

Gas Phase Photochemical Synthesis of II/VI Metal Sulfide Films and *in Situ* Luminescence Spectroscopic Identification of Photofragments

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The wide band gap II/VI semiconductors are of current interest for optoelectronic applications such as blue lasers, light-emitting diodes, and optical devices based on nonlinear properties.^{1,2} In particular, ternary phase materials (e.g., $Zn_xCd_{1-x}S$) have attracted technological interest because the band gap can be tuned and the lattice parameters can be varied. Chemical vapor deposition (CVD) of II/VI materials from pyrolysis of metal complexes with sulfur-chelating ligands (dithiocarbamate, dithiophosphate) has been reported,³ but photoassisted CVD is rare.

Laser-driven photochemical vapor deposition from organometallics enables patterned features to be written directly on thermally sensitive substrates and microelectronic devices to be repaired.^{4–6} By selective energy transfer to the precursor molecule, the photochemical syntheses can proceed at low temperature and give spatial selectivity. The photoreactions involved in the CVD process are poorly understood. When light emission is observed, luminescence spectroscopy can be used to identify gas phase species *in situ* and to elucidate photofragmentation pathways during the photochemical CVD process.^{7–9}

In this paper, we present the facile photochemical synthesis of binary and ternary II/VI metal sulfides from single-source diethyl dithiocarbamate zinc and cadmium precursors, $M(S_2CNEt_2)_2$, $M = Zn, Cd$.¹⁰ We use photoluminescence spectroscopy to simultaneously identify gas phase species present during the CVD process. This study demonstrates one of the first uses of light for both deposition and real time characterization of gas phase species in multiphase materials synthesis.

Photodeposition was initiated by using 308 nm light from a XeCl excimer laser (Lambda-Physik EMG 201). The CVD precursors (~ 0.1 g) in a reservoir cell were heated under vacuum (10^{-2} Torr) to the sublimation temperatures (~ 170 and ~ 185 °C for Zn and Cd precursors, respectively) and introduced into a CVD cell with quartz windows. The photodepositions were carried out by irradiating a circle of 2 cm in diameter on quartz substrates with 30 mJ/pulse at 20 Hz with a resulting fluence of ~ 1 MW/cm². For the growth of ternary phase materials, a dual-source CVD cell was used where each precursor was introduced separately. The films were formed only on laser-irradiated areas of the substrates. CdS films were yellow, and ternary phase $Zn_xCd_{1-x}S$ varied from greenish yellow to brown depending on the composition.

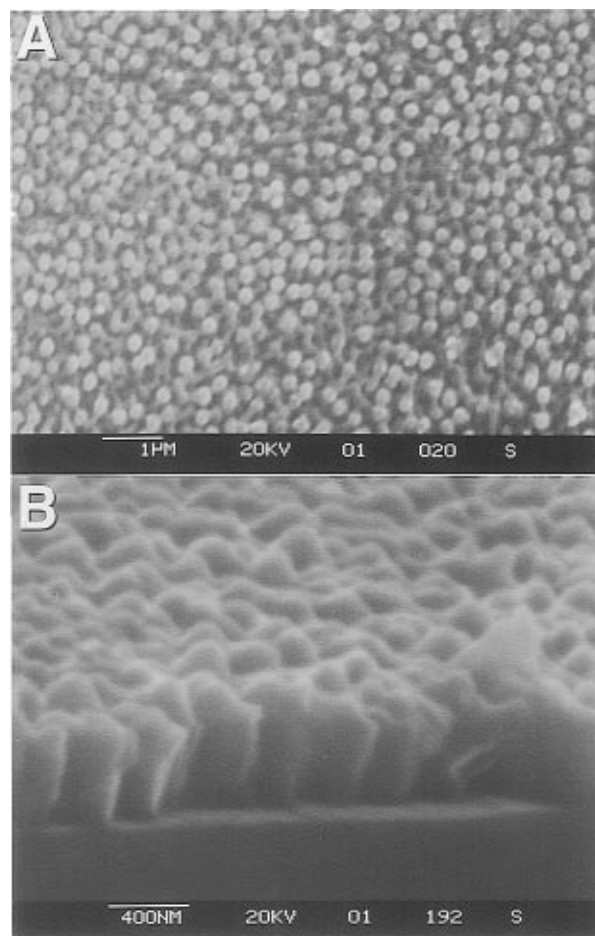


Figure 1. SEM of ZnS films grown on quartz: (a) top view, (b) side view.

The ZnS thin films consist of granules (diameter of ~ 0.2 μm) that exhibit a columnar growth pattern by scanning electron microscopic (SEM) analysis (Figure 1). X-ray diffraction (XRD) analyses reveal that the films are highly *c*-axis-oriented Wurtzite phase materials (Table 1).¹¹ Preferential growth along the *c*-axis, perpendicular to the plane of the substrate, produces a strong (002) diffraction pattern. X-ray photoelectron spectroscopic (XPS) analysis indicates that the films are pure ZnS with $\sim 3\%$ carbon and oxygen contamination. Rutherford-backscattering (RBS) analysis established that the entire film has the stoichiometric composition ZnS. The CdS thin film has a smoother surface without well-defined grain boundaries by SEM analysis. XRD indicates that the films are Wurtzite phase polycrystalline CdS (Table 1).¹¹ Both XPS and RBS analyses indicate that the films are pure stoichiometric CdS.

