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Effects of (002) β-Ta barrier on copper chemical mechanical polishing behavior

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ABSTRACT

This study proposes that the corrosion resistance of copper film correlates well with underlying barrier's orientation. To test the hypothesis, we performed X-ray diffraction, conducted copper removal rate experiments after chemical mechanical polishing, and tested static potentiodynamic polarization. The results all show that copper deposited on strongly (002) oriented β-Ta barrier layer demonstrated better chemical resistance against surface reaction with the slurry for strong copper (111) orientation. The findings were consistent with the result of the chronoamperometric test at 0.3 V in which the more passive film formed on the composite film with (002) β-Ta underlying barrier.

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1. Introduction

Copper has replaced aluminum as the interconnect metal in integrated circuits due to its higher electrical conductivity and superior electromigration resistance. It has recently been reported that the resistance to copper electromigration is closely related to the texture of copper films with the (111) orientation [1,2]. An effectively underlying barrier layer is necessary to prevent the diffusion of copper ions through the dielectric layer. Researchers have pointed out that various underlying barrier materials and textures will affect the microstructure of electroplated copper films [3–8]. Wong et al. [4] demonstrated that the grain boundaries of Ta are often directly aligned with the grain boundaries of copper. Kwon et al. [9] mentioned that using (002) β-Ta as an underlying barrier layer enhances the (111) texture of the copper film with a heteroepitaxial growth.

In most production processes, electrochemical plating is the primary method of copper metallization. After electroplated copper deposition, chemical mechanical polishing (CMP) is a necessary step for surface planarization in microelectronic industry. In a typical CMP process, material is removed from the surface of a wafer through the combined chemical and mechanical actions of slurry containing abrasive particles and weak etchants. The famous polishing principle for the removal rate simulation is Preston's equation, as described below [10,11]:

$$RR = kP^nU^m + RR_0$$

where RR is the material removal rate and k is the Preston's constant. P is the applied wafer pressure and U is the average linear pad-wafer velocity. RR_0 represents the dynamic etch rate of the material in the absence of pressure and velocity. This equation is very general since it relies on essentially one constant, k, to account for all chemical and mechanical intricacies of the process. Although many studies establish various removal models to describe polishing behavior, a simple relationship between the removal rate and CMP parameters can be obtained if we consider only the basic mechanics, which is that the removal rate is direct proportion to the applied polish pressure.

The removal rate of copper during CMP is closely correlated with the corrosion resistance of the electrochemical deposition films. Higher corrosion current density means higher copper removal rate during polishing. To test corrosion, Lin et al. [12,13] used the potentiodynamic polarization for electrochemical measurement and found that copper polished surface with high (111)/(200) ratio has strong chemical resistance. In the potentiodynamic polarization curve [14], using extrapolation method can get corrosion current density (I_{corr}) [15].

While the effect of underlying barrier layer on the performance of the electrochemical plating film has been widely studied, the sequential effect on the CMP behavior has not been fully identified. The objective of this paper is thus to describe the relationship between the textures of tantalum barrier and the behavior of chemical mechanical polishing, with findings from X-ray diffraction analysis, copper CMP removal rate, and potentiodynamic polarization measurements. This paper will conclude that the corrosion resistance of copper film was highly correlated with underlying barrier's orientation.

2. Experimental details

Cu electrochemical deposition on blanket 12-inch Si (100) wafers had the substrate condition with 500 nm thermal oxide. Two series of

