

STRUCTURAL AND SURFACE COMPOSITIONAL CHARACTERIZATION OF SILVER THIN FILMS PREPARED BY SOLUTION GROWTH TECHNIQUE

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Abstract

Silver thin films were deposited on microscope glass slides by the electroless Solution Growth Technique (SGT). The films were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS). The films were found to exhibit a random orientation with peak positions and intensity ratios approximating that of the random JCPDS powder pattern for Ag; a secondary line corresponding to Ag_2O was observed. Calculations from XRD data show the films to have a lattice constant of 4.08608\AA . XPS studies show the film surface to be composed of Ag_2O . The influence of preparation conditions, like bath composition and deposition time on some film properties, has been studied. The bath parameters such as concentration and duration of growth greatly affect film thickness. Some reaction chemistry has been discussed.

Keywords: Solution growth technique, silver films, XRD, XPS

1. Introduction

Silver thin films have generated a lot of interest because of their numerous electrical and optical applications. Solar silver reflective films are easily the most effective and most popular films used today for general-purpose heat control. The films have been used as electrolytes in infrared spectroelectrochemical experiments (Rodes et al, 2003), and as substrates in microcontact printing (CP) of alkanethiolates (Xia et al, 1998). Furthermore, silver thin films have been used as source materials for growing silver selenide (Kulkarni et al, 1995), and in the study of the oxidation process (Pettersson and Snyder, 1995; de Rooij, 1989; Cai et al, 1998), thus leading to other applications.

Solution growth technique, also referred to as electroless chemical growth technique, has become popular due certain advantages over conventional thin film deposition techniques, such as chemical (Xia et al, 1998), magnetron sputtering (Del Re et al, 2002), and vacuum evaporation (Ibe and Mgbenu, 1997). These advantages include low

cost, low temperature application, and easy coating of large surfaces. The technique has been utilized primarily in the growth of chalcogenide thin films, and in recent times, for the growth of oxide thin films (Chopra and Das, 1983; Hartnagel et al, 1995; Chopra et al, 1982).

To achieve thin film growth through ion-by-ion reaction, it is necessary to form a fairly stable complex of the metal ions (M^{n+}), which is then released in a controlled manner into the solution bath. The availability of chalcogen ions (S^{2-} , Se^{2-} , Te^{2-}) in the solution bath then leads to the deposition of metal chalcogenide film, once the ionic product (IP) of the metal and chalcogen ions exceed the solubility product (SP) of the chalcogenide. In the case of oxide films, the metal ions undergo hydrolysis to produce a hydrous metal oxide, which decomposes on heating to yield the corresponding oxide.

Thin film deposition proceeds from the nucleation phase through the growth phase, where film thickness increases, and culminates in a terminal phase. At the terminal phase the film ceases to

increase in thickness as the solution bath is depleted of all constituent ions necessary for thin film deposition. The deposition process and indeed the properties of the resulting films are dependent on the composition of the initial solution, its pH value, and the temperature of the solution.

Properties of the films are further influenced upon exposure to the atmosphere by the process of oxidation. Observations as well as thermodynamic analysis show that at high relative humidity and room temperature (298K), Ag exposed to the atmosphere oxidizes to Ag₂O (de Rooij, 1989; Cai et al, 1998; Peyser et al, 2001). The oxidized silver films have been found to exhibit strong photoactivated emission for excitation wavelengths shorter than 520nm, allowing the films to be applied in data storage and retrieval systems (Peyser et al, 2001).

In this work, we report the growth of silver thin films using the cheap, convenient and highly reproducible solution growth technique (SGT). The effects of bath composition and deposition time on film thickness have been investigated. Furthermore, results of film structure, microstructure, and thin film composition are reported.

2. Experiment

Silver thin films were obtained by reacting 0.1M AgNO₃, 1.0M Triethanolamine (TEA) as complexing agent, 0.01M NaCl, and de-ionized water in a solution bath, which in this case was a 50ml beaker. A glass rod stirrer was used to stir the solution once, at the beginning. The temperature of the solution bath and its pH were also noted using mercury in glass thermometer and a CORNING-pH30 SENSOR-CHECK MITE digital pH meter, respectively. Synthetic foam covers were used to prevent contamination of the growth solution as well to suspend the glass slides used as substrates. Microscope slides, previously degreased in aqua regia (mixture of HCl and HNO₃ in the ratio 3:1) for 24 hours, and washed in detergent and de-ionized water and dried in air, were suspended vertically with the aid of the synthetic foam, in the solution. BDH super premium low Fe microscope glass slides were used in this work. Varying concentrations and volumes of the three precursors made up to 40ml using de-ionized water, and maintained for times ranging from 6-24 hours in the bath, as shown in Table 1, were used to optimize the growth parameters. An optimum pH~10 was observed for the baths maintained at a temperature

of 288±5K. The glass substrates were removed after the prescribed times, washed in de-ionized water and dried in air.