Ternary phase $Zn_xCd_{1-x}S$ thin film can also be prepared with compositions determined by the amount of each precursor delivered to the CVD chamber. By using this method, intermediate compositions are possible. The Cd and Zn compositions can be estimated from band gap (E_g) calculations. The band gaps of the binary (ZnS, CdS) and ternary ($Zn_xCd_{1-x}S$) materials were calculated from optical absorption measurements of the films deposited on quartz substrates.¹² The band gaps for CdS and ZnS were 2.42 and 3.53 eV, in good agreement with the bulk properties of CdS and ZnS (2.43 and 3.66 eV, respectively). The ternary phase materials show band gaps of

(11) JCPDS Powder Diffraction File; McClune, W. F., Ed.; International Center for Diffraction Data: Swarthmore, PA, 1990.

(12) The optical band gaps of the materials are calculated from a plot of $(\alpha)^2$ (where α is absorption coefficient) versus photon energy ($h\nu$): Pankove, J. I. In *Optical Process in Semiconductors*; Prentice-Hall: New Jersey, 1971; Chapter 1.

(1) Neumark, G. F.; Park, R. M.; Depuydt, J. M. *Physics Today* **1994**, (June), 26.

(2) McClean, I. P.; Thomas, C. B. *Semicond. Sci. Technol.* **1992**, 7, 1394.

(3) O'Brien, P.; Nomura, R. J. *Mater. Chem.* **1995**, 5, 1761 and references therein.

(4) Herman, I. P. *Chem. Rev.* **1989**, 89, 1323.

(5) *Laser Chemical Processing for Microelectronics*; Ibbs, K. G., Osgood, R. M., Eds.; Cambridge University: Cambridge, 1989.

(6) Eden, J. G. *Photochemical Vapor Deposition*; Wiley: New York, 1992.

(7) Wexler, D.; Zink, J. I.; Tutt, L. W.; Lunt, S. R. *J. Phys. Chem.* **1993**, 97, 13563.

(8) Talaga, D. S.; Zink, J. I. *Inorg. Chem.* **1996**, 35, 5050.

(9) Cheon, J.; Talaga, D. S.; Zink, J. I. *J. Am. Chem. Soc.* **1997**, 119, 163.

(10) The precursors were prepared by reported methods: Coucouvanis, D. N. *Prog. Inorg. Chem.* **1970**, 11, 233.

Table 1. Lattice Constants and Intensities of the Films

hkl	CdS		Zn _x Cd _{1-x} S		ZnS	
	d spacing (Å)	int. <i>I/I</i> ₀ ^a	d spacing (Å)	int. <i>I/I</i> ₀	d spacing (Å)	int. <i>I/I</i> ₀ ^a
(100)	3.616	0.64 (0.62)	3.579	0.22	3.422	0.23 (1.00)
(002)	3.386	1.00 (0.91)	3.346	1.00	3.143	1.00 (0.84)
(101)	3.184	0.52 (1.00)	3.148	0.47	2.957	0.16 (0.87)
(102)	2.453	0.09 (0.29)	2.436	0.20		(0.28)
(110)	2.074	0.30 (0.48)			1.915	0.17 (0.81)
(103)	1.905	0.12 (0.50)	1.855	0.33	1.764	0.10 (0.54)

^a JCPDS data were included in the parenthesis.¹¹

3.29 eV for Zn rich films and 2.53 eV for Cd rich films. The band gap of the ternary phase is known to vary in a quadratic manner with composition; the band gap of 2.53 eV approximately corresponds to a stoichiometry of Zn_{0.2}Cd_{0.8}S and the band gap of 3.29 eV corresponds to Zn_{0.85}Cd_{0.15}S.¹³

We have performed further characterizations of Cd rich ternary materials by RBS and XRD. RBS analysis indicates that the film consists of Zn_{0.21}Cd_{0.79}S. XRD analysis shows a new Wurtzite diffraction pattern which is not due to either CdS or ZnS (Table 1). The lattice parameters vary linearly with composition for ternary phase materials, and the film composition was calculated as Zn_{0.18}Cd_{0.82}S according to Vegard's law.¹⁴ The optical properties, RBS analysis, and XRD results are all consistent with an approximate stoichiometry of Zn_{0.2}Cd_{0.8}S.