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tantalum barrier films were prepared with 15 nm-thick by physical vapor deposition at room temperature based on the previous study of Wang et al. [16], which described the textures of Ta/TaN barriers sputtered with various N_2/Ar ratios: (1) deposited with 10% N_2/Ar ratio, which was called Barrier A. N_2 and Ar were applied into sputtering at the same time to form TaN structure; (2) deposited with putting Ar into chamber first, then using N2 to make Ta becomes TaN, which was called Barrier B. 100 nm thick copper seed layers used as the conductive layer of sequential electrochemical deposition were deposited on Barrier A and Barrier B with 56 kW DC power and 500 W AC bias, which were called Film AS and Film BS, respectively. Electroplating was carried out using 15 °C bath control with a 12 L/min steady overflow rate. Electroplating studies were performed in a conventional acid copper sulfate electrolytic solution containing 50 g/L copper metal, 20 g/L sulfuric acid, and 80 mg/L chloride ions with a small amount of proprietary organic additives. The thickness of the electroplating copper samples was 200 nm; they were called Film ASP and Film BSP, which were plated on the corresponding copper seed layers. For CMP, the polishing conditions were at head rotation speed of 63 rpm, platen rotation speed of 70 rpm and normalized polishing pressure of 1 to 40 kPa. The copper polishing slurry was prepared with 3.1 wt.% fumed aluminum particle and an acid solution with pH 3–5, which contained ingredients, including 0.2 wt.% hydrogen peroxide, 1 wt.% passivation agent (BTA) and a glycine acid salt which is commonly used in copper CMP slurries as a buffering and chelating agent. The peroxide and passivation agent were used as oxidizer and inhibitor for this study, respectively.

X-ray diffraction method was applied to determine film textures of tantalum barrier layers, copper seed layers, and electroplated copper layers, respectively. The X-ray diffraction apparatus model was Bruker AXS D8 Advance platform with in-situ cell Anton Paar HTK 1200 N, Cu Kalpha for X-ray source, and Bragg–Bentano configuration. The removal rates of copper films after chemical mechanical planarization were measured by the four-point probe method using a 49 point line scan on a Prometrix resistance measurement tools. Potentiodynamic polarization curve and chronoamperometric (applying potential) measurement for corrosion current study were performed with a computer-controlled CHI-602A potentiostat. Three-electrode cell was used for electrochemical measurement. The working electrode (test specimen) was prepared from 12-inch wafer that was processed with barrier, copper seed, and electroplated copper layers (Film ASP and Film BSP). The specimen size was 1×10 cm^2 while the test area was 1×1 cm^2. Not test area was covered with a waterproof tape. A saturated silver/silver chloride electrode (SSCE) and a sheet of platinum were used as reference electrode and counter electrode, respectively. The potentiodynamic polarization sweep of working electrode was performed from -1 to $+1$ V at a scanning rate of 1 mV/s. In the chronoamperometric test, the specimen was applied potential at 0.3 V (vs. SSCE) for 30 s and the change of current density with time was recorded. The test solution contained 0.2 wt.% H_2O_2 and 0.001 M Na_2SO_4. Hydrogen peroxide was used as a copper oxidizer and sulfate sodium was used to reduce solution resistance and to maintain solution conductivity.

3. Results and discussion

In order to investigate the effect of barrier on the chemical mechanical polishing behavior of copper, two barrier films, Barrier A and Barrier B, were prepared at essentially the same time with 15 nm thickness. The other four samples were deposited with 100 nm thick copper seed and 200 nm thick electroplating copper on Barrier A and Barrier B, respectively. X-ray diffraction was used to determine the textures of these six samples, as shown in Fig. 1a to c, respectively. In Fig. 1a, it reveals that Barrier B got very strong β-Ta (002) and bcc-Ta (110) textures. Compared with Barrier B, it is found that Barrier A had the comparable intensity of bcc-Ta (110), but lacked for β-Ta (002) peak. Stavrev et al. [17] mentioned that the interstitially incorporation of small numbers N atoms into Ta films causes the crystal structure change from β-Ta and bcc-Ta to pure bcc-Ta. Fig. 1b shows that Film BS (sputtered copper seed layer deposited on Barrier B) had stronger (111) copper texture than that of Film AS (sputtered copper seed layer deposited on Barrier A). Based on the heteroepitaxial growth study of copper on β-Ta mentioned by Kwon et al. [9], the (111) texture growth of the copper film is enhanced when the underlying barrier layer is (002) β-Ta by a pseudohexagonal atomic arrangement. This strong (111) copper seed orientation developed an intense (111) texture for the sequential copper electroplating layer of Film BSP (electroplating copper deposited on Film BS), as shown in Fig. 1c. According to the research of Hara et al. [18], the (111) texture of the electroplating copper layer is mainly determined by that of the underlying seed layer. Dow et al. [19] demonstrated that the intensity ratio of (111)/(200) texture is in good agreement between electroplating and seed layer. Fig. 1c also shows the same phenomenon that Film BSP had higher (111)/(200) ratio. In the previous studies [12,13], copper polished surface with high (111)/(200) ratio has strong chemical resistance. For face-centered cubic (FCC) copper thin film, (111) texture should exhibit stronger chemical resistance than other planes because (111) is the closest packed plane.

