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GROWTH OF TUNGSTEN SELENIDE FILMS THROUGH
PYROLYTIC CONVERSION AND ANODIC ELECTROOXIDATION
OF AMMONIUM SELENOTUNGSTATE ((NH₄)₂WSe₄)

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ABSTRACT

W_xSe_y thin films have been prepared by the spray pyrolysis and anodic electrodeposition of solutions of ammonium selenotungstate, (NH₄)₂WSe₄, with y/x usually between two and three for the sprayed films and y/x >> 1 for the electrodeposited films. The sprayed films indicated regions of crystalline WSe₂ and have optical absorbance spectra consistent with a mixture of WSe₂, WSe₃, and selenium. The electrodeposited films are totally amorphous, highly photoconductive, and have optical absorbance spectra typical of amorphous or vitreous selenium. The sprayed films transform into WO₃ at temperatures greater than 350°C in the presence of oxygen while the electrodeposited films tend to evaporate and/or decompose upon annealing.

Introduction

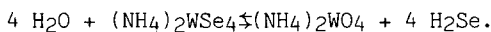
Semiconducting heavy metal dichalcogenides have attracted recent interest as approximations to quasi two-dimensional systems (with associated anisotropic characteristics) and because of their potential usefulness in photovoltaic applications. One of the more studied of these compounds is tungsten diselenide (WSe₂) which has been successfully utilized in both solid-state (1,2) and photoelectrochemical (PEC) photovoltaic cells (3). Unfortunately, the compound is not convenient to produce in a usable macroscopic crystalline form. The method most used previously to produce the material has been halogen vapor transport which has been useful for

preparing small crystals or platelets used in PEC cells (1-3). It would be possible to use hydrogen selenide or selenium tetrafluoride and tungsten halides or tungsten organometallics in a chemical vapor deposition scheme to produce WSe₂ thin films directly (4). However, the extreme toxicity and serious safety problems associated with these gases limit their practical use.

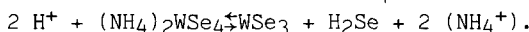
We have successfully produced thin films of W_xSe_y with definite X-ray diffraction evidence of crystalline WSe₂ by the direct thermal decomposition of ammonium selenotungstate, (NH₄)₂WSe₄ (AST), aqueous solutions on heated glass substrates. We have also produced thin films of W_xSe_y with y>>x by the anodic electrodeposition of solutions of AST dissolved in water or N-N dimethylformamide (DMF). We wish to report preliminary results of our investigations as encouraging evidence that the former process could eventually be used as a relatively safe, simple, and practical way to produce WSe₂ thin films.

Chemistry

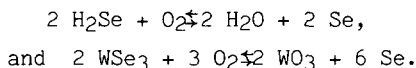
(NH₄)₂WSe₄ is produced by bubbling and saturating a solution of ammonium tungstate, (NH₄)₂WO₄, with hydrogen selenide gas (5). If the solution is not saturated, a red mixed compound, (NH₄)₂WO₂Se₂, may be produced instead of the green AST. AST is unstable in the presence of moisture and slowly decomposes according to



The pungent odor of H₂Se is readily discernible when the compound is dissolved in water and, thus, there are still safety precautions that must be followed in the use of AST. Hydrogen ions increase the rate of decomposition according to



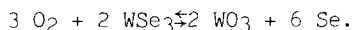
Tungsten triselenide, WSe₃, is a muddy-brown, always amorphous compound with probably a definite composition if it is analogous to WS₃ (6). When an acidic solution of AST is allowed to sit for many hours, the WSe₃ suspension settles to the bottom of the beaker. After a longer period of time, the bright blood red color of a fresh AST aqueous solution changes to a dingy-brick red color indicative of amorphous selenium produced according to



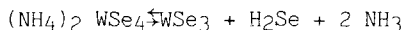
The aqueous solutions usually exhibit the muddy-brown color of WSe₃ for a period immediately following acidification.