X-ray diffraction spectra were obtained by means of a computer interfaced PHILIPS (PW1800) using Cu K α monochromatic radiation. A HITACHI S2300 scanning electron microscope (SEM) was used for imaging the film interface. XPS measurements were performed on the film with the aid of a VG SCIENTIFIC ESCASCOPE using Mg K α excitation, with an analyzer operated in the constant pass energy mode of 30eV. Film thickness was determined using atomic force microscopy (AFM), by creating a groove in the films and measuring the groove height. Sample charging was corrected with the C 1s peak set at 285eV.

3. Results and Discussion

3.2. Film formation and Reaction medium effects

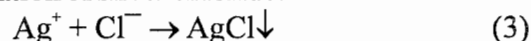
The deposition of silver thin films by means of the SGT was based on the reaction between AgNO₃, Triethanolamine (TEA) and NaCl in an alkaline medium using. Chopra and Das (1983) have given a detailed explanation of the theory of SGT. Ag⁺ ions in solution combine with (HOCH₂CH₂)₃N (TEA) to form a complex with high values of stability constants k₁ and k₂ (Cotton and Wilkinson, 1976; Dean, 1992). The most favoured complex is the linear AgL₂⁺ specie. The formation of the complex Ag[[(HOCH₂CH₂)₃N]₂]⁺ releases Ag⁺ ions in a controlled manner through the equilibrium:



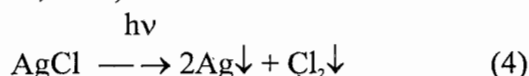
The NaCl ionizes in solution to release Na⁺ and Cl⁻ ions according to the equation:



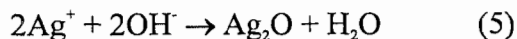
The availability of Ag⁺ and Cl⁻ ions lead to the formation of silver chloride:



Ultraviolet irradiation from sunlight decomposes the AgCl through a slow and complicated mechanism leading to the formation of Ag metal (Svehla, 1979):



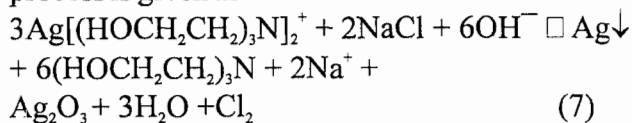
At the same time, the Ag⁺ ions react with OH⁻ ions in alkaline medium to form the oxide (Svehla, 1979):



The silver (I) oxide is oxidized in alkaline solution to give the black oxide $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{O}_2$ (Cotton and Wilkinson, 1976):



The total base reaction involved in the deposition process is given as:



As the three solutions were mixed, a white translucent solution was formed. A gradual transformation of the solution from white to rusty or purplish colour, and eventually, to black was observed after a few minutes, indicating the likely presence of AgCl and Ag_2O . At the end of the deposition period, silver film was found to deposit on the glass substrates as well as the wall of the beakers.

The concentrations of the precursor chemicals were found to have profound effects on thin film formation. In the process of the deposition of Ag thin films it was realized that deviations from the optimum values of the concentrations of TEA and NaCl gave rise to very thin films, non-uniform or probably composite films, or often to no films at all. This observation can be examined against the background that low levels of TEA results in incomplete complex formation with Ag ions; the excess Ag ions precipitating into Ag_2O , which may result in the growth of non-uniform, or to no film at all. At higher concentrations of TEA there is a high degree of complex formation, leading to thinner films because the controlled release of complexed ions becomes highly curtailed. Similar results were obtained for NaCl.

The pH of the growth bath was also found to have an effect on the thickness of films grown. An alkaline medium indicates the presence of OH^- ions. When the OH^- ions participate in the formation of the complex, they stabilize the complex leading to slow release of metal ions into the bath. This in turn leads to low deposition rates and subsequently higher film thickness. If on the other hand the OH^- ions do not participate in the formation of the complex, they precipitate out the metal oxide, thereby lowering the concentration of metal ions required for thin film formation. This ultimately leads to lower film thickness.

The temperature of the growth bath also has an

effect on the film thickness. Increased temperatures lead to increased dissociation of the metal-ion bearing complex. This creates a higher concentration of ions for film growth in the bath. The high concentration coupled with higher kinetic energy of the ions, lead to higher deposition rates and higher film thickness with increased supersaturation of the bath. However, at higher supersaturations precipitation begins to set in, leading to lower deposition rates.

Table 1 shows the values of the various ratios of the molar concentrations of the precursor chemicals (AgNO_3 : TEA: NaCl), along with the values of film thickness obtained. The bath pH and the deposition times are also listed in the table. It is observed that the film thickness increases with increasing concentrations of the reacting chemicals in baths maintained for the same length of time (B1-B4), quite obviously because of the higher proportion of the constituent ions necessary for thin film deposition. The pH of the baths also increase with the concentration of the reacting chemicals, largely due to the increased concentration of TEA and Cl^- ions, which are Lewis bases (Cotton and Wilkinson, 1976). The increased pH (increased OH^- ions) only serves to precipitate the oxide according to equation (5) instead of contributing to film growth according to equation (4), leading to lower film thickness. However, the availability of Ag^+ ions occasioned by the increased concentration of the Ag^+ ion source seem to counter and, in fact, supercede the precipitation, leading to an overall increase in film thickness with concentration of reacting chemicals and bath pH.

