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# Preparation of Semiconducting Materials in the Laboratory

## Part 2. Microscale Chemical Bath Deposition of Materials with Band Gap Energies in the UV, Vis, and IR<sup>1</sup>

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The band gap energy of a semiconductor,  $E_g$  (1, 2) is defined as the separation between its valence and conduction bands (VB and CB) and determines its usefulness. For example, it would be unwise to try to use a semiconductor (SC) with its  $E_g$  in the UV as a visible light detector, or an SC with its  $E_g$  in the Vis in the remote controls of our TV sets. In the first case no response would be observed, whereas in the second any visible light coming from the surroundings would activate the switches that should respond only to the signal from the remote control. Likewise, it would be a major problem if the integrated circuits of an electronic device could respond to any applied potential. Thus, a semiconductor with the appropriate  $E_g$  must be produced for a given application.

There are many methods for the production of SC materials. In a previous paper (3) we described four methods that can be used for teacher demonstrations with CdS. In the following experiments we use the technique of chemical bath deposition (CBD) to produce thin films of three inorganic semiconducting sulfides—ZnS, CdS and Bi<sub>2</sub>S<sub>3</sub>, which have their  $E_g$  values in the UV, Vis, and IR regions of the electromagnetic spectrum, respectively. Devices produced by CBD can be used in optoelectronic devices such as solar cells (4–6) and IR detectors (7) as well as in electroacoustic transducers (8).

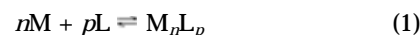
The method of CBD (not to be confused with its vapor phase analogue CVD, chemical vapor deposition) is particularly appropriate for use by students to produce thin films of semiconducting materials in a regular laboratory session and with standard equipment. Reported advantages of this method include (5, 6, 9–12):

1. The deposition rate and film thickness can be controlled by varying pH, temperature, ionic concentrations, and the degree of solution or substrate agitation.
2. The temperatures required are much lower than those used in other methods (like spray pyrolysis, vacuum evaporation, crystal growth from a melt, sintering, and CVD). This permits use of relatively low-melting point substrates (e.g., glass) and low-boiling point media (e.g., aqueous solutions).
3. The stoichiometry of the product is achieved owing to the solubility product; this also produces homogeneous phases.
4. Doping agents can easily be introduced.
5. Large-area, thin, and well-adhered layers can be produced.
6. It is a low-cost, reproducible, and simple process.

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### Theory

The CBD technique was developed during World War II to deposit thin films of PbS for IR detection (7) and is based upon the controlled precipitation of an insoluble compound (3, 7). Here, a saturated solution of an electrolyte in contact with its own solid phase originates a well-defined numerical relationship among the concentrations (or activities) of the ions in solution known as the solubility product ( $K_{sp}$ ). It is well known that precipitation occurs when this product is exceeded. However, this precipitation is usually massive and the solid formed does not grow in a defined, homogeneous pattern. To achieve a controlled precipitation, one can often add a complexing agent (L) to form a stable complex ( $M_nL_p$ ) with the metallic ion (M) that controls its concentration:



(charges are omitted for simplicity).

The formation constant for this equilibrium is given by:

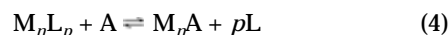
$$K_f = [M_nL_p] / [M]^n [L]^p \quad (2)$$

where the amounts in square brackets have the usual meaning. If  $K_f$  is too large (say,  $10^{25}$ ), the complex is very stable and will not release the metallic ion required for the formation of the SC. On the other hand, if  $K_f$  is too small (say,  $10^0$ ), the complex will be unstable, causing a massive precipitation of the SC.

The concentration of the precipitating anion, [A] can also be controlled in many cases by an exchange reaction as follows:

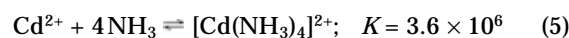


where X and Y denote a suitable cation and anion, respectively. In this way, [A] is governed by the equilibrium and is released in a controlled fashion so as to react with the metal complex to produce the desired SC ( $M_nA$ ):

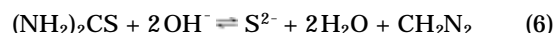


An example of this series of reaction equilibria is given by the production of cadmium sulfide from a solution containing a Cd salt, ammonia, and thiourea or thioacetamide (6, 9, 11, 13):

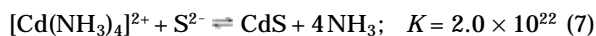
1. Complex formation:



2. Dissociation of thiourea in a basic medium to produce the sulfide ion:



## 3. Formation of solid cadmium sulfide:



In the following experiments, semiconducting thin films that have their  $E_g$  values in the UV, Vis, or IR will be prepared on regular microscope glass slides. These energies will then be calculated from their corresponding absorbance spectra.

