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Synthesis of Metallized Polyimide Films by Surface Chemical Modification

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A novel method is presented for Ag metallization of the polyimide resin via surface chemical modification of polyimide resin using KOH aqueous solution, adsorption of metal ions through cation exchange reaction, and reduction of metal ions using an $NaBH_4$ aqueous solution. Ag films, which were formed on surface modified polyimide resins were characterized by ICP, XRD, GD-OES, SEM and TEM measurements. The amount of adsorbed Ag^+ ions on surface modified polyimide resin could be systematically controlled by initial KOH concentration. XRD measurements and SEM observations showed that island-like metallic Ag were deposited onto polyimide resin surface at early stage of the reduction, and Ag thin film was grown as the reduction time was increased. TEM observations revealed the Ag film that with ca. 300 nm thickness having sufficient surface conductance was uniformly formed on the polyimide resin surface.
Key words: polyimide resin, surface modification, cation exchange reaction, Ag thin film

1. INTRODUCTION

Polyimide resin is known to be a promising material in the microelectronics industry because of its high thermal resistance, excellent mechanical strength, chemical resistance, and low dielectric constant. Thus, polyimide resin films have been widely used in the field of multichip module (MCM) packaging, flexible printed wiring board (PWB), interconnect layers of ultra-large scale integrated circuit (ULSI), and so on [1-12]. On the other hand, silver has been used as a connector in switching device, and lead frame for integrated circuit (IC) in the microelectronics device applications because of its high conductivity, high thermal conductivity, and ease of soldering [13,14]. From these points of view, the process of silver metallization onto polyimide resin surface is of much important technique. Recently, further miniaturization of microelectronics devices has been needed, which will lead to scale down-sizing of circuit patterns. It is difficult to fabricate the silver fine patterns by the process of conventional electroless and/or electroplating. In addition, dry processes such as chemical vapor deposition (CVD) and physical vapor deposition (PVD) require high energy and costly equipment. We have previously studied that metallization of polyimide resin via surface chemical modification of the resin with KOH treatment followed by reduction process [15-17]. The treatment induced hydrolysis of imide ring to form carboxyl groups as cation exchange groups. In this study, we report on silver direct metallization of polyimide resin, by the process of surface modification of the polyimide resin, adsorption of Ag^+ ions through cation exchange reaction, followed by reduction of Ag^+ ions by using an $NaBH_4$ aqueous solution. Obtained Ag/polyimide films were characterized by inductively coupled plasma (ICP) atomic emission spectroscopy, X-ray diffraction (XRD), glow discharge optical emission spectroscopy (GD-OES), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2. EXPERIMENTAL

2.1 Surface modification of polyimide and adsorption of Ag^+ ions

The polyimide films used in this study were Kapton 200-H (Toray-DuPont) of 50 μm thickness. The films were immersed into 5 mol dm^{-3} KOH aqueous solution at 50 °C for 5 min. The samples were then washed with distilled water. Subsequently, surface modified-polyimide films were immersed into 50 mmol dm^{-3} $AgNO_3$ aqueous solution at room temperature for 5 min, and then washed with distilled water.

2.2 Formation of Ag films

The polyimide film containing Ag^+ ions were then immersed into 5 mmol dm^{-3} $NaBH_4$ aqueous solution to reduce the Ag^+ ions. After removal from the solution, the films were washed with water and dried at room tem-

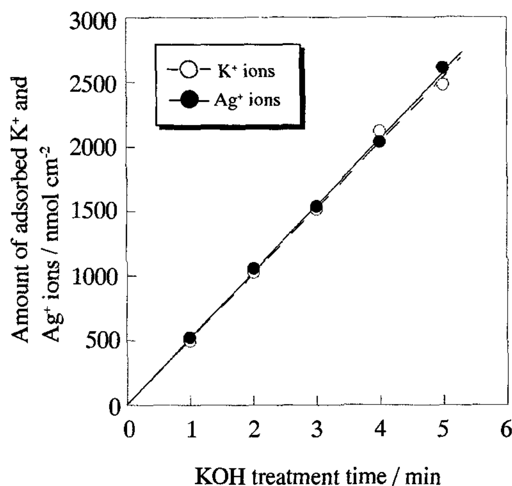

Figure 1. The effect of KOH treatment time of polyimide resin films on the amount of adsorbed Ag^+ ions on surface modified polyimide resins.

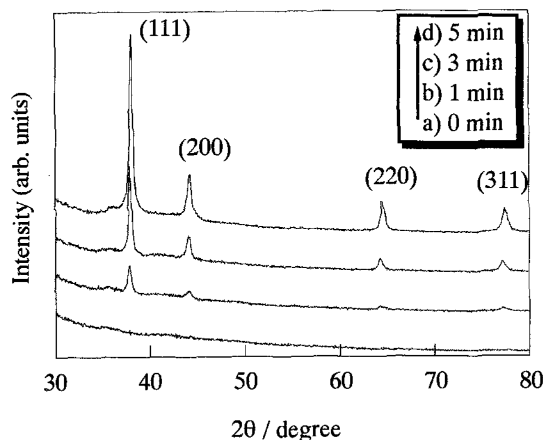

Figure 2. XRD patterns of the Ag films. The films were prepared by soaking polyimide film containing Ag^+ ions into $NaBH_4$ aqueous solutions for 0 min(a), 1 min(b), 3 min(c), and 5 min(d).

perature.