Chemical properties of copper surface play an important role in the CMP process. The mechanism of copper CMP is mechanical abrasion followed by chemical dissolution of the abraded material. Xu and Liang [20] proposed that copper removal mechanism is based on the cyclic sequence of copper passivation followed by the mechanical removal of the passive layer due to abrasion. During CMP, hydrogen peroxide (oxidizing agent) and glycine (complexing agent) form a porous and soft surface layer leading to high removal rate. Thus, the copper removal rate is a useful index to study the CMP behavior. Fig. 2 shows the correlations between the CMP applied pressures and the relative copper CMP

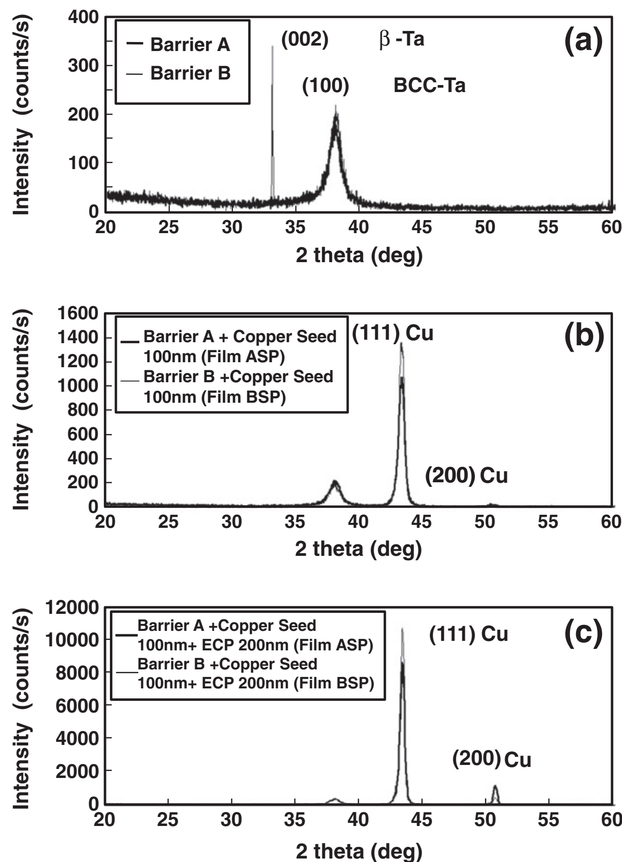

Fig. 1. X-ray diffraction texture patterns for composite films for (a) the barrier layers, (b) the barrier and sputtered copper seed layers, (c) the barrier, sputtered copper seed, and electroplated copper layers, respectively.

removal rates of Film ASP and Film BSP, respectively. It reveals that no matter what the textures of the barrier layer and copper layer were, the copper removal rates increased with increasing applied polish pressure. This matches the Preston's equation that describes the relationship between the polish removal rate and the polish pressure [10]. The increase of pressure raises temperature between slurry and copper surface to naturally speed up etching and passivation layer CuO_x formation. High etching rate and porous CuO_x interface, which can reduce frictional force between pad, slurry and wafer surface, cause linear relationship between removal rate and applied pressure [21]. It also can be seen in Fig. 2 that the removal rate of copper deposited on Barrier A was higher than that deposited on Barrier B which had strong (002) β-Ta texture. This can be explained by the orientation difference shown in Fig. 1c. Copper deposited on Barrier B had high (111)/(200) ratio with stronger chemical resistance because of denser structure of (111) plane. Jindal and Babu [22] reported that the CMP removal mechanism of copper film in slurries is to form a porous surface layer leading to higher removal rate and to reduce friction thus softening the surface layer. Denser structure reduced the chemical effect when polished and made copper not easy to be removed.

