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Growth of CdS crystals by the physical vapor transport method

Cheng Hongjuan(程红娟)†, Xu Yongkuan(徐永宽), Yang Wei(杨巍), Yu Xianglu(于祥潞),
Yan Ruyue(严如岳), and Lai Zhanping(赖占平)

(China Electronics Technology Group Corporation, No. 46 Research Institute, Tianjin 300220, China)

Abstract: Based on the physical vapor transport (PVT) method, the growth of large-size CdS crystals inside a vertical semi-closed tube is studied. Firstly, in order to ensure 1D diffusion-advection transport, multi-thin tubes are used in the growth tube. The XRD spectra of the CdS crystal grown in this configuration indicates that the crystal quality has clearly been improved, where the FWHM is 58.5 arcsec. Secondly, theoretical and experimental growth rates under different total pressures are compared; the results show that the experiential growth rate equation is valid for our semi-tube growth, and it could be used to estimate the growth rate and maximum growth time under different total pressures.

Key words: CdS; growth rate; growth surface; the saturated vapor pressure
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1. Introduction

Cadmium sulfide (CdS) is an important II–VI compound semiconductor, which has a hexagonal structure at room temperature and is chemically stable. Its band gap energy has been known to be about 2.42 eV, which corresponds to the visible region. Based on these fundamental properties, CdS single crystal plays an important role in modern optoelectronic devices and solar cells. Nowadays, high-quality and large-size CdS crystals have already become an international hot research subject.

The growth of CdS by the physical vapor transport (PVT) method has been investigated for many years[1, 2], because of its low growth temperature (about 1050 °C). Since a modification of the PVT method was reported[3, 4], crystals with low dislocation density and second-phase inclusion density can be produced. In this paper, we obtain a single crystal of higher quality and larger size by making further improvements on the growth tube configuration and growth condition.

The PVT method can be classified into three techniques according to different configurations of the ampoule, i.e. self-sealed, semi-closed, and closed. In this paper, a semi-closed tube with a flowing inert gas and a seed crystal is used to accomplish the growth of large-size CdS bulk crystals and study the effects of pressure on single crystal growth rate.

2. Experimental procedure

Figure 1 shows a schematic cross-sectional view of a vertical five-zone furnace and a quartz-made growth tube with an axial temperature profile. A CdS seed is placed in the low temperature zone of the growth tube, and CdS powder (6N) in the high temperature zone. The five growth zones can be adjusted to hold the growth surface at the same temperature and gradient without using the puller[5, 6]. In this experiment, the growth tube is a semi-closed one, in which the total pressure can be adjusted by vacuum pump and the flow rate of argon (Ar). Inevitably, a little CdS material will be extracted by export or deposition in cold areas.

The samples are grown via five steps: heating I, keeping, heating II, growing and annealing. In the keeping step, the temperature is maintained at 950 °C for 2 h to sublime away any volatile impurities and keep an appropriate stoichiometry. After the heating II step, the temperature of the source and growth part are increased to 1080 °C (T_S) and 950 °C (T_C), respectively and the other zones are heated to an appropriate temperature as shown in Fig. 1. During the growing stage, the temperature error is kept within ±0.1 °C and the total pressure is set to 87, 90, 200, 380, 770 and 1000 mbar in the different experiments, respectively. The temperature difference is $\Delta T = T_S - T_C = 130$ °C and T_{avg} is estimated to be about 1050 °C. Finally, in order to avoid samples with cracks, the annealing step is carried out at a rate of 20 °C/h for 30 h. Figure 2 shows a CdS bulk crystal grown in this way.

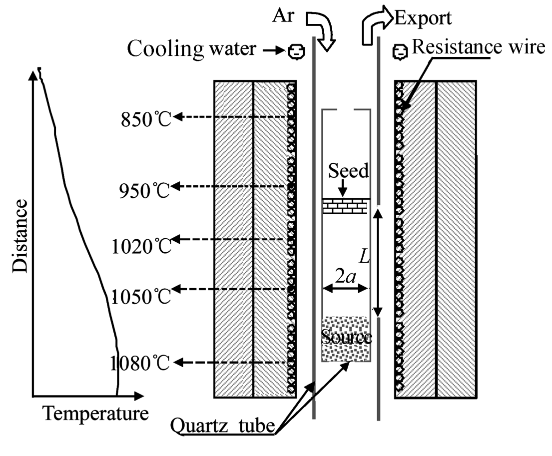

Fig. 1. Experimental arrangement of the five-zone vertical electric furnace and its temperature profile for crystal growth.

