

A simple and low-cost technique for electroless deposition of chalcogenide thin films

Ivan Grozdanov†

Department of Chemical, Bio and Materials Engineering, Arizona State University, Tempe, AZ 85287-6006, USA

Received 12 January 1994, in final form 14 March 1994, accepted for publication 18 March 1994

Abstract. A simple and economical electroless chemical deposition technique for deposition of several metal sulphides and selenides is presented. Aqueous solutions of metal salts and of sodium thiosulphate or sodium selenosulphate were used for the chemical bath. The technique is based on hydrolytic decomposition of the various metal–thiosulphate or metal–selenosulphate complexes in aqueous media, at a suitable temperature, concentration and pH.

The technique presented in this paper has been successfully used for deposition of Cu_2S , CuS , PbS , Sb_2S_3 and $\text{Sb}_{2-x}\text{Bi}_x\text{S}_3$ in acidic media, and Ag_2S , Cu_2Se and PbSe in alkaline media, on various substrates, such as glass, metal, plastics, alumina, silicon and sapphire. Depending on the deposition time and the individual system, films of thicknesses up to $0.3 \mu\text{m}$ were obtained from a single bath. The prospects of this technique are very good for multilayer combinations, solid solutions, and possibly ternary compounds as well.

This technique was found to be suitable for any size and shape of substrate. It is a non-polluting and economical technique, since the bulk precipitates are of a relatively high purity and can be used as semiconducting powders, mineral pigments etc.

The optimal conditions for deposition of each kind of film are described and the corresponding x-ray diffraction patterns are presented. Optical spectra in the wavelength interval between 300 and 2500 nm for each of the films are also supplied. The sheet resistivity and type of conductivity for each kind of film have also been determined.

1. Introduction

The semiconductive metal chalcogenides represent an interesting class of materials which are attractive for large-scale applications because of the easy availability and low cost of the starting materials. In recent years, semiconductive chalcogenide films of different metals have found worldwide application in various fields of science and technology. The utilization of these promising semiconductive materials needs low-cost production and pollution-free techniques.

Most of the semiconducting metal chalcogenides are important materials for applications in various photoelectric and other kinds of devices. Thin films of metal chalcogenides can be deposited on glass, metal, plastics and other substrates by a variety of techniques, such as pyrolysis, sputtering, evaporation and chemical

deposition. The optical and electrical characteristics of the deposited materials often depend on the deposition technique used.

Among the chemical deposition methods, electroless deposition from aqueous solutions is the simplest and most economical one. Successive immersion of the substrate in a solution of metal ions and then in a second solution containing a sulphide agent has been successfully used for thin film deposition of Bi_2S_3 , SnS , Ag_2S and Cu_2O [1–4]. Solution growth of thin films from a single bath which provides both the metal ions and the desired chalcogenide ions has also been used extensively [5–8]. In the latter, the metal ions are usually complexed by a suitable complexing agent, such as triethanolamine (TEA), citric acid, EDTA etc, which would then gradually release metal ions during the course of the reaction. Another agent is used to provide chalcogenide ions: thiourea, sodium thiosulphate and sodium selenosulphate have often been used for this purpose.

The main idea of this work has been to choose an

† Visiting Scholar from University 'Kiril i Metodij', Faculty of Natural Sciences and Mathematics, Institute of Chemistry, Skopje, Republic of Macedonia.

appropriate chemical substance which would be both a complexing agent for the metal ions and at the same time a source of chalcogenide ions. This would make the film deposition less expensive and the deposited materials of higher purity, since fewer chemicals would be used in the chemical bath. Sodium thiosulphate and sodium selenosulphate were found very appropriate for this purpose, since both are known as good complexing agents for the heavy metals and are also capable of releasing sulphide/selenide ions in either acidic or alkaline media. There have been reports in the literature where sodium thiosulphate or sodium selenosulphate has been used in more complex chemical baths [6, 9] and in a similar technique developed for deposition of Cu_xS films [10].

In this paper, a highly simplified and economized electroless technique for deposition of a number of semiconductive metal sulphides and selenides on different kinds, shapes and sizes of substrates is presented. Also, to the best knowledge of the author, this paper contains the first report in the literature on chemical deposition of Cu_2Se films. Additionally, depositions of PbS , Sb_2S_3 and $\text{Sb}_{2-x}\text{Bi}_x\text{S}_3$ films from acidic baths, and Ag_2S and PbSe films from alkaline baths, with this technique were carried out from simpler chemical baths than those previously reported in the literature [11, 12]. The optimal chemical bath composition for each kind of film is specified, as well as other relevant conditions for obtaining uniform, mirror-like thin films. Some basic optical and electrical properties of the various films are also reported, while the detailed optical and electrical characteristics of the films will be a matter of subsequent study and publication.

