JOURNAL OF MATERIALS SCIENCE 26 (1991) 4917–4923

Morphological stability and crystal structure of CVD-grown zinc selenide

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The evolution of micromorphologies has been studied for polycrystalline ZnSe layers grown by low pressure CVD processes in the systems: Zn–Se–H_2–Ar (Se method) and Zn–H_2Se–Ar (H_2Se method). We have found differences in morphological features, apparently due to specific growth and nucleation mechanisms. In technological applications coarse or fine grained materials with homogeneous grain size distribution are often advantageous. Such materials have been successfully prepared under kinetically controlled growth conditions with continuous nucleation, i.e. in contrast to the H_2Se method with deposition temperatures up to 800 °C by the Se method only at $T \leqslant 600$ °C and higher supersaturations. In the system Zn–Se–H_2–Ar the reaction rate constant is comparatively higher, and therefore the layer growth at higher temperatures is mainly diffusion-limited with boundary layer resistance. Correspondingly there is a tendency to morphological instabilities with normal grain growth and texture formation. Abnormal or secondary grain growth occurs as a result of recrystallisation during long-time CVD processes. Results of X-ray texture measurements are analysed in relation to different growth morphologies.

1. Introduction

Polycrystalline CVD-grown layers are of greatest technological importance, and range widely in application. In all of these applications the properties of layers are strongly affected by their microstructure, i.e. the average grain size, grain orientations and grain size distribution. Mostly, homogeneous coarse or fine grained materials are advantageous. It has been commonly found that morphologies showing equi-axed columnar growth and enhanced normal secondary growth of crystallites deteriorate the mechanical material properties.

This paper presents a complete picture of micromorphologies that result from CVD growth of ZnSe. Mechanisms with regard to nucleation and growth of layers with different morphological features have been considered.

In general, these studies are of importance in modelling polycrystalline layer growth from the vapour phase.

2. Material preparation

Polycrystalline ZnSe layers studied in this work were produced by low pressure chemical vapour deposition (LPCVD) using the so-called Se method (system Zn–Se–H_2–Ar) with Se as starting material. In other laboratories the H_2Se method (system Zn–H_2Se–Ar) with H_2Se gas sources has been successfully applied [1–4]. H_2–Ar-gas mixtures are mainly used as transport gases.

The deposition process takes place in horizontal or vertical flow reactors. Substrate materials most usually employed are vitreous carbon and silica glass. In vertical reactors a rectangular box with four plates parallel to the gas flow serves as deposition chamber. Horizontal reactors are used with the deposition surface perpendicular to the incoming gas stream. The reactor conditions were as follows:

$T_{\text{growth}} = 480$–800 °C;
$\Sigma p = 7$–60 torr;
gas flow velocity = 20–300 cm s^{-1} with variable H_2 content up to 75%;
material transport = 3–50 mmol h^{-1} Zn and Se with Se excess up to Se : Zn = 2;
growth time = 10–100 h.

For the H_2Se method the parameter range was similar, but beyond that at lower H_2 gas contents high transport rates up to 800 mmol h^{-1} and increased supersaturation ratios $> 10^{10}$ have been applied.

Samples for micrographic examination of layer surfaces and cross sections were cut from the deposit, lapped, polished, and etched using a solution of 1 part 15% potassium ferricyanide and 1 part 15% potassium hydroxide at 90 °C. For material characterisation microscopic and electron microscopic techniques, X-ray diffractometry and mechanical testing have been applied.

3. Layer growth

3.1. Morphology of polycrystalline ZnSe layers

Typical layer morphologies have been observed: (a) equi-axed columnar growth (Fig. 1a); (b) enhanced

