

Kinetic analysis of Electrochemical Copper Deposition in Etched Ion Track Membranes

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Electrochemical techniques are used for depositing copper during the production process for printed circuits boards in microelectronics industry [1]. Compared to other methods like chemical and physical vapour deposition, electrochemical techniques have several advantages including avoidance of vacuum systems, high flexibility and low costs. Moreover, investigations are being performed for the creation of novel micro- and nanostructures with higher aspect ratios. One suitable method used for this purpose is the electrochemical deposition of a metal in the pores of a template, e.g., etched ion track membranes or anodically oxidised aluminium. Nevertheless, up to now very little is known about the mechanism of this process itself [2], for which some similarities to the behaviour of microelectrode ensembles can be expected [3]. Therefore, the potentiostatic electrochemical process of filling etched ion track membranes with copper is studied in detail.

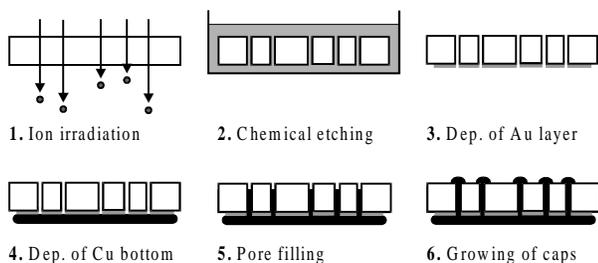


Fig. 1 Template method

Following the template method illustrated in fig. 1 polycarbonate foils with a thickness 30 μm and diameter 5 cm are irradiated at the UNILAC accelerator of GSI with Bi ions (11.3 MeV/u) up to a fluence of $1.25 \cdot 10^7$ ions cm^{-2} . Through a chemical etching process the latent ion tracks develop into cylindrical pores with diameters between 400 and 450 nm. A thin gold layer is then sputtered onto one side of the membrane and subsequently reinforced galvanically with copper. This conductive side acts as cathode during pore filling in a specially designed three-electrode cell. A simple salt electrolyte is used containing 2 mol/l H_2SO_4 but only 0.25 mol/l CuSO_4 to neglect mass transport due to migration.

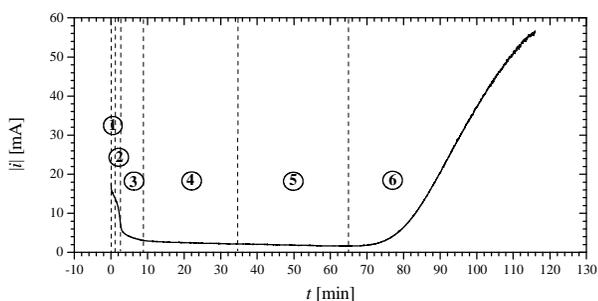


Fig. 2 Current-time-curve for $|\eta| = 120$ mV

In order to analyse the deposition process, current versus time curves are recorded for different applied overvoltages $|\eta|$ (difference between applied and open-circuit potential), namely between 80 and 440 mV. Fig. 2 shows the curve for $|\eta| = 120$ mV. Six different time periods are indicated corresponding to different events determining the overall reaction.

As soon as the potential is applied between cathode and reference electrode, copper is deposited and the electrolyte adjacent to the cathode depletes from copper ions – a concentration gradient starts to develop. For very short times (region 1), this gradient is nearly zero so that the deposition is charge transfer controlled [4]. By plotting the experimentally determined current densities at $t = 0$ versus the chosen overvoltage $|\eta|$ a Tafel-line is obtained. The cathodic reduction of copper takes place in two consecutive steps, so that the exchange current density and the transfer coefficient for the reaction $\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$ are obtained. Then, within region 2, a transition from charge transfer to diffusion control takes place, since both overvoltages become of comparable size.

With increasing time, the depletion zone in front of the cathode (Nernst layer) is growing into the electrolyte – the concentration gradient is increasing and the overall reaction starts to be diffusion controlled. When, for a given overvoltage, the current is plotted versus $1/\sqrt{t}$ (Cottrell-plot), up to three different linear sections (regions 3 to 5) can be clearly distinguished. For relatively short times, the thickness of the Nernst layer is smaller than the remaining pore length, and the diffusion is linear inside the pores (region 3), see fig. 3A. After some time, the depletion zone exceeds the pore length, and a radial diffusion field establishes around each pore (region 4). The ions are diffusing radially towards the pore openings (fig. 3B). For long times (region 5) the radial diffusion fields start to overlap with their neighbours. The diffusion is again linear but now towards the whole membrane surface (fig. 3C). This region is missing for high overvoltages because the deposition is too fast to allow overlapping of the radial diffusion fields. The increase of current in region 6 indicates that caps start to overgrow the membrane surface.

This qualitative model improves the understanding of the metal deposition process in templates of different pore densities and geometries. For a quantitative analysis, new suitable theories are needed.

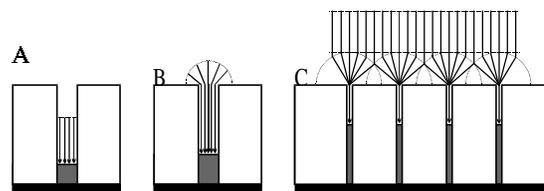


Fig. 3 Diffusion processes during pore filling

References

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