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Monolithic material fabrication by chemical vapour deposition

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The subatmospheric pressure chemical vapour deposition (CVD) process has been used to fabricate theoretically dense, highly pure, void free and large area infrared-optical and ceramic materials such as ZnS, ZnSe, CdS, CdZnTe, Si and SiC. In this paper, an overview of a large scale CVD process is presented emphasizing the important technical and engineering issues such as control of material properties, injector heating and its effect on growth, selection of an appropriate mandrel material, grain growth, material bowing, nodular growth, and storage, transport and scrubbing of a large quantity of hazardous chemicals. Further, the flow pattern in our CVD reactors is described and its importance in achieving good control over thickness and composition uniformity over large areas is discussed.

1. Introduction

Chemical vapour deposition (CVD) offers a proven method to produce theoretically dense crystalline materials for a variety of applications [1–34]. The CVD process has been used to produce metal films (tungsten, aluminium, molybdenum, gold, copper, platinum) to provide protective coatings [1–5]; ceramic materials (Al_2O_3, TiC, SiC, B_4C, TiB_2, HfC, HfN) used for hard or diffusion barrier coatings [6–11]; semiconductors (GaAs, GaP, InP, PbS, Si) with doping necessary to give the desired properties [12–16], refractory oxides (ZrO_2) used for thermal barrier coatings [6, 17]; films (BN, $MoSi_2$, SiC, B_4C) for protection against corrosion [18–20]; powders (Si_3N_4, SiC) used to fabricate complicated shaped parts via sintering and hot pressing [1]; materials (Si, GaAs, HgCdTe, CdZnTe) for solid state and energy conversion devices [21–24]; fibres (B, B_4C, SiC) used to fabricate composite materials [24]; infrared optical materials (ZnSe, ZnS, CdS, CdTe) [25–29] and monolithic ceramic materials (Si_3N_4, SiC, Si) [30–34]. Essentially, four different types of products have been made via CVD. These are fibres, powders, thin film coatings and monolithic materials. While considerable attention has been given to the CVD of fibres, powders and thin film coatings in the past several years, less attention has been directed towards identification and developing an understanding of important issues (described below) involved in the manufacturing of monolithic materials via CVD.

Early research into the fabrication of bulk materials via CVD led to the development of pyrolytic graphite, boron nitride and high purity polycrystalline silicon. The former two materials were developed for the missile nose cone, while bulk silicon was developed as a high purity feedstock for the semiconductor industry. The CVD process was later extended to other bulk materials such as ZnS, ZnSe, CdS, CdTe, SiC, Si_3N_4, B_4C, GaAs and tungsten. While a potential exists to fabricate many more bulk materials via CVD, the relatively high cost for a CVD produced material compared to other techniques precludes its widespread use. The CVD method is attractive when a requirement exists for high purity, near net shape and large area parts which cannot be readily obtained from other technologies.

A large scale CVD process presents unique problems and issues which are quite different from those of the thin film deposition. The aim of this paper is to identify and bring forth these issues to stimulate further research and discussion. In Section 2, techniques to control the properties of CVD materials are discussed. This control can be achieved either inside a CVD reactor by varying certain CVD process parameters or by performing a post deposition treatment. An overview of chemical vapour deposition of several monolithic materials such as Si, SiC, ZnS, ZnSe, CdS and CdZnTe is presented in Section 3. In Sections 4 and 5, important technical and engineering issues relevant for large scale CVD process are discussed. The flow pattern inside a CVD reactor is described in Section 6. Finally, the summary and conclusions are presented in Section 7.

2. Control of material properties

Properties of CVD materials can be controlled by adjusting process parameters such as pressure, reactant concentrations, flow rates, deposition geometry, gas temperature, substrate material and temperature. The most important parameter which controls the properties of the deposited material in a CVD reactor is the deposition temperature. At sufficiently low temperatures, the deposition is kinetically limited and shows a strong dependence on the temperature (Fig. 1). The rate determining step in this regime may be either the nucleation or the decomposition of the adsorbed reactant species on the surface. Relatively uniform deposition profiles are obtained in the kinetically limited

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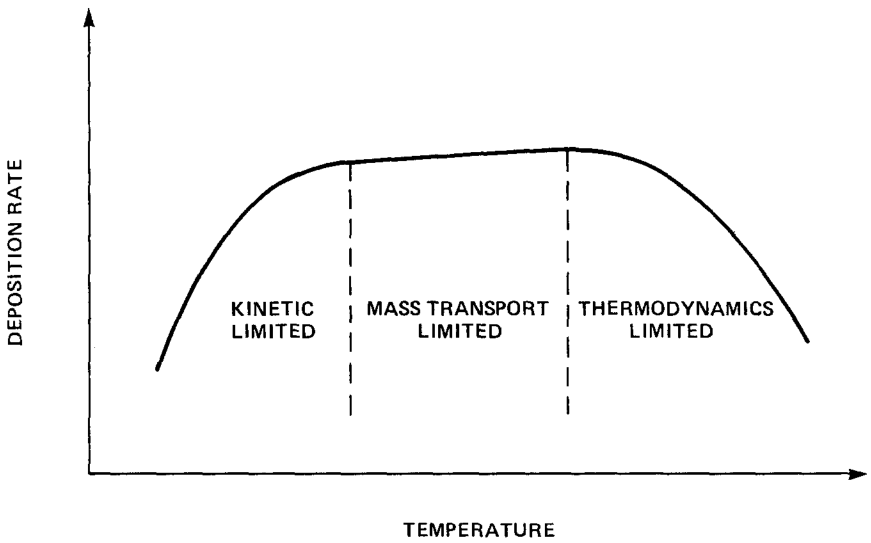

