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Electrogenerated chemical polishing of copper

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ABSTRACT

Stress free polishing method is preferred for a damage free surface of copper with ultra-flatness and ultra-smoothness. Such a surface offers a perfect substrate for integrated circuits and micro-electromechanical systems fabrication. A new polishing method, called electrogenerated chemical polishing (EGCP), is proposed based on the principle of the scanning electrochemical microscope (SECM) and the diffusion controlled chemical reaction. Roughness of a Cu surface is reduced from 100.5 nm to 3.6 nm by the proposed method. To demonstrate the planarization capability of this new method, a patterned Cu surface with an array of micro-columns is planarized with a peak-valley (PV) value from 4.7 μm to 0.059 μm.

1. Introduction

Cu is a promising material for fabrication of micro-electromechanical systems (MEMS) and integrated circuits (IC) due to its good thermal and electrical properties. Copper polishing has been attracting much attention from researchers [1–3]. Chemical mechanical polishing (CMP) is a widely used polishing method in the IC industry, which utilizes the synergistic action between the chemical reaction and mechanical wear to realize polishing of Cu surface. Chemical reaction reduces the threshold force to remove the surface material, but surface defects, such as crack formation and material delamination at the weak interfaces, are still inevitable [3–6]. Mechanical force in the CMP process of the MEMS fabrication may also cause damage to the micro structure on a wafer. Moreover, research reports indicate that mechanical force in the CMP process induces obvious material degradation to the single crystal Cu [7–9]. To solve these problems, many researchers have developed new planarization methods, including abrasive-free CMP (AFP) and electrochemical mechanical polishing (ECMP) [10–12]. It should be pointed out that the new planarization methods have certain technical restrictions, such as difficulties in the reliable supply of an electric power and in achieving material removal without mechanical force during the AFP and ECMP processes. Therefore, stress free polishing/planarization is still difficult to realize.

Material removal by chemical and electrochemical reaction is much gentler than that by mechanical wear. However, the critical roughness of a surface polished by the conventional chemical polishing method is in the sub-micrometer range [13,14], and the electrochemical polishing (ECP) method is inefficient in planarizing the surface with micro scale wavy patterns [15,16]. These methods do not meet the demand in the MEMS and IC manufacturing. It is thus necessary to develop a non-contact and stress free planarization/polishing method.

Within the last 20 years, scanning electrochemical microscopy (SECM) provided attractive ways to patterning Cu surfaces with micrometer and sub-micrometer resolutions [17–19]. The fundamental material removal mechanism in SECM is speculated to be chemical etching, with the etchant being constantly generated at the working electrode surface. Because etchant is only generated over the working area of the electrode surface, the workpiece surface is not etched everywhere except the area facing the working area of the electrode surface [17]. Consequently, the closer the workpiece to the electrode surface, the higher the etching rate. This is so called “gap-sensitive etching”. The accuracy of the micro-scale hole fabricated by SECM depends on the tip-substrate separation distance [18]. However, due to the low ability of the “gap-sensitive etching”, the surface roughness of an etched area, which is in the sub-micrometer scale, does not show much improvement according to the results shown in Ref. [18]. A new method may be developed based on the SECM to reduce surface roughness of an etched area.

According to the fundamental mechanism of SECM, for the first time, we propose a new polishing method, named electrogenerated chemical polishing (EGCP). To develop the new method, several

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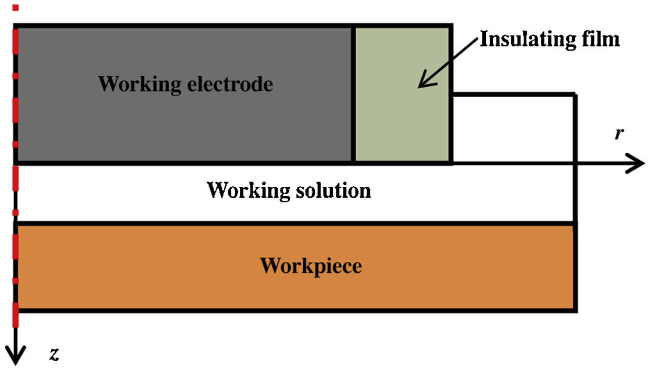

Fig. 1. Schematic illustration of the system under consideration.

issues need to be resolved: (a) A polishing solution needs to be developed, in which the etching rate at surface peaks is obviously higher than that at surface valleys. (b) A method is necessary to align the electrode surface parallel to the workpiece surface with a sub-micrometer gap. (c) Charge propagation in the lateral direction needs suppression for a better control of the polishing process [19].

