
1. Introduction

The importance of copper for next-generation on-chip interconnection has been well established since the first discovery that copper wiring has advantages of lower resistance, higher allowable current density, and increased scalability compared with the Ti/Al (Cu) wiring [1,2]. Much effort has been devoted to copper electrodeposition in recent years because of the technological requirements and scientific interests [3–10].

The growth of branched metal aggregates by electrochemical deposition in quasi-two-dimensional geometries is a complex example of nonequilibrium growth [5–7]. In the thin-layer electrochemical deposition of CuSO₄, a variety of different growth morphologies have been observed depending on the experimental conditions in the quasi-two-dimensionality [5–18]. Electrochemical deposition processes occurring at the interface is determined by diffusion, migration, convection, and chemical processes [5]. To understand and control the deposit formation, it is important to know the various electrochemical and physical processes near the growing interface, for instance, the effect of the cathode over-potential and electrolyte ion electrode potential [12,19–27]. Ions drift in the applied electric field, and electrochemical reactions occur at both cathode and anode. The reactions lead to spatial variations in the concentration of ions near both electrodes and the variety of charge at the electrodes [3–10]. In addition, the change of the ion concentration at the electrodes depending on time can trigger new electrochemical reactions or lead to time dependence on the electrode processes [19]. The electrodeposition can be nucleation controlled [19,22], which is sensitive to the variation of concentration/electric fields at the growing front. These factors would induce oscillatory nucleation and growth, as well as copper/cuprous oxide resulting from nonequilibrium [11,19,22,28,29].

Recently, the electrodeposition of copper in an ultrathin layer of concentrated CuSO₄ electrolyte indicated that the macroscopic fingering branches of deposits consisting of long copper filaments covered with periodic corrugated nanostructures. The copper filaments deposited on an insulating glass substrate without introducing additives in the electrolyte or metallic clusters on the substrate surface. The investigation showed that electrolyte ion electrode potential influenced the formation of periodic structures [22,23].
However, nucleation sites of copper/cuprous oxide in quasi-two-dimensional electrochemical deposition have no direct experimental evidence. Therefore, it is interesting to explore self-assembled structures of copper/cuprous oxide in the copper electrodeposition.

In this paper, the electrodeposition with branched growth was observed on an insulating substrate using an ultrathin layer of concentrated CuSO4 electrolyte. The copper electrodeposition can create periodic self-assembled structures along the branch with the random distribution of Cu/Cu2O nanograins and the spontaneously periodic variations of cell voltage. Phase composition, grain size, surface texture, and distribution of copper/cuprous oxide were investigated further by scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (TEM). The formation mechanism of the self-assembled structure and the periodic variations of cell voltage was also discussed.

2. Experimental

The electrochemical cell for experiments consists of two clean cover glass plates. Separated by the electrodes, the cell gap is determined by the electrodes. Copper foil (99.9%) of thickness 40 μm was generally used as spacers. The experiments were conducted in a cell enclosing two parallel electrodes separated by a distance of 8 mm. The electrolyte solution was prepared from analytical reagent CuSO4 and ultrapure water. The concentration of CuSO4 electrolyte is 0.05 M. A Peltier element and a temperature selector were employed to reduce temperature and to solidify the electrolyte. CuSO4 is partially expelled from the solid in the solidification due to the partitioning effect. Eventually, an ultrathin layer of concentrated CuSO4 electrolyte is formed between the ice of electrolyte solution and the upper or the lower glass plate when equilibrium is reached. The layer thickness is about 200–400 nm and the concentration in this trapped layer does not exceed 0.7 M [22,23]. Experiments are carried out at −4.85 °C. The electrodeposit develops in this layer. A constant Current of 30 μA was applied. The deposited specimen was preserved with nitrogen for SEM and TEM observed.

