Fabrication of IR transparent zinc sulphide plate by chemical vapour deposition (CVD)

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Recent developments in Chemical Vapour Deposition (CVD) processing with its inherent advantages provide a feasible route for producing high quality optically transparent ceramic materials. CVD process feasibility of the reaction between Zn and H_2S in obtaining optical quality ZnS deposits are evaluated with respect to the free energy requirements. Rayleigh number (R_a) of 10^6 corresponding to laminar flow indicated optimum flow velocities during CVD processing. Deposits show desirable thickness uniformity of 0.55% per cm and were found to have a phase pure ZnS XRD phase. EBSD patterns exhibited a highly oriented columnar ZnS grains and the specimens have shown the theoretical transmission values in the IR ranges.

Keywords: Chemical vapour deposition, IR transparent ZnS, Rayleigh number, Free energy, Transport phenomenon

Transparent ceramics by virtue of their unique combination of mechanical and transmission properties have recently gained interest as a new class of advanced ceramics for diverse applications. Some of the high end industrial and strategic applications include high energy lasers, radiation detectors for non destructive testing, transparent armour windows, IR seeking missile domes and medical imaging. The transparent ceramic systems, which are of current interest, include transparent alumina (as polycrystalline sub micron alumina and single crystal sapphire (Al_2O_3)), aluminium oxynitride (AlON), spinel ($MgAl_2O_4$), zinc sulphide (ZnS) ceramics and nano-yttria (Y_2O_3) ceramics. Chemical Vapour deposition is already established for the synthesis of most of these transparent materials[1-3].

Chemical Vapour Deposition (CVD) process with its inherent advantages replaces a series of advanced processing steps and attains the requisites of full densification along with isotropic properties to achieve the desired transmission properties. CVD employs volatile precursors that react in the vapour phase on the heated substrate under optimum CVD parameters. Though CVD mainly operate on chemical engineering principles, it combines several of the engineering and scientific disciplines and deposit properties are strongly depend on process parameters. ZnS for optical applications generally have 4mm thickness or more due to its poor mechanical properties[4,5]. This requires high deposition rate which is generally limited to $100\mu m/h$.

It is evident that the first step of CVD is the mass transport of the vapour precursors to the deposition zone followed by vapour phase reaction resulting in the formation of reactive chemical species. Second step is the mass transport of the reactive species through the boundary layer to the substrate surface followed by the formation of the deposits. Third step is the exit of the byproducts from CVD reactor. Chemical Vapour Deposition reactions can be activated by several methods. Based on the activation and sources the CVD can be classified as hot wall or cold wall CVD and plasma Enhanced CVD (PECVD). Hot wall reactors represent one of the major classes of CVD reactors. In hot wall reactors the components are placed in the chamber surrounded by heating elements. After reaching the deposition temperature the reactant gases are introduced leading to the deposition. In cold wall CVD the components are heated and walls remain cooled through coolant circulation. Under PECVD conditions plasma accelerates the formation of reactive species and modification of reactant surface enhancing the deposition rates. Combination of these effects also lowers the deposition temperatures. The key process parameters are temperature, pressure, flow velocities and reactant concentrations. In

addition uniformity of the deposits is also a function of reactor geometry, substrate configurations and surface specificity and rate of deposition.

Zinc sulphide (ZnS) is a material of choice for optical and electro optic devices by virtue of its transmission properties in the spectral band of 0.4 µm to 14 µm. The most successful route for the preparation of ZnS is chemical vapour deposition (CVD) involving the reaction of zinc vapour and hydrogen sulphide gas at predetermined temperatures and pressures[5-14]. Being a gas phase reaction, CVD provides important advantages over other methods of materials processing in view of the ease of accurately controlling the stoichiometry and purity of the product[15,16]. CVD deposition of optical grade ZnS is discussed in this paper demonstrating the effect of optimum parameters in achieving close to theoretical IR transmission properties.

