

Electrochemical Polishing of Patterned Copper Films

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Abstract

For decades Electrochemical Polishing (ECP) has been used for surface polishing of bulk metal materials such as copper and stainless steel. However, it was found very challenging to planarize patterned copper films electrodeposited on silicon wafers. This work studied the mechanisms of ECP, the surface profiles and ECP effects of copper bulk and films in various electrolyte solutions. Satisfied ECP effect of patterned copper films was obtained. Optimal conditions for planarization of patterned copper films were presented.

Introduction

As device dimensions continue to shrink while speed continues to increase, ultra low-k ILD materials are to be used to reduce RC delay. Unfortunately, these low-k ILDs are too soft to be integrated with conventional CMP technique. Electrochemical Polishing (ECP), as an alternative polishing technique for replacement of CMP, is currently under serious consideration. It was found that ECP effect depends on anode surface profile, anodic layers and their profiles, limiting current and potentials, as well as mass transport limiting species (1, 2). These factors are determined mainly by electrolytes and their concentrations in the solutions. Therefore, in order to find the optimal conditions for the planarization of patterned copper films electrodeposited on silicon wafers, this work studied the ECP effects of copper bulk and patterned films with several electrolytes. Further, ECP mechanisms were analyzed. Optimal conditions for the planarization of copper films electrodeposited on patterned silicon wafers are presented.

Experimental Details

ECP of Cu disks and Cu films electroplated on patterned silicon wafers was performed with chronoamperometry using computer controlled 273A Potentiostat/Galvanostat at room temperature. The controlled potentials are the center points of the limiting current plateaus in the Cu anodic polarization curves, which were measure beforehand (2). Cu films had been electroplated on 200mm patterned wafers beforehand with our in-house wafer plating system. ECP effect (represented by mean roughness R_a) was evaluated with an atomic force microscope (AFM) and electron microscopes, as well as a surface profilometer. Cu removal

rate (R_d) was calculated from the weight loss during ECP and compared with the calculated values determined from the polishing current.

Experimental Results

Fig. 1 shows typical AFM images of bulk Cu surfaces before and after ECP. Table 1 listed limiting current (i_L), R_a , and R_d data obtained with various electrolyte solutions. Very good ECP of copper bulk material were achieved in solutions of phosphoric acid, HEDP, and phosphoric acid with additives copper oxide, ethylene glycol, and sodium tripolyphosphate. However, copper bulk ECP in ethylene glycol - sodium chloride, sulfuric acid, and sulfuric acid - sodium nitrate solutions was not as good. SEM images of Cu film - silicon cross-section before and after ECP in phosphoric acid and HEDP solutions respectively are shown in Fig. 2. A planar surface is obtained from ECP in HEDP solution. However, the ECP in phosphoric acid was not as good. Bumps over dense structures were left behind after ECP. An interpretation of the results will be presented after the discussion of ECP mechanisms in next section.

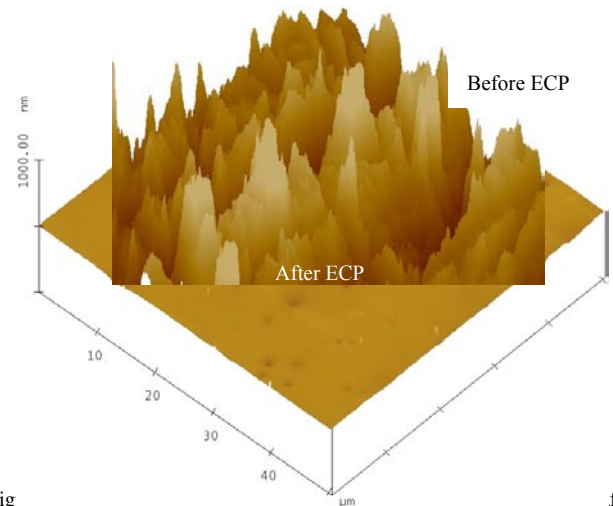


Fig. 1 ECP in 70% phosphoric acid + 15% EG solution ($R_a = 6$ nm).

Table 1 Summary of copper disk ECP data.