Figure1 shows the variation of film thickness as a function of deposition time for films grown from baths of equal constitution (B1, B5, B6, B7, B8). It is seen that the thickness generally increases with time and saturates at about 30 hours, by which time the bath is depleted of ions required for film growth. The deviation from this trend - the film grown for 18 hours - is attributed to temperature effects on thin film deposition. This film was deposited roughly between 4.00pm and 10.00am local time in November, which largely falls within the night when temperatures are generally low. The low temperature of growth will result in the observed low thickness.

Figure2 shows the variation of film thickness with the concentration of individual reacting chemicals, the concentration of the remaining two

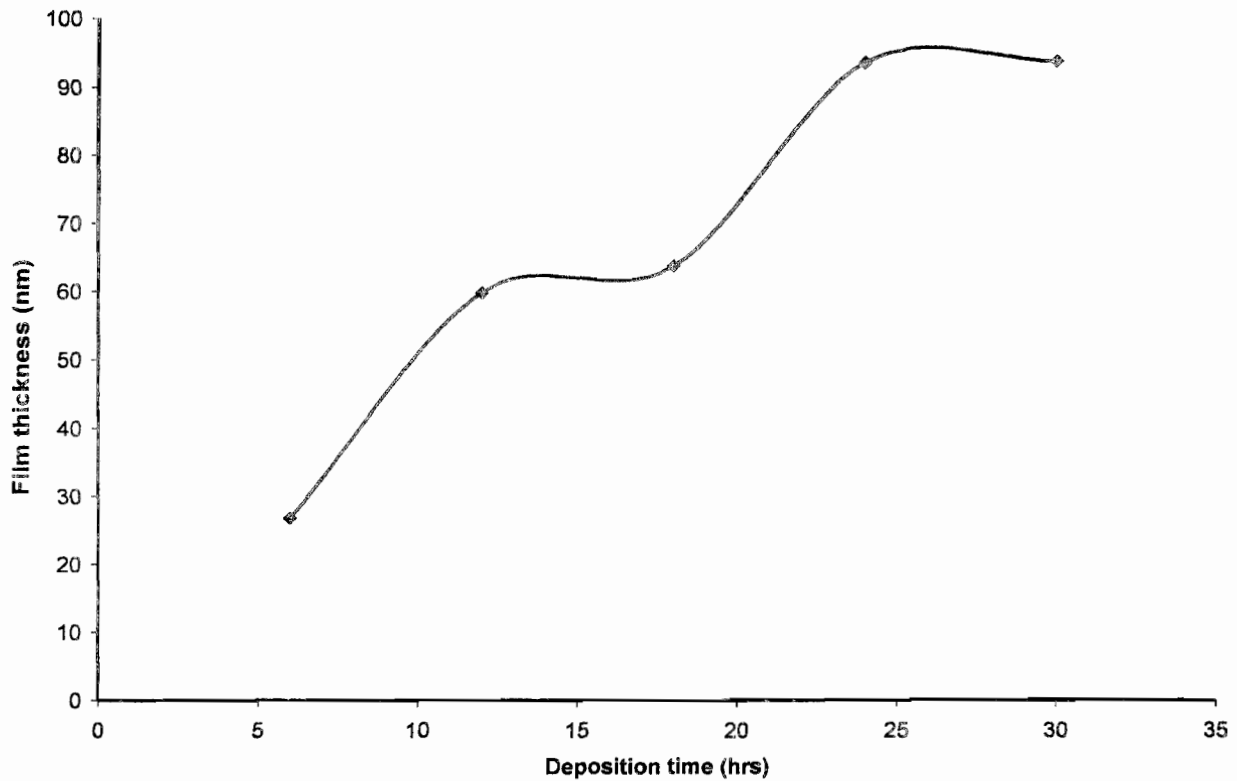


Fig. 1: Variation of film thickness with deposition time for Ag thin films.

(a)

