass slide as substrate to obtain polycrystalline semiconductor films. The glass substrate is heated by another graphite block ($25 \times 18 \times 5$ mm^3). In both steps the CSVT technique has been used. Figure 1 is a schematic view of the apparatus used. All the graphite heaters are made of Ultra Carbon Corporation graphite. At typical semiconductor evaporation temperatures (500–900°C), this graphite will not react with the semiconductor, thereby avoiding contamination of the films. Two holes of 5-mm diameter were made in each end of the graphite block for electrical connections. In Fig. 1 we can see: (1) is the graphite source block with the cylindrical graphite chamber (2) containing the CdTe powder (3). (4) is the graphite substrate-block. (5) is the glass substrate with a ceramic spacer (6), (8) is the graphite substrate heater. (9) represents a revolving plate where the graphite source block and three-graphite substrate heater are supported symmetrically. (12) represents the vacuum passes. The graphite substrate block is coupled to a mechanical arm with up, down, vertical and revolving motion. This motion permits the two *in-situ* steps. This modification has been called double-CSVT (DCSVT).

The second modification is very similar to the first one, only that in this case a hole of 6 mm diameter is made in the center of the semiconductor source to introduce another hollowed cylindrical graphite as doping source. The purpose of this source is to introduce the atoms of the evaporated dopant into the CSVT deposition chamber, where the dopant atoms and the volatile semiconductor compound migrate to the substrate. The dopant source has the shape of a hollowed cylinder with 6-mm o.d., 4-mm i.d., and 10-mm height and hole of 7-mm depth. Figure 2 is a schematic view of the apparatus used. Now, the revolving plate (11) supports symmetrically the cylindrical graphite dopant source (1) and three-graphite substrate heater (10). Both, the semiconductor graphite source and the graphite substrate block, are coupled to two mechanical mobile arms (4) with up, down, vertical and revolving motion. This motion permits to use *in-situ* CSVT-FE and the CSVT steps.

Chromel-alumel thermocouples were used to monitor the temperatures of the substrate, the semiconductor source, and the dopant source. Once the substrate and the semiconductor source temperatures have been selected, based on the sublimation temperature of the semiconductor, the doping level of the film will be a function, primarily, of the dopant source temperature. All the above mentioned temperatures are finely fixed by high-performance temperature control system [16].

TABLE I. Temperatures and time of growth of the CdTe films at $P(O_2) = 2$ mbar, $P(He) = 14$ mbar. □ glass, ◊ ITO/glass, △ CdS/ITO/glass

Substrate kind	T source °C	T substrate °C	Time of grown min.
□	650	580	5
◊	660	585	4
△	650	590	4

3. Application

We have applied the DCSVT and DCSVT-FE techniques to grow indium-doped CdTe films with good properties and to grow non-doped CdTe on different substrates. 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 about 10^{-6} mbar.

3.1. Non-doped CdTe films

The non-doped CdTe thin films are usually used as absorbent in the CdTe solar cells and an oxygen-helium mixture is employed in the preparation process of these devices [8, 9]. Albin *et al.* [7] have used a hydrogen atmosphere during the preparation of the CdTe source. We have used the DCSVT technique and our apparatus to obtain such non-doped CdTe films. Figure 1 shows a schematic view of the used arrangement. Different substrates and atmosphere compositions like those cited above were used. The substrates were: Corning 7059 glass slide (glass), Corning covered by 0.5 μm thickness ITO film (ITO/glass) and the last with a 100 nm thickness CdS (CdS/ITO/glass). The CdS was prepared by chemical bath deposition technique using the method reported by De Melo *et al.* [17].

In all cases, to grow the CdTe source (first step), a hydrogen flow (chamber pressure of 20 mbar) was used. The CdTe powder source and substrate temperature was kept at 700°C and 600°C respectively and 5-min time of growth was used. The growth environment at second step is resumed in Table I.

Figure 3 shows the scanning electron microscopy (SEM) photograph of the CdTe/glass structure. Figure 4 shows the SEM photograph of CdTe/ITO/glass structure. Figure 5 shows the SEM photograph of the CdTe/CdS/ITO/glass. Similar pattern were observed across the whole area of each sample just to the border of the films. In the photographs we can see the good quality of the films and note the influence of the substrate: The grains' shape and size are quite different. The CdTe/glass film has the largest grains (mean value of 7 μm). The majority of the grains are huge and they have good defined hexagonal form. The grains in the CdTe/ITO film are smaller (mean value of 4.4 μm). The density of big grains is less than in the CdTe/glass film and the grain's form is more diffused. The CdTe/CdS film has the smallest grain's size (mean value of 3 μm), and the most diffused form.