2. Experimental details

2.1. Experimental set-up

This technique is very simple and does not require any special set-up. It is convenient for both small and large substrates. For example, a 50 ml beaker can be used for small substrates and a large bath container for large substrates. In this work, glass or plastic containers of up to 1000 ml total volume have been used to insert as many as 15–20 substrates the size of a standard microscope glass slide (75 mm \times 25 mm \times 1.0 mm). Figure 1 shows this kind of set-up. The glass, metal or other kind of substrates were slid into plastic clip binders commonly used to bind documents or similar paper-poster plastic hangers. Several such rows of hanging substrates can be inserted into a 1000 ml container, 15 cm in diameter. Since no stirring is necessary, the bath container can be of any shape, to best suit the substrates used. Also, most of the depositions can be done at room temperature (although this can significantly prolong the deposition time for some of the films), which allows the use of plastic containers, if preferred.

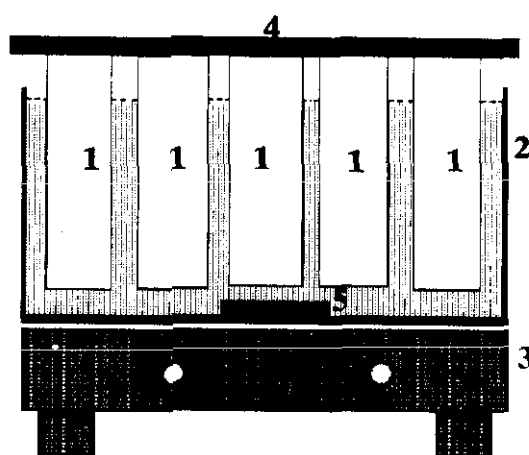


Figure 1. Deposition set-up. (1) Substrate, (2) bath container, (3) hot plate with magnetic stirrer, (4) plastic slide-binder, (5) magnetic stirring rod (optional).

2.2. Preparation of the substrates

Poor adhesion and non-uniform films are common problems when depositing films on smooth substrates by chemical deposition. Therefore, special attention was paid to cleaning and activating the substrate surface. Glass substrates were boiled in chromic acid, washed in deionized water and then activated by soaking in a 0.03% aqueous solution of SnCl_2 for a few minutes. The substrates were then taken out and dried in air. In some cases it was necessary to bake them at this point for about 20 minutes at 250 °C to ensure good adhesion at the surface. Baking creates an ultra-thin layer of SnO_2 on the substrate surface, which proved to be an excellent solution to the problem of poor adherence for some of the materials. Metal substrates (Cu, Al, Ti and Zr) were brushed with an oxygen bleach cleanser, such as 'Ajax' powder, using an ordinary toothbrush. A few dips in chromic acid were also found helpful after this. The pre-treated metal substrates were then dried in air before use. Plastic substrates (pieces of overhead transparencies were used for this purpose), alumina and silicon were first washed in liquid detergent and then activated in SnCl_2 for a few minutes and dried in air before use.

2.3. Deposition of the films

2.3.1. Cu_2S films. Thiosulphate is known to reduce Cu(II) to Cu(I) and then form successive complex thiosulphate compounds with Cu(I) [13]. It was found that at a molar ratio 2:1 of thiosulphate to copper, Cu_2S precipitates upon hydrolytic decomposition of the thiosulphate complexes. The bath parameters were set as follows.

For a 100 ml total volume, 8–10 ml 0.5M aq.sol. CuSO_4 were placed into a beaker and 8–10 ml 1.0M aq.sol. $\text{Na}_2\text{S}_2\text{O}_3$ were added. The blue solution turned green at this point, due to the reduction of Cu(II) to Cu(I) by the thiosulphate. Deionized water was added to make the volume up to 80–100 ml. The pH of the bath should be about 5 and can be adjusted with diluted acetic acid if necessary. Previously cleaned and activated

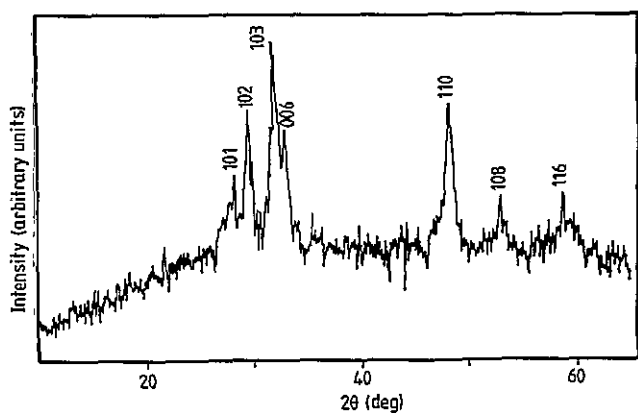


Figure 2. XRD pattern of a CuS film on a glass substrate.

substrates were then inserted into the beaker and the bath was warmed and kept at 40–45 °C. No stirring was applied. At this temperature, the solution turned yellow and soon a brown precipitate began to form in the beaker and golden-yellow films were deposited on the activated sides of the substrates. Once the precipitation began, the reaction at this temperature was completed within 25–35 minutes. The substrates were then taken out, rinsed with distilled water, dried in air and preserved for characterization. The x-ray studies have shown that these films are amorphous. All attempts to produce polycrystalline films, even upon annealing, were unsuccessful. However, chemical analysis (Rutherford backscattering) revealed the ratio of copper to sulphur in the obtained films to be 2:1. The optical spectrum of these films is shown in figure 9, curve a.