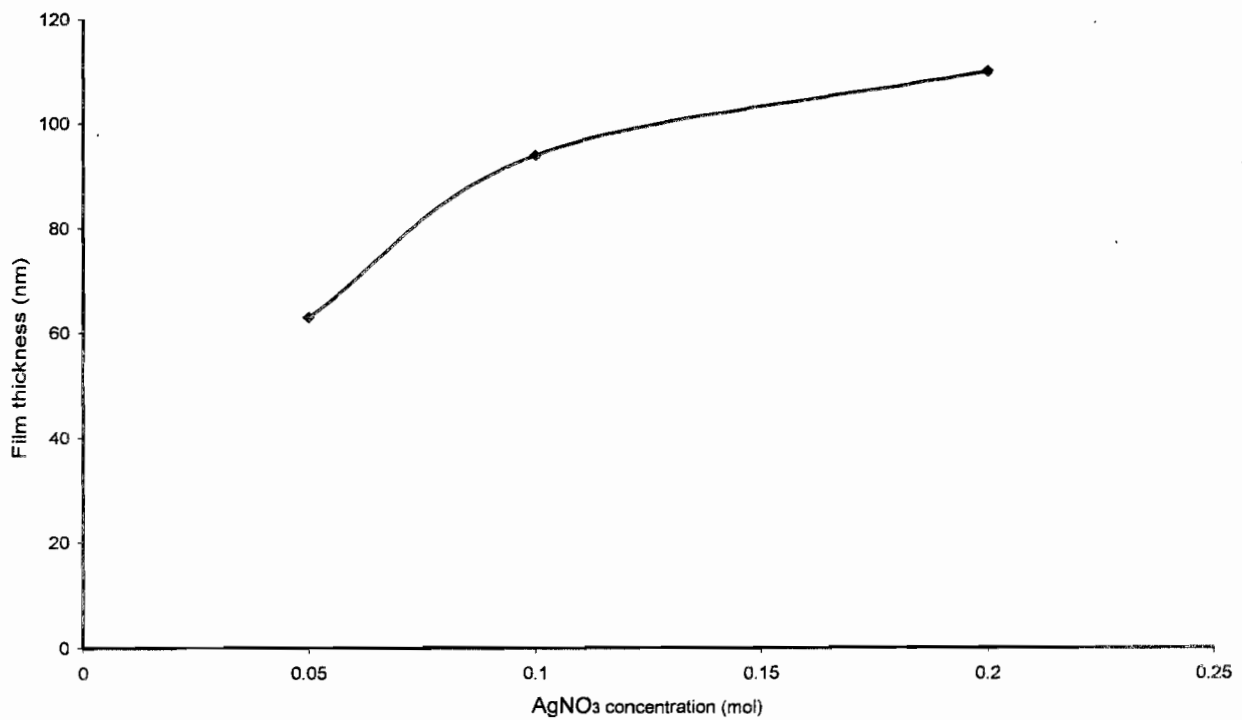


Fig. 2(a) Variation of film thickness with concentration of individual starting chemicals: (a) AgNO₃ (films B1, B9, B10); (b) TEA (films B1, B13, B14); (c) NaCl (films B1, B11, B12).

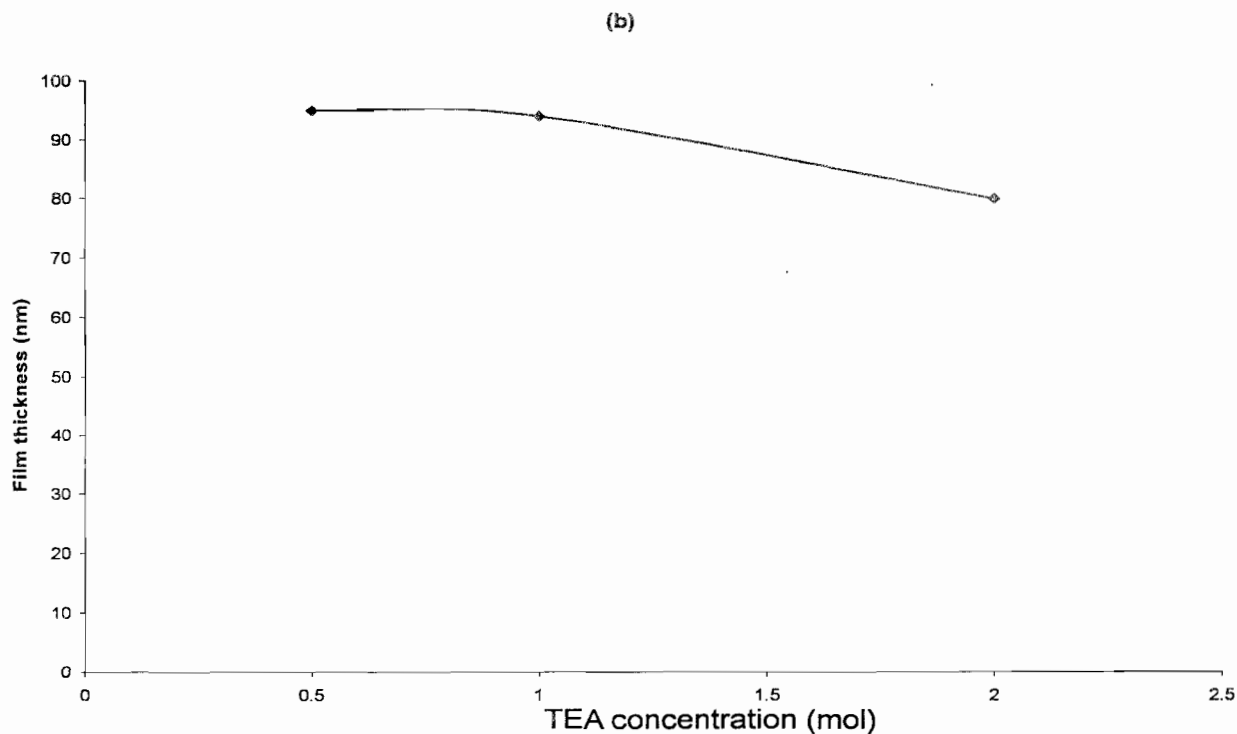


Fig.2(b): Variation of film thickness with concentration of individual starting chemicals: (a) AgNO_3 (films B1, B9, B10); (b) TEA (films B1, B13, B14); (c) NaCl (films B1, B11, B12).