Experimental Section

CVD reaction between zinc vapour and hydrogen sulphide gas at temperatures of 650-750°C and low pressures of around 50 mbar was employed for the preparation of monolithic ZnS samples. Reaction (Reaction 1) for the CVD feasibility was evaluated using free energy (ΔG) calculations. Flow velocities and patterns are estimated through Rayleigh number (R_a) estimations. The samples were deposited on graphite substrates of dimensions of 50 × 50× 5 mm thickness and deposited for 50-60 h to achieve a deposit thickness of 4-5mm.

$$Zn(g) + H_2S\ (g) \rightarrow ZnS(s) + H_2(g) \qquad \dots (1)$$
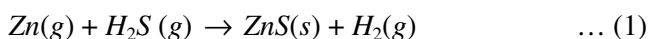
X- ray Diffraction studies (D8 Advanced, Bruker, Germany) were carried out using Cu K alpha radiation, for phase analysis, crystallite size measurements and orientation effects. Electron backscatter diffraction measurements were carried out using an EDAX-TSL system attached to a Hitachi S-4300 scanning electron microscope equipped with a field emission gun. Studies were conducted on the CVD ZnS specimens. The samples were mounted using resin and were polished using standard ceramographic procedures. For the final polishing step, colloidal silica suspension (0.05 µm) was used and the polishing was carried out for approximately 20 min on the specimen. Infrared transmittance was measured in the wavelength range of 3-10 µm using Fourier Transform Infrared spectrophotometer (Spectrum GX, Perkin-Elmer, Shelton, CT).

Results and Discussion

CVD Process feasibility

Prior to the selection of CVD process it is very important to determine the feasibility of the CVD reaction. Feasibility of reaction 1 for ZnS CVD deposition was determined based on the calculated Gibbs free energy ΔG. In reaction (g) and (s) refer to gas and solid reactants. The first step of theoretical analysis is to ensure that the desired CVD reaction will take place. This will happen if the thermodynamics is favorable, i.e. if the free energy change (ΔG) of the reaction is negative. To calculate ΔG of reaction (ΔG_r) it is necessary to know the thermodynamics properties of each component, specifically their ΔG. The relationship can be expressed by the following equation –

$$\Delta Gr^\circ = \sum \Delta\,G^\circ\ products - \sum \Delta\ G^\circ\ reactants \quad \dots (2)$$

The free energy of formation is not a fixed value but varies as a function of several parameters which includes the type of reactants, molar ratio of reactants, process temperature and process pressure. The relationship is represented by the following equation –