Figure 1 Different reaction regimes in a CVD process involving an exothermic reaction to produce crystalline materials.

regime because the depletion of reagents in the direction of flow does not affect the deposition rate. For this reason, many CVD reactors used to produce electronic devices are operated in the kinetically limited regime. However, when high growth rates are more important than thickness uniformity, the CVD reactor is operated in the mass transport limited regime, where the rate determining step is now the diffusion or transport of the reactant gases to the substrate surface. It is because the transport phenomenon is relatively independent of temperature that the deposition rate does not change much as the substrate temperature is varied. Since the deposition profiles now depend on the flow pattern of the reactant gases, it is important to understand and control the flow to obtain fairly uniform profiles over large deposition areas. Monolithic materials are usually produced in a CVD reactor in the mass transport limited regime.

At high temperatures the net reaction rate (forward rate − reverse rate) decreases as a function of temperature for an exothermic reaction, and the thermodynamically limited regime is obtained (Fig. 1). This occurs because the free energy of the reaction, ΔG, increases with temperature, (i.e., becomes less negative) reducing the driving force of the reaction. Epitaxial or single crystal growth is usually performed in the thermodynamically limited regime. However, for an endothermic reaction, at high temperatures, the net reaction rate increases because the free energy of the reaction, ΔG, decreases with temperature (i.e., becomes more negative). If ΔG becomes very negative, a gas phase homogeneous reaction occurs producing a powder deposit instead of a crystalline material. Finally, at very high temperatures, ΔG, becomes positive for an exothermic reaction and instead of deposition, etching occurs.

The structure of the deposited material can be controlled by varying the substrate temperature and reactant gas concentrations [1]. In general, for an exothermic reaction, as the temperature increases, the structure of the deposited material changes from a gas phase nucleation powder, to fine grained polycrystals, to dendrites, to epitaxial growth. The dependence on reactant gas concentration is the opposite, i.e., as the gas concentration increases, the structure changes from epitaxial growth to gas phase nucleation powder at very high reactant gas concentrations. For bulk CVD materials, a polycrystalline structure is generally preferred because good material uniformity is obtained with this structure at a high deposition rate. The CVD polycrystalline structure consists of columnar grains possessing a high degree of preferred orientation. This preferred orientation develops even though the substrate surface is randomly oriented. Preferentially oriented grains grow at a more rapid rate at the expense of less favourably oriented grains [1].

Some control of mechanical properties can be achieved by adjusting the CVD process parameters. Since the hardness and the flexural strength of a polycrystalline material are inversely related to the average grain size, the goal is to produce fine-grained materials via CVD. In general, as the deposition temperature decreases or the growth rate increases, the grain size decreases. Thus, the fine grained CVD materials are produced by maximizing the parameter, J/DN_0 where J is the incoming gas phase flux (atoms $\text{cm}^{-2}\,\text{sec}^{-1}$), D is the surface diffusion coefficient of the adsorbed atoms ($\text{cm}^{-2}\,\text{sec}^{-1}$) and N_0 is the number of surface sites per cm^2 [31, 36].

Properties of CVD materials can also be controlled by incorporating appropriate dopants or a second phase in the material. Dopants or a second phase are usually incorporated by adding an appropriate amount of volatile compound to the carrier gas stream along with other reagents. Since the deposition occurs on an atomic scale, layer by layer, dopants or a second phase are dispersed uniformly throughout the volume of the material. For instance, manganese doped layers of ZnS and ZnSe have been produced for applications as optoelectronic devices [37]. Further, doping of ZnS or ZnSe with excess zinc, indium or aluminium has been proposed as a technique to obtain conducting layers of ZnS or ZnSe [38–39]. When a second dispersed phase is incorporated into CVD materials, the resulting composite material may or may not possess properties which fall in between the properties of the two phases. Examples of the former include alloys ZnSSe [40] and CdZnTe [22, 35] while those of the latter include composites SiC–TiSi_2 [41] and Si_3N_4–TiN [42–43]. Properties of CVD SiC have also been varied by incorporating different dispersed phases such as $TiSi_2$, TiC, Si_3N_4, B_4C and carbon.

Often it becomes necessary to perform a post-deposition treatment on CVD materials to obtain the desired properties. For instance, the standard CVD ZnS has a reddish-orange milky colour and considerable scattering in the near infrared. The poor short-wavelength transmission of CVD ZnS is believed to be due to a combination of zinc and anion vacancies at normal lattice sites [44]. Subjecting this material to a high temperature and pressure post-deposition process produces "water clear" ZnS with improved optical properties, particularly in the visible. This treatment also eliminates the 6.3 μm ZnS absorption band, although the grain size of the material increases, thereby decreasing its flexural strength. In a similar manner, Nanba *et al.* [45] have improved properties of their CVD ZnSe.