## Experimental Procedure (14)

All glassware (slides and beakers) must be meticulously cleaned. It is advised that the glassware be immersed in a KOH/alcohol bath overnight. (CAUTION: Highly corrosive. Wear gloves.) Remove the glassware from the KOH bath using tongs. Rinse the glassware with tap water and immerse it in dilute nitric acid. Rinse again with tap water and finally with deionized (or distilled) water. An ultrasonic cleaning bath containing a detergent solution is an alternative to the KOH bath. After the glass slides are clean and dry, cut them lengthwise into halves. The slides must be cut so that they can easily fit into spectrophotometer cuvettes. (CAUTION: Take care while handling the cut glass slides. Their edges are sharp!) Half of the slide is used for depositing the semiconducting film and the other half is used as a reference for the absorption spectrum of the film. Alternatively, Kodak transparency film can be used in place of the glass slides. We have used a double-beam Cecil series 5000 UV-Vis spectrophotometer, which goes from 190 to 900 nm.

## General Procedure

**CAUTION:** Perform the following experiments in a well ventilated hood. These reactions may generate toxic  $\text{H}_2\text{S}$  gas. Moreover, avoid contact with thioacetamide, which is a cancer suspect agent. Set up a water bath in a 100-mL beaker on a magnetic-stirring hot plate. Begin heating. At the same time, prepare three 10-mL beakers each containing a stirring bar and the corresponding mixture for each of the three desired semiconductors (reaction mixtures 1, 2, and 3 [see below]).

**Reaction mixture 1 (ZnS).** Add 1.0 mL of 0.1 M thioacetamide (or thiourea) solution to 1.0 mL of 0.1 M  $\text{ZnSO}_4$ , followed by 1.5 mL of a 6M  $\text{NH}_3$  solution.

**Reaction mixture 2 (CdS).** **CAUTION:** Many cadmium-containing compounds are toxic and cancer suspect agents; avoid breathing or touching Cd-containing vapors or dusts. For disposal of small amounts of Cd compounds, see ref. 3. Alternatively, CdS films can be prepared by the instructor, for students' use or as a teacher demonstration only. Mix 1.0 mL of 0.1 M cadmium sulfate (or cadmium acetate) solution and 1.0 mL of 0.1 M thioacetamide (or thiourea). Add 2.0 mL of a 6M  $\text{NH}_3$  solution.

**Reaction mixture 3 ( $\text{Bi}_2\text{S}_3$ ).** **CAUTION:** Many bismuth salts are toxic. Do not touch them or breath their vapors or dusts. Triturate a mixture of 50 mg of  $\text{Bi}(\text{NO}_3)_3$ , 500 mL of triethanolamine (use hood), and 2.5 mL of water in a mortar. Using a Hirsh funnel, filter the solution (if necessary) to obtain a clear filtrate. Using a pipet, transfer 1.0 mL of this solution into one of the 10-mL beakers. Add 1.5 mL of a 0.1 M thioacetamide solution, followed by 1.0 mL of a 6M  $\text{NH}_3$  solution.

Insert each beaker in the bath and allow the temperature to reach approximately 80–85 °C. (Lower temperatures—down to 50 °C—work as well for CdS, whereas higher temperatures facilitate the deposition of  $\text{Bi}_2\text{S}_3$ . Ob-

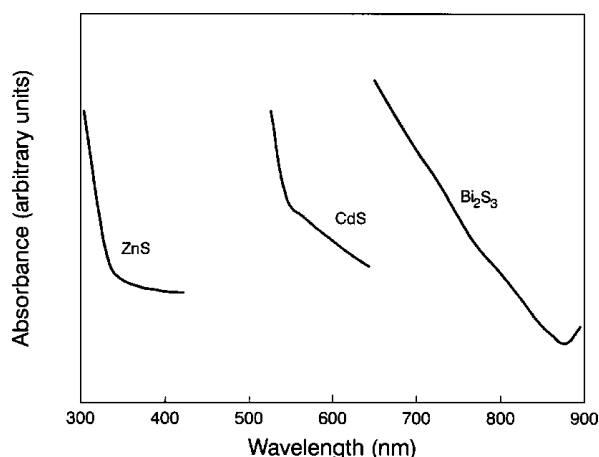


Figure 1. Absorbance spectra for the semiconducting films.