$$\Delta Gr = \Delta G^{\,o} + RT \ln Q \qquad \dots (3)$$

By definition ΔG_r at equilibrium is zero so, $\Delta G = -RT \ln Q$

Based on the available thermo-chemical data ΔG of the reaction was estimated as per Eqn. 2 and the ΔG of the reaction is found to be –37.3 kcal/mol at a temperature around 680°C (Eqn. 4). Acceptable quality of bulk CVD materials in the temperature of 650-700°C can be produced in the temperature regime which ΔG of the reaction is negative and is within the range of 35-45 kcal/mol. It is well known that as a thump rule a good quality CVD deposits can be produced when ΔG is negative and further its magnitude is around –30 kcal/mol. If the temperatures is below 630°C deposition rate as low as >50 µm/h following Arrhenius law and cost of the process will become exorbitant due to excessive deposition time when a self standing optical monolith is to be fabricated[17]. On the other hand with very high deposition rates the deposits will have inherent microstructural defects as well as microcracks which can be attributed to the bowing of the deposits from the substrates. A schematic of the hot wall reactor along with deposition sequence is shown in Fig. 1. XRD pattern recorded on the surface of the CVD ZnS specimen is shown in Fig. 2. It is evident from XRD patterns that the homogeneous ZnS sphalerite phase
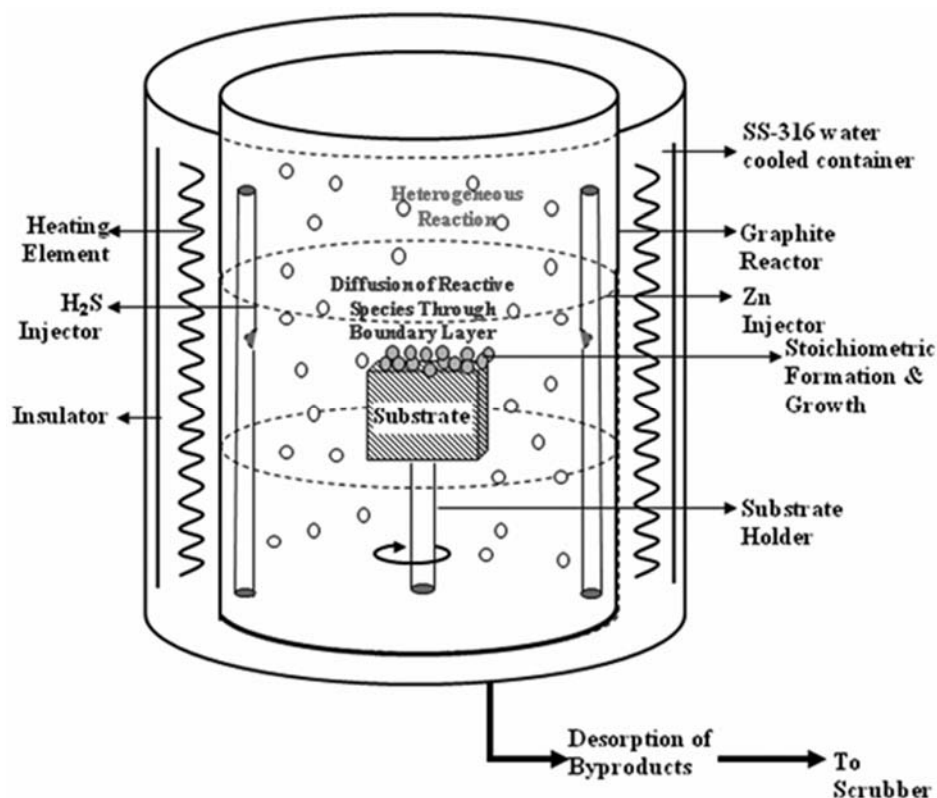
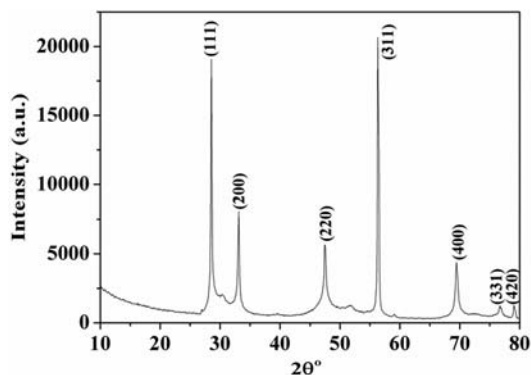Fig. 1 — Schematic of CVD Reactor and deposition sequence

Fig. 2 —XRD Pattern of CVD grown ZnS Specimen

confirming the isotropic nature of sample and effectiveness of CVD temperature regime for desired phase formation from the precursors.

$$\Delta G = 82.1T - 5.9T\,lnT - 0.62 \times 10^{-3}\,T^2 - 76400\,cal/mol$$
$$\dots (4)$$

Crystallite sizes were also estimated using the Scherrer formula (Eqn. 5). Where k is the shape factor, λ is the wavelength of the incident x-rays, FWHM is the calculated width at half height, FW is the broadening from equipment and θ the Bragg angle. The crystallite size of the samples was found to be 37.2274 Å.

$$D_{hvl} = k \times \lambda \backslash (FWHM - FW) \times cos\theta \qquad \dots (5)$$

Precursor transport phenomena

Not only the flow velocities but also flow pattern is also expected to play a major role in achieving the desired bulk properties especially in the mass controlled regime suitable for monolithic self standing ceramics. The flow pattern due to natural convection can be characterized by Rayleigh number (R_a)