3. Monolithic materials fabrication via CVD

Five bulk materials ZnS, ZnSe, CdS, Si and SiC were produced using the following reactions [28]

$$H_2S(g) + Zn(g) \rightarrow ZnS(s) + H_2(g) \qquad (1)$$

$$\Delta G = 82.1T - 5.9T \ln T - 0.62 \times 10^{-3}T^2 - 76\,400\,\text{cal mol}^{-1}$$

$$H_2Se(g) + Zn(g) \rightarrow ZnSe(s) + H_2(g) \qquad (2)$$

$$\Delta G = 86.4T - 5.95T \ln T - 0.69 \times 10^{-3}T^2 - 85\,800\,\text{cal mol}^{-1}$$

$$H_2S(g) + Cd(g) \rightarrow CdS(s) + H_2(g) \qquad (3)$$

$$\Delta G = 85.2T - 6.64T \ln T - 0.45 \times 10^{-3}T^2 - 50\,000\,\text{cal mol}^{-1}$$

$$SiHCl_3(g) + H_2(g) \rightarrow Si(s) + 3HCl(g) \qquad (4)$$

$$CH_3SiCl_3(g) \xrightarrow{H_2} SiC(s) + 3HCl(g) \qquad (5)$$

where (g) and (s) refer to gas and solid respectively, T is the temperature in Kelvin and ΔG is the Gibb's free energy for the reaction. The CVD process conditions for these materials are listed in Table I. It can be seen that the deposition temperature, reactor pressure and the average flow velocity vary considerably from material to material but the deposition rate remains relatively constant. To obtain good quality CVD materials in a cost-effective manner, it is important to maintain the growth rate in a narrow range. If the growth rate is too small, the time to deposit a given thickness of material may become quite large, thereby increasing the cost. On the other hand, if the growth rate is too large, defects such as voids, inclusions and bands may be incorporated in the material, thereby degrading its optical or mechanical performance.

Table I also lists ΔG values for exothermic reactions [1-3] at the corresponding deposition temperatures. These calculations do not include the effect of reactant partial pressures and molar ratio. Although it is difficult to obtain quantitative information about a reaction from its thermodynamic data, qualitative trends can still be inferred. For instance, the deposition temperature for ZnSe is larger and the reactant partial pressures smaller than the corresponding values for ZnS because the ΔG value for ZnSe is more negative. The deposition data of CdS also show the same trends. Good quality bulk material has been produced in our reactors when ΔG for the reaction is negative and that its magnitude is less than 30 kcal mol^{-1}. This is true for ZnSe, ZnS and CdS because when the respective reactor pressure and reactant molar ratios for reactions 1-3 are taken into account, the magnitude of ΔG as given in Table I falls below 30 kcal mol^{-1} [25]. Production of pyrolytic BN by the reaction of BCl_3 and NH_3 is another example where the deposition temperature is kept high ($\sim 1850°$C) and the reactant's partial pressures quite low to bring ΔG to an acceptable value for obtaining good quality pyrolytic BN.

Fig. 2 shows a schematic view of a CVD furnace which has been used to produce monolithic materials. For fabricating ZnS, ZnSe and CdS, a graphite retort is used to contain the metal. A graphite mandrel box is placed on top of this retort. The deposition occurs on the interior surfaces (mandrels) of this box. A carrier gas is used to transport metal vapours from the heated retort into the mandrel area. The H_2S or H_2Se gases along with argon are introduced into the mandrel box through a central injector. While fabricating silicon or SiC, a graphite retort is not required and a mixture of $SiHCl_3$ or CH_3SiCl_3 and H_2 is transported through a central injector directly into the mandrel box.

A large scale CVD process is usually performed at subatmospheric pressures (as opposed to atmospheric pressures) because the emphasis is on material properties. Other parameters such as thickness and composition uniformity are less important if their effect on material properties is minimal. For elements such as silicon and binary compounds such as ZnS, ZnSe, CdS, stoichiometric deposits can be obtained over a wide range of reagents molar ratio. For instance, stoichiometric ZnS has been produced in a large CVD

TABLE I CVD process parameters used to fabricate polycrystalline ZnS, ZnSe, CdS, SiC and silicon. Deposition area = 1000 cm^2.

S. No.	Material produced	Flow rates (Slpm)			Deposition temperature (°C)	Reactor pressure (torr)	Deposition rate (μm min^{-1})	ΔG for Reactions [1-5] kcal mol^{-1}
		H_2S/H_2Se/ $SiHCl_3$/ CH_3SiCl_3	Zn(v) or Cd(v) or H_2	Ar				
1	ZnSe	0.2-0.4	0.2-0.4	2	730-825	20-40	1.0	−40.3 (750° C)
2	ZnS	0.2-0.4	0.2-0.7	2	630-730	30-60	1.2	−37.3 (680° C)
3	CdS	0.2-0.4	0.2-0.4	2	550-650	70-100	1.2	−15.2 (600° C)
4	Si	0.8-1.5	3.0-9.0	2	950-1150	100-400	1.25	−
5	SiC	0.6-1.2	2.0-5.0	2	1250-1400	100-400	1.50	−

