Chapter 2
Technical Issues in Processing of CVD ZnS

2.1 Introduction

In order to appreciate the complexities associated with chemical vapor deposition of ZnS and the subsequent heat treatment of the material, one must first examine the characteristics and reactions of the main components of the system (Zn, S, H_2S, and Ar). Trace components in the gas system (e.g., H_2O, H_2, and O_2) that provide alternative reaction paths must be considered as well.

It is well known that the presence of hydrogen is a controlling factor for the chemical potential of sulfur, and hydrogen has been widely used in this respect to study the reactions of sulfides in the geochemical field,[1] where the reaction is $2H_2S = 2H_2 + S_2$. This reaction determines the fugacity (i.e., activity at low pressure) for sulfur. Increasing the $[H_2]/[H_2S]$ ratio in the gas phase must then lower the partial pressure of sulfur and further prevent the H_2S from dissociating.

For ZnS, the reaction of sulfur with zinc to form ZnS, $2Zn + S_2 = 2ZnS$, is known as univariant because at constant temperature and pressure it depends only on the activity of sulfur.[2] The free-energy change for the sulfidation of zinc, per the equation above, has been shown by Vaughan[2] to be

$$
\begin{aligned}
\Delta G^{\circ}_{rxn,II,25-420C}(kJ) &= \Delta H_{rxn,II,25-420C} - T\Delta S_{rxn,II,25-420C} \\
&= -537.88 + 0.19T(K), \\
\Delta G^{\circ}_{rxn,II,420-1200C}(kJ) &= \Delta H_{rxn,II,420-1200C} - T\Delta S_{rxn,II,420-1200C} \\
&\quad -548.87 + 0.21T(K).
\end{aligned}
\tag{2.1}
$$

These values agree with those in commercial thermodynamic properties databases.[3] This database also includes thermodynamic data for the similar formation of ZnO. That ZnO has a lower-standard-state Gibbs energy of formation implies that, other factors being equal, zinc has a preference for oxygen over sulfur.

The presence of oxygen in ZnS has been alluded to before in the context of luminescence. Because ZnS forms a solid solution with oxygen, dissolving about 1 mol% O, ZnS-O can be hard to detect and will not show up as a separated phase in x-ray diffraction.[4] There has been some debate as to whether the weak extrinsic absorption in CVD ZnS around 9.1 μm (1100 cm^{-1}) is due to ZnO,[5] Si-O,[6] or SO$_3$.[2–7] Absorption bands in ZnSe between 850–1100 cm^{-1} have been attributed to ZnO.[8] Low-temperature deposits ($\leq$670 °C) are said to have higher [O] present. Annealing in Zn vapor increases dissolved oxygen and decreases density, whereas annealing in S vapor reduces dissolved oxygen to 10^{18} cm^{-3} but does not affect density.[9] Additionally, the ZnS-O solid solution is said to be noticeable in photoluminescence, as a red shift to the free exciton due to the bandgap shrinkage of ZnS from accommodation of oxygen.[10] As mentioned in Chapter 1, diBenedetto *et al.* have experimented with deliberate doping of CVD ZnS with oxygen, which produced colorless material with lower visible scatter than material grown using only hydrogen sulfide and zinc.

2.1.1 Vapor phase equilibrium

Homogeneous decomposition of hydrogen sulfide is severely restricted below 500 °C, and at 800 °C conversion to the elemental components is only 25% at 110-kPa pressure (825 torr).[11] Trace amounts of O$_2$ are known to greatly accelerate the decomposition of H$_2$S at high temperature (> ~2100 °C).[12] It has been observed that when H$_2$, O$_2$, and H$_2$S are present in equal volumes, the H$_2$S will be oxidized before the H$_2$.[13] However, the reaction mechanisms in the H$_2$S-O$_2$ system are very complex, and at least thirty possible reactions have been identified involving several paths.[14,15]

Sulfur vapor is extremely complex in its constituency, as it exhibits a number of allotropes, the distribution of which varies strongly with temperature. At low temperatures, S$_8$ is the most stable species, with significant fractions of S$_7$ and S$_6$, but above 720 °C S$_2$ becomes the most prevalent species.[16] Reaction enthalpies for conversion from S$_8$ to lower molecular weight forms have been reviewed recently, comparing experimental and calculated values.[17] S$_2$ is the largest mole fraction above 1000 K,[18] and individual sulfur atoms are unlikely to be present at temperatures lower than 2000 K due to their high enthalphy of formation.[17] However, a different conclusion was reached by Wiedemieir[19] in studying the reaction of ZnS, who stated that sulfur atoms were an important fraction of the equilibrium gas phase above the ZnS reaction from H$_2$S and Zn.