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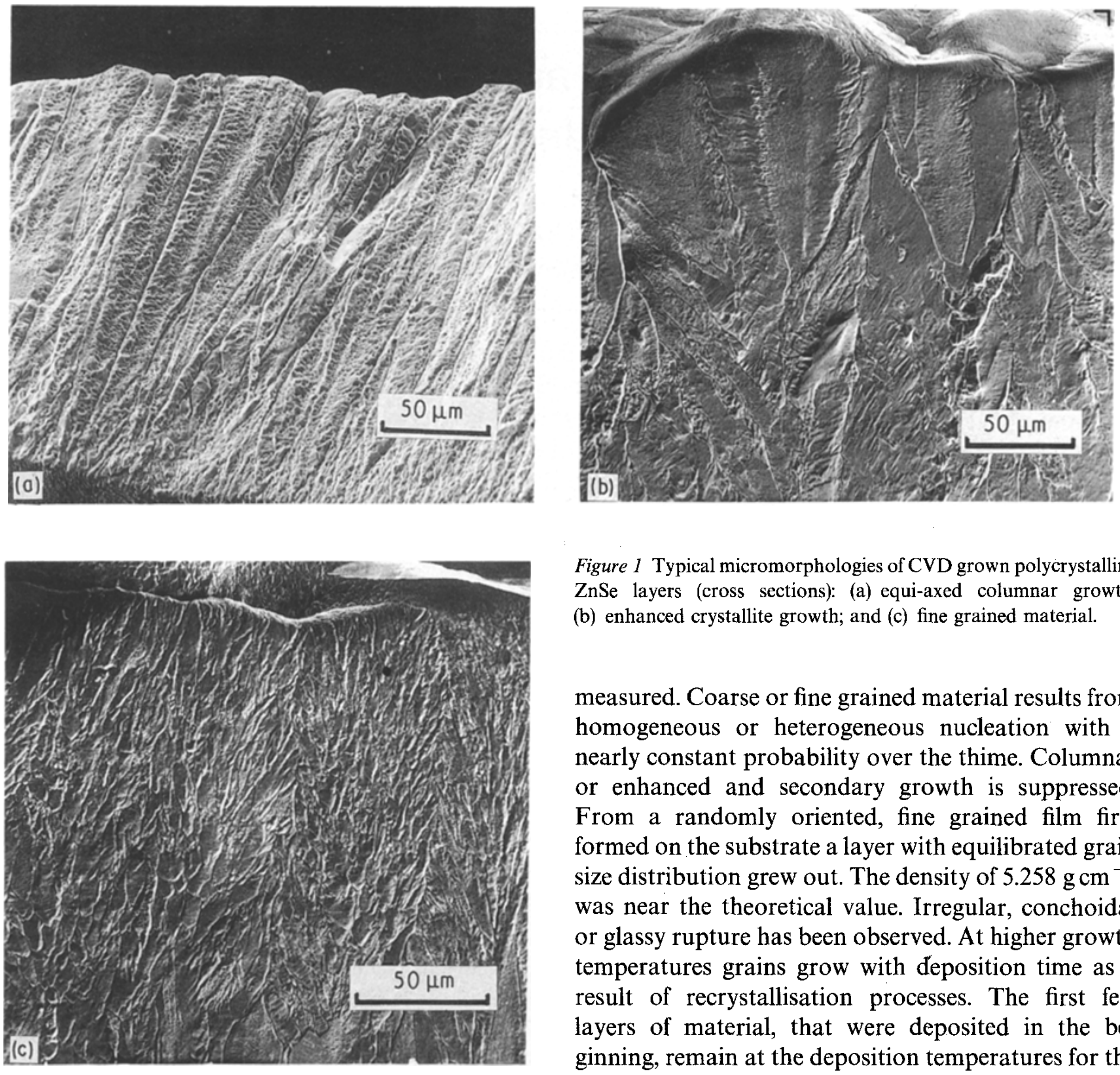

Figure 1 Typical micromorphologies of CVD grown polycrystalline ZnSe layers (cross sections): (a) equi-axed columnar growth; (b) enhanced crystallite growth; and (c) fine grained material.

grain growth, resulting in high surface roughness (Fig. 1b); and (c) coarse or fine grained material with homogeneous grain size distributions (Fig. 1c).

Intermediate between these types a series of different microstructures was produced.