2.3.2. CuS films. Increasing the molar ratio of thiosulphate to copper to 3 or higher yields a black precipitate in the bath and olive-green film deposition. The x-ray diffraction pattern of these films (figure 2) revealed that the material is CuS. Thus, in excess of thiosulphate, the 'sulphur-rich phase' of the copper-sulphur phase diagram was obtained upon hydrolytic decomposition of the thiosulphate complexes. The optimal bath conditions for these films were found to be as follows.

8–10 ml 0.5M CuSO₄ aq.sol. were placed in a 100 ml beaker and 15–20 ml 1.0M sodium thiosulphate aq.sol. were added. 0.2 ml glacial acetic acid were also introduced into the bath and distilled water was added to make a total volume of 80–100 ml. The bath was slowly heated to about 60–70 °C and kept within this temperature interval. Once the precipitation begins, the films should be ready in 30–40 minutes. The optical spectrum of these films is presented in figure 9, curve b.

The details of this interesting copper-thiosulphate system with respect to the formation of copper sulphide films of a different chemical composition are under further investigation.

2.3.3. PbS films. The chemical bath for growth of PbS films with this technique was composed as follows. For a total volume of 100 ml, 30 ml 1.0M aqueous

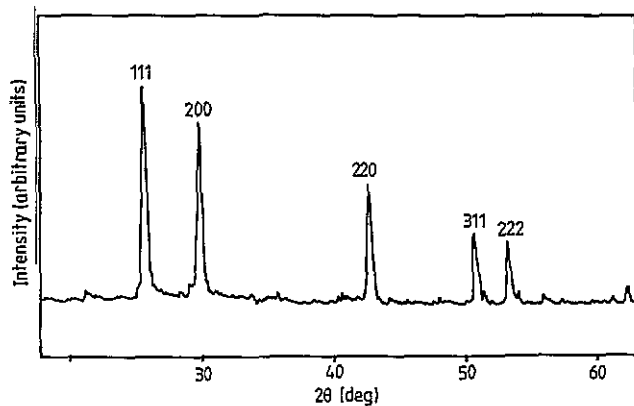


Figure 3. XRD pattern of a PbS film on a glass substrate.

solution of sodium thiosulphate were placed in a beaker and 12 ml 0.5M aqueous solution of lead(II) nitrate were slowly added with constant stirring. This gave a colourless, clear solution of lead thiosulphate complexes. The pH of the bath should be 4–6 and small amounts of diluted acetic or nitric acid can be used to adjust it if necessary (this will happen if lead(II) acetate is used instead of lead(II) nitrate, for example). The optimal temperature for this system was found to be in the range 65–75 °C. A grey, mirror-like thin film began to be deposited at the surface of the substrate after 40–65 minutes, depending on the temperature of the bath. Once deposition began, the film growth within the specified temperature range could go on for up to three hours, depending on the thickness desired. Upon removal, the films were rinsed with distilled water and soaked under water for a few hours to ensure thorough cleansing. The x-ray diffractograph of the obtained films revealed a mixture of both amorphous and polycrystalline phases of the as-prepared films. Annealing of the films at 100 °C led to further crystallization and a polycrystalline phase was thus obtained (figure 3). The optical spectrum of PbS films in the range 300–2500 nm is shown in figure 9, curve c.

2.3.4. Sb₂S₃ films. The difficulties of using antimony salts in aqueous media arise from the strong tendency of antimony salts to hydrolyse in water solutions and precipitate insoluble hydroxy salts. Clear solutions can be obtained only in strongly acidic media or in complexing agents. For this method, solid antimony(III) chloride was dissolved in a small volume of glacial acetic acid and then complexed by sodium thiosulphate.

The following bath parameters were found to be optimal. 3.5–4.0 g of SbCl₃ were dissolved in 7–8 ml glacial acetic acid and a 1.0M aqueous solution of sodium thiosulphate was slowly introduced with constant stirring until a clear solution was obtained. As much as 100 ml of 1.0M sodium thiosulphate may be needed. Then 400–450 ml of cold (10–15 °C) distilled water were added and the substrates were introduced into the bath. Vertically supported substrates had films deposited on both sides, while horizontally mounted substrates had films deposited on the side facing the bottom of