The equilibrium composition of the gas phase above ZnS in the presence of H$_2$, H$_2$O, and CO$_2$ has been investigated recently using a total energy minimization method[19] (see Figure 2.1). The study began by simulating the equilibrium vapor phase composition above ZnS(s) including all of the allotropes of sulfur along with zinc and zinc sulfide. It was found that Zn and
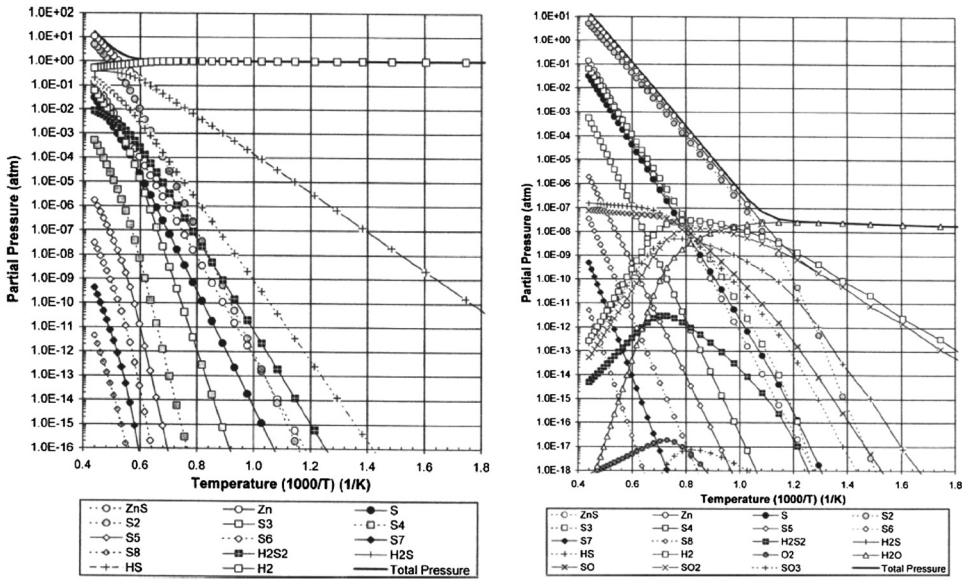
Figure 2.1 Calculated partial pressure of species in a ZnS chemical vapor reaction in the presence of hydrogen (left) or water (right) (image from Wiedemeier[19] used with permission; copyright 2006 American Vacuum Society).

S_2 are the dominant species by several orders of magnitude and are very close in partial pressures throughout the simulated temperature range (~588–2000 K). A simulation was then performed assuming the addition of 10^{-3} atm (~1 torr at 298 K) of H_2 gas, which significantly changed the equilibrium such that the dominant species below 1000 °C are H_2 and H_2S, followed by Zn, and then HS or S_2, depending on the temperature. The partial pressure of zinc (p_{Zn}) was significantly greater than the partial pressure of sulfur (p_{S_2}). Additions of H_2 gas at the 10^{-8} atm (~10^{-5} torr) level did not significantly alter the equilibrium of the ZnS (s) system alone, but larger concentrations on the order of 1 atm (~10^3 torr) of H_2 resulted in even more depletion of sulfur gas in the vapor. Similar results were found when adding 10^{-8} atm (at 298 K) of $H_2O(g)$, in that the sulfur was much depleted below about 700 °C, and the major constituents of the vapor in order of concentration were H_2O, H_2, SO_2, Zn, S_2, and H_2S, with the order differing slightly with temperature. When both H_2O and H_2 were added at the 10^{-3} atm (at 298 K) level, the vapor was almost entirely H_2O and H_2, with concentrations of H_2S and Zn being next. Finally, the addition of 10^{-8} atm (at 298 K) of $H_2O(g)$ and H_2 along with 10^{-5} atm (~10^{-2} torr at 298 K) of CO_2 resulted in an extremely complex equilibrium consisting of CO_2 and CO, with Zn and S_2 being the next greatest component and very close in concentration due to sublimation down to about 650 °C when $H_2O(g)$, H_2, COS, and H_2S become important. In this last case, only at temperatures below 560 °C is there a return to the $p_{Zn} \gg p_{S_2}$.

   This example illustrates the profound effect of trace impurity gases in vapor equilibria. Conventional vacuum deposition reactors that do not use careful outgassing techniques can expect to have 10^{-8} atm of $H_2O(g)$ and H_2 from the chamber walls, along with 10^{-5} atm of CO_2 in a continuous supply from pumps, furnaces, and graphite crucibles.[19] If the deposition system is dynamic, it is unlikely to be at equilibrium. Defect concentrations will be inhomogeneous and vary spatially in the chamber. Overall, any present $H_2O(g)$ and H_2 will lower the chemical potential of sulfur by forming gases with sulfur, leaving a great excess of zinc in the vapor. Assumptions in this study included a congruently vaporizing ZnS (i.e., Zn and S ratios upon sublimation are equal) and that no other solid phases were formed. This already has limited applicability to the CVD ZnS system because ZnO and Zn-H species were not considered. However, this study is one that must be performed and compared to experimental mass spectrometer data from actual CVD depositions.