Layers comprising equi-axed columnar growth exhibited texture formation with preferred [1 1 1] orientation. The growth rate was approximately constant over the deposition time with values $\geqslant 50\ \mu m\, h^{-1}$. In most cases, at early stages of growth a randomly fine grained layer was deposited with a thickness of a few micrometres. Enhanced grain growth with deposition time was observed when the nucleation rate decreases during the CVD process, modelling the progressive exhaustion of a finite number of nucleation sites.

Preferred nucleation generally occurs at tips of growing crystallites and at intercrystalline boundaries. With increasing layer thickness texture formation and high surface roughness were particularly favoured. The faces of crystallites became faceted. Smooth cleavage planes have been observed. Grown-in boundary porosity was caused by relatively large crystallites ($> 100\ \mu m^3$) as a result of enhanced grain growth. In relation to the theoretical density of $5.266\ g\, cm^{-3}$ values between 5.230 and $5.248\ g\, cm^{-3}$ have been measured. Coarse or fine grained material results from homogeneous or heterogeneous nucleation with a nearly constant probability over the thime. Columnar or enhanced and secondary growth is suppressed. From a randomly oriented, fine grained film first formed on the substrate a layer with equilibrated grain size distribution grew out. The density of $5.258\ g\, cm^{-3}$ was near the theoretical value. Irregular, conchoidal or glassy rupture has been observed. At higher growth temperatures grains grow with deposition time as a result of recrystallisation processes. The first few layers of material, that were deposited in the beginning, remain at the deposition temperatures for the long-time CVD process, while a few of the grains outstrip and consume their neighbours (abnormal or secondary grain growth). This behaviour is typical for the H_2Se method [6].

3.2. Nucleation and growth mechanisms

The evolution of different micromorphologies of polycrystalline layers depends strongly on the conditions of nucleation and growth. Fig. 3 is a schematic diagram of the morphological dependence on reactor

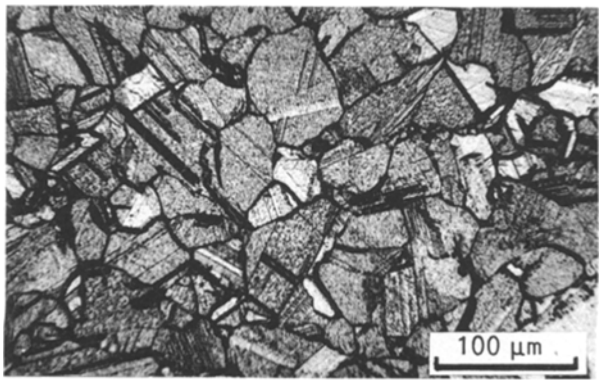

Figure 2 Surface morphology of a CVD grown polycrystalline ZnSe layer after grain boundary etching; fine grained material.

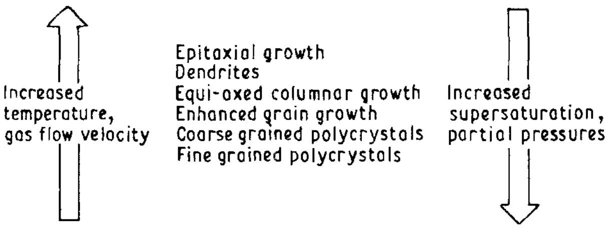

Figure 3 The effect of growth conditions on micromorphology of CVD grown ZnSe.

conditions for materials prepared by the Se and H_2Se methods. For both processes, the experimental values are related to different parameter ranges. In the preparation of ZnSe by the Se process enhanced grain growth, resulting in high surface roughness, was accomplished at $T_{\text{growth}} \geqslant 600\,^\circ\text{C}$ and $\sigma \leqslant 10^7$.

$$\sigma = (p_{\text{Zn}})(p_{\text{Se}_2})^{1/2}/(p_{\text{Zn(eq)}}(p_{\text{Se}_2\text{(eq)}})^{1/2}$$

denotes the supersaturation ratio with experimental and equilibrium partial pressures.

At relatively low temperatures ($T \leqslant 600\,^\circ\text{C}$), Se excess and higher supersaturations, brought about by higher p_{Zn} and $\Sigma p_{\text{Se}} = p_{\text{H}_2\text{Se}} + 2p_{\text{Se}_2}$ at the substrate surface, relatively fine grained material of random orientation can be produced. With decreasing temperature the grain structure became finer.

