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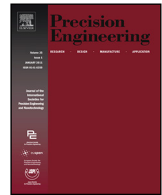

Analysis of the polishing ability of electrogenerated chemical polishing

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A B S T R A C T

Electrogenerated chemical polishing (EGCP) had been proved effective in improving both the smoothness and the flatness of copper surface in our previous work. In this paper the polishing ability, defined as the ratio between the material removal rate at the peak and at the valley of a rough surface, is studied theoretically and experimentally. In a mathematical model, the effects of the special wavelength L, the peak-to-valley height h of the workpiece surface profile and the working distance d between working electrode and workpiece surface on the polishing ability are studied. The results show that the polishing ability decreases with increasing the working distance and finally approaches the value $(d+h)/d$, if L is much larger than d. However, the effect of the working distance on polishing ability is negligible, if L is close to or less than d. The polishing ability also decreases with h decreasing. Based on the above analysis, an analytical expression of the polishing ability of EGCP is given. For validating the theoretical analysis, a copper surface is polished by EGCP and the change of the surface profile is measured and analyzed using the analytical expression. The measured polishing ability agrees well with the simulation results.

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1. Introduction

Copper, due to its good thermal and electrical properties, is widely used as a substrate material for fabricating micro-electromechanical systems (MEMS) devices and as a conducting material in integrated circuits (IC). Copper surfaces should be polished or planarized in the fabrication of MEMS [1] and IC [2] devices for layered structures formation using lithography technology, or as a substrate for film epitaxial growth using chemical vapor deposition (CVD) [3,4]. Chemical mechanical polishing (CMP) is a common method to obtain an ultra-smooth copper surface, and it reduces the force to remove the surface material by the assistance of chemical reaction. However, the mechanical force is still necessary to remove the material in CMP process. When CMP is used in the fabrication of MEMS and IC, the mechanical force will cause damage to the micro structure, such as material delamination and even crack formation at weak interfaces [5,6]. When polished single crystal copper surface is used as the substrate material for graphene or diamond growth, the amorphous layer induced by the mechanical force of CMP on single crystal substrate surfaces [7] will influence the quality of the epitaxial grown graphene and diamond [8–10]. To solve these problems caused by the mechanical force, many researchers have developed various stress-free polishing methods, including chemical polishing, electrochemical polishing (ECP) and others. However, the minimum roughness of a surface polished by the chemical polishing method is in the sub-micrometer range [11,12]. The ECP method can reduce the roughness to less than 10 nm for Cu surfaces [13,14] or even to less than 1 nm for stainless steel surfaces [15,16], but it is inefficient in planarizing the surface of micro scale wavy profile and difficult in the reliable supply of electric power for an ultra-thin copper layer on insulated substrate. Therefore, it is necessary to develop a new non-contact and stress-free polishing/planarization method.

Scanning electrochemical microscopy (SECM) provided attractive ways to process Cu surfaces with micrometer and sub-micrometer resolution [17–19]. According to the fundamental mechanism of SECM, our prior work proposed a new polishing method named electrogenerated chemical polishing (EGCP) [20,21]. As shown in Fig. 1, the fundamental polishing mechanism of EGCP is chemical etching. Firstly, the redox mediator (R) is oxidized to the etchant (O) by electrochemical reaction on the working electrode surface. Then the etchant diffuses to the workpiece surface and reacts with the workpiece material. In the chemical reaction, the etchant and the workpiece material react to form the redox mediator and the product (P). The closer the workpiece surface to the working electrode surface, the higher the etchant concentra-

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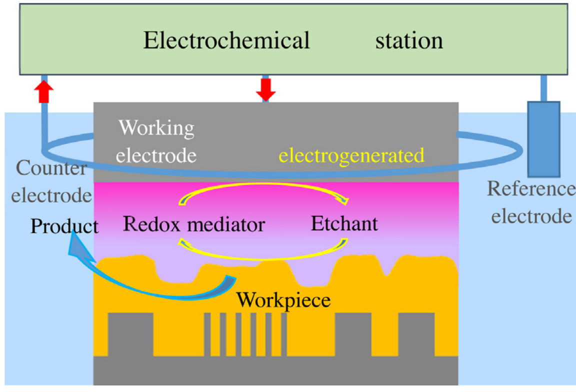

Fig. 1. Schematic illustration of EGCP.