We also dissolved AST in N-N dimethylformamide. The color of this solution is much more orange than that of the aqueous solution. The odor of H₂Se is still present but is much less noticeable than for the aqueous solutions. The decomposition of this solution is slow with little evidence of WSe₃ formation but with eventual formation of a red selenium suspension because of reactions with oxygen and trace amounts of water.

WSe₃ is unstable when heated and eventually transforms into WSe₂ and selenium in the absence of oxygen. Oxygen produces the competing reaction



The extent to which this latter reaction interferes with the creation of WSe_2 depends upon the temperature and amount of O_2 present. WSe_2 is stable in air to temperatures above 500°C . $(\text{NH}_4)_2\text{WSe}_4$ will directly transform into W_xSe_y upon heating in the absence of oxygen, probably according to



The initial objective was to investigate if aqueous solutions of AST would directly decompose into W_xSe_y thin films when sprayed onto heated substrates.

Experimental

The apparatus used in the spray pyrolysis technique has been previously described (7) and consisted of a glove box, a gas-fed spraying nozzle, and a substrate heater system with thermocouples. Deionized water and Alfa (Danvers, Massachusetts) $(\text{NH}_4)_2\text{WSe}_4$ were used along with hydrochloric acid, acetic acid, and ammonium hydroxide. Hydrazine (N_2H_4) was tried as a reducing agent but had little noticeable consistent effect. N_2 was the propellant gas. Corning 7059 glass pieces served as substrates. Various pH's were utilized with no definite pH dependence in film characteristics noted. At acidic pH's, there were problems with H_2Se generation and WSe_3 formation within the spray solution, thus, clogging the nozzle and making it difficult to keep AST in solution.

Unfortunately, our apparatus was not originally designed for use in an inert atmosphere due to various added ports for wiring, tubing, etc., so a completely oxygen free atmosphere was not possible. However, the N_2 propellant was emitted with the solution from a nozzle and enveloped the heated substrate with a very N_2 rich local atmosphere. The consistency of the spray was usually selected to be a fine uniform mist in a conical pattern that totally covered the small ($<1 \text{ in}^2$) substrates. The solution usually consisted of 50-100 mg of AST in 250 ml of solvent.

The glass substrates were placed inside a metal well for temperature stabilization. Substrate temperatures ranged from 100°C - 500°C and the minimum spray rate was approximately 4 ml/min. Low temperatures and high spray rates favored "puddling" of the spray on the substrate and associated nonuniformities. However, for temperatures much above 350°C , the deposits were thin, smooth, and yellow films of tungsten trioxide (WO_3), thus, reflecting the oxygen presence in the atmosphere. For lower temperatures, the films were a lustrous dark gray color with a grainy consistency. If a gray film was initially grown and the temperature suddenly increased, the film would quickly change to a yellow color. There seemed to be a critical temperature for this transformation near 350°C . The fact that higher spray rates favored the gray films was probably due to the lower substrate surface temperature under these conditions. The best gray films were grown at temperatures between 250° and 350°C because of the problems with vaporizing the water quickly enough at lower temperatures. Those films grown at temperatures between 100°C and 200°C tended to be blacker, thicker, and less uniform than those grown at higher temperatures due to the "puddling" problem and a higher selenium content.

Sprayed Film Data

Figure 1 exhibits the X-ray diffraction spectrum for one of the more uniform gray films on glass after annealing in air at temperatures between 200°C and 300°C. Note the peak near 13.6° which is the dominant Cu- α WSe₂ peak. The peak is broad and weak but definite and is increased upon annealing. Thus, the bulk of the film material is probably amorphous WSe₃ with possibly some amorphous selenium and small amounts of crystalline WSe₂ present. Annealing converts WSe₃ into WSe₂ and selenium. Higher temperature air annealing has been initially avoided because of the strong possibility of converting our better films into WO₃. Figure 2 shows the X-ray microprobe analysis spectrum for one of the gray films. Note that appreciable tungsten and selenium are present with a Se/W ratio near 2.5. The large silicon peak and smaller barium peaks are due to the substrate.