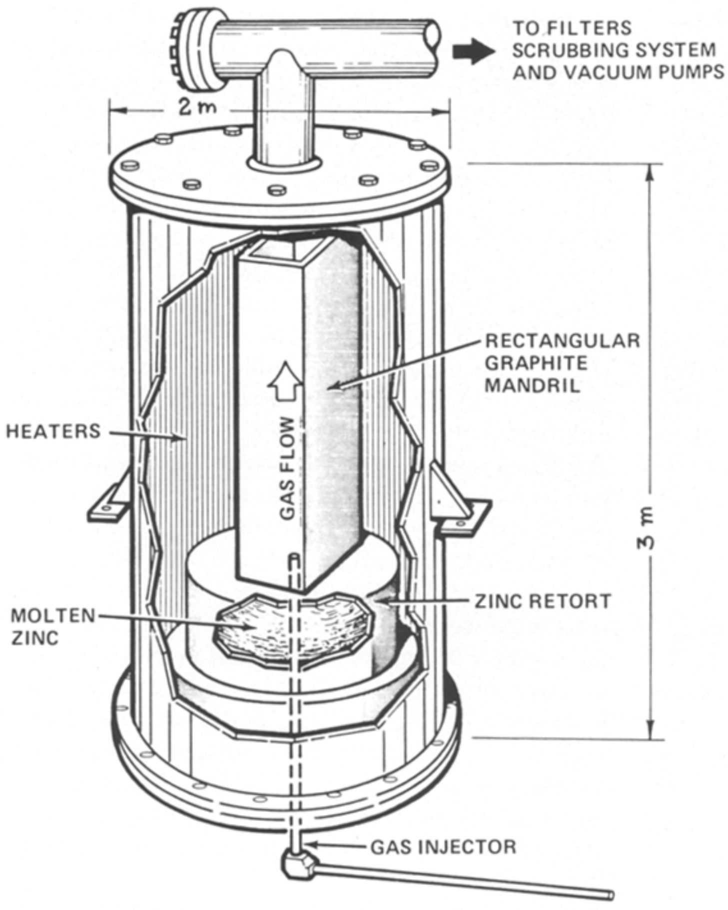

Figure 2 A schematic view of the CVD production furnace used to produce monolithic materials.

reactor when the Zn(g) to H_2S molar ratio varied in the range 0.6 to 1.0. For ternary compounds, such as CdZnTe and ZnSSe, however, a small variation in composition affects the material properties considerably. For such materials, the substrate is usually rotated and kept perpendicular to the flow to obtain good composition control.

4. Technical issues

Production of a good quality material via large scale chemical vapour deposition process requires successful resolution of several issues as follows.

4.1. Selection of a suitable substrate material

A good substrate material should have the following properties: (i) its coefficient of thermal expansion should closely match that of the material to be deposited, (ii) it should be able to withstand high temperature, low pressure and the chemicals present in the CVD environment, (iii) it should not react with the reagents, products and deposited material, (iv) it should be dense enough to prevent diffusion of the deposited material into the substrate, and (v) it should separate readily from the deposited material. This last requirement is in contrast to thin film deposition in which one desires the coating to adhere to the substrate. While several materials, such as silicon, SiC, Si_3N_4, molybdenum, tantallum, platinum, nickel, tungsten, quartz and graphite have been used as substrates, quartz and graphite are particularly attractive because they can be readily separated from the deposited material. For instance, quartz can be etched away by using hydrofluoric acid, while graphite can be burned in air. There are obvious disadvantages to both of these latter approaches. First, the deposited material must be inert to these substrate removal conditions, and second, the substrate is not reusable. This becomes expensive when large area depositions are made. To prevent loss of the substrate after each deposition, mould release coatings made of amorphous carbon and aqueous SiO_2 have been used to coat graphite and quartz respectively. More than ten depositions have been performed using these coatings on the same substrate in a CVD reactor. A comparison of quartz and graphite as substrates shows graphite is more attractive because it is relatively inexpensive, easier to fabricate and available in large pieces. Quartz is useful when replication of complex or fine patterns is performed.

4.2. Injector heating and growth

When thick ($\sim$2.5 cm) depositions are performed, the CVD process must be continuously operated for several weeks. The tip of the injector which introduces the reactants into the deposition chamber becomes quite hot during this time. If the injector is not cooled, deposition occurs inside the tube, thus clogging the injector. When water cooled injectors are used, growth inside the injector tube is inhibited, but considerable growth on and around the injectors is still observed. This growth often leads to flow diversion and impingement on the mandrel walls. This increases the deposition rate at the impingement points, and also affects the flow pattern inside the deposition area which can degrade the material quality. Excessive growth on the injectors has also caused cracking of the deposited material on the mandrel walls. Fig. 3 shows

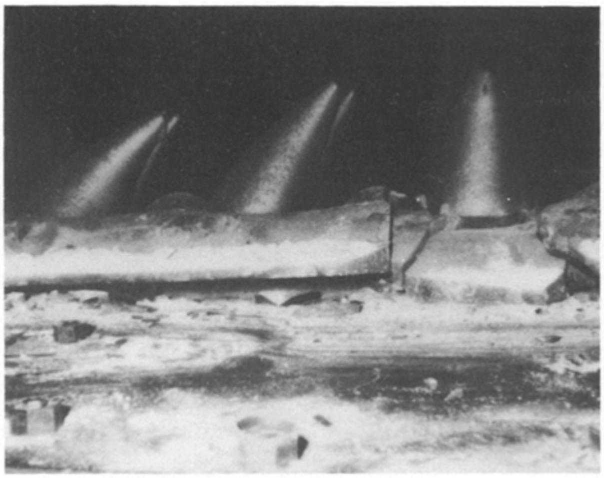

Figure 3 Injector growth after 854 h of ZnSe deposition. The growth cones are around zinc injectors.

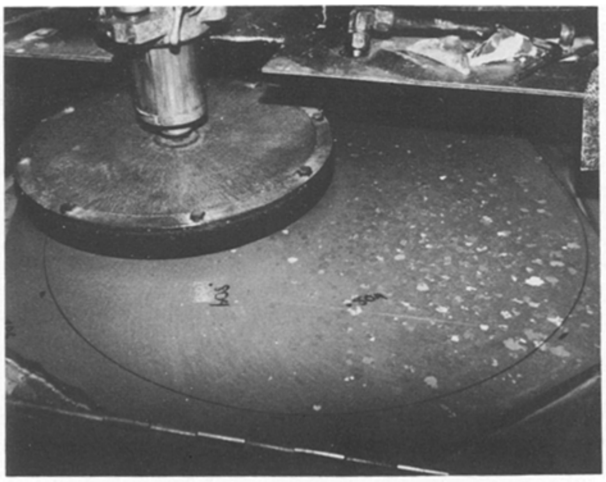

Figure 4 Large grains produced during CVD growth of ZnSe become visible during polishing.

an example of injector growth after 850 h of ZnSe deposition. The growth cones have been formed around the zinc holes, while very little extra growth has occurred around the H_2Se holes. Further, the left two pairs of growth cones have deflected their flow towards the side of the box. Excessive growth around zinc holes as opposed to H_2Se holes occurs because (i) the zinc vapours are at a high temperature and (ii) the flow velocity of zinc vapours is smaller in comparison to that of H_2Se gas.