Optical microscopy (OPM; Leitz, Orthoplan-pol) was employed in situ to observe the ice blocking and the growing process of the deposits. The growing process of deposits was kinescoped by a CCD camera, and the growing velocity were measured. At the same time, the cell voltage and time was recorded with computer. Temperature was controlled by circulators with a programmable or digital controller (Polystat).

The structure and phase composition of the electrochemically deposited formation were identified by electron diffraction analysis, bright-field imaging, dark-field imaging, and high-resolution electron microscopy image in a FEG 2000 transmission electron microscope. The surface morphology at these experimental conditions was observed in a LEO-1550 scanning electron microscope.

3. Results and discussion

Fig. 1(a) shows the SEM morphology of typical electrodeposition with branched growth. The branch structure grows on a substrate with relatively regular branches and breaches within a two-dimensional plane. The branched structures have distinctly periodic structure along the branch with nanograins, as shown in Fig. 1(b). The fine polycrystalline features are made of carpet gains arranging...
Fig. 2. TEM images and electron diffraction pattern.

side by side. The size of the nanograins is <60 nm. The TEM diffraction patterns made up of the polycrystalline diffraction ring of Cu and Cu$_2$O suggest the existence of Cu and polycrystalline Cu$_2$O (Fig. 2). Fig. 1(c) indicates a plot of the cell voltage ($V$) as a function of time ($t$), when the deposits grew on a cathode at a constant current (30 mA). It has been confirmed that the periodic structure and the periodic variations of cell voltage have a close connection by in situ observations of the growth velocity and recorded relationship between the cell voltage and time. The growth velocity is about 300 nm/s. It took 1 s for the aggregate to develop one unit. The periodicity of the cell voltage is 1 Hz. The aggregate develop one unit, and at the same time, the periodicity of the cell voltage oscillates one time.

The results illustrated above suggest that the growth process includes nucleation and growth events. The nucleation frequency is random in nature, while the growth occurs within a specified interval. The newly triggered nucleation and the size of new grain were dependent on nucleation and growth kinetics. When the driving force reaches a critical value, nucleation and growth events occur, otherwise the growth process is totally inhibited.

In the electrocrystallization process, the over-potential is the driving force, which leads to the formation of a new phase (nucleation or growth) at the electrode–electrolyte interface [26]. We make the assumption that the anode potential remains fixed during the process [12]. The most interesting changes in the cell voltage are due to cathode processes [12]. When a constant current (30 mA) was applied in the two poles of the cell, the cathode is charged, and the cell voltage increases. The potential of cathode becomes more negative with respect to the anode, and the cathode over-potential also becomes more negative. At the same time, the concentration of Cu$^{2+}$ ion was improved near cathode by the electric field effect. According to the Nernst equation, the standard electrode potential of Cu and Cu$_2$O is a function of the Cu$^{2+}$ concentration. The standard electrode potential was increased by increasing the concentration of Cu$^{2+}$. When the cathode over-potential reaches the reaction over-potential ($V_f$) and the standard electrode potential reaches the standard electrode potential of reaction (the deposition potentials), the nucleation and growth events take place. The segment curve MN in Fig. 1(c) indicates the cell voltage increases by charging in the cathode, the cathode over-potential reaches the deposition potentials for Cu and Cu$_2$O (about 3.9 V) under the experiment condition, and the deoxidization occurs at the top of the curve. In the growth process, the cation and the charge are rapidly depleted. Therefore, the concentration of the ion close to the region of the cathode is lower than in the bulk [18]. When the transport velocity of cation is less than the deposition velocity at the growing interface, the concentration gradient becomes stronger very close to the cathode, and new nucleation events are totally inhibited.

