Alkahest for $V_2VI_3$ Chalcogenides: Dissolution of Nine Bulk Semiconductors in a Diamine-Dithiol Solvent Mixture

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3 Supporting Information

**ABSTRACT:** The ability to solution deposit semiconductor films has received a great deal of recent attention as a way to potentially lower costs for many optoelectronic applications; however, most bulk semiconductors are insoluble in common solvents. Here we describe a novel and relatively nonhazardous binary solvent mixture comprised of 1,2-ethanediol and 1,2-ethylenediamine that possesses the remarkable ability to rapidly dissolve a series of nine bulk $V_2VI_3$ chalcogenides ($V =$ As, Sb, Bi; $VI =$ S, Se, Te) at room temperature and atmospheric pressure. After solution deposition and low-temperature annealing, the chalcogenides can be fully recovered as good quality, highly crystalline thin films with negligible organic content, as demonstrated for Sb$_2$Se$_3$ and Bi$_2$S$_3$.

Solution processing of semiconductor thin films holds great promise for various optoelectronic applications, such as photovoltaics, thin-film transistors, nonlinear optics, and nonvolatile phase-change memory. Liquid inks comprised of true molecular solutions are an especially promising medium for semiconductor deposition because they can lead to very homogeneous films; however, most metal chalcogenide semiconductors are totally insoluble in “normal” solvents. As exceptions to this statement, it is known that $N$-$N$-dimethylformamide will dissolve (K,Rb)PSe$_6$ and (K,Rb,Cs)-ZrPSe$_6$, methanol will dissolve $(Li,Na)$AsSe$_2$, and primary amines will dissolve As$_3$S$_5$. While the dissolution of other metal chalcogenides is generally much more difficult, a number of these materials (e.g., SnS$_2$, In$_2$Se$_3$, Cu$_2$S, etc.) can be dissolved with hydrazine in the presence of stoichiometric elemental chalcogen via “dimensional reduction.” In this process, soluble chalcogenometallate anions are formed by reaction of $M$,$E$ metal chalcogenides with $E^2-$ ($E^2-$ = $S^{2-},$ Se$^{2-},$ Te$^{2-}$; formed by the *in situ* reduction of the chalcogen with hydrazine). The dissolution of metal chalcogenides by the hydrazine/chalcogen route allows for the solution deposition of high-quality metal chalcogenide thin films, but the explosive, highly toxic, and carcinogenic properties of hydrazine make scale up difficult. Alternatively, colloidal dispersions of semiconductor nanocrystals can be used as inks, but this also presents serious scalability challenges as compared with using molecular solutions. Thus, new alkahests (or “universal” solvents) for the solution processing of bulk metal chalcogenide semiconductors are required.

Both crystalline and amorphous $V_2VI_3$ chalcogenides possess considerable importance in areas as diverse as thermoelectrics (Bi$_2$Sb$_3$Te$_3$), photovoltaics (Sb$_2$S$_3$, Sb$_2$Se$_3$, Bi$_2$S$_3$), photodetection (Bi$_2$Te$_3$), and infrared optics. Herein, we present a novel binary solvent mixture comprised of 1,2-ethylenediamine (en) and 1,2-ethanediol (edtH$_2$) that possesses the remarkable ability to rapidly dissolve nine bulk $V_2VI_3$ semiconductors ($V =$ As, Sb, Bi; $VI =$ S, Se, Te) at room temperature and ambient pressure. We describe the dissolution and subsequent solution redeposition of these $V_2VI_3$ chalcogenides, with specific focus placed on the facile solution processing of Sb$_2$Se$_3$ and Bi$_2$S$_3$ thin films from bulk material.