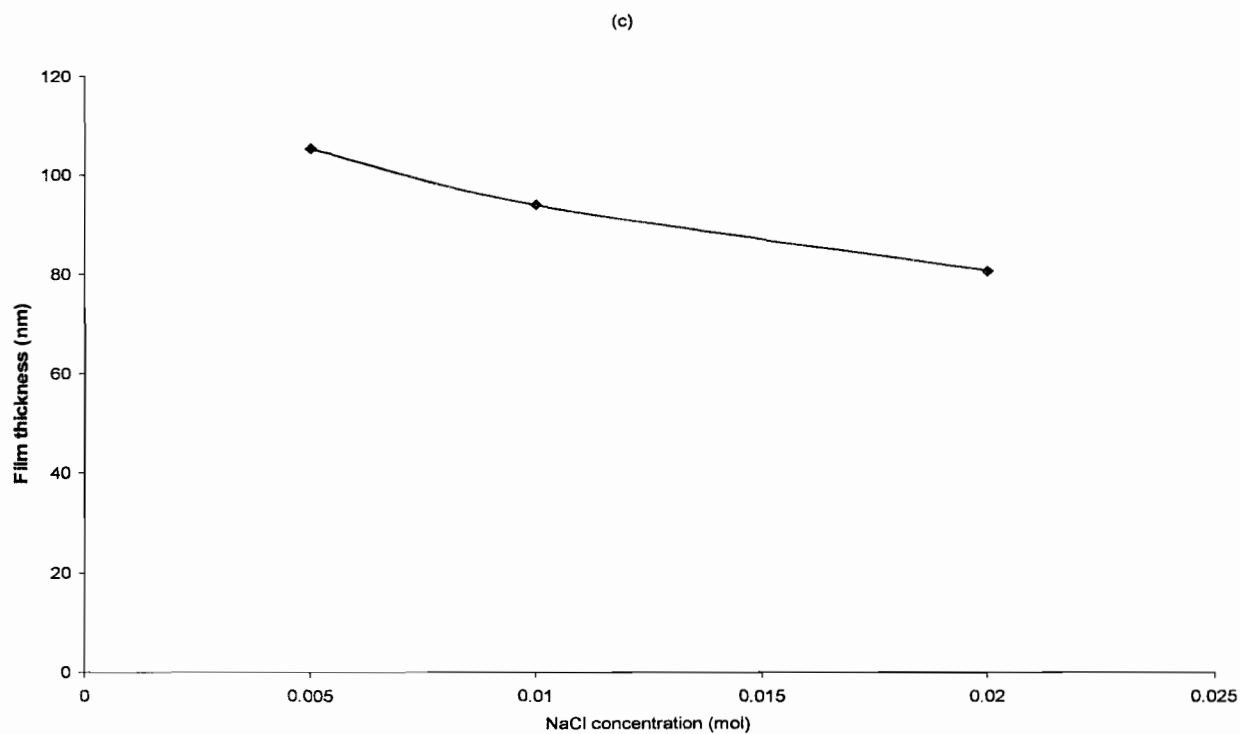


Fig. 2(c): Variation of film thickness with concentration of individual starting chemicals: (a) AgNO_3 (films B1, B9, B10); (b) TEA (films B1, B13, B14); (c) NaCl (films B1, B11, B12).

Table 1: Thickness of Ag films grown under varying condition

Sample	Molar ratio AgNO ₃ : TEA: NaCl	pH	Deposition time (Hrs)	Approximate film thickness (nm)
B1	4 : 40 : 0.4	10.15	24	93.64
B2	3 : 30 : 0.3	10.02	24	92.30
B3	2 : 20 : 0.2	9.68	24	91.28
B4	1 : 10 : 0.1	9.40	24	47.34
B5	4 : 40 : 0.4	10.15	6	26.80
B6	4 : 40 : 0.4	10.15	12	59.90
B7	4 : 40 : 0.4	10.15	18	63.81
B8	4 : 40 : 0.4	10.15	30	93.93
B9	8 : 40 : 0.4	9.62	24	110.02
B10	2 : 40 : 0.4	10.22	24	62.96
B11	4 : 40 : 0.3	10.08	24	80.63
B12	4 : 40 : 0.2	9.99	24	105.30
B13	4 : 80 : 0.4	10.32	24	79.76
B14	4 : 20 : 0.4	9.52	24	94.69

Table 2: X-ray diffraction data for Ag film (100~ nm)