Luminescence is observed in the path of 308 nm laser beam. This luminescence provides a method of identifying excited photochemical products and intermediates that are formed during the CVD process.¹⁵ Under CVD conditions, emissions due to Cd atomic lines were observed at 509 and 480 nm from the cadmium dithiocarbamate precursor (top trace of Figure 2a).¹⁶ Less-intense regularly spaced bands (~720 cm⁻¹ spacing) from 330–550 nm are also detected and assigned as vibrationally hot S₂ (B → X).¹⁷ Very similarly, emission due to Zn atomic lines (472 and 481 nm) and regularly spaced bands (~720 cm⁻¹ spacing) due to vibrationally hot S₂ (B → X) were observed from the zinc dithiocarbamate precursor (top trace of Figure 2b). The production of metal atoms in the gas phase requires multiple ligand dissociations. The emission from S₂ in the gas phase arises from fragmentation steps involving the free dithiocarbamate ligand radical (•S₂CNEt₂). Analogous solution phase UV-photoactivated ligand dissociation and the generation of the free ligand radical from the metal dithiocarbamate compounds have been reported.^{18,19} The radical can fragment yielding CS₂ and a NEt₂ radical. Absorption of a UV photon by CS₂ results in fragmentation yielding CS and S. The S atom

(13) The formula $E_g(x) = xE_{g(\text{ZnS})} + (1-x)E_{g(\text{CdS})} - x(1-x)b$ is used for the calculation, where x is the fractional composition and b is a bowing parameter which represents the non-linearity of the band gap changes (0.61 for Zn_xCd_{1-x}S system).

(14) Brinkman, A. W. In *Growth and Optical Properties of Wide-Gap II-VI Low-Dimensional Semiconductors*; McGill, T. C., Sotomayor Torres, C. M., Gebhardt, W., Eds.; NATO ASI Series B, Physics; Plenum: New York, 1989; Vol. 200, p 97.

(15) The instruments for gas phase photoluminescence measurements are described in ref 8.

(16) *Wavelength and Transition Probabilities for Atoms and Atomic Ions*; U.S. Department of Commerce, National Bureau of Standards: U.S. Government Printing Office: Washington, DC, 1980; NSRDS-NBS 68.

(17) Pearse, R. W. B.; Gaydon, A. G. *The Identification of Molecular Spectra*; Chapman and Hall: London, 1976.

(18) Schwendiman, D. F.; Zink, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 4439.

(19) Given, K. W.; Mattson, B. M.; McGuiggan, M. F.; Miessler, G. L.; Pignolet, L. H. *J. Am. Chem. Soc.* **1977**, *99*, 4855.

(20) Sapers, S. P.; Andraos, N.; Donaldson, D. J. *J. Chem. Phys.* **1991**, *95*, 1738.

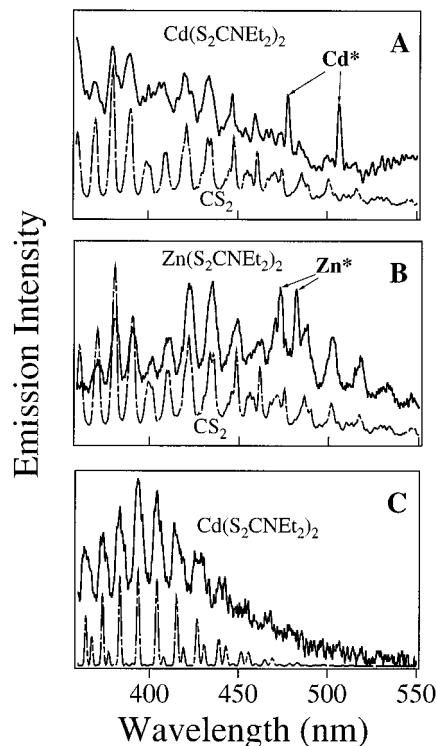


Figure 2. (a) The top trace is the *in situ* luminescence spectrum recorded during photolytic CVD from Cd(S₂CNEt₂)₂. The bottom trace is the spectrum observed from photolysis of CS₂ under identical conditions. (b) The top trace is the *in situ* luminescence spectrum recorded during photolytic CVD from Zn(S₂CNEt₂)₂. The bottom trace is the spectrum observed from photolysis of CS₂ under identical conditions. (c) The top trace shows a luminescence spectrum observed from Cd(S₂CNEt₂)₂ under high-pressure conditions (collisionally cooled S₂ emission). The bottom trace shows a calculated spectrum of the S₂ B → X luminescence.

can further react with CS₂ to produce luminescent S₂.²⁰ Our photofragmentation control study of CS₂ under identical CVD conditions reproduces all of the nonmetal features present in the metal dithiocarbamate photofragmentation spectra which are assigned to S₂ (bottom traces of Figure 2a,b). The top trace of Figure 2c shows that the spectrum from the cadmium dithiocarbamate precursor under higher pressure conditions with Ar buffer gas (~100 Torr) contains a congested progression from 340–500 nm with substantial cooling of S₂ as a result of collisions. The bottom trace of Figure 2c shows a calculated S₂ (B → X) luminescence including contributions from $\nu = 0, 1, \text{ and } 2$ in the excited state.

In conclusion, we demonstrate that ternary Zn_xCd_{1-x}S films as well as ZnS and CdS can be prepared photochemically under mild conditions and only in the area irradiated by the laser beam. Luminescence spectra show that the elements composing the films are produced in the gas phase. The simultaneous use of light to both drive the deposition reactions and to identify intermediates may be applicable to a wide variety of laser-driven materials preparations.

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