— Communication —

Morphology Change of Silver Deposit from BMITFSI Ionic Liquid

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The electrodeposition of silver was investigated with 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide containing Ag:TFSI at 150 °C. The influence of current density on the morphology of the silver deposit was studied by cyclic voltammetry and scanning electron microscopy. The size of the silver crystallite became smaller and dendrite-like growth was suppressed with increasing current density.

Key Words : Ionic Liquid, Silver, Electrodeposition, Cyclic Voltammetry

1 Introduction

To increase the device speed and reduce the chip size in Ultra Large Scale Integration (ULSI), new interconnect materials as a replacement for copper are desirable. Silver is regarded as a good choice because of its low bulk resistivity at room temperature and its high corrosion resistance. Among numerous silver coating methods, electroplating is thought to be the simplest and cheapest method for producing homogeneous silver deposits.

In an aqueous plating bath, cyanide is indispensable as the complexing agent for the Ag⁺ ion; without it, smooth and flat deposits are not obtained. However, almost all cyanide-containing baths used industrially for silver electroplating are highly toxic. Additionally, the disposal of the waste plating solution is becoming more difficult.

Ionic liquids are a new class of compounds that can serve as replacement media for various applications, including electroplating, because of their thermal stability, good conductivity, low toxicity, non-volatility, and recyclability. The electrodeposition of metals from ionic liquids has been investigated by many researchers, and a book has recently been published about progress in the field.¹

In this paper, we report the results of a study on the electrodeposition of silver from 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide (BMITFSI) containing silver bis[(trifluoromethyl)sulfonyl]amide (AgTFSI). Cyclic voltammetry (CV) was used to characterize its electrochemical behavior. The morphology of the electrodeposited silver was investigated by scanning electron microscopy (SEM). The composition was determined using energy dispersive X-ray analysis (EDX).

2 Experimental

2.1 Chemicals

BMITFSI was prepared by an anion metathesis method.² An aqueous solution of lithium bis[(trifluoromethyl)sulfonyl]amide (LiTFSI) was added to a solution of 1-butyl-3-methylimidazolium chloride in water and stirred for 4 h at 70 °C. A separating funnel was used to separate the organic phase from the aqueous phase containing the chloride ion. The organic phase was repeatedly washed with distilled water until the chloride salt was completely removed and then dried in vacuo at ca. 80 °C for 4 h. The obtained ionic liquids were characterized by ¹H-NMR and cyclic voltammetry.

The AgTFSI was prepared as follows: a solution of bis[(trifluoromethyl)sulfonyl]amine (HTFSI) was added to an aqueous solution of silver carbonate (Ag,CO₃) and stirred for 4 h at 70 °C. Then the suspension was heated at 100 °C in vacuo in a rotary evaporator for 72 h. The obtained AgTFSI was characterized by FTIR.

2.2 Measurement procedures and apparatus

A solution of BMITFSI with 0.5 mol% AgTFSI was obtained by adding an appropriate amount of AgTFSI to BMITFSI in an air-tight glass vessel inside a glove box, where the oxygen and moisture levels were less than 1 ppm.

All electrochemical experiments were performed using a voltammetric analyzer (CV-50, BASi Co., Ltd.). For the CV measurements, a glassy carbon electrode (φ, 3 mm) and a Pt electrode (φ, 1 mm) were used as working electrodes; a Ag wire and a Ag/AgTFSI electrode were used as the counter electrode and reference electrode, respectively. For electrodeposition, a glassy carbon (GC) plate (5 × 10 × 1 mm) and a Pt plate (10 × 10 × 0.1 mm) were used as working electrodes. The CV measurements were conducted inside the air-tight electrochemical cell of a cell stand (CS-3, BASi Co., Ltd.) under N₂ flow and at room temperature. Electrodeposition measurements were performed inside an argon-filled glove box or under atmospheric conditions at 150 °C by the constant current method. A Hitachi S-4300 FESEM with EDAX Genesis2000 EDS analyzer was used to examine the surface morphology and chemical composition of the deposits. The electrical resistance of the silver deposits was measured using a four-probe method.
3 Results and Discussion

A typical cyclic voltammogram for BMITFSI with 0.5 mol% AgTFSI on a platinum disk electrode at a sweep rate of 50 mV s⁻¹ is shown in Fig. 1. The width of the electrochemical window of this solution is about 4.3 V, which is compatible with that of commercially available BMITFSI chemicals. The cathodic peak at ~0.32 V corresponds to Ag deposition, whereas the anodic peak at 0.14 V may be related to the dissolution of silver. By increasing the temperature of the solution, the cathodic peak for silver deposition shifted in the anodic direction and the shape of the peak became sharper.

The obtained deposits had a metallic/silver color and their compositions, almost pure Ag, were determined by EDX. Figure 2 shows SEM images of silver deposits from 0.5 mol% AgTFSI in BMITFSI on the GC plates at 150 °C. The sizes of crystallites were determined by examining the SEM image of each deposit. At 0.08 mA cm⁻², relatively large crystallites were observed, but the surface of the GC substrate was only partially covered with silver deposits.

Figure 3 shows the relationship between the size of the deposited silver crystallite and the current density. With increasing current density, the size of the crystallite became smaller. At a current density of 0.88 mA cm⁻², the surface of the GC substrate was fully covered with dense silver deposits. At a current density of 1.0 mA cm⁻², the color of the solution changed to brown, which might have been attributable to decomposition of the solvent, and no deposit was observed.

To characterize the transport properties, the diffusion coefficient of the Ag⁺ ion in the solution was estimated. Using a micro Pt electrode (0.01 mm), a series of cyclic voltammograms was recorded at various sweep rates (0.01 to 5 V s⁻¹). According to the following equation, which corresponds to an irreversible process,

$$j_\text{p} = \frac{0.4958 \times 10^{-7} n F^2 (RT)^{1/2}}{(a_n)^{1/2} C^* a_{Ag} D^{1/2} a_{Ag}^{1/2}}$$

the diffusion coefficient of the Ag⁺ ion in BMITFSI at 25 °C was calculated to be $3.5 \pm 2.0 \times 10^{-6}$ cm² s⁻¹. This value is very low compared with that in aqueous solution.

The electrical resistance of the Ag film deposited at 0.88 mA cm⁻² was $1.72 \times 10^4$ Ωm, which is comparable to the intrinsic resistance of silver ($1.59 \times 10^4$ Ωm).

4 Conclusions

The electrodeposition of silver was investigated in BMITFSI containing AgTFSI at 150 °C. A thin film of white/silver metallic color was obtained at current densities greater than 0.8 mA cm⁻². The electrical resistance of the deposit was comparable to that of the intrinsic material. The diffusion coefficient of Ag⁺ in this solution was rather low.

References