

Cadmium Sulfide and Cadmium Phosphide Thin Films from a Single Cadmium Compound

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S Supporting Information

ABSTRACT: Aerosol-assisted chemical vapor deposition of Cd[(SPⁱPr₂)₂N]₂ leads to the growth of cadmium sulfide and/or phosphide thin films on glass. Decomposition of the precursor has been studied by pyrolysis–gas chromatography/mass spectrometry and modeled by density functional theory.

The use of single-source precursors for the growth of cadmium chalcogenide thin films or nanoparticles has been widely studied.¹ Numerous chemical vapor deposition (CVD) methods have been used to grow thin films at reduced or atmospheric pressure involving delivery at low pressure, from an aerosol or by entrainment. Substrates have ranged from glass to oriented single crystals, with the latter often acting as templates for epitaxy. A recent evolution in this methodology involved supercritical-fluid CVD with hexyl dithiocarbamate and demonstrated the deposition of high-quality, near-stoichiometric, CdS films.²

Mixed chalcogenide compounds for thin films of more complex structures have received scant attention. We recently showed that dichalcogenoimidodiphosphinato compounds of nickel, [Ni-{Pr₂P(X1)NP(X2)Pr₂}]₂ (X1 = S, X2 = Se, X1 = X2 = S, and X1 = X2 = Se), can be used to deposit thin films of nickel sulfide, selenide, or phosphide,^{3,4} dependent upon both the temperature and method of deposition. In light of the recent results with a transition metal, we decided to revisit the related dithio complex of cadmium, Cd[(SPⁱPr₂)₂N]₂,⁵ initially reported to deposit only CdS films by low-pressure CVD experiments.⁶ In this Communication, aerosol-assisted (AA)CVD studies of cadmium complex decomposition onto glass substrates are reported and confirm the formation of either cadmium sulfide or cadmium phosphide films, depending on the growth temperature. Both cadmium sulfide and cadmium phosphide are considered to be useful materials for solar cells and are potentially important components of optoelectronic devices.^{8,9} A mechanism is also proposed for the formation of different materials based upon both computational and pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) studies.

AACVD studies were carried out on glass substrates at 500 and 525 °C under a dynamic argon flow rate of 160 sccm using a 2.7 mmol precursor solution in toluene. Films were found to be adherent but could be removed by scratching the surface of the films. Little or no film growth was seen at temperatures <500 °C. Powder X-ray diffraction (XRD) analysis confirmed the growth of hexagonal CdS (ICDD no. 01-075-1545) films at 500 °C with some phosphorus contamination (Figure 1a). However, at

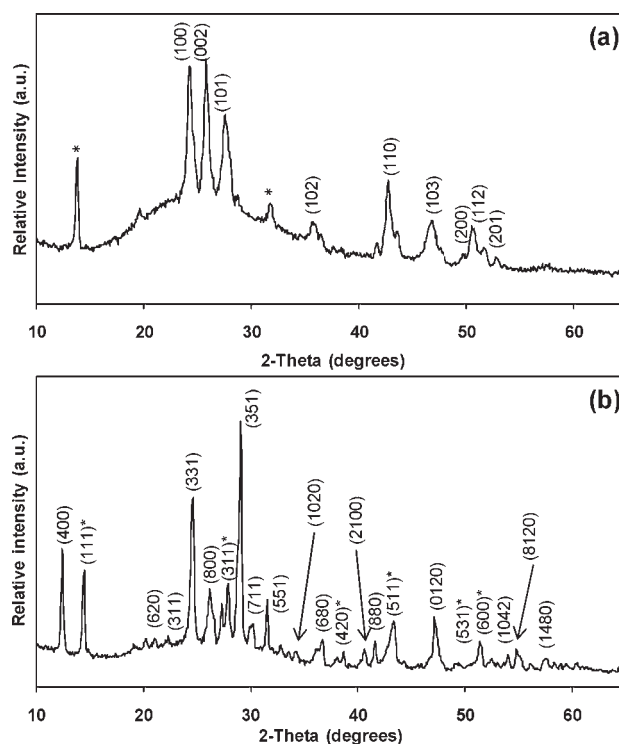


Figure 1. XRD of (a) hexagonal CdS at 500 °C and (b) orthorhombic Cd₇P₁₀ at 525 °C. Peaks marked in part a are due to phosphorus, and those in part b are due to the presence of cubic Cd₆P₇.

525 °C the growth of cubic Cd₆P₇ (ICDD no. 022-0126) and orthorhombic Cd₇P₁₀ (ICDD no. 054-0206) was observed (Figure 1b). The deposition experiments were repeated several times under similar growth conditions to confirm their reproducibility.