2.2 Chemical Vapor Deposition of ZnS

Chemical vapor deposition methods of zinc sulfide can be separated into static and dynamic methods, as well as transport methods and conventional methods.[20] Static methods involve sealing the reactants in a furnace, whereas dynamic methods involve continuously feeding reactants and removing spent gases. Transport CVD requires combining solids of ZnS with hydrochloric acid vapor (for example) to produce zinc chloride and hydrogen sulfide gases that are held at a high temperature. These gases are then recombined such that the ZnS solid re-deposits in a bulk solid on substrates at a lower temperature, leaving hydrochloride acid that can be evaporated off. The process works well for growing small single crystals and some polycrystalline material, but it is limited in the size of parts that can be grown: zinc sulfide grown this way tends to have undesirably large grain size.

   The standard dynamic ZnS CVD process as practiced today involves a liquid zinc metal that combines with hydrogen sulfide gas in a higher-temperature deposition area; the growth of ZnS proceeds by the reaction

$$Zn\ (g) + H_2S\ (g) \Rightarrow ZnS\ (s) + H_2(g). \qquad (2.2)$$
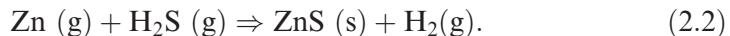
Hydrogen gas is given off in the process, some of which ends up being incorporated in the solid ZnS, especially at lower deposition temperatures.

   ZnS CVD growth is carried out in a hot-wall CVD reactor, with a heated retort of zinc metal, hydrogen-sulfide gas injectors, and argon carrier gas for the vapors.[21] Complex models of the transport phenomena have been simulated recently that show dependence of geometries on deposition rates.[22,23] Despite this, the details of the reaction kinetics, thermodynamics, and transport phenomena are still poorly understood today.

2.2.1 Homogeneous and heterogeneous CVD reactions

There is considerable debate as to how the ZnS forms. The relative importance of the homogeneous versus heterogeneous reaction in CVD ZnS has never been resolved. CVD processes in general can be completely homogenous, completely heterogeneous catalytic, or in between.[24] The fact that CVD reactions generally show deposition of material on all internal surfaces and not just those that are meant to catalyze the reaction suggests that CVD reactions typically involve at least some homogeneous reaction.[25]

In a *homogenous* reaction, ZnS forms in the gas phase and either condenses into a powder or diffuses to the substrate to form a film.[25] Higher gas-phase concentrations (supersaturation) will favor self-collisions of gaseous products and powder formation, wheras low concentrations favor diffusion and film formation. With a cold-wall CVD process, the diffusion to the substrate is known as thermophoresis and is used in producing silica optical waveguide fiber. The CVD ZnS process, however, is a hot-wall CVD process. In recent modeling of ZnS growth using transition state theory (TST) to estimate the configuration of transition state complexes between H_2S and ZnS, Sharifi[26] assumed that ZnS forms in the gas phase and then diffuses and deposits on the substrate. It has been argued that the gas phase reactions in ZnS are undesirable from an optical standpoint, and that heterogeneous reactions and low growth rates are preferred to produce a more-cubic material.[27] There is experimental evidence that gas phase nucleation and heterogeneous deposition do occur in CVD ZnS under certain conditions, resulting in some hexagonal material. Figure 2.2 shows electron micrographs
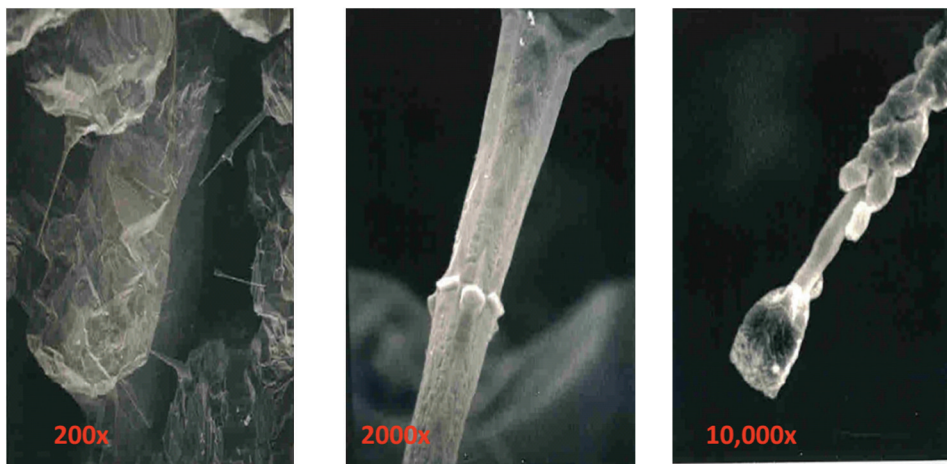

Figure 2.2 Evidence of gas phase nucleation of ZnS_xSe_{1-x} particles which then stick to hexagonal needles and become incorporated into bulk CVD material (photos courtesy of Barney diBenedetto, c. 1973).