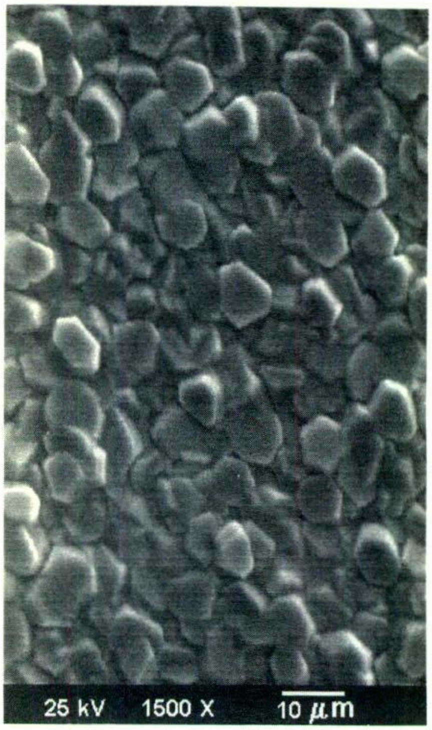


FIGURE 3. SEM microstructure of the CdTe film (10.8 μm) deposited by DCSVT) on the Corning glass substrate (CdTe/glass) under the following conditions: T(source) = 650°C, T(substrate) = 580°C, $P(O_2) = 2$ mbar, $P(He) = 14$ mbar, time = 5 min.

3.2. Indium-doped CdTe films

To obtain In-doped CdTe films we used the DCSVT-FE technique as can be seen in Fig. 2. In our experiments we used high-purity Balzers metallic indium (99.999 at. % pure). The CdTe powder, (99.999 at. % pure Balzers), sublimes at a temperature of 600°C and it is deposited in the first step on the substrate of graphite at the temperature of 500°C. The time of the first step was 5 min. The temperature of the In source was ranged between 600 to 725°C. For the second step we use 600°C as temperature of the packed In-doped CdTe source and 500°C for the substrate, (Corning 7059 glass slide), with deposition time of 5 min. The control gas used during the film growth was Matheson argon 99.999 at. %. The pressure during deposition was below 10^{-5} mbar.

Figure 6 shows the variation of lattice parameter of the In-doped CdTe films with the indium source temperature. As we can see, the lattice parameter decreases when the indium source temperature increases indicating a substitutional incorporation of In atoms into the unitary cell of the CdTe film. We also have investigated the thermal properties of these polycrystalline indium-doped CdTe films, using the photo acoustic technique (in the heat transmission configuration),

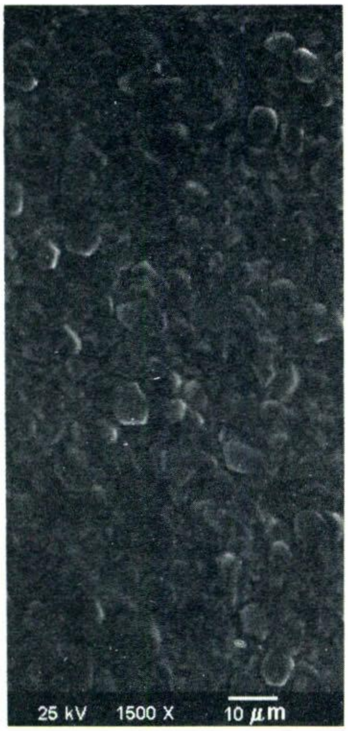


FIGURE 4. SEM microstructure of the CdTe film (9,8 μm) deposited by DCSVT on the ITO substrate (CdTe / ITO / glass) under the following conditions: $T(\text{source}) = 660°\text{C}$, $T(\text{substrate}) = 585°\text{C}$, $P(\text{O2}) = 2$ mbar, $P(\text{He}) = 14$ mbar, time = 4 min.

FIGURE 5. SEM microstructure of the CdTe film(16 μm) deposited by DCSVT on the CdS substrate (CdTe / CdS / ITO / glass) under the following conditions: $T(\text{source}) = 650°\text{C}$, $T(\text{substrate}) = 590°\text{C}$, $P(\text{O}_2) = 2$ mbar, $P(\text{He}) = 14$ mbar, time = 4 min.