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† Corresponding author. Email: hongjuan@mail.nankai.edu.cn

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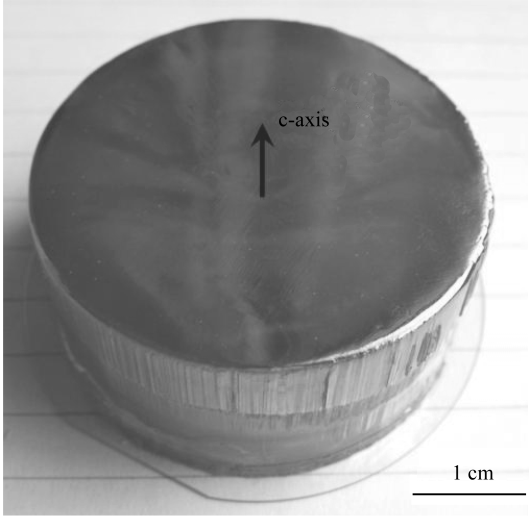

Fig. 2. Φ40 mm × 30 mm CdS single crystal.

3. Results and discussion

3.1. Hydrodynamic state inside the growth tube

The growth mechanism for PVT can be characterized by sublimation of the source material, transport of the vaporized species, and coagulation at the growth surface. The actual growth rate is limited by the slowest step. In general, equilibrium is always assumed to be established immediately, so the growth rate is limited by the transport process. Meanwhile, transport is characterized by three theoretical hydrodynamic models[7]: 1D diffusionless, 1D diffusion-advection, 2D or 3D diffusion-convection. Convection can induce an unsteady vapor transport process, which causes asymmetrical growth and crystal defects, so the convection flow should be reduced in experiments.

Before applying these theoretical models to study the transport process, we can judge the state inside the growth tube by a dimensionless number, the Rayleigh number (Ra):

$$\mathrm{Ra} = \frac{g\beta}{\nu\kappa}\frac{\Delta T}{AR}a^3, \tag{1}$$

where β is the coefficient of volume expansion, ν is the kinematic viscosity, κ is the thermal diffusivity for the gas inside the ampoule[7, 8], g is the gravitational acceleration, and AR is the aspect ratio of the growth tube, $AR = L/a = 10$.

In a horizontal furnace, because the temperature gradient is vertical with gravity, a complicated 2D or 3D convection flow pattern always occurs. For a vertical one, only when Ra reaches a critical value ($\mathrm{Ra_c} = 230$) will the onset of convection occur[9]. So a five-zone vertical furnace is adopted.

In the large-size CdS crystal growth process, the radius of the growth tube is 2 cm, which is bigger than traditional ampoules[7, 8, 10]. Under the six growth conditions (CdS-1 to CdS-6) mentioned above, the corresponding Ra is smaller than $\mathrm{Ra_c}$, but it is bigger than the ampoules. Thus, the transport is based on the 1D diffusion-advection model, but the contribution of convection cannot be neglected.

To optimize the growth conditions, the multi-thin tube method is applied. Multi-thin tubes are added to divide the growth tube space into several more reedy ones, which can reduce the average Ra, ensure the main form of 1D diffusion-advection vapor transport, and avoid the effects of convection. Figure 3 shows perspective micrographs of CdS crystal cross-sections grown under the two configurations, and the corresponding full-width at half-maximum (FWHM) of the XRD rocking curve peaks which can reflect the structural quality of the CdS crystal. We find that many long or short empty direct tubes and empty variform wrappages exist in Fig. 3(a), which are caused by dislocations and thermally created defects in the CdS crystal. The corresponding (002) XRD FWHM is 96.79 arcsec. Compared with Fig. 2(a), the numbers and volumes of empty tubes and wrappages in Fig. 3(b) become smaller. The corresponding (002) XRD FWHM is 58.5 arcsec, which means that the crystal quality becomes better. So we can draw the conclusion that when adding multi-thin tubes into the growth tube, crystal growth quality can be clearly increased.