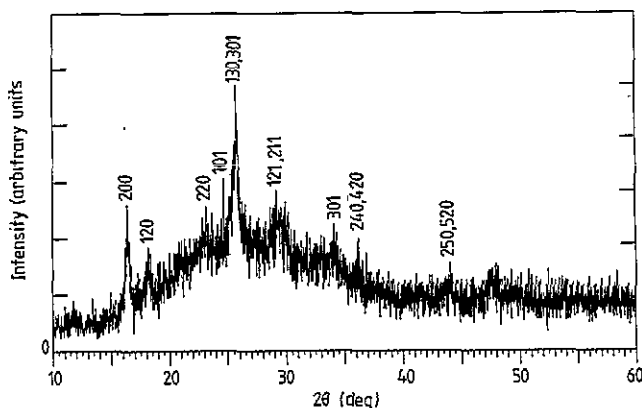


Figure 4. XRD pattern of an Sb_2S_3 film on a glass substrate, annealed in air for 6 h at 170 °C.

the bath container. In about 10–20 minutes, a yellow-orange precipitate of amorphous Sb_2S_3 began to fill the bath. For good adherence of the films to the substrates, they need to be left in the bath for at least five and up to 24 hours, depending on the desired thickness in the range 0.1–0.3 μm . It is important to note that cold distilled water should be used for the bath, otherwise precipitation begins immediately, which is inconvenient for film deposition. Plastic bath containers can be used for this system.

The as-deposited films were transparent, yellow-orange in appearance and amorphous. Polycrystalline films were obtained by post-deposition annealing of the films at 170–200 °C. The x-ray diffraction pattern of an annealed film is shown in figure 4, and the optical spectrum of the as-deposited film is shown in figure 9, curve d.

2.3.5. $\text{Sb}_{2-x}\text{Bi}_x\text{S}_3$ films. The compounds Sb_2S_3 and Bi_2S_3 both have an orthorhombic crystal lattice. These isomorphous compounds can form solid solutions of a desired mixed composition, giving materials of variable bandgaps [11].

The chemical bath for growing these films was similar to the one described for growth of Sb_2S_3 , except bismuth(III) nitrate was also added along with antimony(III) chloride. The value of x in $\text{Sb}_{2-x}\text{Bi}_x\text{S}_3$ can be varied between zero and 1.90. However, pure Bi_2S_3 films were difficult to obtain, because of poor adherence of the films to the substrate surface. The as-deposited films were amorphous and up to 0.3 μm thick.

2.3.6. Ag_2S films. The precipitation reaction for Ag_2S from thiosulphate solutions in acidic media was too fast even at lower temperatures of the bath and thus inconvenient for film growth. Therefore, the Ag_2S films were grown in alkaline media. The typical bath for a total volume of 100 ml was composed as follows.

1.0 g of AgNO_3 was placed in a 100 ml beaker and dissolved in a small amount of distilled water. Aqueous ammonia solution (1:3) was gradually added just until the forming precipitate of AgOH was dissolved (complexed by NH_3). The pH of the solution should be 9–11. Filtering of the solution at this point was

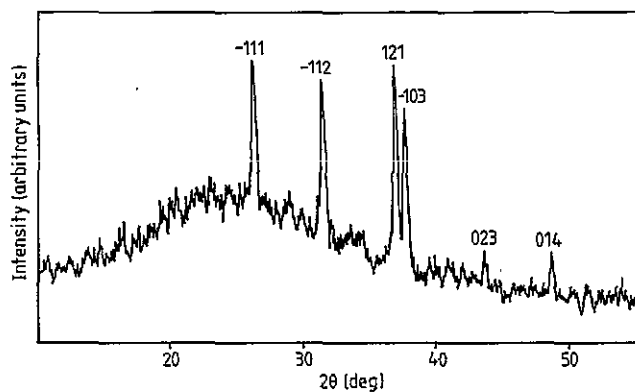


Figure 5. XRD pattern of an Ag_2S film on glass, annealed in air for 3 h at 150 °C.

found helpful. Then 5.0 ml of 1.0 M aqueous solution of sodium thiosulphate were introduced and distilled water was added to make a total volume of 90–100 ml. The substrates were introduced vertically into the bath and the bath was warmed and kept at 45–55 °C. At this temperature the solution starts to develop a yellow-brown colour, and soon a brown precipitate fills the beaker. The reaction was completed within 20–30 minutes after precipitation began, and yellow-brown films of Ag_2S were deposited onto the substrates. The films were then taken out, washed in distilled water and dried in air.

X-ray studies of the films showed that the as-prepared films were a mixture of amorphous and polycrystalline phases. Annealing of the films at 150 °C led to further crystallization. The x-ray diffractograph of an annealed Ag_2S film is shown in figure 5.

The optical spectrum of an as-deposited Ag_2S film in the range 300–2500 nm is shown in figure 10, curve a. It is apparent that the transmittance of the Ag_2S film in the infrared region increases with increasing wavelength. Thus, Ag_2S films resemble PbS films in this respect.

2.3.7. Cu_2Se films. Bright yellow to reddish Cu_2Se films were obtained from a copper-selenosulphate chemical bath, following the procedure to be described.