The success of obtaining thick and good quality material via the CVD process depends upon how well the growth on and around the injectors is controlled. The challenge is to design a CVD reactor in which the growth around the injectors is controlled and does not alter the flow pattern inside the reactor. Much empirical experimentation is required to achieve a successful design.

4.3. Grain growth

As mentioned in Section 2, the morphology of CVD produced bulk materials is polycrystalline. In such materials, grains grow with deposition time. The first few layers of the material, that were deposited in the beginning, remain at the deposition temperature for the remaining duration of the deposition while small grains combine to form large grains. If one examines the cross-section of the material, one finds the grain size decreasing from the substrate side to the deposition side. In the case of ZnSe, after an 850 h of deposition, grains as large as 1 cm were obtained on the mandrel side, although the grain size on the deposition side was only a few micrometres. These large grains distinctly appear during polishing as shown in Fig. 4. Since the flexural strength of a material typically decreases as the grain size increases, the control of the grain size is very important for obtaining a material with good and uniform mechanical properties. Resistance to grain growth is provided by grain boundary voids, bubbles, impurities or second-phase particles. The presence of voids, bubbles and impurities, also degrade the mechanical properties. However, the second-phase particles not only retard grain growth but, in certain cases, also increase the fracture toughness of the material [41].

4.4. Material bowing

In a CVD reactor under certain conditions, such as a low deposition temperature, it has been observed that the deposited material is lifted and separated from the substrate forming in an arch shape. This phenomenon is called "bowing". Often the bowed material contains cracks particularly on that surface which faces the substrate. These cracks usually do not go through the entire thickness of the material but are about 0.5 mm deep.

Bowing has been observed while depositing ZnS, ZnSe and SiC. However, to date, the most pronounced bowing has been observed in ZnS. Fig. 5 shows a bowed CVD ZnS plate which has lifted to a distance of 5 cm from the graphite substrate. Such bowing is observed when the deposition temperature is in the range of 630–670° C.

Several factors have been suggested as possible causes for the bowing in ZnS. These include: (i) Use of a coating on the graphite mandrel prior to starting deposition [31]. (ii) *Growth stresses.* At a low temperature the number of nucleation sites are large. Growth occurs on these nucleation sites in a columnar fashion. Since the growth is polycrystalline, the crystallites grow and expand in all directions. Since the ends of the substrate are constrained, requirements of increased dimension on the deposition surface causes the material to lift from the substrate. Thus, as the deposition thickness increases, the degree of bowing should also increase. In conformity with this mechanism, the bowing has been reduced by first starting the deposition at a high temperature followed by slowly lowering the deposition temperature to the optimum temperature. (iii) Trapping of a process gas such as hydrogen in between the deposited material and the substrate. When zinc vapours react with H_2S gas, hydrogen is produced which could be trapped underneath the deposited material. There is some evidence in favour of this mechanism because the infrared transmission curve of the bowed ZnS material show a more pronounced zinc hydride (ZnH_2) band. (iv) Thermal expansion mismatch between the deposited material and the substrate. (v) Zinc condensation underneath the bowed plate. (vi) Deposition geometry. Thus far, none of these factors have been examined in

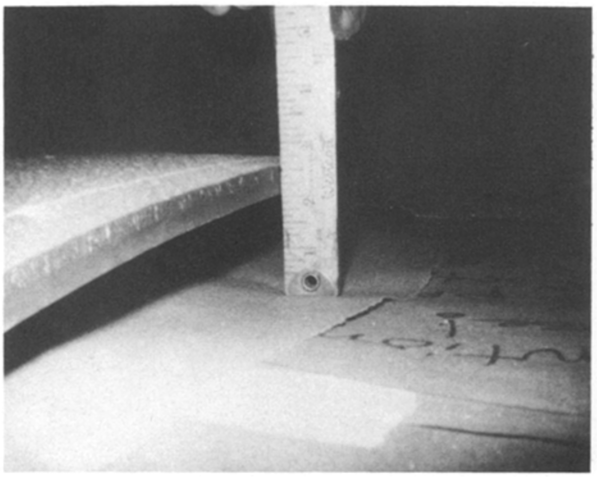

Figure 5 Bowing in CVD ZnS plate.

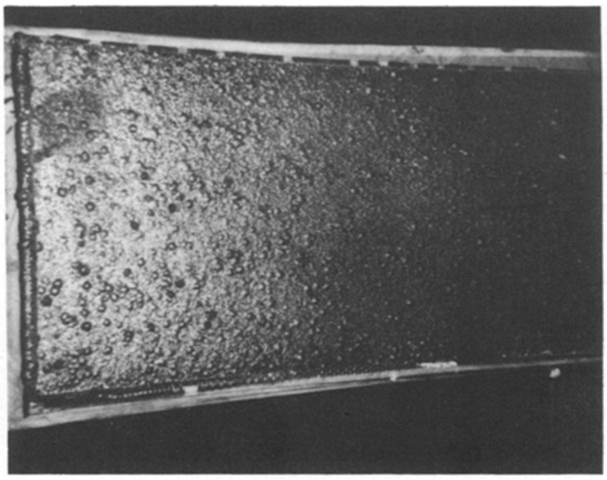

Figure 6 Nodular growth in CVD plate. The plat is 60 cm wide and 120 cm long.

detail to see if they could be related to the occurrence of the bowing phenomenon. Currently, work is underway at CVD Inc. to develop a fundamental understanding of this phenomenon.