Standard pattern (ASTM card: 4-0783)			Prepared film		
(hkl)	Average d (Å)	I/I ₀	d (Å)	I/I ₀	Peak widths (2θ)
100 (Ag ₂ O)	2.64	4	2.6368	1.8	0.800
111	2.359	100	2.3653	100	0.140
			2.3582	86.5	0.060
200	2.044	40	2.0471	28.3	0.240
220	1.445	25	1.4466	15	0.160
311	1.231	26	1.2348	13.8	0.100
222	1.1796	12	1.1817	3.5	0.240
400	1.0215	4			
331	0.9375	15	0.9384	2	0.800
420	0.9137	12	0.9155	2	0.640
422	0.8341	13	0.8233	1	0.320

being constant. The result shows that the film thickness (B1, B9, B10) increases with the concentration of Ag^+ ions as depicted in Fig. 2a, as the corresponding bath pH decreases. The decreasing pH leads to less precipitation of the oxide, allowing proportionally more of the Ag^+ ions to be used in thin film deposition. This is in addition to the increased availability of Ag^+ ions from increasing concentration of AgNO_3 in the bath.

The results in Fig. 2b (B1, B13, B14) and Fig. 2c (B1, B11, B12) show the film thickness to be decreasing with concentrations of TEA and Cl^- ions, respectively, even as the pH is increasing. The increasing pH leads to more precipitation of the oxide, allowing proportionally fewer of the Ag^+ ions for thin film deposition. This quite obviously led to decrease in film thickness with pH as observed. An exception to this trend is observed for film B12 plotted in Fig. 2c. The pH of this bath would suggest that the film thickness would be higher than the obtained value when compared to the other two films. The lower than expected thickness becomes obvious when it is realized that this bath has at least twice the concentration of NaCl of any of the other two baths. This leads to higher chlorine gas yields according to reaction (4), which is known to dissolve in water and aqueous bases to produce chlorine oxo acids (Cotton and Wilkinson, 1976). These acids are strong oxidizing acids in which silver is known to dissolve (Cotton and Wilkinson, 1976). This leads to lower than expected film thickness for the bath, as observed.

3.2. Film Structure, Morphology, and Composition.

Figure 3 shows the ex-situ x-ray diffraction (XRD) spectra of a typical silver thin film, and Table 2 shows the observed d spacing and peak widths along with the standard data (ASTM card 4-0783). The diffractogram shows well defined peaks corresponding to (111), (200), (220), and (311) planes of reflection, as well as other peaks, obscured by the heavy background, corresponding to (222), (331), (420), and (422) planes of reflection, all of which are consistent with the known structure of cubic silver. The broad peak seen between 15 and $\sim 38^\circ$ is due to the amorphous glass substrate. The heavy background of the XRD spectra seems to suggest the growth of semi-amorphous or poorly crystallized films (Taylor, 1960), probably due to the low temperatures of growth. Diffraction spectra of poorly crystallized

films will necessarily show heavy background as the small crystallite sizes broaden the peaks, which merely contribute to the background. This suggestion is clearly supported by the observation (Table 2) that all the obscured peaks have peak widths significantly higher than the sharper peaks. The lattice parameter was calculated and its value is $a=4.08608\text{\AA}$, which is very close to the reported value. A secondary silver oxide Ag_2O phase is observed as characterized by the planar separation $d = 2.6335\text{\AA}$, corresponding to the (100) plane of reflection (ASTM card 19-1155). Fig. 4 shows a high resolution SEM micrograph of a thin film ($\sim 90\text{nm}$ thick). Continuous granular films with a rough surface morphology were formed. This is in agreement with the observations of Xia et al (1998).

$\text{Ag } 3d$ XPS spectra is illustrated in Fig. 5 for the as-deposited silver films. There are two peaks, a result of spin-orbit splitting, designated $\text{Ag}3d_{5/2}$ and $\text{Ag}3d_{3/2}$, respectively, corresponding to the strongest photoelectron lines. These peaks are observed at 367.8eV and 373.8eV, respectively, shifted to lower binding energy (BE) values in relation to metallic Ag, and could be assigned to Ag^+ oxidation state in Ag_2O (Gaarenstroom and Winograd, 1977).

Figure 6 shows the XPS O 1s peak for a typical as-deposited film. There are two components observed for the peak. The first peak located at a binding energy of 529.9eV is the low binding energy (LBE) component for O 1s. This LBE peak has been assigned as corresponding to the lattice oxygen in Ag_2O , again in agreement with the XRD data and the Ag 3d XPS spectrum. The second peak that appears at a BE of 532.1eV 532.6eV is the high binding energy (HBE) component, ascribed to surface adsorbed oxygen or oxygen containing components like H_2O and OH, and grain boundary impurities.

The results of the Ag 3d and O 1s XPS spectra, coupled with the secondary oxide phase observed with XRD seem to suggest the presence of silver (I) oxide on the surface of the films.