A 1:10 vol/vol mixture of chelating edtH$_2$/en was found to possess marked solvent ability for all nine $V_2VI_3$ chalcogenides. Metal chalcogenide solubilities, expressed as wt% solute in the saturated solution (at 25 °C, 1 atm), are extraordinarily high for As$_3$S$_5$, As$_3$Se$_5$, As$_2$Te$_5$, Sb$_2$S$_3$, Sb$_2$Se$_3$, and Sb$_2$Te$_3$ (21–32 wt%), moderate for Bi$_2$S$_3$ (9.8 wt%), and lower but still significant for Bi$_2$Se$_3$ and Bi$_2$Te$_3$ (0.75 and 1.5 wt%, respectively) (see Supporting Information, Table S1). Significantly, the $V_2VI_3$ chalcogenides can be dissolved very rapidly under these conditions (e.g., on the order of minutes for the As$_2$E$_3$ and Sb$_2$E$_3$ chalcogenides), as compared to substantially slower dissolution sometimes required with the hydrazine/chalcogen route. Dilute solutions of As$_3$S$_5$ and Sb$_2$S$_3$ are both nearly colorless, while As$_3$Se$_5$, Sb$_2$Se$_3$, Bi$_2$S$_3$, and Bi$_2$Se$_3$ give golden yellow solutions, and the tellurides all give dark brown solutions (Figure 1). All nine $V_2VI_3$ chalcogenide solutions in edtH$_2$/en were optically transparent and free of visible scattering at all concentrations. For the detailed investigation described below, solutions of Sb$_2$Se$_3$ were prepared under nitrogen by the complete dissolution of 125 mg of the chalcogenide in an empirically chosen solvent mixture of 1.0 mL en and 0.1 mL edtH$_2$; however this volume ratio of edtH$_2$/en can be deviated empirically chosen solvent mixture of 1.0 mL en and 0.1 mL edtH$_2$; however this volume ratio of edtH$_2$/en can be deviated

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flowing nitrogen, 5 °C min⁻¹ to 125 °C, 20 min isothermal) and then cooled to 30 °C before commencing analysis (60 mL min⁻¹ flowing nitrogen, 10 °C min⁻¹ to a sample-specific maximum temperature; see Figures S1–S3). The solids recovered via evaporation from the V₂VI₃ chalcogenide solutions all showed negligible mass loss above 300–350 °C, indicating end-point of decomposition. The solid recovered via evaporation of the dissolved Sb₂Se₃ solution shows a multistep mass loss of 24% from 30–350 °C (Figure 2a). Similarly, the solid recovered via evaporation of the dissolved Bi₂S₃ solution shows a multistep mass loss of 31% from 30–325 °C (Figure 2a). These mass loss events very likely correspond with elimination and/or decomposition of organic species from the dried solid. To test this hypothesis, dissolved solutions of Sb₂Se₃ and Bi₂S₃ were drop-cast on an IR-transparent disc and dried at 100 °C, a temperature at which no thermal decomposition is observed by TGA. FT-IR spectra of the films displayed strong ν(C–H) and ν(N–H) stretches at 3300–2800 cm⁻¹ along with other bands corresponding to organics; however, heat treatment to 350 °C resulted in elimination of the organic species as evidenced by complete loss of the ν(C–H) and ν(N–H) stretches (Figure 2b,c), in accordance with TGA data. The temperatures corresponding to organic mass loss for all these systems are comparable with literature precedent set by the hydrazine/chalcogen route, where a temperature of 350 °C is typically employed to volatilize excess chalcogen that must be added in order to dissolve the metal chalcogenide.⁸a

Solutions of all nine V₂VI₃ chalcogenides investigated here were dried and heat-treated under nitrogen, with sulfur vapor being used in the case of Bi₂S₃ to remove the small amount of elemental Bi present as an impurity in the as-bought material. Powder X-ray diffraction (XRD) revealed that As₂S₃, As₂Se₃, Sb₂S₃, Sb₂Se₃, Bi₂S₃, and Bi₂Se₃ can be recovered as phase pure material after deposition and annealing to temperatures ranging from 270–350 °C (see Figures S4–S10). In the case of Sb₂Se₃ and Bi₂S₃, which share identical orthorhombic stibnite (or bismuthinite) crystal structures, they were recovered from solution as crystalline and completely phase pure materials after annealing to 350 °C (Figures 3a,b). The elemental composition (at %) of the recovered chalcogenides was also compared against that of the as-bought materials by energy dispersive X-ray spectroscopy (EDX). For example, EDX analysis revealed a high degree of compositional agreement between the as-bought material and that recovered from solution for Sb₂Se₃ (41% Sb, 59% Se as bought; 39% Sb, 59% Se, 2% S recovered from solution); however, significant Bi and S peak overlap in the EDX spectrum precluded quantitative elemental analysis for Bi₂S₃.