Scanning electron microscopy (SEM) studies showed that the films grown at 500 °C are composed of dense, ribbon-like primary crystallites (Figure 2a). In contrast, films at 525 °C are composed of randomly oriented crystallites (~0.75 μm in size), and poor coverage of the substrate is seen (Figure 2b). Different morphologies may suggest that the conversion of initial deposition of CdS metathesis to Cd_xPy is not a likely reaction. Energy-dispersive analysis of X-rays showed the growth of cadmium-rich films along with phosphorus contamination at 500 °C. At 525 °C,

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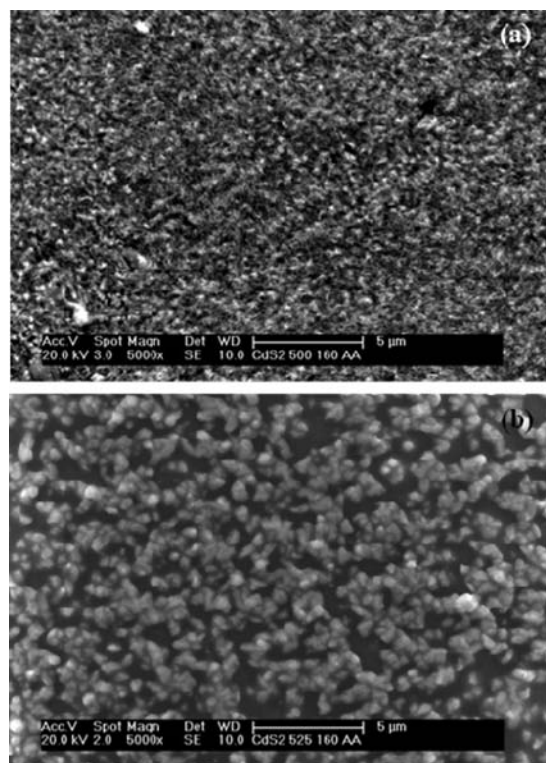


Figure 2. SEM images of (a) cadmium sulfide and (b) cadmium phosphide thin films deposited at 500 and 525 °C.

the ratio of phosphorus to cadmium is greater than 1:1. Traces of sulfur (~2%) are also detected in the same films.

To probe the electronic structure of the deposited material, X-ray photoelectron spectroscopy (XPS) of the films was carried out (Figures S1–S4 in the Supporting Information, SI). The film grown at 500 °C showed Cd 3d_{5/2} and 3d_{3/2} peaks at 405.1 and 411.9 eV, respectively (Figure S1 in the SI).¹⁰ The S 2p spectra exhibited two peaks arising from a spin–orbit splitting of 1.17 eV between the S 2p_{3/2} (161.4 eV) and S 2p_{1/2} (162.57 eV) states. The binding energies of the cadmium and sulfur peaks are indicative of CdS chemistry (Figure S2 in the SI).¹⁰ Moreover, the oxidized species of sulfur (165.8 eV) and phosphorus (133.7 eV) are also detected in the same film. However, for the film deposited at 525 °C, two different environments for Cd 3d_{5/2} (405.4 and 407 eV) and Cd 3d_{3/2} (411.9 and 413.8 eV) are observed. The low-energy peaks of Cd 3d are indicative of CdO species, whereas the high-energy peaks have unusually high binding energies for cadmium (Figure 3).¹⁰ The P 2p_{3/2} spectrum at 134.9 eV suggests P₂O₅ bonds (Figure S3 in the SI).¹¹ The atomic concentration of cadmium in the sample was found to be 43% and that of phosphorus 57%. A minor sulfur signal at ca. 162 eV (<1% surface coverage) is seen for this sample (Figure S4 in the SI). Carbon contamination is also apparent, but the origin is uncertain. Although the precursor itself is a likely source, it could also occur during the handling procedure.

To understand the factors responsible for the materials formed in the system, Py–GC/MS and complementary density functional theory (DFT) calculations have been carried out. We have computed the free energies of the dissociative and rearrangement reactions of the species that may lead to the deposition products. The proposed scheme (Figure 4) gives a plausible decomposition mechanism based upon an analysis of the Py–

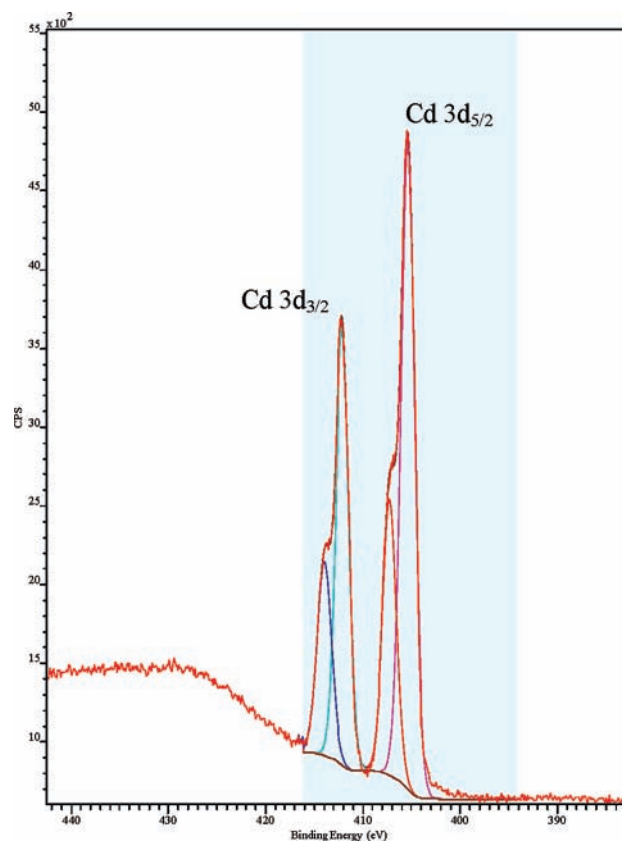


Figure 3. XPS of Cd 3d peaks for the film deposited at 525 °C.