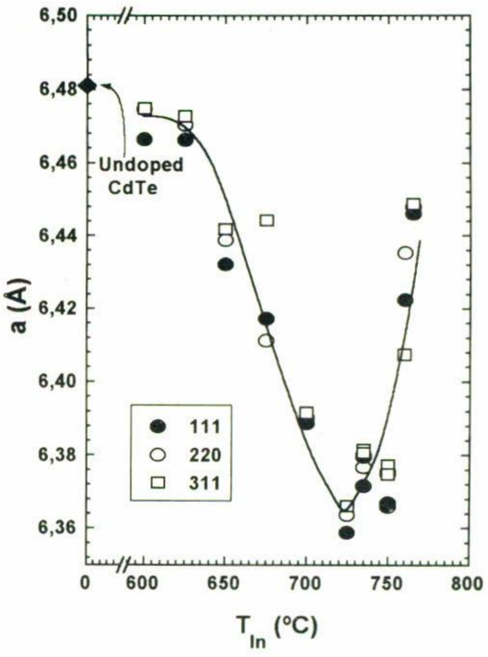


FIGURE 6. Typical variation of the lattice parameter of the In-doped CdTe films as a function of indium source temperature.

in order to associate the observed signal variation with crystalline imperfections and the role played by this imperfection on the thermal transport properties of the films.

To understand the PA signal and be able to monitor the homogeneity of our non-doped and doped CdTe samples we should examine the modulation frequency dependence of the detected signal. As it is well known, the modulation frequency dependence of the PA signal is the usual way for extracting information about the thermal diffusivity of the sample under study. For rear-side illumination the thermal diffusion model of Rosencwaig *et al.* [18] predicts that, for an opaque sample of thickness l_s and thermal diffusivity α, the PA signal follows the equation:

$$S = \frac{\text{Constant}}{f} \cdot \exp\left(-a\sqrt{f}\right) \qquad (1)$$

For a thermal thick sample ($l_s a_s \gg 1$), where $a_s = (\pi f/\alpha)^{1/2}$, $a = l_s(\pi/\alpha)^{1/2}$, and f is the frequency of the modulated light beam. Knowing the coefficient a from the fitting procedure, the thermal diffusivity α is readily obtained.

Figure 7 shows the PA signal amplitude as a function of the square root of the modulation frequency for non-doped CdTe sample. The PA signal of the In-doped CdTe samples, were similar to the Fig. 7. The solid curve in this figure represents the fitting of the experimental data to Eq. (1). From this processing a value of $\alpha = 0.069 \pm 0.003\,\text{cm}^2\,\text{s}^{-1}$ was found. Figure 8 shows the room-temperature-measured values of the diffusivity of the non-doped and doped-CdTe samples as a function of the In content. We can see that the thermal diffusivity first decreases monotonically when the In concentration rises and reaches a minimum. Afterwards, the thermal diffusivity increases and reaches a maximum. Later, the ther-

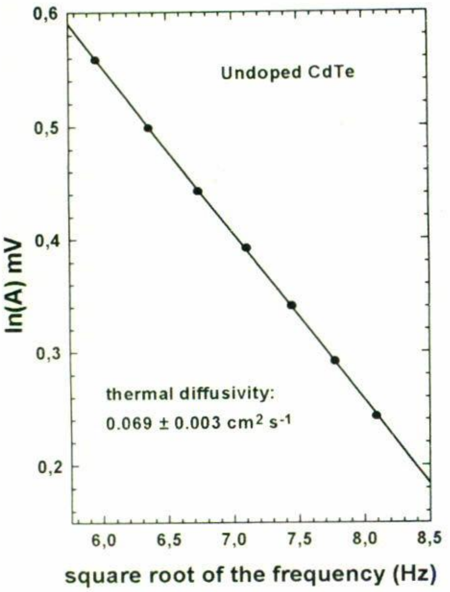


FIGURE 7. Photo acoustic signal amplitude as a function of the square root of the modulation frequency for undoped CdTe sample. The solid line represent the data fitting to Eq. (1).