For a total volume of 100 ml, 8–10 ml 0.5 M aqueous solution of CuSO_4 were introduced in a 100 ml beaker and 1:3 aqueous solution of ammonia was added until a clear, deep-blue colour solution was obtained. The pH of the bath should be in the range 9–11. Then 4–5 ml 1.0 M aqueous solution of sodium selenosulphate were added and the solution turned yellowish. The substrates were then vertically mounted in the bath and the bath was warmed and kept at 40–45 °C. Soon, a brown to red-brown precipitate began to form, and within a few minutes transparent yellow to reddish films were deposited onto the substrates. 25–40 minutes later, the films were taken out, washed with distilled water and dried in air. Mirror-like, uniform films with excellent adherence to the substrates were obtained in this way.

The x-ray diffraction pattern of a fairly thick film ($\sim 0.3 \mu\text{m}$) is presented in figure 6. It shows that the obtained films are Cu_2Se , as expected from a bath of 1:1

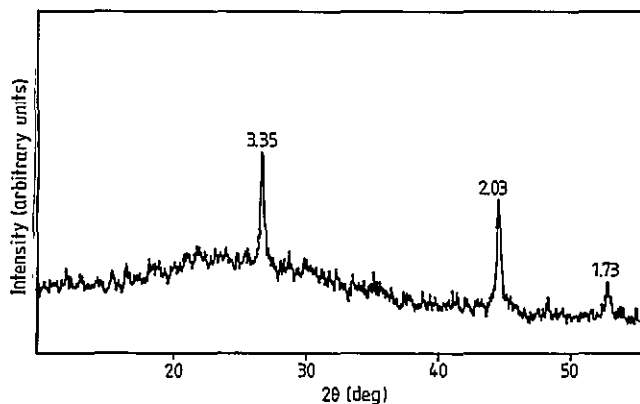


Figure 6. xRD pattern of a Cu_2Se film on glass.

ratio between copper(II) and selenosulphate. The optical spectrum of these films is included in figure 10, curve b.

2.3.8. CuSe films. Increasing the molar ratio of selenosulphate to copper to 1:3 or higher, in a chemical bath similar to the one previously described for Cu_2Se films, produced a deep-green precipitate in the bath and olive-green colour films on the substrates. The adherence of this material to the substrates was poor, so that the obtained films could hardly be kept on the substrate after washing with distilled water. Another way these films were produced was by following the procedure for Cu_2Se films until the desired thickness was achieved; at that point, excess of sodium selenosulphate was introduced into the bath, with stirring. In a matter of minutes the films turned olive-green, and x-ray analysis confirmed that CuSe films were produced. The adherence of the films obtained in this way was much better.

The x-ray diffraction pattern shown in figure 7 was produced from scraps of the film material and confirmed the expected CuSe (the hexagonal Klockmannite phase) identity of these films. Thus, similar to the copper-thiosulphate system, Cu_2Se films were obtained on the 'copper-rich' side of the copper-selenide phase diagram, while CuSe films were produced on the 'selenium-rich' side.

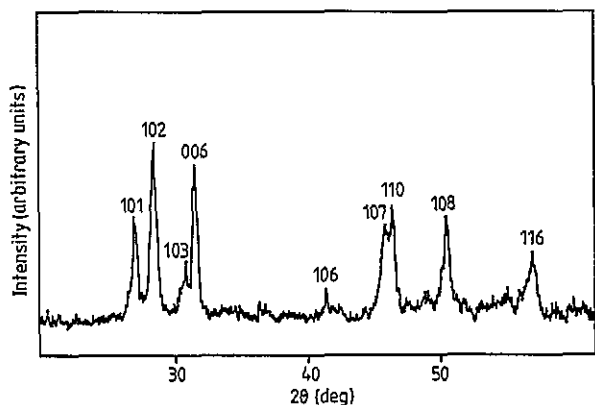


Figure 7. xRD pattern of CuSe , scraped from films.

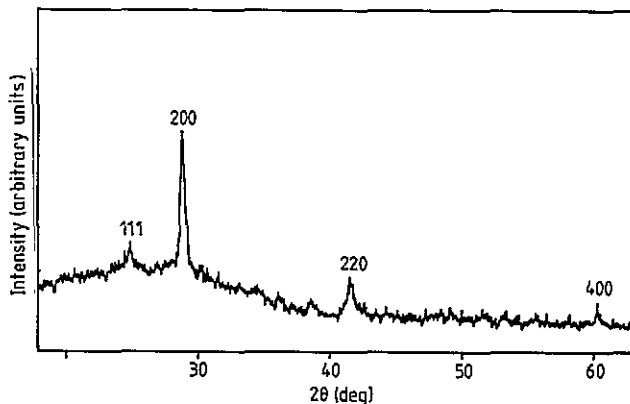


Figure 8. xRD pattern of a PbSe film on a glass substrate.