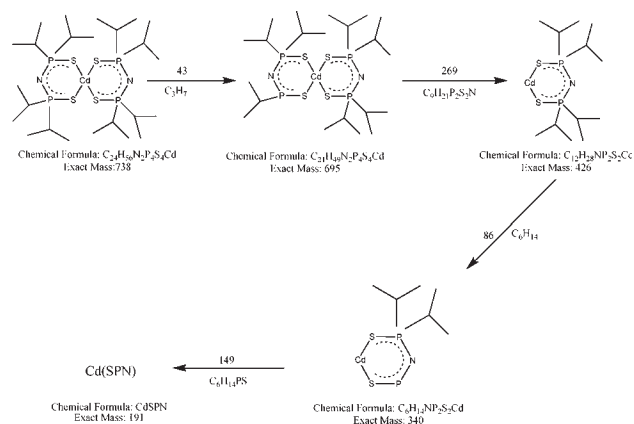


Figure 4. Summary of the proposed fragmentation pattern of Cd[(SP'Pr₂)₂N]₂ under Py–GC/MS conditions.

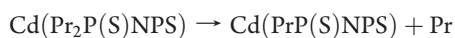
GC/MS results; the main intermediates and products are shown. Each intermediate species is postulated from a corresponding fragment in the Py–MS experiment and is shown with the corresponding *m/z* value. The key steps are as follows:

- (1) The initial loss of an isopropyl group.
- (2) Elimination of the close-shell molecule ⁱPr₃P₂S₂N.
- (3) The loss of two further isopropyl groups from the same atom.
- (4) Removal of the closed-shell ion ⁱPr₂PS⁺, which gives a major peak in the MS spectrum, to leave the neutral species Cd(SPN).

We have computed the free energies associated with each of these proposed steps by DFT calculations employing a locally

implemented version of the M06¹² functional in the *Gaussian03* suite of programs,¹³ together with a SDD pseudopotential and based on cadmium and a 6-31G** basis on all other atoms. For simplicity, the isopropyl groups were modeled as methyl groups. The free energies of each of the optimized structures were determined using the harmonic oscillator and rigid rotor approximations, at a temperature of 800 K. We find that each of the four steps shown are endergonic by 20, 109, 221, and 332 kJ mol⁻¹, respectively. The low values for the first two steps can be attributed to the formation and subsequent loss of the stable molecule Pr₃P₂S₂N. We find that for the corresponding neutral species that are postulated to be involved in the CVD process the values are 178, 82, 197, and 223 kJ mol⁻¹, respectively. Reaction energies of this magnitude suggest that the mechanism that we have proposed is not unreasonable.

We have also investigated a modification of the first and final steps in our proposed mechanism. For the first step, we have considered removal of one of the ligands entirely rather than a single isopropyl group and find it to be energetically more costly, but by only 34 kJ mol⁻¹. An alternative to the final step is

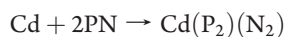


followed by



We compute these two steps to be endergonic by 71 and 215 kJ mol⁻¹, respectively, suggesting that such a two-step mechanism might be somewhat more favorable than the single step 4 mechanism, which is endergonic by 223 kJ mol⁻¹.

We may speculate as to how the formation of Cd(SPN) in step 4 leads to the deposition of both CdS and CdP species. We find that the formation of (PN)CdS from Cd(SPN) is energetically uphill, but by only 5 kJ mol⁻¹, so that Cd(SPN) may isomerize to (PN)CdS, with the latter losing the stable species PN upon deposition of CdS. In order to form the Cd_xP_y species observed, having a P/Cd ratio greater than unity, we suggest that some of the remaining cadmium in the atmosphere can catalyze the reaction converting the gaseous PN into P₂ and N₂. Thus, we predict that the reaction



is exergonic by 144 kJ mol⁻¹ and suggest that the Cd–P species are formed via decomposition of this complex. The conversion of CdS to Cd_xP_y phases is also possible. However, earlier studies with the nickel complex seem to suggest that this is not the dominant route.⁴

In summary, we have sought to try to develop an understanding of the processes which lead to different materials being deposited at different temperatures in a ligand containing only sulfur donors. Our preliminary mass spectrometry and DFT studies suggest a plethora of pathways which could easily lead to a reaction that switches over a short range of temperature, and could lead to either direct deposition or metathesis to the phosphide. The former being held to be, on balance, more likely.

■ ASSOCIATED CONTENT

● **Supporting Information.** Physical measurements, XPS and mass spectra, and a plausible decomposition mechanism of

Cd[(SPⁱPr₂)₂N]₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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