A theoretical model is proposed for evaluating the polishing characteristics of the polishing solution that is to be developed. The study proposes a novel polishing method based on electrogenerated etchant in which an ultra-flat electrode and a nano-precision positioning system are adopted to precisely control the position of the working electrode relative to the workpiece surface. An inhibitor is used to suppress lateral charge propagation. Rough and patterned Cu surfaces are polished with the new method, and the evolved surface profiles are observed and evaluated.

2. Theoretical model of EGCP

The whole process of EGCP can be expressed as follows:

1) Electrochemical generation reaction

$$R \rightleftarrows O + ne \tag{1}$$

where R is redox mediator, O is etchant, e means an electron, and n is the electron number.

2) Etching reaction

$$O + W \xrightarrow{k_e} R + P \tag{2}$$

where W is the atom of workpiece material to be etched; P is the product of etching reaction; k_e is the rate constant of the irreversible etching reaction.

In the electrochemical reaction system, the species in solution are transported by diffusion, convection and electrical mobility. Because velocity of the electrolyte is near zero, mass transfer caused by convection in static etching is negligible. For a high concentration of ions in the working electrolyte, the strength of the electric field in solution is too low to drive the charged species. Thus, for the static etching, it can be assumed that the diffusive mass transfer is the only dominant factor of species transport in solution. Mathematical formulation of EGCP is created based on this assumption.

Fig. 1 shows the electrochemical system proposed in this study. As illustrated in Fig. 1, a cylindrical electrode (with radius a) is coated with an insulating film. At the beginning, the redox mediator has a concentration of C_R^0 in the solution. Distance between the working electrode and workpiece is d.

During etching, the potential on the working electrode is kept high enough to rapidly oxidize the redox mediator. Consequently, R concentration at the surface of the working electrode is near zero, which leads to the polarization boundary condition as

$$C_{R(z=0)} = 0 \tag{3}$$

The current response can be formulated as

$$I_t = \int_0^a D_R(\partial C_R/\partial z)_{z=0} nF2\pi r dr \tag{4}$$

where F is Faraday's constant (96,485 C/mol); D_R is the diffusion coefficient of R.

When the system approaches its steady state, etching rate $V_{etching}$ is equal to diffusion rate $V_{diffusion}$. As $a \gg d$ in this study, the concentration gradients of O and R are constants in the uniform sub-micron gap.

The expression of $V_{etching}$ and $V_{diffusion}$ are

$$V_{etching} = k_e C_{O(z=d)} \tag{5}$$

$$V_{diffusion} = D_O(\partial C_O/\partial z) = D_R(\partial C_R/\partial z) \tag{6}$$

where

$$\partial C_O/\partial z = 2(C_{O(z=d/2)} - C_{O(z=d)})/d \tag{7}$$

$$\partial C_R/\partial z = 2C_{R(z=d/2)}/d \tag{8}$$

$$C_{O(z=d/2)} + C_{R(z=d/2)} = C_R^0 \tag{9}$$

D_O is the diffusion coefficient of O.

Then Eq. (4) can be solved to obtain steady current

$$I_t = 2\pi n C_R^0 F a^2/(k_e^{-1} + d(D_O^{-1} + D_R^{-1})) \tag{10}$$

From the above solution, it is found that when $k_e \gg d^{-1}(D_O D_R)/(D_O + D_R)$ the etching current is sensitive to the distance between the working electrode and the workpiece surface, which facilitates selective etching between the peak and valley features on a workpiece surface. Selective etching is also named diffusion-controlled reaction in the published literature [19,20]. Eq. (10) provides a convenient method for evaluating polishing solution system for EGCP.

3. Experimental preparation

3.1. Chemicals and materials

All chemicals ($FeSO_4 \cdot 7H_2O$, H_2SO_4 and benzotriazole (BTA)) used in the study were of analytical grade or better and provided by Aladdin Co., China. The physical vapor deposition technique was used to prepare Cu workpieces on silicon wafers. Ultra-pure water was obtained in the laboratory (Milli-Q grade). The glassy carbon electrode of 6 mm in diameter was used as the working electrode. A ring counter Pt electrode of 250 μm in diameter and a reference electrode (mercury/mercurous sulfate electrode, abbreviated as "MSE") were also used. A 3D surface profiler (New View 5022, ZYGO Co., USA) was used to characterize the polished workpiece surface.

3.2. EGCP apparatus

A schematic diagram of a lab-made EGCP apparatus is shown in Fig. 2. The apparatus was composed of a mechanical motion system, an electrochemical system, a monitoring system and an information processing computer. In the mechanical motion system, a macro–micro dual positioning stage (stepper and piezo motor) drove the working electrode in the vertical direction. A workpiece was fixed on the working stage. A PAR2273 electrochemical workstation (Princeton Applied Research Co., USA) was used to perform the polishing process, including controlling the potential of the tool