Solution	i_L (mA)	R_d ($\mu\text{m}/\text{min}$)	R_a (nm)
30~100 % Phosphoric acid + 0~2 M CuO	20 ~200	0.44~4.4	5~29
70% Phosphoric acid + 5~25% EG	14 ~50	0.3~1.1	5~8
70% Phosphoric acid + 0.1~0.5MNa ₃ P ₃ O ₁₀	32 ~50	0.7~1.1	7~17
20~80% HEDP + 10~30% Phosphoric acid	14 ~167	0.3~3.7	6 ~243
20 ~ 100% EG + 1~2M NaCl	20 ~50	0.44~1.1	63 ~91
20% H ₂ SO ₄ + 0~2M NaNO ₃	70 ~80	1.54~1.75	72 ~279

ECP Mechanisms and Interpretation of ECP Results

ECP can be achieved under ohmic control or mass transport control (3). Under ohmic control, a leveling effect of surface roughness, *ohmic leveling*, due to the fact that the protruding areas have higher current density (J) than the recesses, can be achieved. As illustrated in Fig. 3, the current densities at protruding point P and recessed point Q are different due to the different electrical resistance between P and Q to cathode. Accordingly, there is a difference of anodic dissolution rate (R_d) between P and Q, which can be expressed as (1, 2)

$$\Delta R_d = R_d(P) - R_d(Q) = \frac{MV}{nFd} \frac{2b}{\rho_e(l^2 - b^2)} \quad (1)$$

where M is the atomic weight (63.5 g for Cu) and d is the density of the anode material (8.96 g/cm³ for Cu), V is the applied anode potential, ρ_e is the resistivity of the electrolyte solution, n (2 for Cu - 2e → Cu⁺⁺ reaction) is the number of electrons transferred in the oxidation reaction, and F (= 96485 C) is the Faraday constant. Under normal ECP conditions, assuming $\rho_e = 10 \Omega\text{-cm}$ [7], $2b = 0.5 \mu\text{m}$, $l = 20 \text{ cm}$, and $V = 2\text{V}$, we calculated $\Delta R_d = 9.18 \times 10^{-9} \mu\text{m/s}$, which is negligible compared to the average removal rate $R_d = 4.4 \times 10^{-3} \mu\text{m/s}$ at limiting current density $i_L = 12 \text{ mA/cm}^2$ for phosphoric acid (85% H₃PO₄) solution.

Under mass transport control, anodic dissolution rate is controlled by migration/diffusion of Cu ions or acceptors in the anodic layer(s). Fig. 4 shows the normal electrical field (E_n) variation along a sinusoidal anode surface obtained by computer simulation. E_n at peak point P, $E_n(P)$, is larger than that at valley point Q, $E_n(Q)$. Hence, the Cu⁺⁺ at P get a larger force applied by the electric field and move towards

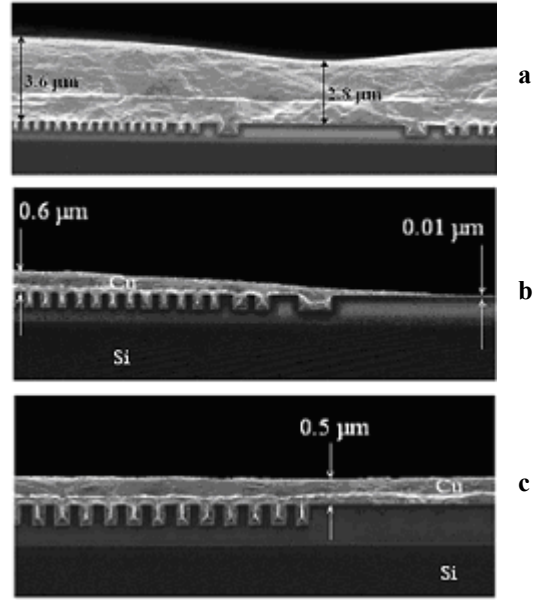


Figure 2 SEM images of copper film - silicon cross section (a) before and after ECP (b) in phosphoric acid and (c) HEDP solutions.

cathode faster than the Cu⁺⁺ at Q. Therefore, Cu dissolution rate at peak area (P) is expected to be greater than that in the valley area (Q), which results in surface leveling or *Migration Smoothing*. The simulation data (1, 2) showed that $\Delta E_n, E_n(P) - E_n(Q)$, depended on the frequency of the anode surface profile. As shown in Fig. 5, shorter wave (higher frequency) has greater ΔE_n than longer wave (lower

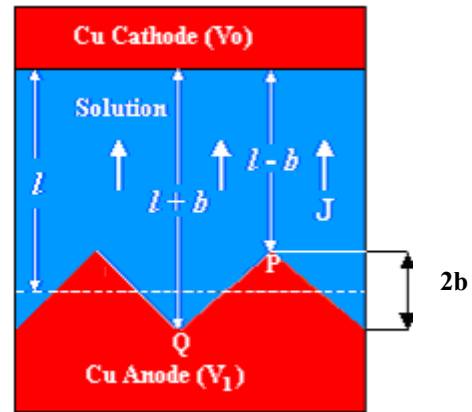


Figure 3 Schematic of an ECP cell with rough anode surface.