2.3.9. PbSe films. These films were obtained in alkaline media from a chemical bath of the following composition. 10–12 ml 0.5M aqueous solution of lead(II) nitrate were placed in a 100 ml beaker and enough 2M sodium hydroxide was added to obtain a clear solution. The pH should be about 10 and can be adjusted, if necessary, with acetic acid. Then 5–6 ml 1.0M aqueous solution of selenosulphate were introduced into the beaker and the substrates were mounted vertically in the bath. The temperature of the bath was raised and kept at 50–70 °C. Within this temperature range, a dark precipitate begins to form and brown to red, mirror-like films are deposited on both sides of the substrates. Once precipitation begins, the deposition process at the specified temperature range is completed in 40–50 minutes.

The x-ray diffraction pattern of a PbSe film is presented in figure 8 and its optical spectrum is shown in figure 10, curve d.

2.4. Characterization of the film materials

Identification of the deposited film material was carried out by x-ray diffractometry, on a Jeol Model JDX diffractometer, using nickel filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.54050 \times 10^{-10}$ m). The films used for this purpose were deposited on a glass substrate. They were $\sim 0.3\text{--}0.4$ μm thick. In one case (Cu_2S films) Rutherford backscattering (RBS) analysis was used to determine composition of deposited material. The thickness of the films was determined either by ellipsometry or by the weighing method, assuming the same density of materials as that of the corresponding bulk material.

Optical studies were carried out on a CARY 5 UV-VIS-NIR spectrophotometer. Films deposited on a glass substrate were used and transmission spectra were recorded against plain glass as a reference. In this way, the obtained spectra are those of the deposited materials only.

To examine the electrical properties of the deposited materials, gold electrodes, 1 cm long, 1 mm wide and 1 cm apart, were pasted on the surface of films deposited on a glass substrate. Sheet resistance was measured between the two electrodes by an electrometer

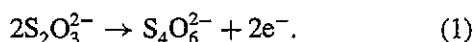
(Keithley 616). Standard two-probe thermoelectric measurements were also performed, to determine the type of conductivity.

3. Results and discussion

3.1. Chemical considerations

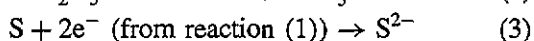
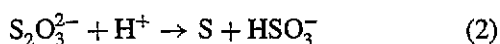
The deposition of the metal chalcogenide films described in this paper was based on three important properties of the thiosulphate/selenosulphate:

(1) The reducing ability of these agents, described for example using thiosulphate by the following half-cell reaction:

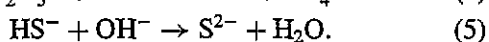
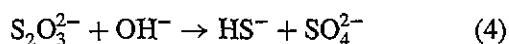


(2) The complexing ability of these agents, whereby metal-thiosulphate and metal-selenosulphate complexes are formed in excess of the complexing agents.

(3) The ability of these agents to gradually release sulphide/selenide ions upon hydrolytic decomposition, both in acidic media:



and in alkaline media:



These chalcogenide ions then combine with the metal ions released from the thiosulphate/selenosulphate complexes, upon hydrolysis, precipitating the corresponding chalcogenides. Due to the differences in the stability of the metal-chalcogenide complexes initially formed, the optimal concentrations, pH and temperatures convenient for film deposition are different for each system under consideration and need to be established.

Glass, plastics, alumina and several kinds of metal substrates (Cu, Al, Ti, Zr, Ni) were successfully used with this technique, to deposit thin films up to $0.3 \mu\text{m}$ thick from a single bath deposition. Multiple dips in

fresh baths, with the purpose of obtaining thicker films, were successful with most of the systems described in this paper, with the exception of CuS and CuSe films, where detachment of the initially deposited layers was observed upon immersion in a fresh bath. It is possible that the substantial excess of thiosulphate/selenosulphate in the fresh baths with these two systems was corrosive to the films.

Different shapes and sizes of substrates were also tried with this technique and it was concluded that thin films could be deposited with equal ease. For example, tubular substrates were used to deposit these films either on the inside or on the outside; these films were also deposited on the outside of ordinary electric bulbs. Pieces of thermo-stable overhead transparency sheets were also used successfully as substrates, and neat 'colour filters' and conductive plastic surfaces were produced. With the metal substrates, electroless colouring of the metal surfaces was observed in a variety of colours (green, blue, purple, grey etc), depending on the thickness of the deposited layers.

3.2. X-ray studies of the films

Since relatively low temperatures were applied for the deposition of the described film materials, most of them were obtained either in their amorphous phase or as amorphous/polycrystalline mixtures.

Most of the materials deposited in acidic media (Cu_2S , Sb_2S_3 and $\text{Sb}_{2-x}\text{Bi}_x\text{S}_3$) were amorphous, with the exception of CuS and PbS films in which the polycrystalline phase was predominant. Crystallization of the films was achieved by post-deposition annealing, at temperatures between 100 and 200 °C. However, no XRD pattern could be obtained for the Cu_2S films, and RBS chemical analysis was used to identify this material. The ratio of copper to sulphur was found to be 2:1.