5. Conclusion

The growth of Silver thin films on microscope slides has been achieved by the cheap and readily accessible SGT. This is confirmed by X-ray diffraction results, which show the films to be randomly oriented and polycrystalline in nature, with a lattice constant of 4.08608\AA . Other results

indicate that the properties of the films such as the thickness can be tuned easily by varying the deposition parameters. The surfaces of the films exhibit a rough surface morphology, and show evidence of contamination with silver (I) oxide (Ag_2O) phase, as confirmed by XRD and Ag 3d and O 1s XPS studies of the films. It would appear that

the SGT is well suited for the growth of silver films, which have numerous applications as reflecting surfaces.

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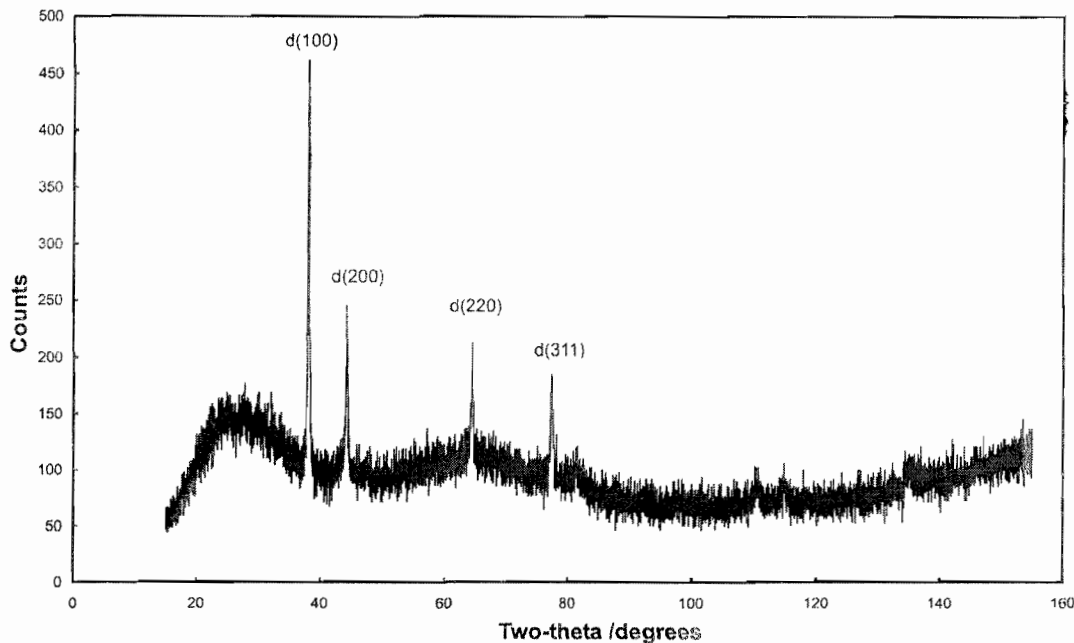


Fig.3: X-ray diffraction spectra for a silver thin film deposited on glass.

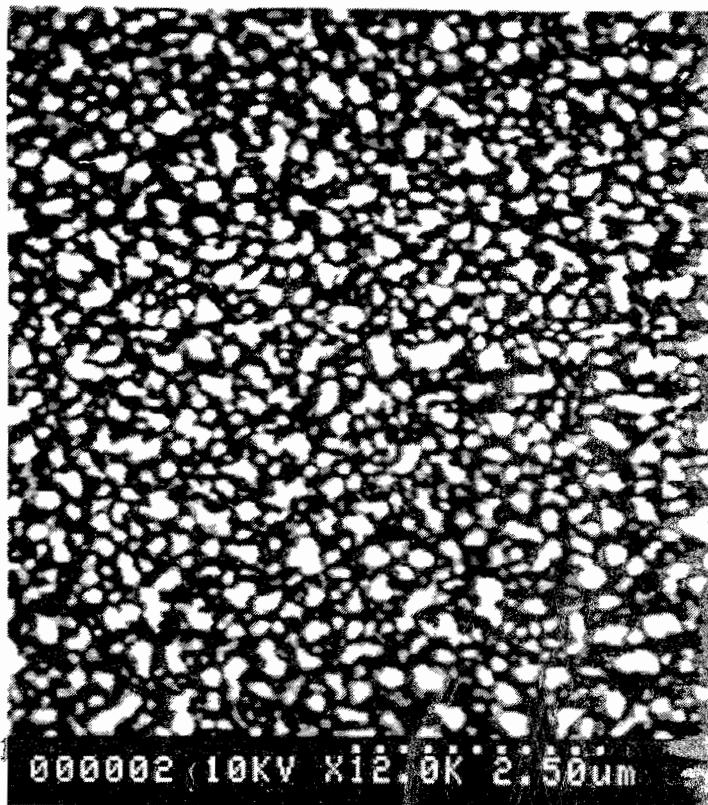


Fig.4: A high resolution SEM micrograph of a silver thin film.