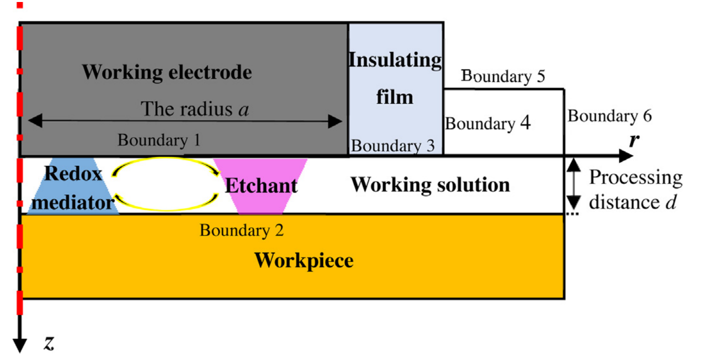

Fig. 2. Schematic illustration of a half cross-section of a rotationally symmetric model under consideration.

tion will be. Therefore the material removal rate at the top of a peak is higher than that at the bottom of a valley. The regenerated redox mediator will diffuse back to the working electrode surface. Consequently, the polishing of workpiece surface can be realized by repeating the process above.

EGCP has been proved successful in the copper polishing and patterned copper surface planarization [20,21]. But the polishing and planarization mechanisms of EGCP still need to be further elucidated, especially regarding polishing ability and gap control. In this paper, a one-dimensional analytical model and a two-dimension numeric simulation model are developed for studying the polishing ability of EGCP. The effects of relevant parameters such as the wavelength L, the peak-to-valley (PV) value height h of the workpiece surface profile and the working distance d between the working electrode and the workpiece surface on the polishing ability of EGCP are analyzed systematically. A mathematical expression of the polishing ability is given based on the numerical solution. Finally, some experimental validations are performed.

2. Theoretical model of EGCP

2.1. EGCP process sequence

The whole process of EGCP can be expressed as follows:

1) Electrochemical reaction

$$\mathrm{R} \underset{\longleftarrow}{\overset{\rightarrow}{}} \mathrm{O} + n_1 e \quad (1)$$

where R is the redox mediator, O is the etchant, e is electron, and n_1 is the number of electrons.

2) Etching reaction

$$n_2\mathrm{O} + n_1\mathrm{W} \overset{k_{b,s}}{\rightarrow} n_2\mathrm{R} + n_1\mathrm{P} \quad (2)$$

where W is an atom of the workpiece material to be etched; P is the product of the etching reaction; $k_{b,s}$ is the rate constant of the irreversible etching reaction, therefore ion concentration of product (P) almost has no effect on reaction process; n_1 and n_2 are the stoichiometric numbers.

2.2. One-dimensional analytical model

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 static etching, it can be assumed that the diffusive mass transfer is the only dominant factor of species transport in solution. And in Ref. [18], the convection and electrical mobility are also neglected when the SECM theoretical model is used to predicts the etched profile. The mathematical formulation of EGCP is created based on this assumption.

Fig. 2 shows the electrochemical system proposed in this study. As illustrated in Fig. 2, 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. The distance between the working electrode and the workpiece is d. The shape marked "R" and "O" schematically represents the corresponding concentration distribution of redox and etchant, respectively.

The current response I_t can be formulated as

$$I_t = \int_0^a D_R \left(\partial C_R/\partial z\right)_{z=0} n_1 F 2\pi r \mathrm{d}r \quad (3)$$

where F is the Faraday's constant (96485 C/mol), D_R is the diffusion coefficient of redox mediator.

When the system approaches its steady state, $V_{etching}$ (etching rate) = $V_{diffusion}$ (diffusion rate) = V_{rxn} (electrochemical generation rate). As $a \gg d$ in this study, the concentration gradients of O and R are constants in the uniform micro gap.

The expressions of $V_{etching}$ [22], $V_{diffusion}$ and V_{rxn} [23] are

$$V_{etching} = {}_{b,s}C_{O(z=d)} \quad (4)$$

$$V_{diffusion} = D_O\left(\partial C_O/\partial z\right) = D_R\left(\partial C_R/\partial z\right) \quad (5)$$

$$V_{rxn} = k^0\left(C_{R(z=0)}e^{(1-a)f\left(E-E^{\ominus'}\right)} - C_{O(z=0)}e^{-af\left(E-E^{\ominus'}\right)}\right) \quad (6)$$

where $f = F/R_0T$, D_O is the diffusion coefficient of the etchant, k^0 is the standard rate constant, α is the charge transfer coefficient, R_0 means the universal gas constant (8.314 J/mol/K), T is the room temperature (298 K), E is the potential of the working electrode and E' is the equilibrium potential. It is assumed that the diffusion coefficients for both species are equal, i.e., $D_O = D_R$, and the lateral ion transportation is negligible, thus,

$$\partial C_O/\partial z = \left(C_{O(z=0)} - C_{O(z=d)}\right)/d \quad (7)$$

$$C_{O(z=0)} + C_{R(z=0)} = C_R^0 \quad (8)$$

Combining with $V_{etching} = V_{diffusion}$, one obtains

$$C_{O(z=d)} = D_O C_{O(z=0)}/\left(k_{b,s}d + D_O\right) \quad (9)$$

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