The film materials deposited from alkaline baths were predominantly polycrystalline. Further crystallization was easily achieved by short-time (less than one hour) annealing and at lower temperatures (≤ 100 °C). Thus, most of the XRD patterns presented in figures 2–8 were obtained from annealed films, to make sure good reflections were produced. The XRD pattern of each film was compared against the standard JCPDS-ICCD

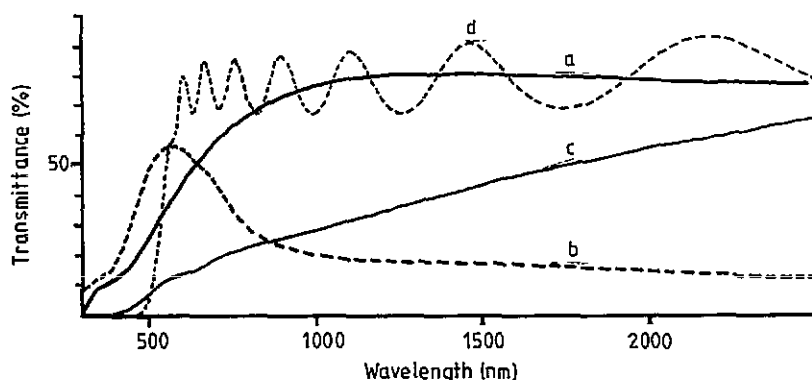


Figure 9. Optical transmission spectra of some chalcogenide thin films on glass substrates. (a) Cu_2S , (b) CuS, (c) PbS, (d) Sb_2S_3 .

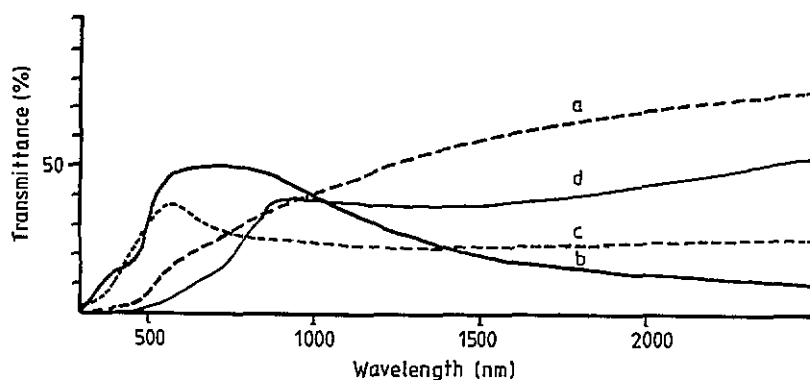


Figure 10. Optical transmission spectra of some chalcogenide films on glass substrates. (a) Ag_2S , (b) Cu_2Se , (c) CuSe , (d) PbSe .

diffraction patterns from the PDF-2 Database. The hkl indexes are shown above the reflections in the supplied figures. The only exception was made with the XRD of the Cu_2Se films, where the corresponding d -values in angstroms are displayed above the reflections; this was done because the obtained reflections fit all three forms of Cu_2Se displayed in the JCPDS list.

3.3. Optical and electrical considerations

The detailed optical, electrical and other relevant characteristics of these film materials are going to be a matter of further study. However, the optical spectra in the entire visible–near-infrared region for most of the

films described in this paper are presented in figures 9 and 10. These spectra reveal the basic characteristics of the films under consideration. The spectrum of Cu_2S (figure 9, curve a) shows that this material has high transmission in the spectral region 600–2500 nm. This feature of Cu_2S , coupled with our preliminary results on its high conductivity (of the order of $10^{-4} \Omega^{-1} \text{cm}^{-1}$), makes this material suitable as an electroconductive window coating. The optical spectrum of CuS films, on the other hand, (see figure 9, curve b) reveals that this material exhibits low transmission ($\leq 20\%$) throughout the near-infrared region (800–2500 nm). Thicker films of CuS ($\geq 0.25 \mu\text{m}$) had close to zero transmittance in the near-infrared region. Similar optical features to

Table 1. Optical energy gaps for the chalcogenide films.

Compound (formula)	Description of film (phase, colour)	Energy gap (eV)	Best fit
Cu_2S	amorphous, golden yellow	1.70	$\alpha^{1/2}$ versus $h\nu$
CuS	polycrystalline, green	2.20	$\alpha^{1/2}$ versus $h\nu$
PbS	mixture, gray	undetermined	
Sb_2S_3	amorphous, yellow-orange	2.48	$(\alpha h\nu)^2$ versus $h\nu$
	polycrystalline, gray	1.70	$(\alpha h\nu)^2$ versus $h\nu$
$\text{Sb}_{2-x}\text{Bi}_x\text{S}_3$	amorphous, orange to red	2.4–1.6	$(\alpha h\nu)^2$ versus $h\nu$
Ag_2S	polycrystalline, brown	2.20	$(\alpha h\nu)^2$ versus $h\nu$
Cu_2Se	polycrystalline, yellow	2.33	$(\alpha h\nu)^2$ versus $h\nu$
CuSe	polycrystalline, olive-green	2.40	$(\alpha h\nu)^2$ versus $h\nu$
PbSe	polycrystalline, yellow-red	undetermined	

Table 2. Basic electrical characteristics of the chalcogenide films.