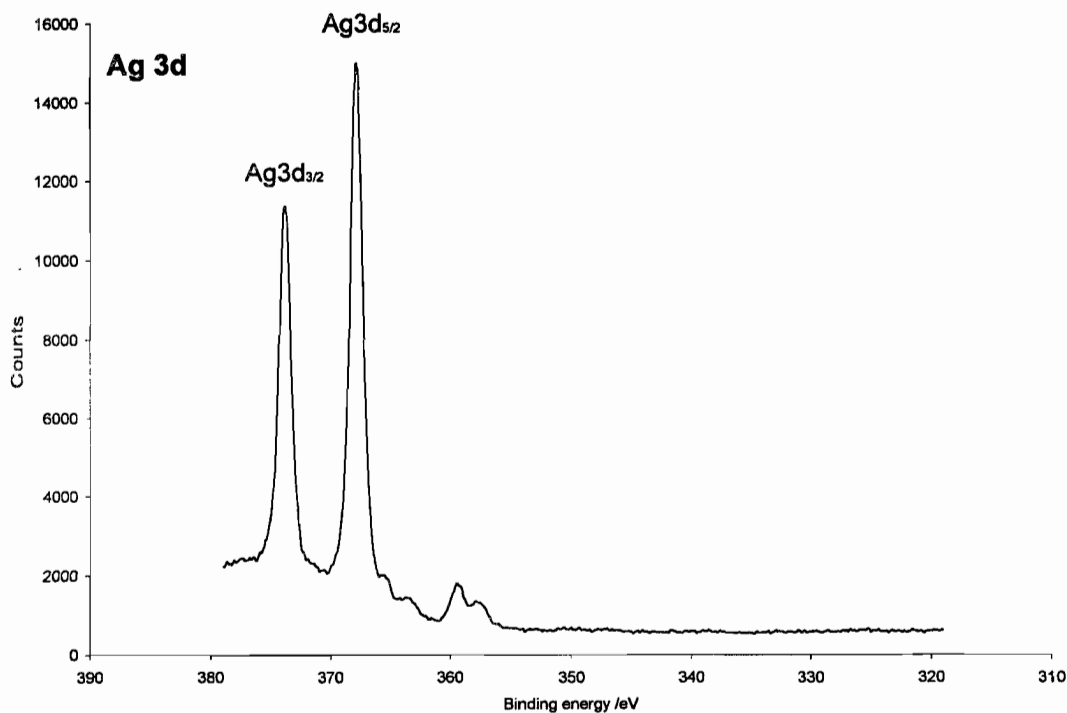


Fig.5: The Ag 3d spectra for a silver thin film corresponding to Ag⁺ oxidation state.

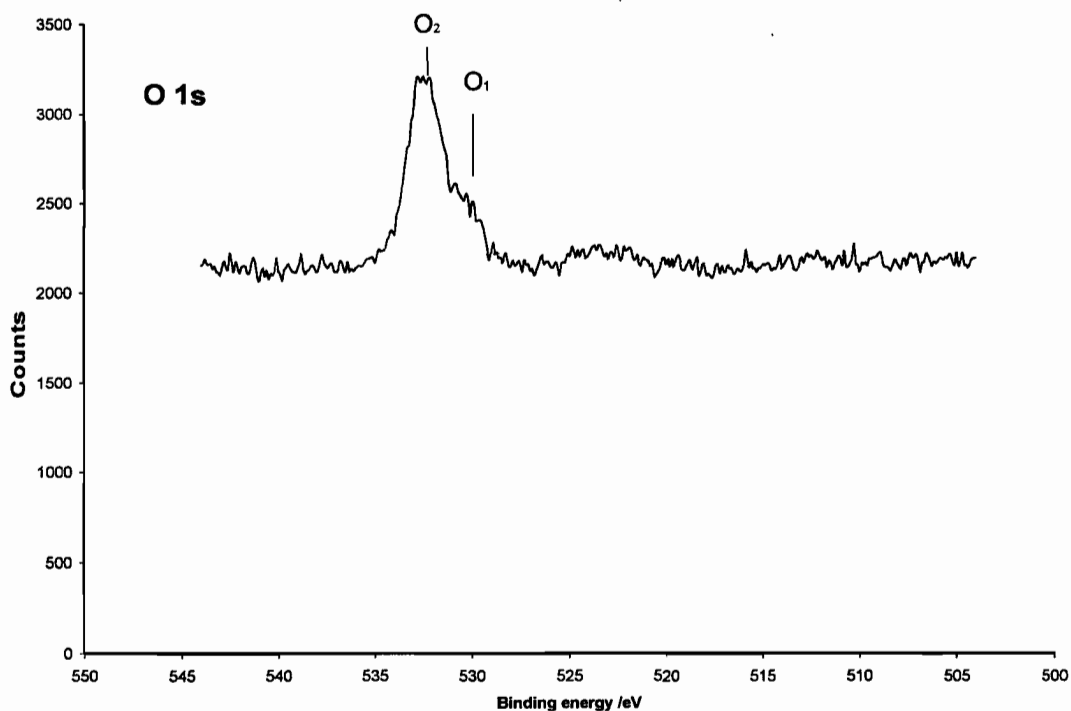


Fig. 6: The O 1s spectra for polycrystalline silver thin film.

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