4.5. Nodule growth

When thick layers ($\geqslant 1.5$ mm) of ZnS, ZnSe, CdS and silicon are deposited in a CVD reactor, large nodules sticking out of the as-deposited surface of the material have been observed. The nodular growth is not observed when thin layers ($\leqslant 0.5$ mm) of these same materials are deposited. In general, the nodular growth is not desirable, because it (a) inhibits growth of the bulk material, (b) degrades mechanical properties by developing internal stresses in the material, (c) reduces the material yield, and (d) requires additional work during optical fabrication. The nodular growth has been found to be more pronounced in CdS and silicon than in ZnS and ZnSe. Thus far, the largest length of the nodule (~ 10 cm) has been obtained in silicon while the largest diameter (~ 2.5 cm) has been obtained in CdS. Fig. 6 shows the nodular growth on the "as-deposited" surface of a CdS plate. Large nodules scattered all over the surface are clearly visible.

The nodular growth is believed to occur when there is an appreciable difference in growth rates of different crystallographic planes. For instance, if the growth rate of a particular crystallographic plane is much larger than that of the other planes, more material will grow in the direction of that plane leading eventually to the formation of a nodule. The nucleation sites for the nodular growth are often impurity inclusions or gas phase particles formed by the homogeneous reaction which are swept to the surface and stick there. Since the particle or the nodule sticks out of the surface, it encounters a higher concentration of reagents in the flow stream which increases its growth rate even further. This may explain why the average growth rate of some nodules is an order of magnitude larger than that of the bulk material.

In cubic materials such as silicon and ZnSe we have been able to control the nodular growth by (i) optimizing the deposition temperature [31], and (ii) pulsing the flows. This latter technique also produces bands in the material. However, if the flows are pulsed at a fast rate, the bands may not degrade the optical or mechanical properties of the material. Deposition temperature optimization has not worked very well with hexagonal (wurtzite) materials such as CdS, Si_3N_4 and α SiC [32] and all these materials exhibit poor mechanical properties due to nodular growth.

5. Engineering issues

Chemical vapour deposition is a slow process and considerable processing time is required to grow monolithic materials of reasonable thickness. Typically, the deposition rate in a CVD reactor is about 1 μm min^{-1}. Therefore, to grow a material 1 cm thick, the CVD process is operated continuously for about 170 h (~ 7 days and 7 nights). If during this time, the process stops due to any unforeseen reasons such as power outage, equipment failure, leakage in the reactor, gas transport or scrubbing systems, restarting the process serves no useful purpose because bands are produced in the material. These bands affect the transmission characteristics of materials such as ZnS and ZnSe and they may also affect the mechanical properties. Consequently, if thick materials are required, the process must be designed to operate continuously (without interruption) for the total duration of deposition. This requires provisions for storage, transport and scrubbing of a large quantity of reagents.

Many reagents used in CVD of ZnS, ZnSe, Si, SiC and CdS are toxic, pyrophoric, corrosive and flammable. These reagents require special handling procedures. For instance, in large scale production of silicon via CVD, thousands of kilograms of $SiHCl_3$ and hydrogen are required. The $SiHCl_3$ is very reactive with air and water while hydrogen is a potentially explosive gas. Elaborate safety procedures are required to handle such materials.

Scrubbing of a large quantity of toxic reagents is another potential problem in a large scale CVD process. In the production of ZnSe, thousands of kilograms of H_2Se are routinely used. The tolerable limit for H_2Se as listed in the safety handbook is about 50 parts per billion (p.p.b.). Therefore, if we assume that the scrubber's efficiency is about 99%, for

$1\,\mathrm{l\,min^{-1}}$ of H_2Se flow, we require 2×10^5 l of diluent gases per minute to bring the toxic level of the exhaust to the tolerable limit. If diluent gases are not used, it must be ensured that a proper dilution of the exhaust is obtained by natural dissipation process in the atmosphere. Other techniques, such as thermal decomposition of toxic gases before they reach the scrubber, have also been used to partially remove them from the exhaust.

A CVD reactor operating at subatmospheric pressures requires a vacuum pump to control the reactor pressure. The use of chlorine-based reactant gases, such as $SiHCl_3$, CH_3SiCl_3, $SiCl_4$, CCl_4, BCl_3 in the processing of ceramic materials creates liquid, gaseous and solid byproducts which must be handled properly for trouble-free operation of a vacuum pump. The exhaust drawn from a CVD reactor may react with the pump oil, corrode the pump components or condense in the pump, thereby increasing the volume of the pump oil and deposit solid particulates which may be abrasive. The hot exhaust also increases the pump oil temperature which affects its viscosity and thus the lubricating properties. Several techniques which minimize corrosion of pump components, prevent pump seizer, ensure trouble free operation of mechanical pumps have been proposed and are discussed in references [30, 47–49].

Monolithic materials have been fabricated using both hot and cold wall reactors. In both types of reactors, the deposit not only occurs on the substrate, but may also occur on the reactor walls. In a hot wall reactor, the deposit on the reactor walls is usually of the same material as on the substrate. However, in a cold wall reactor, the condensation of metal vapours or volatile reagents such as $SiHCl_3$ occurs. Often these deposits on the walls are considerably thicker than those on the substrate. Cleaning of the reactor walls after every deposition is cumbersome and increases the processing time and cost. Therefore, coatings which inhibit deposition on reactor walls and techniques which isolate reactor walls from the reagents have been used in large scale CVD processing.