Sufficiently high values of reactant concentrations (p_{Zn}, $\Sigma p_{\text{Se}} > 5 \times 10^{-4}$ atm) caused powder formation in the gas phase. Columnar growth and texture formation has been favoured by high gas flow rates.

The rate constant of the relevant reaction in the case of the Se method

$$\text{Zn(g)} + \tfrac{1}{2}\text{Se}_2\text{(g)} \rightarrow \text{ZnSe(s)}$$

was estimated to be 2 to 3 orders of magnitude greater than the corresponding one of the reaction

$$\text{Zn(g)} + \text{H}_2\text{Se(g)} \rightarrow \text{ZnSe(s)} + \text{H}_2\text{(g)}.$$

Indicative of this is the fact that equal growth rates in the H_2Se method compared to the Se method were brought about only by increased reactant concentrations at $\sigma > 10^{13}$. The estimation was based on experimental growth rate characteristics related to the given reactor parameters. Non-equilibrium conditions were assumed between the Se source and the gas stream with regard to the H_2Se formation. At higher flow velocities the gas was not in contact with the charge bed long enough to reach thermodynamic equilibrium. Therefore, the experimental transport rates were clearly lower than the theoretical ones (cf. [7] and [8]).

The growth rate dependence on process parameters for experiments with $T > 600\,^\circ\text{C}$ indicates that the layer growth is mainly diffusion-limited. The growth rate was found: (i) to be directly proportional to the square root of the flow velocity ($u^{1/2}$); (ii) to increase with the H_2 content as a result of higher diffusion coefficients (D); (iii) to alter only slightly with T; and (iv) to decrease with increasing Σp.

The calculated Sherwood numbers are seen to be near the critical value 1 ($Sh < 1 \rightarrow$ surface-actived process; $Sh > 1 \rightarrow$ diffusion-limited process).

A system pressure up to 80 torr could be used due to the retardation effect with regard to powder formation in the system Zn–H_2Se–Ar. Comparatively, for the Se method and concentration dependent growth rates $> 50\ \mu\text{m h}^{-1}$ a pressure of about 20 torr seems to be upper limit, which results automatically in lower partial pressures of reactants.

The results of experiments on growth by the Se process indicate that prerequisites for increasing the kinetic control are the following parameters: $T \leqslant 600\,^\circ\text{C}$ (reduced k): $\Sigma p \leqslant 20$ torr (higher D, lower boundary layer thickness); sufficiently high gas flow velocity and H_2 content (higher D); and relatively high supersaturation ratios ($\gtrsim 10^7$).

For the H_2Se method, conditional upon lower k values kinetic limited growth has been found up to $T \approx 750\,^\circ\text{C}$ and $\Sigma p \approx 80$ torr [1–4].

Homogeneous grain size distributions can be successfully prepared under kinetically controlled conditions and continuous nucleation. In this case the nucleation rate remains constant throughout the CVD process. The deposition is induced by heterogeneous or homogeneous nucleation. Heterogeneous nucleation is particularly favoured for systems with relatively low rate constants under conditions of lower supersaturation. Stable nuclei form at preferred sites on the substrate surface, and at a later stage at the surface of the growing ZnSe layer. In contrast, depending on the system pressure at sufficiently high combined values of supersaturation and temperature homogeneous nucleation in the gas phase is favoured. The critical σ- and T-values have been found to

TABLE I Morphology and growth mechanisms of polycrystalline ZnSe layers

Morphology	Nucleation, growth	Growth mechanism	Crystal structure
Equi-axed columnar	Simultaneous nucleation, followed by crystallite growth	Diffusion control (boundary layer resistance)	Strong [1 1 1] texture
Enhanced, abnormal grain growth	Continuous nucleation decreasing with time, growth to impingement and secondary growth	Diffusion control (boundary layer resistance)	Strong [1 1 1] texture or randomly oriented with preferred [1 1 1] direction
Coarse or fine grained material	Continuous nucleation (homogeneous or heterogeneous nucleation), growth to impingement	Kinetic control	Randomly oriented, often with several preferred directions