2.3 Characterization of the films

Formation of carboxyl groups and amide bonds caused by KOH treatment were confirmed with XPS. Amount of adsorbed Ag^+ ions on polyimide resin was measured by ICP atomic emission spectroscopic measurements (SPS7700 plasma spectrometer, Seiko Instruments). XRD measurements were carried out with a Rigaku Geigerflex diffractometer using Cu Kα radiation. The voltage and current of the X-ray source were 45 kV and 35 mA, respectively. Crystallite sizes were calculated from the Ag (111) diffraction line using Scherrer's equation, $L=\lambda/(\beta \cos\theta)$, where L is the mean dimension of the crystallites, β is the integral width of the diffraction peak, θ is the diffraction angle, and λ is the wavelength of the Cu $K\alpha_1$ radiation (0.1540 nm). Depth profiles of specimens were measured by GD-OES (JY5000RF, Horiba, Ltd.). The Ar pressure and reflected power were 240 Pa and 15 W, respectively. The surface morphology of the Ag films on polyimide resins was observed using an FE-SEM (JSM-6340F, JEOL), operating at 15 kV. Cross-sectional transmission electron microscope (TEM) observations were performed with a JEM-2000EX (JEOL), operating at 200 kV. Thin cross-sections were prepared by conventional microtome technique using a diamond knife.

3. RESULTS AND DISCUSSION

3.1 Surface modification of polyimide and adsorption of Ag^+ ions

Figure 1 shows the effect of KOH treatment time of polyimide resin films on the amount of adsorbed Ag^+ ions on surface modified polyimide resins. The amount of adsorbed K^+ ions increases linearly with increasing the KOH treatment time, due to an increase in modified thickness. After ion exchange, the amount of adsorbed Ag^+ ions is almost same as that of initially-adsorbed K^+ ions, indicating that the adsorption of Ag^+ ions essentially proceeds through ion exchange reaction between both monovalent K^+ ions and Ag^+ ions. The amount of adsorbed Ag^+ ions reaches ca. 2500 nmol cm^{-2} after the KOH treatment for 5 min.

3.2 Formation of Ag films

The XRD patterns of the Ag films are shown in figure 2. The films were prepared by soaking polyimide film containing Ag^+ ions into $NaBH_4$ aqueous solutions for various times. Before reduction (figure 2a), no distinct diffraction peak can be seen, indicating amorphous nature of the film containing Ag^+ ions. Upon reduction by $NaBH_4$ aqueous solutions, diffraction peaks are observed at 38°, 44°, 64°, and 77°, which are assigned to the (111), (200), (220), and (311) reflections of metallic Ag, respectively. As the soaking time increases, these peaks increases in intensity due to growth of Ag film on the modified polyimide surface. For the films obtained after reduction for 5 min, crystallite size was estimated from (111) reflection using Scherrer's formula, the value of which was ca. 17 nm.

The growth of Ag films was also confirmed by SEM observation, and the results are shown in figure 3. At the initial stage of reduction, small particle-like Ag deposits are formed on the polyimide surface. Upon increase in soaking time in $NaBH_4$ aqueous solution, these Ag deposits are found to be grown as larger particles, which is caused by further reduction of Ag^+ ions remaining in the underlying modified polyimide film. Uniform formation of continuous Ag film can be achieved after soaking for 5 min (figure 3f).