6. Flow pattern

An understanding of the flow pattern inside a CVD reactor is critical to control the transport of the various reagents to the deposition surface and to develop the scaling laws for the process. Fig. 7(a) shows a simplified model of a typical gas injector geometry used in the fabrication of ZnS, ZnSe and CdS. It consists of a cylindrical deposition box into which are transported a mixture of H_2Se/H_2S and argon through the central injector, and Zn/Cd vapours (carried by the carrier gas, argon) through the ring injector surrounding the central injector. The central injector is cooled with water to ensure that the H_2Se/H_2S gas remains cold and that it does not dissociate before reaching the deposition surface. The cold gas also keeps the average temperature of the gas inside the deposition chamber low, and thus, prevents gas phase nucleation. The flow velocity through the central injector is usually kept much larger than that used in the ring injector. Consequently, the flow through the central injector (the primary flow) largely determines the overall flow pattern. As the primary jet expands, its temperature increases due to both radiative heating from the hot mandrel walls and mixing with the surrounding medium. Thus, an axial temperature gradient develops inside the deposition chamber. Since the walls of the deposition chamber are maintained at a much higher temperature than the gas along the cylindrical axis, radial temperature gradients also exist. These temperature and concentration gradients will tend to develop currents due to natural or free convection. In a horizontal CVD reactor, these currents will be in a plane perpendicular to the axisymmetric flow pattern due to the forced convection. Therefore, both effects can be studied separately and later superimposed to obtain the actual flow pattern in the reactor.

The important parameter which characterizes the flow pattern due to natural convection is the Rayleigh number (R_a) which is defined by [12]

$$R_a = \frac{\alpha g C_p d^3 \Delta T \varrho^2}{\eta K} \qquad (6)$$

where α is the thermal expansion coefficient ($= 1/T$ for an ideal gas), g is the acceleration due to gravity, C_p is the specific heat at constant pressure, ϱ is the density, d is a characteristic distance, ΔT is the temperature difference between the hot and the cold regions, K is the thermal conductivity and η is the viscosity. For ZnSe deposition, the Rayleigh number is less than 10^4. Therefore, due to natural convection, the flow is laminar [12]. Fig. 7(b) shows the cross-section of the deposition chamber and the flow pattern due to natural convection. We see that two flow vortices develop which transport the cool H_2Se gas from the centre to the deposition surface, and simultaneously, remove products of reaction from the deposition surface to the center of the cylindrical box.

The important parameter which characterizes the flow pattern due to forced convection in a confined jet configuration (Fig. 7(a)) is the jet parameter, H, first suggested by Hill, and defined below [50–51].

$$H = \left(\frac{2}{\pi}\right)^{1/2} \frac{Q}{(W/\varrho)^{1/2} D} \qquad (7)$$

where Q is the total flow rate, W is the sum of pressure and momentum integrals at any cross-section, ϱ in the density and D is the diameter of the circular cylinder. For ZnSe, H is of the order of 3×10^{-4} which is quite small. Further, $D/D_i = 49$ and $V_0/V_1 \geqslant 10$, where D_i is the central injector diameter, and V_0 and V_1 are the flow velocities at the exit of the central and the ring injectors, respectively. These flow parameters will result in a flow pattern [50] which is shown in Fig. 7(a). Three flow regimes exist. First, there is a flow developing region, in which the core of the flow has velocity V_0. At the end of Region 1, the turbulence generated on the boundaries penetrates to the axis, and the flow velocity on axis begins to decay as the distance from the injector increases in the downstream direction. In Region 2, the central jet entrains the surrounding fluid, an adverse pressure gradient develops in the axial direction and a recirculating pattern is

