Electroless Deposition of Ag Thin Films

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I. INTRODUCTION

Surface deposition processes that take place during the deposition of semiconductor or metallic films from solution is an area known as chemical bath deposition (CBD) or alternatively, electroless deposition. Film formation commences with the deposition of nanoparticles onto a substrate surface and these particles then continue growing laterally to form the film. A thorough understanding of the chemistry of solution deposition processes of semiconductor and metallic films is required in order to design optimal thin films in a cost effective manner. This paper reports the SERS data obtained from growing silver metal films during the reduction of ammoniacal silver nitrate by propionaldehyde.

A well-known example of CBD is the Tollen’s test for aldehydes, where propionaldehyde (CH₃CH₂HO) was used as the reductant. The aldehyde was obtained from Aldrich and used without further purification. All glassware was washed in 2 M HNO₃, rinsed with deionised water and dried in air prior to use. Deposit morphology was investigated using three different methods:

Method 1. The following solutions were added to a glass vial in the following order: 4000 μL 0.25 M AgNO₃, 3x100 μL aliquats of 0.1 M NaOH to form a fine brown precipitate of Ag₂O, 3x100 μL aliquats of 0.05 M NH₃ to completely dissolve the precipitate, 9x100 μL 0.25 M AgNO₃ aliquats were added until the solution became pale brown/yellow. Various amounts of 0.0097 M CH₃CH₂HO were then added to the ammoniacal silver nitrate solution and a glass substrate was placed in the vial. After 1 hour the substrate was removed, rinsed with deionised water and dried in air.

Method 2. The following solutions were added to a glass vial in the following order: 4000 μL 0.25 M AgNO₃, 3x100 μL aliquats of 0.1 M NaOH to form a fine brown precipitate of Ag₂O, 3x100 μL aliquats of 0.05 M NH₃ to completely dissolve the precipitate, 9x100 μL 0.25 M AgNO₃ aliquats were added until the solution became pale brown/yellow. Various amounts of 0.0097 M CH₃CH₂HO were then added to the ammoniacal silver nitrate solution and a glass substrate was placed in the vial. After 1 hour the substrate was removed, rinsed with deionised water and dried in air.

Method 3. A glass substrate was placed at the bottom of a glass container. 3 aliquats of ammoniacal silver nitrate solution as prepared in methods 1 and 2 were placed on the substrate. Several aliquats of concentrated CH₃CH₂HO (97 M) were also placed beside but not on the substrate at the bottom of the container. The container was then sealed and the substrate removed after 1 hour to be rinsed with deionised water and dried in air.

Propionic acid was obtained from Ajax and used without further purification. Silver propionate was made by mixing the acid with 1% AgNO₃.
Raman Spectroscopy and SERS. Raman and SERS studies were conducted on a Renishaw System 100 Raman spectrometer where the incident radiation was conveyed from a HeNe laser of 633 nm excitation. Power at the sample was ~6 mW with a laser spot size of ~50 μm. Raman scattered light was detected with a Peltier-cooled charge coupled device (CCD) detector with spectral resolution 2 cm⁻¹ and the light was focused with an ultra-long working distance x20 Olympus Plan FI lens with a numerical aperture of 0.4. Raman spectra were also collected on a Renishaw 2000 system Raman microprobe spectrometer that has a rotary encoded grating stage and an internal two stage Peltier cooled (-70°C) CCD detector with a spectral resolution of 1 cm⁻¹. A 442 nm He-Cd laser was used as the excitation source. The laser power at the sample was in the range 0.5-10 mW. Data was processed using GRAMS32 software (Galactic Industries, Salem, NH, USA). The laser beam was focused inside a glass vial for solution samples and focused on the inside surface of the vial for SERS studies.

Scanning Electron Microscopy. SEM images of the silver mirrors were obtained using an FEI Quanta 200 environmental scanning electron microscope (ESEM). Back scattered images were taken with the instrument in environmental or high vacuum mode using an accelerating voltage of 25 keV. Various magnifications and scanning areas were used.

III. RESULTS AND DISCUSSION

The normal Raman spectrum of propionaldehyde is presented in Figure 1, together with SERS spectra taken from a silver mirror depositing on glass after 2 minutes and 5 minutes of growth. In the SERS spectra a very strong band is observed at 879 cm⁻¹ that appears during the initial deposition stage and then decreases in intensity over time. This band is attributed to the C-CH₃ stretch. The band at 1560 cm⁻¹ was attributable to the HOH bending mode of water.

The SERS spectra arise from the formation of silver particles as the silver cations are reduced and the aldehyde is oxidized to the acid. Unreacted silver ions precipitate the propionate as the insoluble silver salt at the metal surface.

Figure 2 presents Raman spectra for the solid silver propionate, propionic acid, propionaldehyde and the SERS spectrum obtained after ten minutes of film growth. The \( \nu_{\text{as}} \) CO₂⁻ group exhibits a strong band at 1400 cm⁻¹ for the silver propionate, and weaker \( \nu_{\text{as}} \) and \( \nu_{\text{s}} \) bands at 1460 cm⁻¹ and 1440-1420 cm⁻¹ for the dimeric acid and aldehyde species respectively. The SERS spectra show tate formation of silver propionate was occurring during silver mirror deposition.