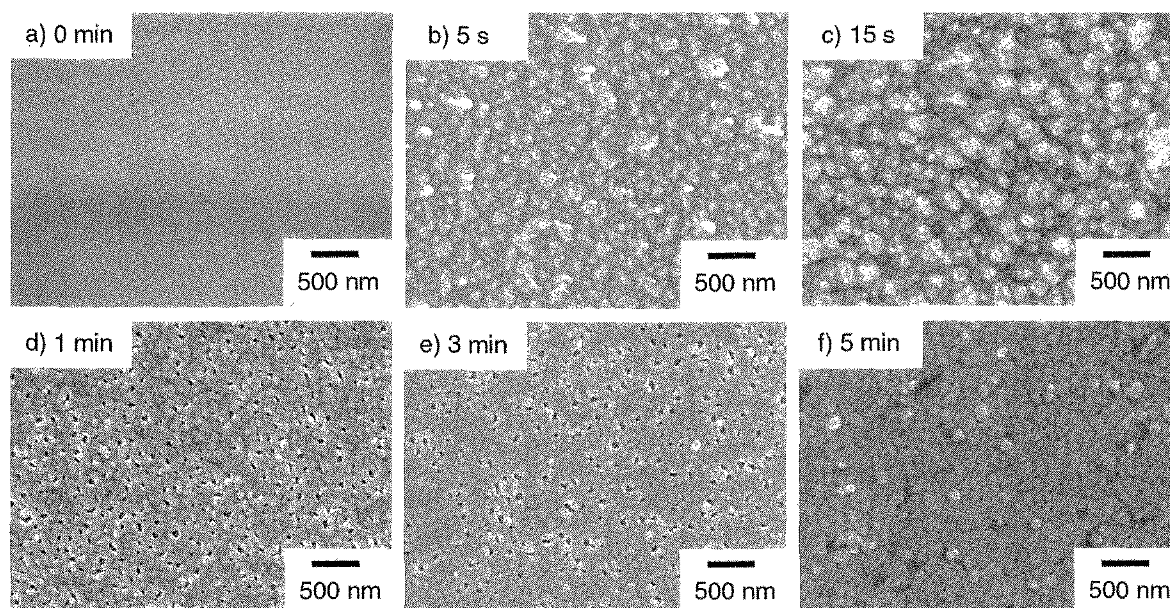

Figure 3. Surface morphology of the Ag films formed on the polyimides. The films were prepared by soaking polyimide film containing Ag^+ ions into $NaBH_4$ aqueous solutions for 0 min(a), 5 s(b), 15 s(c), 1 min(d), 3 min(e), and 5 min(f).

Figure 4 shows cross-sectional TEM image of the Ag film on the polyimide resin surface after reduction using $NaBH_4$ for 5 min. It can be seen that the Ag film with ca. 300 nm in thickness successfully formed on polyimide resin surface and nano-sized particles also formed within subsurface of polyimide resin. Selected area electron diffraction analysis for these nano-sized particles revealed that these particles were fcc metallic Ag (results not shown).

Figure 5 shows GD-OES depth profiles of Ag in the films before and after soaking into $NaBH_4$ aqueous solution. For the film containing Ag^+ ions (before reduction), Ag intensity profile shows a constant magnitude, indicating Ag^+ ions are homogeneously dispersed in surface modified region. Upon reduction treatment, Ag intensity becomes much larger in the surface region (after reduction for 1 min), and finally localized only at the top surface of the resin (5 min). For the films obtained after reduction for 5 min, significant Na signal can be detected in deeper side of the modified layer (inset in figure 5), of which distribution parallels corresponding decrease in Ag intensity. From there results, formation mechanism of Ag film on polyimide surface is proposed as follows ; at the initial stage of soaking in $NaBH_4$ solution, Ag^+ ions located near the surface are reduced to metallic Ag to form small islands. Since the $NaBH_4$ aqueous solution is alkaline, Na^+ ions then bind to carboxylic acid anions instead of H^+ ions. Subsequently, the Ag^+ ions located at

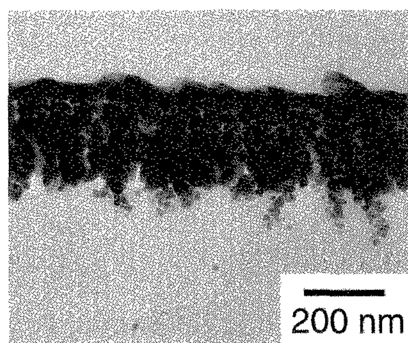

Figure 4. Cross-sectional TEM image of the Ag film on the polyimide resin surface after reduction using $NaBH_4$ for 5 min.

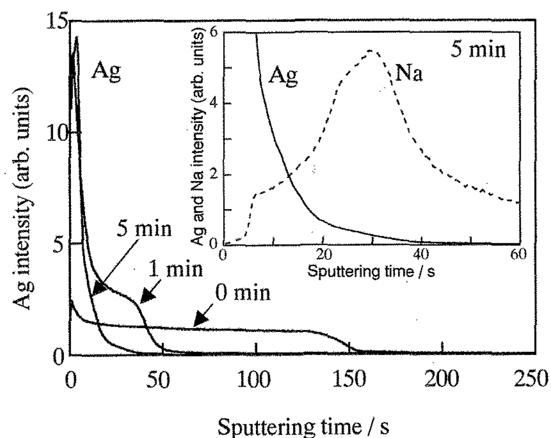

Figure 5. GD-OES depth profiles of Ag and Na intensity in the films before and after soaking into $NaBH_4$ aqueous solution and enlargement (inset) of the 0 to 60 s region.

deeper side of the modified layer can diffuse towards surface region of the resin through ion exchange reaction with bound Na^+ ions, and then reduced to metallic Ag to grow Ag islands. Finally, Ag thin films form on the surface and the underlying layer consists of modified polyimide resin containing Na^+ ions. Formation of nano-sized Ag particles in subsurface of the film can be presumably due to diffusion of BH^{4-} ions into the film during reduction but further experimented study is needed to verify this assumption.

4. CONCLUSION

We have developed a noble method for the preparation of the Ag film on polyimide resin by surface modification and chemical reduction. The amount of adsorbed Ag^+ ions on polyimide resin film were systematically controlled by initial KOH treatment time. Metallic Ag thin films were successfully formed on the resin surface by the reduction of adsorbed Ag^+ ions using a $NaBH_4$ aqueous solution. This process can be described as fully additive-based metallization process and useful for the formation of various kind of metal thin films. Patterned formation of the metal films is also possible by using resist and photolithographic techniques. Potential applications of this approach are currently being investigated.

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