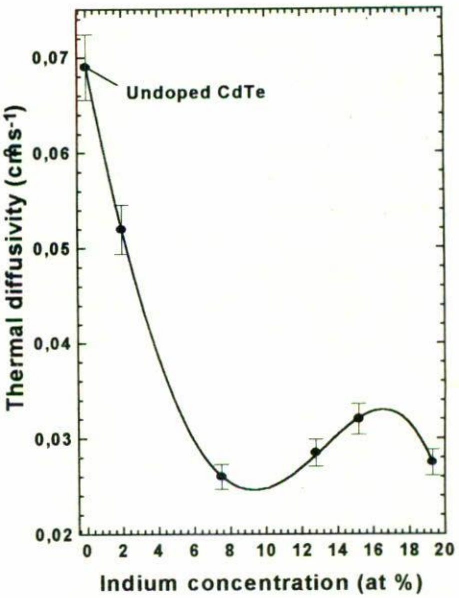
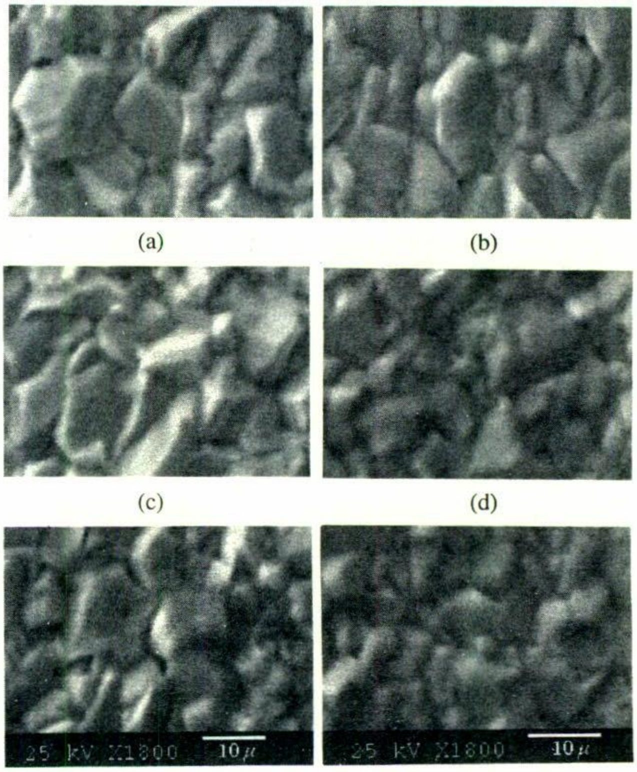


FIGURE 8. Effective thermal-diffusivity data as obtained for the In-doped CdTe samples as a function of In-at. % concentration. The solid curve represents the fit to the data.

mal diffusivity shows a saturation tendency. In order to explain the above behavior, we analyzed in detail the structure of the films, using X-ray diffraction techniques, and found that the deposited films have zinc-blende (ZB) type structures with a preferential orientation of the (111) planes parallel to the substrate. These measurements show a linear decrease of the unit cell parameter with the indium source temperature increment (see Fig. 6). We note that the decrease is larger than the expected one, obtained assuming a single substitutional model, with a CdTe distance of 0.2806 nm and In-Te distance of 0.2730 nm. The shortest reported In-Te distance for a compound containing both In and Te (see Fig. 6). Such a rapid decrease in the unit cell parameter with dopant concentration has been reported in other II-VI doped semiconductors and has been related to the presence of point defects. The decrease in the thermal diffusivity of the films is thought to be due to this effect. In other words, the lattice becomes greatly distorted because the radius of the In ion is smaller than the Cd ion radius, the distorted lattice may enhance the phonon scattering and decreases the thermal diffusivity. Therefore, a CdTe lattice doped with substitutional In atoms may shrink and become distorted. When the Cd vacancies in CdTe evaporated films are completely compensated by In atoms, they can dope interstitially into the films. Therefore, the spacing of principal lattice planes corresponding to the (111) plane can become larger upon further doping. This effect decreased the phonon scattering. Then the thermal diffusivity increases and reaches a maximum. The last behavior can be explained due to the formation of the new phase $CdIn_2Te_4$ in the CdTe matrix, as was reported by [19]. Figure 9 shows SEM photographs of the films, as can be seen, the morphology of the films are very uniform.



(a) (b)

(c) (d)

(e) (f)

FIGURE 9. SEM microstructure of the In-doped CdTe film with: (a) $T_s = 600°C$; (b) $T_s = 625°C$; (c) $T_s = 650°C$; (d) $T_s = 675°C$; (e) $T_s = 700°C$; (f) $T_s = 725°C$.

4. Conclusions

We have reported a modification of the CSVT-FE technique for doping semiconductor films and for the production of interfaces. We have applied this technique to grow Indium-doped CdTe and to grow non-doped CdTe on different substrate films with good structural and morphological properties. The potential of application of this technique for the control of the growth of doped semiconductors from the vapor phase and the production of interfaces to obtain semiconductor materials, as required for semiconductor devices, is promising.

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