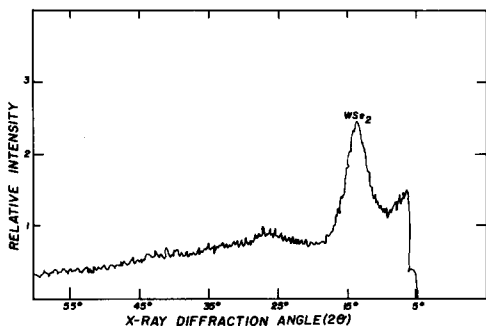


FIG. 1

Typical Cu- α X-ray diffraction data for sprayed W_xSe_y films.

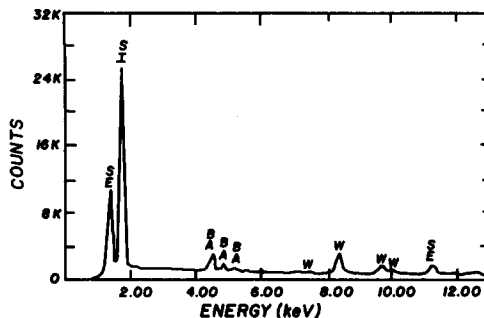


FIG. 2

Representative X-ray microprobe analysis data for sprayed W_xSe_y films on glass substrates.

Figure 3 exhibits the optical absorbance spectrum of one of the sprayed films corrected for the substrate but not for the film reflectance. The absorption edge near 1200 nm is rather broad indicating the predominantly amorphous nature of the film but is approximately consistent with that of WSe₂ with a lowest indirect band gap of 1.16 eV ($\lambda \approx 1100$ nm) (8).

Further required work on the spray process includes the spraying of the films at higher temperatures in a completely oxygen free atmosphere and the use of an organic solvent to avoid hydrolysis of the AST. Higher temperature annealing in an inert or reducing atmosphere is also warranted.

A two nozzle system where a neutral or basic aqueous solution of AST and an acid and/or reducing solution are separately sprayed onto the substrate at individually controlled rates would be advantageous. A more detailed analysis of the film characteristics as a function of the process parameters is also needed as well as detailed evaluations of the films' optical and electrical properties.

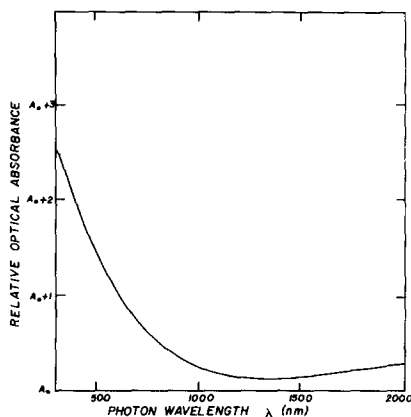
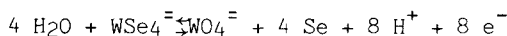


FIG. 3

Relative optical absorbance spectrum for a sprayed W_xSe_y film.

Electrodeposition Process and Results

We have also conducted preliminary experiments on the electrodeposition of W_xSe_y from aqueous or DMF solutions of AST using an apparatus previously described (9). No cathodic deposits were obtained except for a thin brick-red film of selenium, after prolonged electrolysis, resulting from minor oxidation of the anodic deposits into selenium cations and subsequent cathodic reduction of these cations. However, we were successful in anodically producing thick, smooth, and adherent gray-brown deposits on transparent, conductive $In_2O_3:Sn$ (ITO) coated glass substrates. The films grown from DMF solutions were less adherent and redder than those grown from aqueous solutions but were similar in gross optical absorbance characteristics. Figure 4 exhibits the absorbance spectrum for a film electrodeposited from an aqueous solution. Note the sharp and strong absorbance starting near 1000 nm. All of these films were totally amorphous and strongly photoconductive. Figure 5 exhibits data for the X-ray microprobe analysis of one of these films. Note the strong predominance of selenium but definite evidence of some tungsten. Annealing tended to destroy the films. From these observations, we concluded that the deposits were predominantly vitreous or amorphous selenium produced by the oxidation of the WSe_4^- ion according to



or a similar reaction involving WO_3 in strongly acidic solutions. An analogous oxidation reaction involving dissolved O_2 or DMF probably exists in the DMF solution. It is possible that small amounts of WSe_2 or WSe_3 are present but the tungsten may also be in an occluded or impurity form. Thorough rinsing precludes any adsorbed solution solutes contributing to the tungsten signal.