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

where,

α: Thermal expansion coefficient (= 1/T for an ideal gas) (7.1×10^{-6} /°C)

g: Acceleration due to gravity

C_p: Specific heat at constant pressure

Q: Density

d: Characteristic distance

ΔT: Temperature difference between the hot and cold region

K: Thermal conductivity

η: Viscosity

Critical parameters that affect the vapour precursor transport are reactor temperature and distribution within the reactor, reactor pressure, reactor geometry, flow velocities and properties of the gases. As the gaseous reactants are injected into the reaction chamber through the orifice located in the injector flow velocity along the axis is expected to high and as the distance from the orifice increase the flow pattern decays and as enters into the rotating boundaries of the substrate turbulence are generated which results in intermixing generating a recalculating flow. Flow rates of carrier gas and revolution per minute of the substrate are major factors play the major role in maintaining the velocities and hence the flow patterns. The flow velocities of the gaseous reactants along with argon carrier gas are kept in the range of 1.54×10^{-6} m/sec for the CVD reaction 1, in the present study. Further, Rayleigh number (R_a) is estimated to be in the range of 10^6 confirming to the laminar flow. A typical ZnS deposit obtained on the graphite substrate showing (Fig. 3) the thickness uniformity for deposits was around 0.55% per cm.

Micro-structural development

CVD deposition rate and microstructural developments are generally controlled by the temperature of deposition as well as the molar concentrations of the reactants. At relatively low temperatures deposition is kinetically limited and shows a substantial dependence on temperature.

The rate determining step in this regime may be either the nucleation or decomposition of adsorbed reactant species on the substrate surface. As the temperature increase to the mass controlled regime kinetics of the reaction becomes faster, and the deposition is limited by the diffusion of the reactants through the depleted boundary layer to the substrate surface. On further increasing the temperature, the deposition rate is limited by thermodynamics and the free energy of the reaction increases with temperature which in-fact reduces the driving force of the reaction. If ΔG shift towards positive side gas phase nucleation occurs and when ΔG becomes positive for an exothermic reaction the reaction may result in etching rather than deposition.

Typical colour-coded crystal orientation map (COM) of the CVD ZnS at deposition temperature of 650-680°C and the deposition rate of 50-80 µm/hr obtained with EBSD scan is shown in Fig. 4(a). Further, the inverse pole figure (IPF) is shown in Fig. 4(b). Each colour in the COM refers to a unique orientation of the grain as read from the IPF. These

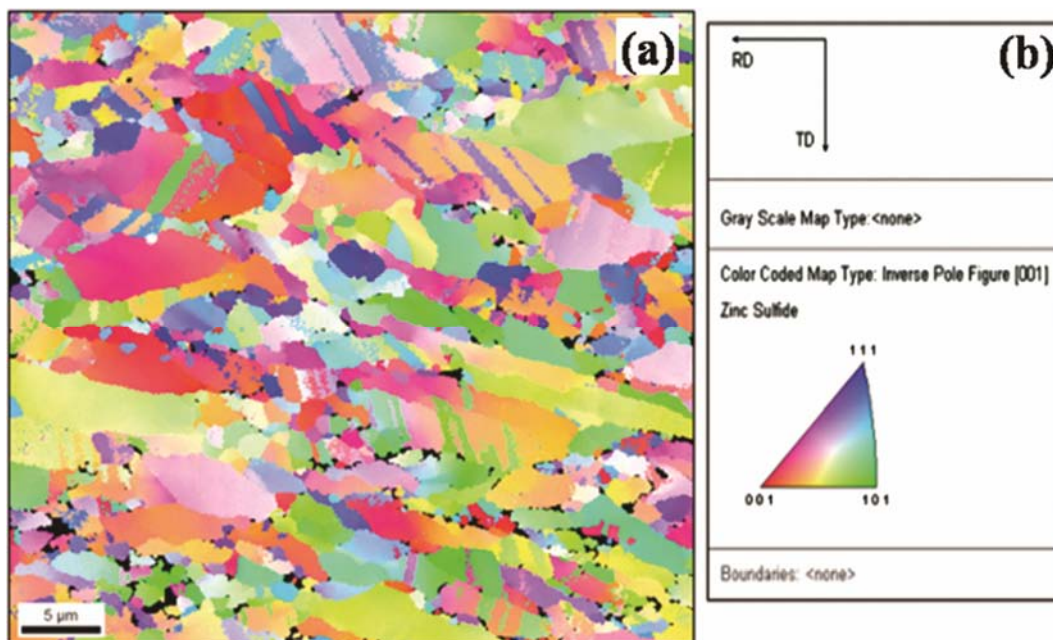Fig. 3 — Thickness uniformity on the substrate