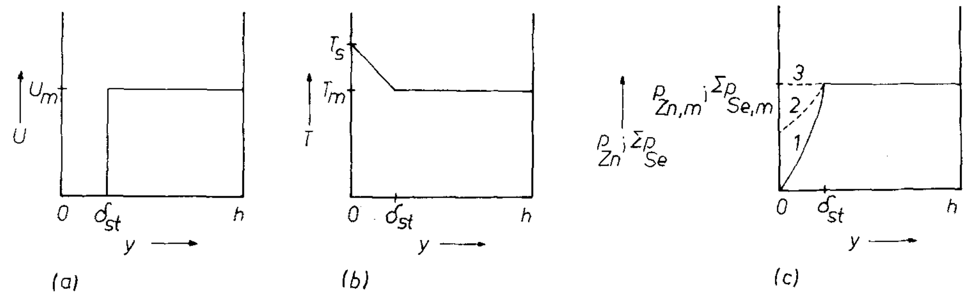

Figure 4 Boundary layer model. Change perpendicular to the substrate surface (*O*) in *y*-direction: (a) of the forced convection velocity, *u*: (b) of the gas temperature, *T*; (c) for reactant partial pressures, *p*, under diffusion controlled conditions (1), under kinetically controlled conditions without (2a) and with (2b) thermal diffusion.

decrease with increasing pressure. Further prerequisites to avoid homogeneous reaction with powder formation are relatively low H_2 concentrations, and definite high—but not too high—reactant concentrations. High surface qualities of substrates suppress heterogeneous nucleation. For CVD growth of polycrystalline, fine or coarse grained ZnSe it can be inferred therefore that homogeneous nucleation is likely dominant. Enhanced grain growth was observed under diffusion-limited deposition with simultaneous nucleation (spontaneous nucleation before any significant growth of crystallites occurs) or with transitions between simultaneous and continuous nucleation (nucleation rate decreases with time) [9].

Studies of boundary layer effects can help in understanding the mechanisms of diffusion controlled layer growth (Fig. 4). Mass transport is assumed to take place by diffusion over a boundary layer and by transfer at the interface. This layer coincides with the thermal and momentum boundary layers [10]. Between the bulk gas and the substrate relatively large concentration and thermal gradients are present. The concentration decreases towards the growing surface. For our experimental conditions the boundary layer thickness was found to fluctuate between 1.0 and 1.5 cm.

For typical CVD conditions values of p_{Zn} and Σp_{Se} in the gas phase were calculated in the range 10^{-5} to 10^{-3} atm. Moreover, the gas phase is slightly cooler than the substrate owing to the high gas velocities and large entrance length in LPCVD reactors. The supersaturation rises with the distance away off the substrate as a result of increasing reactant concentrations and decreasing temperature over the boundary layer thickness. Analogous temperature dependent concentration profiles were caused by the exothermic character of the dominant chemical reactions in the Se and H_2Se CVD systems. From Fig. 5 it can be seen that the effect is larger for the system Zn–Se–H_2–Ar than in the H_2Se process. Correspondingly there is a tendency to morphological instabilities with enhanced grain growth and texture formation. Protrusions and crystallites will show enhanced growth.

A first-order perturbation stability analysis in which the coupling between heat and mass transfer is taken into account has been presented by van den Brekel [10].

The stability function is composed of three terms:

1. a positive term, which represents the mass-gradient effect favouring growth of the perturbation;
2. a negative term, which represents the capillarity effect favouring decay of perturbations, and
3. a term with the critical parameter *l* which represents the effect of heat transport.

$$l = c_{eq}^{\infty}\frac{\Delta H}{RT_0^2} + (c_0 - c_{eq}^{\infty})\frac{\Delta E}{RT_0^2} \qquad (1)$$

l consists of an equilibrium term, containing the reaction enthalpy ΔH and a kinetic term, containing the activation energy ΔE of the process. The van't Hoff constants express the temperature dependence of the chemical equilibrium and of the reaction rate, respectively.