Hydrogen peroxide is commonly used as an oxidizer in commercial copper CMP slurries [23]. An aqueous solution containing 0.001 M Na_2SO_4 solution with 0.2 wt.% H_2O_2 was prepared to investigate the corrosion behaviors of copper films ASP and BSP by the measurement of potentiodynamic polarization curves in this study. Fig. 3 displays the static potentiodynamic polarization behaviors for Film ASP and Film BSP. The results reveal that the corrosion current density of Film BSP (79 μA/cm^2) was lower than that of Film ASP (142 μA/cm^2). Lower corrosion current means better chemical resistance. This implies that the composite film (BSP) with strong (002) β-Ta underlying barrier layer and (111) copper orientation had relatively high chemical resistance against surface reaction with slurry, which caused lower copper CMP removal rate as shown in Fig. 3. Furthermore, the data in Fig. 3 also indicated that the passive film formed on Film BSP might be more passive than that on Film ASP in the solution containing H_2O_2. When scanning in the positive potential direction, the formation of passive film in both Film ASP and Film BSP was observed based on the existence of a substantial peak in the anodic region. It appears that the passive layer started to grow for Film BSP around 0.51 V and Film ASP around 0.55 V, respectively, since the current density started to rise slower as the potential increased. The passive current densities of both films were significantly different, indicating that Film BSP was protected well compared to Film ASP at the region.

Several studies have mentioned that copper reacts in the presence of H_2O_2 or O_2 can form a weak passivation layer. The most likely cathode reductions may include oxygen reduction and decomposition of H_2O_2 [24,25]:

$$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \quad (1)$$

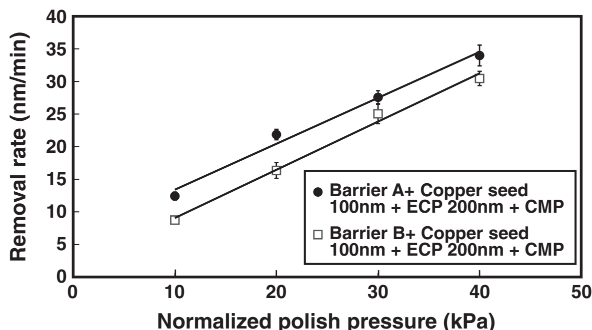

Fig. 2. The correlations between the CMP applied pressures and the relative copper CMP removal rates of Film ASP and Film BSP.

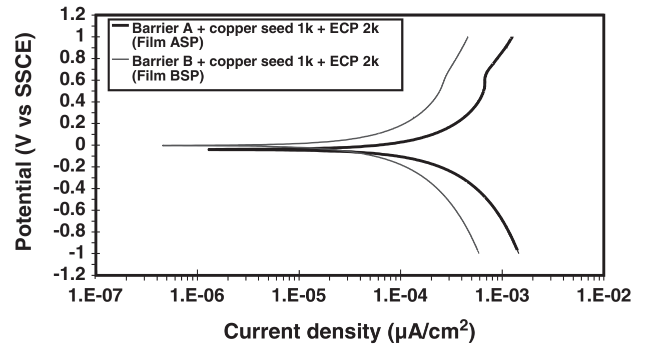

Fig. 3. The static potentiodynamic polarization behavior for Film ASP and Film BSP.

$$H_2O_2 + 2e^- \leftrightarrow 2OH^-. \quad (2)$$

Anodic reactions depending on the electrode potentials displayed in Fig. 4 may include active dissolution of copper and oxidation of cuprous oxide. Both reactions compete with the variation of sweep potential. While potential swept just after the corrosion potentials of Film ASP and Film BSP, the dominated anodic reaction was Eq. (3) as shown below, dissolution of copper. Therefore, current density increased with raising potential.

$$Cu \rightarrow Cu^{2+} + 2e^- \quad (3)$$

$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^- \quad (4)$$

Furthermore, as potential scanning close to 0.51 V or 0.55 V, the turning point of current density of Film BSP and Film ASP, the dominated anodic reaction changed to Eq. (4), which is the oxidation of cuprous oxide. Because the passive layer formed on copper surface and even protected surface probability, current density started to rise slowly with increasing potential. The existence of passivation region in both films also implies that the oxidation occurs on copper surface without applying potential. Previous research also detected oxides formed on copper immersed in H_2O_2 based slurries when no electric field was applied [26].