Since the conductivity of the electrolyte goes to zero and the current remains constant, the cathodes are charged and $V(t)$ must diverge at this time. In practice, the cell voltage increases, and the cathode over-potential is decreased. The concentration gradient becomes stronger very close to the cathode, and then diffusive transport across the depletion region becomes important. Owing to migration of cations in the once again growing interface, the concentration of Cu$^{2+}$ increases, $p$H decreases, and the electrode potential is increased. A large field is formed again on the surface, up to the point when a new nucleation is fired, and the process repeats itself. As a result, the aggregate have distinct periodic structure and the cathode over-potential has a spontaneously periodic potential.
Fig. 3. Bright-field image and dark-field TEM images: (a) the bright-field image consists of nanograins; (b) the dark-field image of Cu$_2$O was obtained by diffraction ring of Cu$_2$O(210) (the polycrystalline diffraction ring location a in Fig. 2); and (c) the dark-field image of Cu was obtained through the diffraction ring of Cu(200) (the polycrystalline diffraction ring location b in Fig. 2).

Fig. 3 is the TEM bright-field image and dark-field image of one unit. Fig. 4 is a high-resolution electron microscopy image. The bright-field image (Fig. 3(a)) shows the morphology consisting of nanograins, while the dark-field image indicates that nanograins of Cu and Cu$_2$O (bright area) were scattered at a difference site, which is shown in Fig. 3(b) and (c). Figs. 3 and 4 indicate that nanograins of copper and cuprous oxide were irregular size and arrangement.

In the process of nucleation and growth, the cathode over-potential reaches the reaction over-potential; the standard electrode potential Cu/Cu$_2$O reaches the standard electrode potential of reaction; and the nucleation of copper and cuprous oxide compete. The two electrode reactions are written in Eqs. (1) and (2):

$$\text{Cu}^{2+} + 2e^- = \text{Cu} \quad (1)$$
$$2\text{Cu}^{2+} + 2e^- + 2OH^- = \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad (2)$$

Higher nucleation rates and larger nucleation sites in the electocrystalization process will lead to depositing with a polycrystal nature. In the growing process of each periodic structure, the equilibrium electrode potential of Cu$_2$O (0.17 V) is higher than that of Cu (0.34 V), so the deposition of Cu$_2$O is priority. According to Eq. (2), the formation of Cu$_2$O would deplete OH$^-$ and Cu$^{2+}$ in the migration layer, decreasing the local pH. The standard electrode potential of Cu$_2$O becomes lower than the standard electrode potential of reaction with OH$^-$ depletion. When the nucleation of
Cu occurs, the formation of Cu would deplete Cu$^{2+}$ in the migration layer, according to Eq. (1). The concentration of OH$^-$ ion is refreshed again, and the standard electrode potential of Cu$_2$O exceeds the reaction over-potential. The formation of Cu/Cu$_2$O electrochemical deposition is oscillatory nucleation and growth. However, due to the crystallite capture the amount of ion is different, the formation of every crystal (Cu$_2$O) differ in depleting OH$^-$ and Cu$^{2+}$, the crystal differ in size, they result in the front of the growing interface is irregular. In accordance, the nucleation sites of Cu crystal are too irregular. Thereby, the distribution of Cu/Cu$_2$O nanograins is random to all appearances (see Fig. 3). A mixture of copper and cuprous oxide is deposited and grains form on the uncoated cover glass substrate from a copper sulfate solution. The changes in the local Cu/Cu$_2$O rate are too weak for the cell potential curve to be the cause of the changes (see Fig. 1c).

4. Conclusions

In the presence of an ultrathin layer of concentrated CuSO$_4$ electrolyte, the depositing have a distinct periodic structure with randomly distributed Cu/Cu$_2$O nanograins, and relatively regular branch and breach were formed on two-dimensional plane.

In the electrocrystallization process, the change of the cathode over-potential and the standard electrode potential for Cu$_2$O and Cu result in a periodic structure and spontaneously periodic variations of cell voltage. In the front of the growing interface, the presence of copper and cuprous oxide can be justified a competition between the two electrode reactions because the electrode potentials for Cu$_2$O and Cu are different. A mixture of copper and cuprous oxide is deposited as a structure with the randomly distributed Cu/Cu$_2$O nanograins.

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References