The stability analysis indicates morphological instabilities for CVD growth with exothermic ZnSe formation on hot substrates with respect to the gas phase under diffusion-limited conditions.

Crystallites and protrusions show enhanced growth, because the supersaturation at the cooler peaks is greater than at the hotter valleys of the layer.

The second term of equation (1) only contributes to *l* when the deposition process is kinetically controlled. For the exothermic ZnSe formation the sign of *l* depends on the supersaturation $(c_0 - c_{eq}^{\infty})$. At sufficiently high supersaturations *l* becomes positive. In

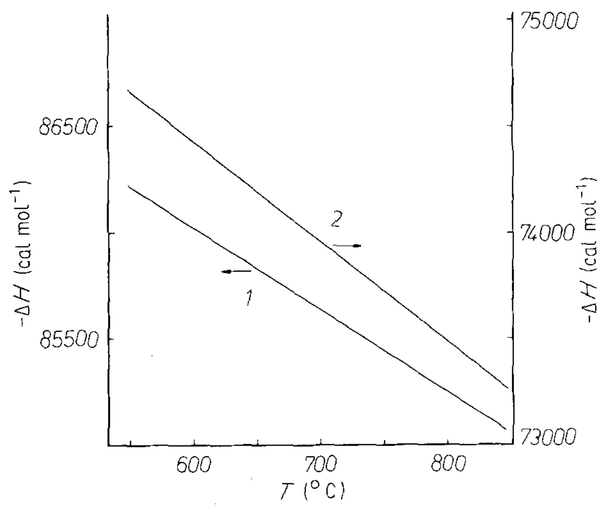

Figure 5 ΔH as a function of temperature. (1) $Zn_{(g)} + Se_{2(g)} \rightarrow ZnSe_{(s)}$; (2) $Zn_{(g)} + H_2Se_{(g)} \rightarrow ZnSe_{(s)} + H_2(g)$.

this case, morphological stability conditions can be satisfied at decreased interface temperature T_0 (reduced k), reduced concentration and thermal gradient effects. This is in agreement with our experimental results. Growth of coarse or fine grained layers has been observed as a result of continuous nucleation.

From our experiments it is apparent that deviations from stoichiometry in the form of Zn excess have the effect of favouring crystallite growth. It is reasonable to expect a modification of nucleation and growth mechanisms under conditions of non-stoichiometry.

For Zn excess it is possible that this effect is simply associated with the activated chemisorption of Se_2 molecules, depending upon the dissociation energy. On the other side, relatively fine grained material is favoured in kinetic activated CVD processes with Se excess (Se:Zn $\leqslant 2$). Therefore, precise control of stoichimetric conditions by the partial pressure of reactants is needed for morphological stability. Moreover, layers of material grown by processes with kinetic control, particularly by the H_2Se method, show decreasing grain sizes from the substrate side to the deposition side. Further grain growth occurs by the abnormal or secondary growth. A few of the grains strip out and consume their neighbours by recrystallisation. The material, that was deposited in the beginning, remain at the deposition temperature for the whole experimental time. In the case of ZnSe, after