3.2. Growth rate

By assuming complete dissociative vaporization for CdS, the predominant vapor species are Cd and S_2[8] inside the growth tube: $\mathrm{CdS_{(g)}} = \mathrm{Cd_{(g)}} + \frac{1}{2}\mathrm{S_{2(g)}}$, and the equilibrium source pressure for stoichiometric vapor P_S^0 is the sum of the partial pressure of Cd and S_2, i.e. $P_S^0 = P_{Cd} + P_{S_2}$. Meanwhile, the reaction constants K_P can be expressed as[11]:

$$\lg K_P = \lg P_{Cd}^2 P_{S_2} = -3.45 \times 10^4/T + 20.86. \tag{2}$$

So, P_S^o can be described experimentally as a function of temperature[7] by the Antoine equation:

$$P_S^0 = 1.0588 \times 10^{10} \times e^{-26141/T}, \tag{3}$$

where P_S^o is in units of Torr and T in K. Because the crystal interface temperature (T_c) is lower than that of the source (T_s), the phenomenon of local super-saturation will exist near the crystal interface ($P_S^0\big|_{x=0} < P_S^0\big|_{x=L}$), which illustrates the main mechanism of CdS crystal growth.

In the closed growth ampoule, when there are no inert gases, the growth rate can be calculated from Poiseuille's equation, and is given in cm/h as:

$$V_g = 9.6 \times \frac{a^2 M\left[\left(P_S^0\right)_{x=0}^2 - \left(P_S^0\right)_{x=L}^2\right]}{\eta L \rho_c (T_S - T_C)}, \tag{4}$$

with the dimensions of a and L in cm, dynamic viscosity of the vaporized source η in poise, the molecular weight M and density ρ_c of crystal in g/mole and g/cm^3, respectively.

However, the growth rate is very large under this condition. In actual growth, a slight difference in components or stoichiometry can change the growth rate by one to two orders of magnitude, so it is hard to obtain high-quality crystal[6, 7]. An inert gas such as Ar is introduced to obtain a transport-controlled regime in the closed growth. Then the growth rate

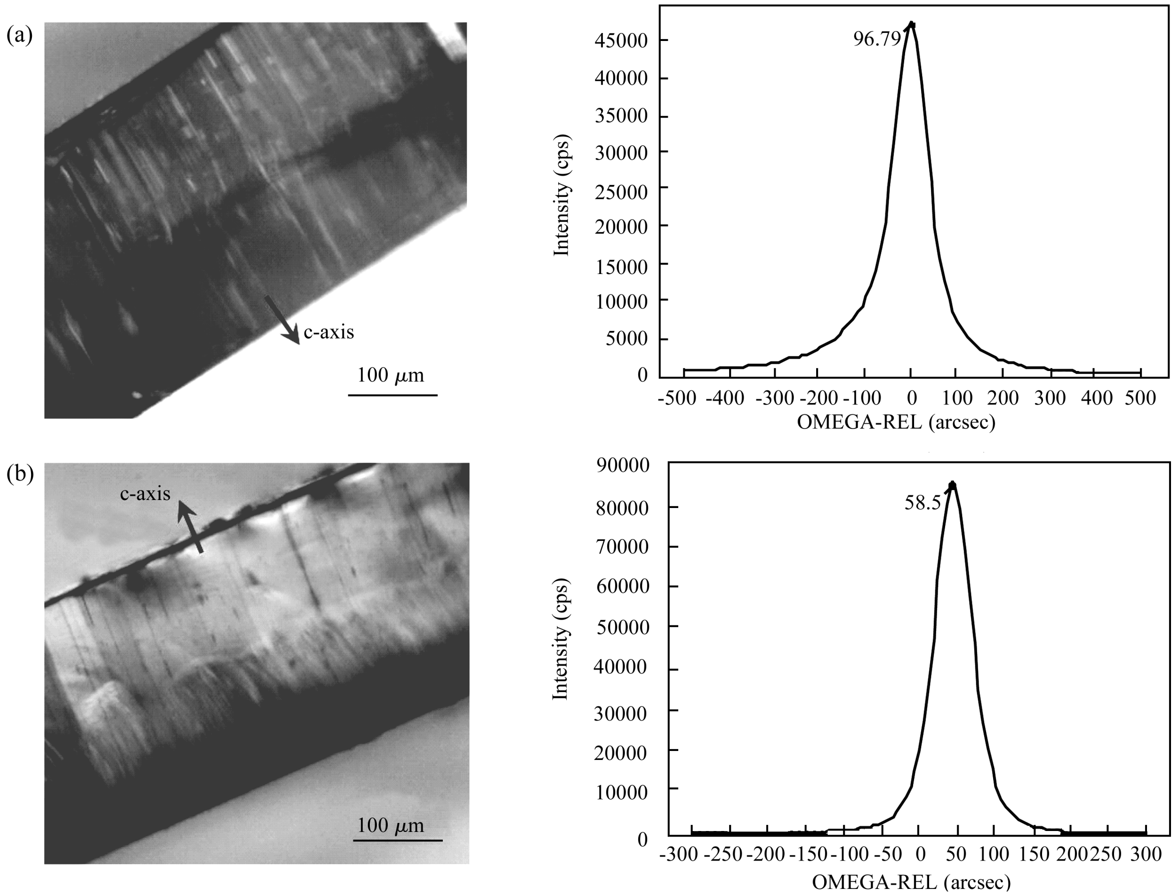

Fig. 3. Perspective micrographs and corresponding double diffraction X-ray rocking curves (ω scan) of CdS wafers growing (a) without and (b) with multi-thin tube.