viously the deposition times will be a function of temperature.) Then, begin stirring the solution. At the same time, place a glass slide halfway into each solution. Maintain the temperature of the bath as constant as possible. A precipitate will start forming in a few minutes (ZnS is white, CdS is yellow,  $\text{Bi}_2\text{S}_3$  is gray-black). After 10–20 min, slowly and cautiously remove each slide from the beaker using forceps, rinse it with deionized water, and allow it to air dry (except for the ZnS, which needs to be dried under an  $\text{N}_2$  atmosphere in a desiccator, since it can get oxidized to  $\text{ZnSO}_4$  in the presence of moist air). After the slide has dried, place it in a cuvette and obtain its absorption spectrum (3) using its twin half (not coated with SC) as a reference. See Figures 1a, b, and c, respectively. Each band gap energy,  $E_g$ , can be estimated as described in our earlier paper from the corresponding wavelength,  $\lambda_g$  (i.e.,  $E_g = hc/\lambda_g$ ) (3). The onset of photoconductivity plots can also yield this information, although this falls outside of the scope of the present experiment.

## Results and Discussion

Values of  $E_g$  for each semiconducting film were obtained (see Table 1) and compared with literature values (15). The relative magnitude of  $E_g$  and the color of each SC can be understood as follows.  $E_g$  is a measure of the energy required to transfer an  $e^-$  from the valence band (VB) to the conduction band (CB). If the CB is assumed to be fundamentally associated with the cation and the VB with the anion in binary compounds (16), then  $E_g$  will be smaller as the band formed by the unoccupied orbitals of the metal is closer in energy to the band formed by the occupied orbitals of the anion (sulfide, in this case). These bands will be closer as the difference in electronegativities (DEN) be-

Table 1. Characteristics of SCs Produced

SC	$\lambda_g$ (nm)	$E_g$ (eV)		Color
		Calcd	Lit. (15)	
ZnS	331	3.7	3.4	white
CdS	542	2.3	2.42	yellow
$\text{Bi}_2\text{S}_3$	870	1.4	1.47	gray-black

comes smaller. This qualitatively explains the experimental observation that  $E_g$  varies in the order  $\text{ZnS} > \text{CdS} > \text{Bi}_2\text{S}_3$ , since DEN varies in the same order. Likewise, the observed colors can be explained by noting that a large value of  $E_g$  (i.e., in the UV) means that the compound does not absorb (and therefore reflects) visible light and thus is white (ZnS). On the other hand, a small  $E_g$  (i.e., in the IR) means that the compound absorbs all the visible light and thus is gray-black ( $\text{Bi}_2\text{S}_3$ ). A compound with an intermediate value of  $E_g$  shows the color resulting from the visible light not absorbed by it. A more thorough discussion of this phenomenon can be found in refs 16 and 17. An empirical equation relating DEN with  $E_g$  is (16):

$$E_g = 3.7[X^{\text{anion}} - X^{\text{cation}}] \text{ eV} \quad (8)$$

where  $X^*$  is the corrected optical electronegativity (see ref 16 for a table of values of  $X^*$ ). Using this equation and  $X^*$  values of 2.15, 1.1, and 1.45 for S, Zn, and Cd, respectively, gives  $E_g$  values of 3.9 eV for ZnS and 2.6 eV for CdS. These agree reasonably well with the values reported in Table 1. (The value for  $X^*$  of Bi is not reported in ref 16).

## Conclusions

The microscale chemical bath deposition (CBD) technique used in these experiments has proved to be simple, fast, reproducible, and inexpensive. CBD can also be used for the production of other binary ( $\text{ZnO}$  [8, 18],  $\text{MoS}_2$  [19],  $\text{MoSe}_2$  [19],  $\text{PbS}$  [20]) as well as ternary ( $\text{Cd}_2\text{SnO}_4$  [19],  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$  [21]) semiconducting films.

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## Note

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