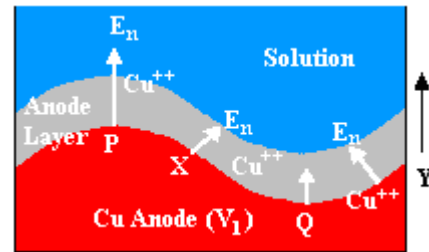


Figure 4 Schematic of the distribution of normal electric field on a sinusoidal anode surface.

frequency). Therefore, migration smoothing effect, driven by ΔE_n , approaches a sine wave profile involving the largest wavelength of the original pattern, since shorter waves disappear faster than the longer waves.

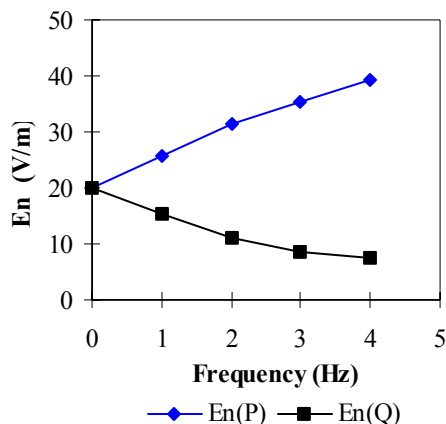


Figure 5 The amplitude of normal electric field at peak (P) and valley (Q) points of a sinusoidal anode surface.

Under mass transport control, a concentration gradient of the mass transport limiting species is developed in the anode boundary layer. Wagner (5) calculated the distribution of concentration gradient and the dissolution rate (driven by concentration gradient of acceptor) along a sinusoidal anode surface. It was shown that ECP due to diffusion smoothing mechanism is similar to migration smoothing effect. That is, shorter waves disappear faster than the longer waves.

From the above discussion, it seems impossible to get an absolute flat surface through migration smoothing and diffusion smoothing mechanisms. However, the situation can be improved if the anode layer has a macro profile. In this case, the migration and/or diffusion distance of the mass transport limiting species at peak points is shorter than that at the valley points (Fig. 6).

Mechanically polished bulk Cu surface has sharper geometrical profiles (Fig. 1) and thus better ECP effect can be achieved, due to migration and/or diffusion smoothing mechanisms. This explains why very good ECP effect of copper disks was obtained with most of the solutions (Table 1). For electroplated copper films on patterned wafers, as shown in Fig.7, the surface profiles consist of gentle geometrical undulation, i.e., longer wavelength of sine waves. Hence, ECP efficiency is largely reduced. When phosphoric acid solution was used, ECP efficiency was not as good due to the lack of ion migration mechanism since water molecules instead of Cu^{++} worked as the mass transport limiting species (6). When HEDP solution was used, an electrically resistive salt film with macro profile formed on the anode surface and Cu^{++} worked as the mass transport limiting specie (1), all the above three ECP mechanisms take effect. Therefore, a good ECP efficiency was achieved, even though the surface had a gentle

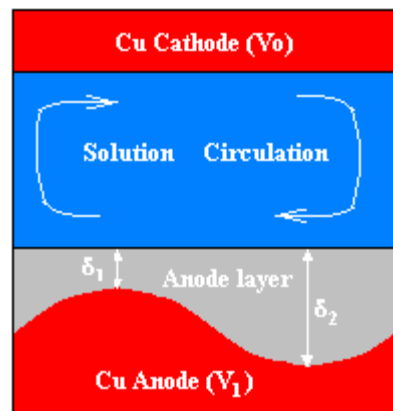


Figure 6: Schematic of an ECP cell with non-conformal anode layer.



Figure 7 AFM image of copper film electroplated on patterned silicon wafer.

geometric profile (Fig.2).

Summary

Very good electropolishing results ($R_a < 10$ nm) of bulk copper were obtained in solutions of phosphoric acid, HEDP and phosphoric acid with additives copper oxide, ethylene glycol, and sodium tripolyphosphate.

ECP of electroplated Cu films on patterned silicon wafers is more challenging. Gently protruding areas were not planarized by an ECP process with phosphoric acid while a good planarization was obtained in HEDP solutions, where a salt film formed on the anode surface (1). An anodic salt film with macro profile may enhance planarization due to migration smoothing and diffusion smoothing effects.

References

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