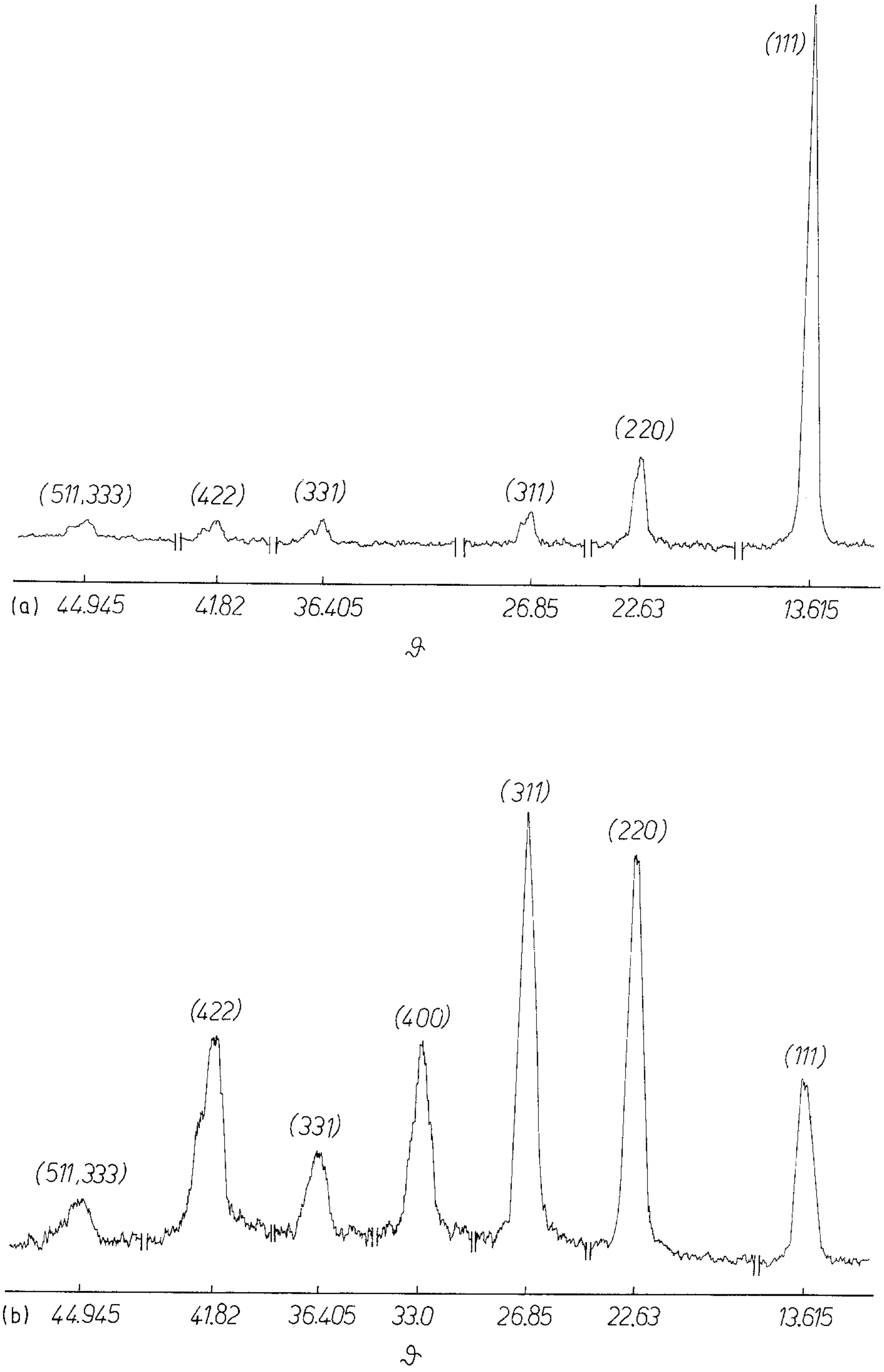

Figure 6 X-ray diffraction patterns (Cu $K_{\alpha 1}$) from CVD grown ZnSe layers: (a) material with enhanced secondary crystallite growth; and (b) fine grained polycrystalline layer.

850 h of deposition, grains as large as 1 cm were obtained [6]. Factors which contribute to this behaviour are:

1. The abnormal growth might result for a particular grain if it is much larger than other grains in the microstructure.
2. The abnormal grain is surrounded by grain boundaries which have a higher mobility than the other grain boundaries in the structure.
3. A driving force exists in addition to that provided by the grain boundary energy, which drives the boundaries surrounding the abnormal grain outward.

4. X-ray diffraction

The crystal structure of polycrystalline ZnSe layers with different morphological features has been studied using X-ray diffractometry (Fig. 6). The orientation factor O_{hkl} was calculated from

$$O_{hkl} = \frac{I_{hkl}}{I_{ohkl}} \Big/ \Sigma \frac{I_{hkl}}{I_{ohkl}}$$

where I_{hkl} and I_{ohkl} are the measured and theoretical (ASTM standard) intensities of diffraction peaks. The intensity of the (1 1 1) reflections was appointed to 100%, respectively.