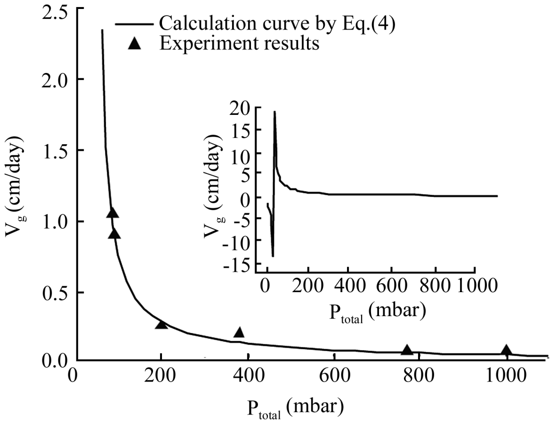

Fig. 4. Theoretical and experimental growth rates as a function of pressure for experimental conditions.

equation will be modified as[7]:

$$V_g = 5.76 \times 10^{-2} \times \frac{M D_{AB} P_S^0 \left(\dfrac{B}{T_{avg}} - 1 \right)}{\rho_c (T_{avg})^2 (1 - X_S)} \left| \left(\frac{dT}{dx} \right)_{x=L} \right|, \qquad (5)$$

where X_S is the mole fraction of the source components in the presence of the inert gas, and D is the diffusivity of the vapor through the inert gas in cm^2/s.

In our experiments, the temperature gradient near the growth surface (dT/dx) is -11.5 °C/cm, $T_{avg} = 1050$ °C, and the total pressure P_T is the total pressure inside the growth tube, $P_T = P_{Cd} + P_{S_2} + P_{Ar} = P_S^0 + P_{Ar}$. According to Eqs. (2) and (5), we can obtain theoretical curves representing the variation of the growth rate with total pressure inside a closed tube (Fig. 4). We can see that the crystal grows quickly at low pressures, and the growth rate reach a maximum value when the total pressure equals the equilibrium source pressure, $P_T = P_S^0$. That means when there are no inert gases in the growth tube, $X_S = 1$, the crystal growth rate will be very large. But on increasing the total pressure, the growth rate becomes slower.

Table 1. Comparisons of CdS crystal growth rates in different experiments.

Experiment number	P_T (mbar)	Growth rate (cm/day)
CdS-1	87	1.05
CdS-2	90	0.9
CdS-3	200	0.25
CdS-4	380	0.192
CdS-5	770	0.07
CdS-6	1000	0.072

In this study, some experimental growth rates in a semi-closed tube displayed in Table 1 are shown by triangles (▲) in Fig. 4. This chart shows that the triangles coincide reasonably well with the theoretical curve. This agreement confirms that Eq. (5) applied to the closed-tube condition is also valid for the condition of semi-closed growth tubes. So we can use this equation to calculate growth rates under different total pressures (P_T), and crystal lengths and growth surface positions at different growth times. For example, if $P_T = 60$ and 600 mbar, the growth rates are about 2.3 and 0.08 cm/day, respectively. Based on this information, we can adjust the growth zone temperature with the help of computer simulation to keep the temperature and temperature gradient near the growth surface at the same value. In addition, according to the gross weight of CdS powder and P_T, we also can estimate the maximum growth time, which can help us to avoid a surplus of CdS powder and resublimation of CdS crystal in our experiments.

4. Summary

In this paper, we use the multi-thin tube method to optimize the configuration of the growth tube, which can reduce the average tube Ra and ensure the main form of 1D diffusion-advection vapor transport during the growth process. As a result, dislocation density and second-phase inclusion density are reduced, and the quality of the CdS crystal is improved.

Meanwhile, the growth rate is also an important factor during CdS crystal growth. From published papers, we can obtain experiential equations which can be applied in the closed-ampoule system with/without inert gas to calculate the crystal growth rate. In this study, the experiment results prove that Equation (5) is applicable to the semi-closed tube system. Hence, the CdS crystal growth rate, the crystal length, and the maximum growth time can be estimated with different P_T, growth times and total weight of CdS powder.

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