Vapour Phase Electrolytic Deposition: A Novel Method for Preparation of Orientated Thin Films

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A novel method of electrolysis in the vapour phase which is carried out using glow-discharge plasma as conductive fluid has been devised for the preparation of orientated Ag^+ ion conductive thin AgI films.

Considerable attention has been focused on the preparation of orientated thin films including CVD,[1,2] plasma CVD,[3] molecular beam epitaxy[4] and reactive ion beam deposition.[5] Here we describe the novel preparation of oriented, uniform thin films using glow-discharge plasma as a conductive medium.

Glow discharge plasma is a conductive fluid, whose charge carriers consist not only of ionic species, but also of electrons. Under certain conditions, the electric conductivity of plasma reaches values as high as 10^{-3} S cm^{-1}.[6] Thus glow-discharge plasma could be used as conductive fluids in electrochemical systems. We developed a novel electrolysis using glow-discharge plasma for the preparation of yttria-stabilised zirconia films.[7,8]

The principle of vapour phase electrolytic deposition for orientated AgI films is shown in Fig. 1. The AgI layer grew on the surface of a Ag^+ ion conductive glass (70% AgI–30% Ag_2MoO_4)[9] under various DC current densities flowing through the circuit consisting of Ag/Ag^+ ion conductor/glow-discharge plasma/Ag. Ag is anodically oxidised at the interface between the Ag electrode and the Ag^+ ion conductive glass, forming Ag^+. The Ag^+ is directed to the glass surface facing the plasma which was generated by applying AF power of 12 W of 10 kHz at 0.9 Torr on a gaseous mixture of Ar and I_2. A potential gradient across the glass, caused by an applied DC bias, drove the migration of Ag^+. After reaching the surface, the Ag^+ ion reacted with an electron and I_2 to form AgI which is also Ag^+ conductive.

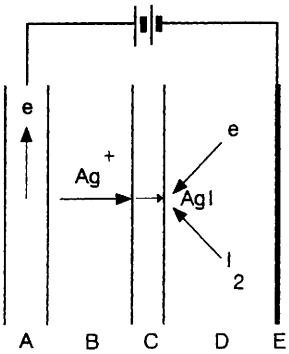

Fig. 1 Principle of AgI layer deposition by vapour phase electrolytic deposition under applied DC bias voltage through a DC circuit. A: Ag electrode, B: Ag^+ ion conductive glass (70% AgI–30% Ag_2MoO_4), C: growing AgI layer, D: argon glow-discharge plasma containing I_2 vapour, E: counter Ag electrode.

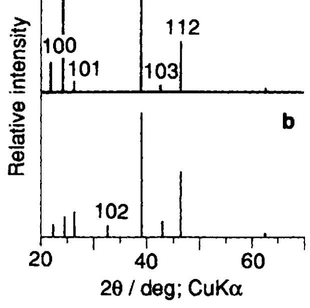

Fig. 2 X-Ray diffraction patterns for AgI formed at DC current density of (*a*) 0.49 and (*b*) 2.1 mA cm^{-2}

The layers formed on the Ag^+ ion conductive glass at different DC current densities were characterised by electron probe micro analysis (EPMA), X-ray photoelectron spectroscopy (XPS), X-ray diffraction, and scanning electron micrograph (SEM). EPMA and ESCA measurements indicated that the composition of the layers, Ag : I, were 1 : 1. These results indicate that the layers were stoichiometric AgI. A cross-sectional SEM photograph showed that the layer was uniform. The current efficiency for AgI deposition was 100% independent of DC current density.

X-Ray diffraction patterns for the AgI at different DC current density are shown in Fig. 2. The diffraction pattern for the film shows peaks at the (100), (002), (101), (102), (110), (103), and (112) position of β-AgI.[10] The peak ratio (110)/(002) is 0.71, 0.76, and 5.3 for β-AgI powder of ref. 10, the AgI film formed at DC current density of 0.49 mA cm^{-2}, and the AgI film formed at DC current density of 2.1 mA cm^{-2}, respectively. A peak corresponding to the (110) plane of the film formed at high current density was stronger than all the other peaks. This indicates that the film formed at high current density (Fig. 2b) had a remarkable orientation of the crystallographic *c*-axis parallel to the substrate plane, as compared with non-orientated β-AgI.

Ionic conductivity of Ag^+ ion conductive glass (70% AgI–30% Ag_2MoO_4) and electric conductivity of the Ar glow-discharge plasma were estimated by AC impedance measurement and Faraday probe method.[11] The room temp. ionic conductivity of the glass and electric conductivity of the plasma were 9.0×10^{-3} S cm^{-1} and 9.5×10^{-4} S cm^{-1}, respectively. Practical resistance of the glass and the plasma is 2.2×10 (thickness of the glass = 2 mm) and 9.3×10^2 Ω (distance between C and E of Fig. 1 is 4.0 cm), respectively. On the other hand, the room temp. ionic conductivity of β-AgI is about 10^{-6} S cm^{-1},[12] which is lower than those of the glass and the plasma. Ionic transport through the growing β-AgI layer should affect the morphology, especially in high DC current density, because of the high potential gradient inside the layer. The bulk conductivity of β-AgI single crystals perpendicular to *c*-axis is higher than that parallel to *c*-axis.[13] For this reason, the film formed at high current density had a *c*-axis orientated parallel to the substrate plane, because this orientation is favourable for ion transport through the film.

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