To demonstrate the utility of this approach for solution processing V₂VI₃ chalcogenides, thin films of Sb₂Se₃ and Bi₂S₃ were produced by spin coating the dissolved species, followed by heating and annealing, as described above.
by rapid annealing to 350 °C. For example, a dilute Sb2Se3 solution (~4 wt %) proved very easy to spin-coat onto glass or silicon substrates. Subsequent heat treatment to 350 °C (under nitrogen) produced a dark gray, specularly reflective film, shown to be dense and polycrystalline by scanning electron microscopy (SEM). Cross-sectional and plane view SEM of the resulting thin film revealed it to be ~150 nm in thickness and composed of grains ranging from ~50–200 nm in width (Figures 3c and S11a). Similarly, spin coating a saturated Bi2S3 solution (~9.8 wt %) followed by rapid annealing to 350 °C (under nitrogen) produced a ~270 nm thick film comprised of ~30–100 nm grains (Figures 3d and S11b). The optical properties of the resulting Bi2Se3 and Bi2S3 thin films were characterized by transmission UV–vis NIR spectroscopy using an integrating sphere. The direct optical band gap transitions were estimated from Tauc plots (i.e., $a(h\nu)^2$ vs $h\nu$), giving values of $E_{g,dir}$ = 1.7 and 1.5 eV for Bi2Se3 and Bi2S3, respectively (see Figures S12 and S13). These values agree well with the direct band gaps previously reported for Bi2Se3 and Bi2S3 ($E_{g,dir}$ = 1.7–1.9 and 1.4–1.7 eV, respectively).12

To investigate why this edtH+/en binary solvent mixture possesses high solvent power for the V2VI3 chalcogenides, a number of informative control experiments were performed by qualitatively gauging the solubility of the metal chalcogenides in various solvent mixtures over the course of several minutes. Generally, the V2VI3 chalcogenides were insoluble in the absence of edtH2 with the exception of As2S3 and As2Se3, which were soluble in neat en. This demonstrates the need for a thiol component in the solvent mixture. Experiments with mixtures of 2,3-butanedithiol with en, or mixtures of edtH3 with diethylenetriamine, showed good solvent ability for Bi2S3. This is consistent with the observed solvent power of edtH+/en since all these binary solvent mixtures possess 1,2-dithiol/1,2-diamine functionality. On the other hand, mixtures of edtH+ with n-butylamine possessed much poorer solvent ability for Bi2S3 as did mixtures of 1,3-propanedithiol or n-propanethiol with en. Moreover, it was found that mixtures of n-propanethiol and n-butylamine, or using edtH3 alone without amine, did not possess any appreciable solvent power for Bi2S3. It therefore appears that a 1,2-chelating dithiol and 1,2-chelating diamine are both essential for maximum solvent power for these materials.

It was found that the addition of edtH2 to en (1:10 vol/vol) resulted in a ~15 000× increase in electrolytic conductivity (i.e., the observed solution resistance fell from 2.04 MΩ to 136 Ω), suggesting that extensive ion formation occurs in this binary solvent mixture. The formation of ionic species upon mixing the observed solution resistance fell from 2.04 MΩ to ~9.8 MΩ. The dissolution mechanism would then be expected to increase the overall concentration of ions in solution, which is consistent with electrolytic conductivity data. Resistances of 94 and 86 Ω were observed for solutions of Sb2Se3 and Bi2S3, respectively, which are lower than the 136 Ω measured for an identical volume of the 10:1 vol/vol en/edtH2 solvent mixture (i.e., conductivity increased by a factor of ~1.4–1.6 upon V2VI3 dissolution). Thioloathiomellitate anions are well established by the literature,14 and the formation of analogous species in V2VI3/en/edtH2 systems is plausible, but further work is required to confirm this hypothesis.

In summary, this work describes a simple and general method for the solution processing of bulk V2VI3 chalcogenides using a relatively nonhazardous binary solvent mixture. Specifically, we have discovered an ionic solvent mixture resulting from 1,2-ethylenediamine and 1,2-ethanethiol that can be used to dissolve and redeposit nine bulk V2VI3 semiconductors. Among the nine semiconductors that can be dissolved with this solvent mixture, As2Se3, As2S3, Sb2Se3, Sb2S3, Bi2Se3, and Bi2S3 can be recovered as phase pure material after deposition and annealing. The V2VI3 solutions hold promise for direct-thin film deposition via spin coating, which was demonstrated for the deposition of Sb2Se3 and Bi2S3 thin films. We believe these initial results indicate that the chemistry can be further extended to other families of chalcogenide materials and may hold promise for applications that would benefit from the solution deposition of semiconductor thin films.

**ASSOCIATED CONTENT**

1 Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.
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