The main Raman bands for the aldehyde and acid are assigned in Table 1. The strongest bands arise from methyl and methylene antisymmetric and symmetric C-H stretches (\( \nu_{\text{as}} \) CH₃, \( \nu_{\text{s}} \) CH₃, \( \nu_{\text{s}} \) CH₂, \( \nu_{\text{as}} \) CH₂) and antisymmetric and symmetric anion stretches (\( \nu_{\text{as}} \) and \( \nu_{\text{s}} \) RCO₂⁻).

The Raman bands that appear in the range 1380-1150 cm⁻¹ are due to methylene twisting vibrations, those between 1080-880 cm⁻¹ are due to methylene rocking and C-C stretches while those between 460-330 cm⁻¹ are due to CCC bending modes and C-C stretches [8].

The C-CH₃ stretch for propionic acid occurs at 845 cm⁻¹ and is clearly lower than the corresponding band observed (879 cm⁻¹) in the SERS spectra from Figure 1. The band shift to lower wavenumber is due to the acid existing as a dimer species. The fact that there is no Raman band attributed to \( \nu_{\text{as}} \) C-CH₃ observed in the spectrum for propionaldehyde demonstrates that this mode is enhanced by the presence of the large silver cation, enabling the alkyl chain C-C stretch to be easily observed.

Figure 3 presents SEM micrographs of silver mirrors taken with the microscope in environmental mode (ESEM) and high vacuum mode (SEM). The environmental mode was used to help reduce charge buildup in the glass while the high vacuum mode was specifically used to obtain higher resolution images.
Silver mirror thin films deposited on glass using deposition methods 1, 2 and 3 (as outlined in the experimental section) were all composed of three different silver phases: (i) fine grained nanoparticles, (ii) larger string-like particles and clusters, and (iii) micron-sized crystals. The SEM micrograph in Figure 3(c) provides a good image of well formed octahedral silver crystals. The films are therefore not continuous but were rather formed by nanoparticles growing laterally on the glass substrate, which grow even larger to form the elongated particles and subsequently crystals. The amount of reducing agent, between 1600-2200μL 0.00097 M propionaldehyde, had an effect on the amount of each phase present in the films. Generally, the amount of phase (ii) and (iii) increased with the volume of aldehyde used, and more of these two phases were yet again observed in films made from method 2 compared to method 1. This may have been due to the supply of aldehyde to the surface and therefore to the growth centers on the surface. The films produced using method 3 reacted very quickly and this would have been due to a combination of uniform vapour pressure and solubility. The film shown in Figure 3(b), made from method 3 using a silver ammonical solution from method 1, demonstrates that although a large amount of phase (i) and (ii) were present, the crystals were smaller.

The silver mirror shown in Figure 3(b) was later sonicated for 2 minutes in deionised water. After drying in air, the SEM micrograph taken from the film showed that the large silver crystals and a considerable amount of phase (ii) were removed after sonication.

<table>
<thead>
<tr>
<th>Vibration frequency (cm⁻¹)</th>
<th>Description of vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Propionaldehyde</strong></td>
<td><strong>Propionic acid</strong></td>
</tr>
<tr>
<td>2968 m</td>
<td>ν₁ CH₃</td>
</tr>
<tr>
<td>2941 vs</td>
<td>ν₁ CH₂</td>
</tr>
<tr>
<td>2919 sh</td>
<td>ν₁ CH₃</td>
</tr>
<tr>
<td>2882 vs</td>
<td>ν₁ CH₂</td>
</tr>
<tr>
<td>2734 m</td>
<td>ν C=O</td>
</tr>
<tr>
<td>1643 vw</td>
<td>νₕ CH₂</td>
</tr>
<tr>
<td>1460 s</td>
<td>νₕ CH₂</td>
</tr>
<tr>
<td>1439 s</td>
<td>νₕ CH₂</td>
</tr>
<tr>
<td>1380-1150 w</td>
<td>ρ₂ CH₃</td>
</tr>
<tr>
<td>1080-880 w</td>
<td>ρ₂ CH₃, ν C-C</td>
</tr>
<tr>
<td>845 vs</td>
<td>ν C-CH₃</td>
</tr>
<tr>
<td>603 w</td>
<td>δ(O=C-O)</td>
</tr>
<tr>
<td>484 w</td>
<td>δ CCC, ν C-C</td>
</tr>
<tr>
<td>460-330 m</td>
<td>τ CH₂-CH₂</td>
</tr>
</tbody>
</table>

Figure 3. ESEM micrograph of silver mirrors as deposited using (a) method 1 with 1600μL of propionaldehyde, (b) method 3 and SEM micrograph of octahedral silver crystals on surface of mirror (c), as deposited on glass using method 2 with 2200μL of propionaldehyde.
IV. CONCLUSION

The use of Raman spectroscopy and SERS are novel techniques with which to investigate the electroless deposition of silver thin films on glass. ESEM results show that the deposition technique produces fine grained particulate films. Propionate influences the structure of the silver deposit. ESEM investigations demonstrated that the silver film forms by first nucleating silver nanoparticles on the glass surface which then grow outwards. The fine grained films exhibited three distinct structures, fine nuclei on the glass, isolated strands of small crystals above these nuclei and a number of individual octahedral micron-sized single crystals distributed over the surface.

During the Ag⁺ reduction process, SERS from aldehyde species was not observed. The Raman signal obtained was derived from silver propionate species enhanced on the depositing silver film. This indicates that the aldehyde species are oxidized in the solution at a distance from the silver deposit. Silver propionate is formed by reaction of the acid anion with silver cations and adsorbs onto the growing silver film surface.

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REFERENCES