It should be noted that AST might serve as a good complexing agent for selenide ion, thus, shifting the Se/Se^- reduction potential to more positive potentials. This is especially important considering that tungsten cannot

normally be electrodeposited as a separate metallic phase and would not present strong interference in an electrochemical analysis.

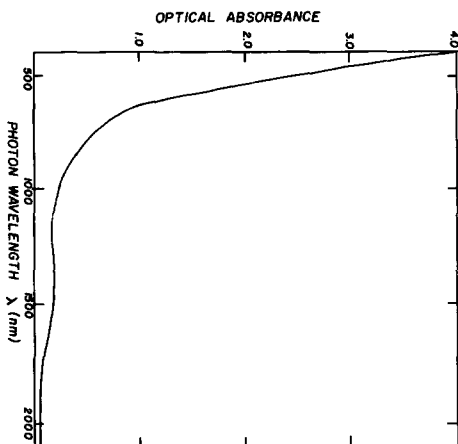


FIG. 4

Optical absorbance spectrum typical of anodically electrodeposited W_xSe_y films.

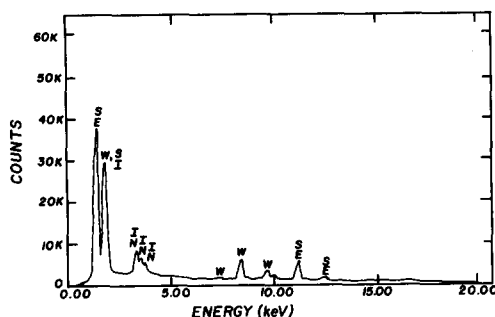


FIG. 5

Microprobe analysis data for an electrodeposited W_xSe_y film on an ITO substrate.

Further needed work in the electrodeposition scheme includes detailed voltammetric and/or polarographic analysis of the various AST solutions. The use of other organic solvents with large decomposition voltages is needed to see if WSe_4^{2-} can be reduced to WSe_2 . The analogous compounds $(NH_4)_2WS_4$, $(NH_4)_2MoS_4$, and $(NH_4)_2MoSe_4$ also warrant investigation in both the spray and electrodeposition processes.

Conclusions

W_xSe_y thin films consisting primarily of a WSe_3/WSe_2 mixture have been spray pyrolyzed from aqueous solutions of ammonium selenotungstate, $(NH_4)_2WSe_4$. The films are gray in color and grainy but decompose into smooth WO_3 upon heating above $350^\circ C$. There exists definite X-ray diffraction evidence of crystalline WSe_2 present in the films and X-ray microprobe analysis indicates a Se/W ratio not unreasonable for such a mixed film although excess selenium may exist in some films. Optical absorbance spectra indicate an absorption edge consistent with WSe_2 but broadened and shallowed by the amorphous nature of the deposits and probably indicative of WSe_3 and amorphous selenium.

Primarily vitreous or amorphous thin films of selenium have been anodically electrodeposited from aqueous or N-N dimethylformamide solutions of $(NH_4)_2WSe_4$ although there are definite amounts of tungsten in the deposits as evidenced by X-ray microprobe analysis data. The optical absorbance spectra indicate a sharp and strong increase in absorption near 1000 nm similar to that of selenium. The films are very photoconductive and are very adherent and uniform.

It should be reemphasized that $(\text{NH}_4)_2\text{WSe}_4$ will produce trace amounts of toxic hydrogen selenide gas upon exposure to water and/or hydrogen ions and, thus, appropriate safety procedures must be used in dealing with the material. Otherwise, the spray pyrolysis and electrodeposition techniques seem attractive potential methods of producing WSe_2 and selenium, respectively, thin films.

Acknowledgements

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