Fig. 4 — (a) EBSD colour-coded crystal orientation map and (b) Inverse Pole Figure
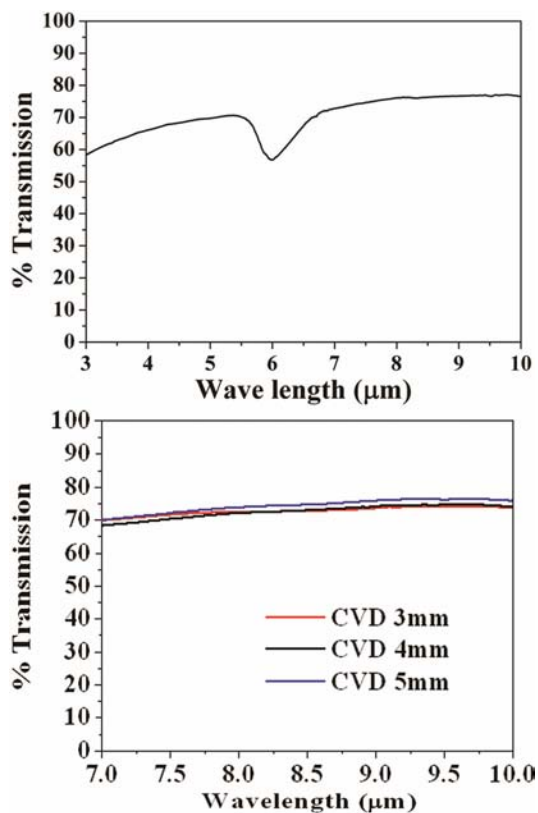
Fig. 5 — FTIR Pattern of CVD grown ZnS Specimens of different thicknesses

grains are composed of many ZnS crystallite of 37.2274Å. Fig. 4(a) shows the growth direction in this case is from left to the right, as indicated by the reference direction (RD) in the IPF. As can be seen from the Fig. 4(a), columnar grain structure is clearly evident signifying the mass controlled regime deposition. It is also to be seen that, a large fraction of grains is oriented along the (001) direction. Preferentially oriented grains grow at a more rapid rate at the expense of less favorably oriented grains.

IR transmission properties

FTIR transmission pattern of the optically polished CVD ZnS sample of different thicknesses is provided in Fig. 5. It shows the %IR transmission in the wavelength region of 3-10 µm. The %transmission is >60% in the 3-5 µm region and ~75% in the 7-10 µm region (close to theoretical) .The pattern clearly shows an absorption band at 6 µm which is the fingerprint of Zn-H stretch. When the Zn vapours react with H_2S according to the reaction 1 the byproduct hydrogen (H_2) during ZnS formation gets trapped within deposits. This H_2 which reacts with Zn results in the formation of undesirable

Zn-H. A uniform % IR transmission in the entire 3-10 µm region can be achieved through post thermal CVD treatment of specimens. These samples do not posses visible transparency.

Conclusion

Free energy calculations for the reaction 1 at 680°C exhibited a ΔG of –37.3 kcal/mol clearly exhibiting the feasibility for CVD processing of ZnS and is confirmed by the phase pure XRD patterns. Rayleigh number (R_a) in the range of 10^6 corresponding to laminar flow and resulting in the thickness uniformity for deposits was around 0.55% per cm indicating optimum flow velocities and flow patterns. EBSD patterns exhibiting the growth direction from left to the right and the columnar grain structure clearly signifies the mass controlled regime of deposition. Theoretical transmission values indicated the superiority of CVD processing in achieving the optical quality ZnS IR Transparent ceramics.

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