Compound (formula)	Phase	Film thickness (μm)	Sheet resistance (Ω/square)	Type of conductivity
Cu_2S	amorphous	0.1	600	p
CuS	polycrystalline	0.1	105	p
PbS	polycrystalline	0.1	4000	p
Sb_2S_3	amorphous	0.3	10^{12}	n
$\text{Sb}_{2-x}\text{Bi}_x\text{S}_3$	amorphous	0.3	10^{13} – 10^{11}	n
Ag_2S	polycrystalline	0.1	10^8	n
Cu_2Se	polycrystalline	0.1	300	p
CuSe	polycrystalline	0.1	50	p
PbSe	polycrystalline	0.2	2000	p

those of CuS films are exhibited by Cu₂Se and CuSe films (see figure 10, curves b and c). This opens the door to possible application of these films as microwave shielding coatings or selective solar control coatings in regions with warm climates, as already suggested for CuS by other authors [15, 16]. The optical spectra of PbS (figure 9, curve c), Ag₂S (figure 10, curve a) and to some extent PbSe (figure 10, curve d) display a continuous increase of transmittance with increase of wavelength in the near-infrared region, a characteristic useful for application in infrared detectors [17].

Preliminary work has been done to determine the optical energy gaps for each kind of film material. Various fitting methods have been applied to determine energy gaps and the best fitting method is specified for each kind of film along with the obtained values, shown in table 1. Continuing investigations are in progress.

Sheet resistance and type of conductivity were also determined for the films under consideration in this paper. The obtained results are presented in table 2. Investigations continue, to determine free carrier concentrations, dependence of conductivity on film thickness, illumination, temperature etc.

4. Conclusions

A simple and low-cost electroless technique to deposit thin chalcogenide films on small or large substrates of different materials has been described. The technique presented in this paper has been successfully used for deposition of Cu₂S, CuS, PbS, Sb₂S₃ and Sb_{2-x}Bi_xS₃ in acidic media, and Ag₂S, Cu₂Se and PbSe in alkaline media, on various substrates, such as glass, metal, plastics, alumina, silicon and sapphire. Depending on the deposition time and the individual system, films of thickness up to 0.3 μm were obtained. The prospects of this technique are very good for multilayer combinations, solid solutions, and possibly ternary compounds as well. It is also convenient for both small- and large-scale fabrication of metal chalcogenide films.

The XRD patterns of each deposited material have also been presented, for its identification. Also, the optical spectra of each film in the spectral range 300–

2500 nm have been provided. Estimated optical energy gaps, sheet resistance and type of conductivity for each kind of film are also reported.

The detailed study and characterization of each system referred to in this paper is continuing, and the results will be published consecutively.

Acknowledgments

Part of this work has been carried out under a US Government (Fulbright) Grant, for which the author is indebted. The author's special gratitude goes to Dr Sandwip Dey of Arizona State University for providing facilities for this research work.

References

- [1] Ristov M, Sinadinovski Gj, Grozdanov I and Mitreski M 1989 *Thin Solid Films* **173** 53
- [2] Grozdanov I 1991 *Chemtronics* **5** 71
- [3] Ristova M and Toshev P 1992 *Thin Solid Films* **216** 274
- [4] Ristov M, Sinadinovski Gj and Grozdanov I 1985 *Thin Solid Films* **123** 63
- [5] Racheva T M, Dragieva I D, Djoglev D H and Dimitrova P P 1973 *Thin Solid Films* **17** 85
- [6] Kainthla R C, Pandya D K and Chopra K L 1980 *J. Electrochem. Soc.* **127** 277
- [7] Mondal A and Pramanik P 1983 *J. Solid State Chem.* **47** 81
- [8] Nair P K and Nair M T S 1992 *Semicond. Sci. Technol.* **7** 239
- [9] Gadave K M and Lokhande C D 1993 *Thin Solid Films* **229** 1
- [10] Lal M, Goyal N and Vohra A 1993 *Thin Solid Films* **225** 177
- [11] Lokhande C D 1991 *Mater. Chem. Phys.* **28** 145
- [12] Lokhande C D 1991 *Mater. Chem. Phys.* **27** 1
- [13] Nayak B B, Acharia H N, Mitra G B and Mathur B K 1983 *Thin Solid Films* **105** 17
- [14] 1964 *Spravochnik Chimika* vol III (Moscow: Chimia) p 136
- [15] Nair M T S and Nair P K 1989 *Semicond. Sci. Technol.* **4** 191
- [16] Nair P K, Nair M T S, Fernandez A and Ocampo M 1989 *J. Phys. D: Appl. Phys.* **22** 829
- [17] Bube R H 1962 *Photoconductivity of Solids* (New York: Wiley) p 233