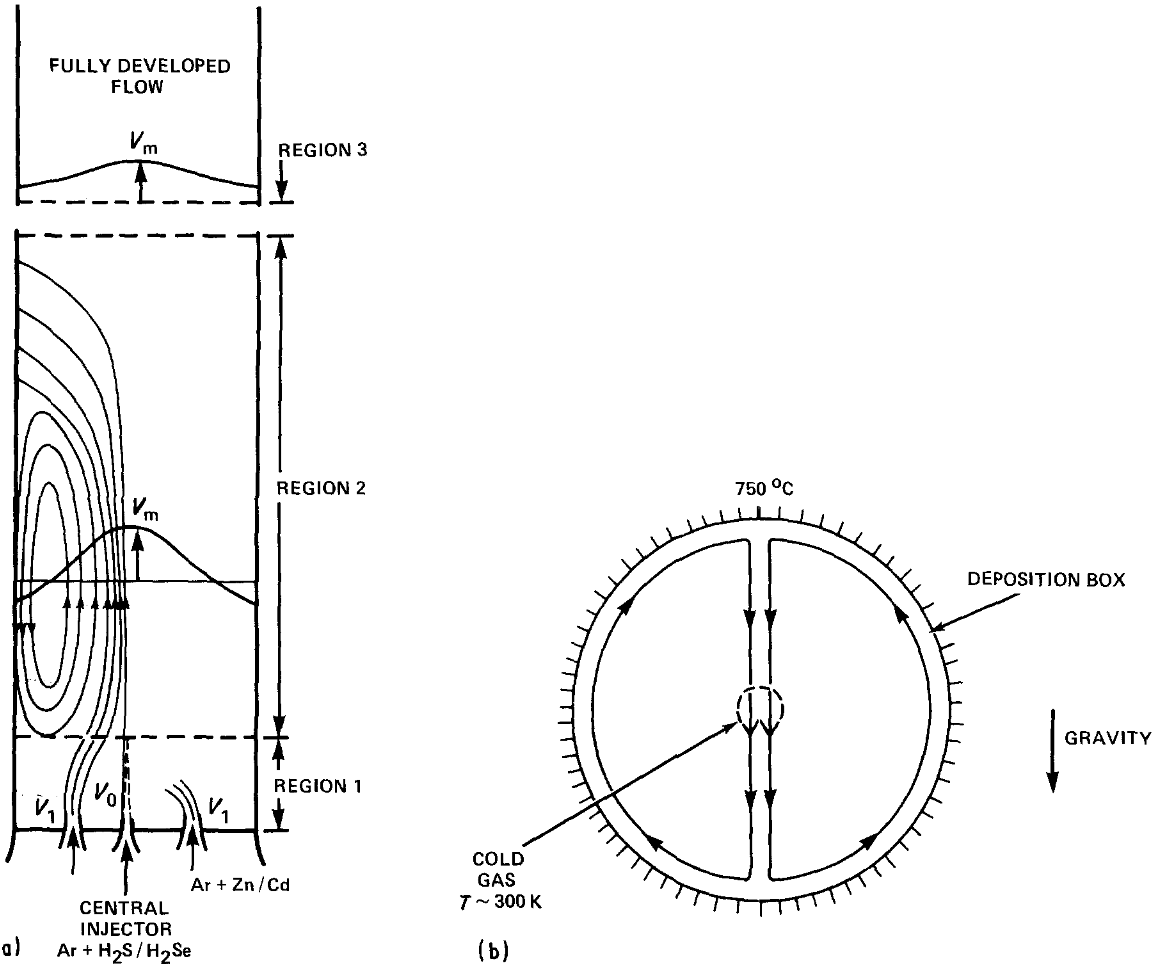

Figure 7 Flow pattern (a) inside a CVD chamber used to produce monolithic infrared optical materials and (b) due to natural convection in a cylindrical CVD chamber placed horizontally. The flow direction is perpendicular to the plane of the paper in (b).

generated. When V_0/V_1 is large, the length of Region 2 is much larger than that of Region 1. If the CVD chamber is long enough, eventually a fully developed flow is established (Region 3). In this region, the velocity profile is parabolic. The chamber length should be chosen such that Region 3 is not obtained. Thus, in the deposition chamber the flow is essentially dominated by the recirculation pattern. This pattern is very important to the successful performance of the CVD chamber, since it provides a flow mechanism to transport the cool H_2Se/H_2S to the hot walls with minimum gas phase decomposition or reaction, and, at the same time, it transports the products of reactions away from the surface.

Superimposing the flow patterns in the cross-sectional plane of the chamber with those along its axis, we find that the resultant flow is quite complex. An important aspect of this flow pattern is that it tries to make the deposition uniform, particularly in the flow direction. Fig. 8 shows a typical deposition profile for ZnSe obtained in a large CVD reactor. We see that the maximum deposition occurs in the middle of the substrate. By varying the flow rate of the carrier gas through the central injector, we can shift the maximum deposition area from one end to the other. However, when the maximum deposition occurs in the centre, an optimum deposition profile is obtained. From Fig. 8 we see that a 100% variation in thickness occurs over a plate 125 cm in length. This provides a thickness uniformity of about 0.8% cm^{-1} which is quite good for a large scale CVD process.

7. Summary and conclusions

An overview of monolithic material fabrication via

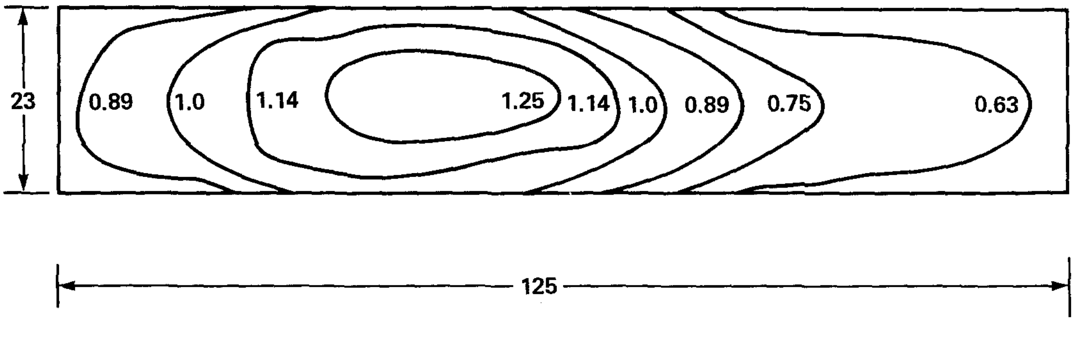

Figure 8 A typical ZnSe deposition profile in a large CVD reactor. All dimensions are in cm.

chemical vapour deposition emphasizing the fabrication of CdS, ZnS, ZnSe, silicon and SiC has been presented. The properties of CVD materials can be varied to some extent by controlling the CVD process parameters, by incorporating dopants or a second phase in the material or by performing a post deposition treatment. The large scale CVD process presents unique engineering and technical issues which are quite different from those of the thin film deposition. A recirculating type of flow pattern is crucial to the successful operation of the CVD process. There is a need to develop a fundamental understanding of phenomena such as the bowing and nodular growth to further improve properties of the CVD materials.

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