In order to differentiate the passive potential for both films, the chronoamperometric test at 0.3 V, which was in the narrow passive potential range, was carried out on film A and film B in the H_2O_2 solution. The variation of current densities with time during the test was recorded simultaneously as well, as shown in Fig. 4. The current density of Film ASP decayed from 89 μA/cm^2 to 41 μA/cm^2 speedily

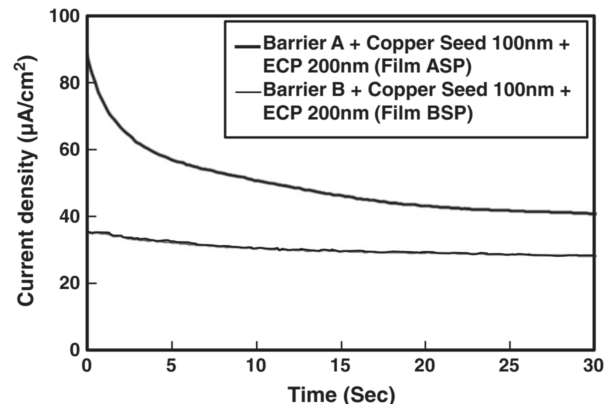

Fig. 4. The change of current densities with time of Film ASP and Film BSP at applying potential 0.3 V in the H_2O_2 solution.

while that of Film BSP always kept almost constant and was lower than Film ASP. Higher current density that represented more electron exchange occurred on the sample surface. The result indicates that the passive film formed on Film ASP could offer more paths than Film BSP to induce oxidizer contacting fresh Cu surface so that oxidation–reduction reaction occurred on Film ASP easier than that on Film BSP. This also consisted to the result of corrosion current density that was displayed in Fig. 3.

From the above study, it reveals that strong (002) β-Ta underlying layer produced strong (111) copper orientation, which has lower copper removal rate and better chemical corrosion resistance. This is because the (111) texture is the closest packed plane in the copper FCC structure, which means dense film structure. Thus, the film structure density is an important factor for copper CMP behavior understanding. Denser structure can resist chemical attack and reduce the removal rate. Currently several techniques are used to analyze film quality, such as X-ray diffraction, scanning electron microscope, and transmission electron microscope. Most of them take a long time for sample preparation and tool operation. How to analyze film density with higher efficiency is worth studying in next paper.

4. Conclusion

This study indicated the correlation between the barrier texture and copper corrosion behavior. X-ray diffraction analysis reveals that if the texture of underlying barrier layer was (002) β-Ta, the subsequent copper layer got strong (111) orientation. This strong (111) texture had high chemical resistance ability, which was proved by the results of copper removal rate after the chemical mechanical planarization and the static potentiodynamic polarization analysis. The removal rate measurement result, which matched the Preston's correlation under different polish pressure, shows that the removal rate of copper plated on strong β-Ta was low; this is because copper plated on strong β-Ta has high (111)/(200) ratio with stronger chemical resistance because of the closest packed structure of copper (111) plane. Denser structure reduced the chemical effect when polished and made copper not easy to be removed. The measurement of potentiodynamic polarization for corrosion behavior, which in an aqueous solution containing 0.001 M Na_2SO_4 solution with 0.2 wt.% H_2O_2, demonstrates that the corrosion current density of film plated on (002) β-Ta (79 $\mu A/cm^2$) was lower than that on the barrier without β-Ta (142 $\mu A/cm^2$), hence better chemical resistance against the surface reaction with slurry. This was coincidence with the result of the chronoamperometric test at 0.3 V that the passive film formed on the film with (002) β-Ta barrier was more passive.

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