Layers comprising columnar grains or enhanced grain growth are strongly oriented in [1 1 1] direction (Fig. 6a).

On the other hand the diffraction patterns from coarse or fine grained, irregular microstructures closely resembles that of a powder sample with several preferential growth directions, which belong to the same crystallographic zone (Figs 6b and 7).

The orientation factors for different reflections vary in the range of 20–80%. Moreover, the available maximum percentages were found to decrease in the sequence of rising angular deviations of growth directions from [1 1 1] (*cf.* Table II).

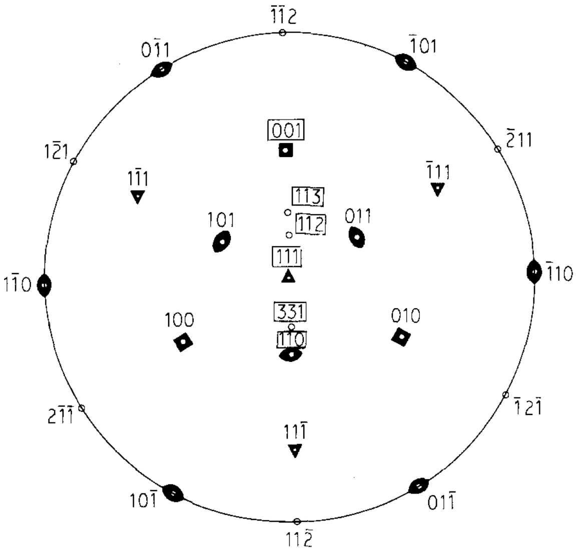

Figure 7 Stereographic projection of preferred growth directions (□).

TABLE II Preferred growth directions of CVD grown polycrystalline ZnSe layers

Preferred growth direction	Angular deviation with regard to [1 1 1]	Observed maximum percentage of orientation
[1 1 1]	—	100%
[2 1 1]	19.47°	80%
[3 3 1]	21.95°	77.3%
[3 1 1]	29.50°	35%
[1 1 0]	35.27°	23%
[1 0 0]	54.73°	22.5%

Studies on polycrystalline ZnSe layers have shown percentage fluctuations of structural orientations for various samples or ranges of the same sample. Particularly, the reflections (1 1 1), (4 2 2), (3 3 1) are favoured. All ZnSe layers exhibit the zinc blend structure.

At early stages of growth, there was a strong [1 1 1] layer texture. When a thickness of 5 to 10 μm has been reached, a randomly oriented layer is formed. Micrographs of cross section views displayed transitions between fine columnar and fine grained microstructures.

These different growth morphologies were apparently caused in the initial phase by the influence of vitreous carbon substrates, and at a later stage, by nucleation on the growing polycrystalline ZnSe layer.

5. Conclusions

Polycrystalline ZnSe layers were grown by low-pressure CVD processes. Typical layer morphologies have been observed: 1. equi-axed columnar growth; 2. enhanced grain growth; and 3. coarse or fine grained material with homogeneous grain size distributions.

Morphological stability effects have been studied in the CVD systems Zn–Se–H_2–Ar and Zn–H_2Se–Ar. The formation of different micromorphologies was found to be dependent on growth and nucleation mechanisms.

Coarse or fine grained material (case 3) has been prepared under kinetically controlled growth conditions with continuous nucleation and Se excess. In this case, morphological stability is realized.

X-ray diffraction patterns from such layers closely resemble that of a powder sample with several preferential growth directions. Particularly, the reflections (1 1 1), (4 2 2), (3 3 1) are favoured.

Layers comprising columnar grains (case 1) or enhanced grain growth (case 2) exhibit strong [1 1 1] texture. In these cases layer growth was found to be limited by diffusion processes with boundary layer resistance resulting in morphological instability effects. For long-time CVD processes at relatively high temperatures it is found that there was abnormal or secondary grain growth.

Studies on microstructural evolution in polycrystalline layers are being undertaken with a view to preparing technological material with definite grain size distributions.

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Received 24 May 1990
and accepted 31 January 1991