Effects of Cu Self-Capping and Ta Capping on Nanometer-Sized Cu Films Sputter-Deposited on β -Ta

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The Cu(111) texture evolution in Cu films sputter-deposited on 35-nm β -Ta barrier layers on Si(100) (Ta/Cu) and in those capped by 5-nm Ta (Ta/Cu/Ta) were studied by X-ray diffraction (XRD). The Cu thicknesses (t_{Cu}) ranged from 5 to 500 nm. For Ta/Cu, the intensity of the Cu 111 reflection exhibited a step-like increase for t_{Cu} between 22 and 33 nm, indicating that subsequent deposition of Cu caused the Cu(111) texture evolution in the already-deposited Cu film (Cu self-capping effect). For Ta/Cu/Ta, the 5-nm Ta capping caused the Cu(111) texture evolution in the already-deposited Cu films for t_{Cu} between 10 and 30 nm (Ta capping effect). These capping effects indicate that the texture evolution took place at room temperature in nanocrystalline Cu films. The capping effects and the initial growth stage of Cu on β -Ta are discussed as they relate to Ta and Cu interfacial and grain boundary energies in the nanocrystalline structures.

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1. Introduction

Understanding the properties and structures of Cu thin films deposited on barrier films made from materials such as Ta and TiN is important for developing high-performance microelectronic devices. The Cu-Ta system is a typical immiscible example; therefore, its microstructure is also of great interest from a scientific perspective. Many studies have focused on the resistivity and electromigration,^{1–3)} mechanical properties,^{4–6)} and microstructures^{7–10)} of Cu films formed on Ta. Interconnections between films with sizes of less than a few tens of nanometers, such as nanometer-thick Cu films on nanometer-thick Ta barrier layers, require control of their microstructures for use as strong heterogeneous film-barrier systems. The growth behavior is very important for the preparation of nanometer-thick metallic films, and it depends on the interfacial state between the film and its underlayer. There are three well-known modes of growth for metallic thin films prepared by deposition: a layer-by-layer growth (Frank-van der Merwe (FM) mode), a three-dimensional-island growth (Volmer-Weber (VM) mode), and a transitional mode from the initial layer-by-layer growth to the three-dimensional-island growth with increasing deposition thickness (Stranski-Krastanov (SK) mode). For Cu growth on a clean Ta surface, the formation of approximately one conformal Cu monolayer with high thermal stability has been reported from experiments^{7,11,12)} and calculations.^{10,13,14)} These reports suggest that Cu grows in the SK growth mode on Ta. The crystallographic texture and elastic property of Cu films sputter-deposited on Ta are expected to change with the Cu thickness in the nanometer-thick range.

The Cu thickness dependence of the crystallographic texture and elastic property of Cu films sputter-deposited on 35-nm-thick Ta barrier films (Ta/Cu) and 5-nm-thick Ta capped films (Ta/Cu/Ta) were studied for Cu thicknesses

between 10 and 1000 nm in our previous investigations.^{4,15)} Reed-shaped Si substrates were used to measure the elastic property of the Cu thin films using the complex reed vibration method.^{16,17)} After intensive chemical etching, the Si substrates exhibited undulated surfaces, and the deposited 35-nm-thick Ta barrier films were composed of equilibrium α -Ta and nonequilibrium β -Ta.⁴⁾ For Cu film thicknesses (t_{Cu}) below ~ 80 nm, both the crystallographic texture and elastic property exhibited considerable changes with the Cu film thickness, as well as after Ta capping. For example, the in-plane Young's modulus of the Cu films decreased with t_{Cu} for Ta/Cu and was enhanced after 5-nm Ta-capping for Ta/Cu/Ta. The Cu (111) plane distance (d_{Cu111}) normal to the film surface decreased with t_{Cu} for Ta/Cu ($\sim 0.3\%$ from the bulk value at t_{Cu} of 20 nm), and such a decrease in d_{Cu111} almost disappeared after 5-nm Ta capping for Ta/Cu/Ta. Because the Cu thin films were not only prepared on the barrier film but also capped or surrounded by the barrier layers in the microelectronic devices, it is important to understand these phenomena from the previous work.

During Ta deposition on Si, the nonequilibrium β -Ta phase is preferentially formed by sputter-deposition on Si or SiO₂.^{12,18–22)} In our previous work, the Ta barrier layers deposited on Si reed substrates with undulated surfaces consisted of an equilibrium α -Ta phase and β -Ta phase.⁴⁾ In contrast, the Ta barrier layers deposited on Si reed substrates with a mirror surface consisted solely of the β -Ta phase.¹⁵⁾ On the other hand, on α -Ta, but not on β -Ta, the formation of a superstructured Cu layer has been reported in a recent computer simulation study of the deposition of an fcc Cu film on Ta.¹⁰⁾ These results indicate that further study of the microstructure of Cu films deposited on β -Ta films formed on Si substrates with a mirror surface is technologically and scientifically relevant. In the present study, we used Si wafers with a mirror surface as substrates and investigated the Cu thickness dependence of the microstructure of nanometer-thick Cu films deposited on β -Ta and of those capped with 5-

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nm thick Ta by X-ray diffraction (XRD). For $t_{\text{Cu}} < 100$ nm, all Cu films exhibited a preferred (111) texture in which the (111) planes of most crystallites were parallel to the flat surface of the sample. For Ta/Cu, the Cu-thickness dependence of the intensity of the 111 reflection exhibited a step-like increase at t_{Cu} between 22 and 33 nm, indicating spontaneous improvement of the preferred (111) texture in the already-deposited Cu films by subsequent deposition of Cu (Cu self-capping effect). For Ta/Cu/Ta, the spontaneous improvement of the preferred (111) texture in the already-deposited Cu films by 5-nm-thick Ta capping occurred at t_{Cu} between 10 and 30 nm (Ta capping effect).

2. Experimental Procedure

Si (100) wafers ($\phi = 2$ in., 0.4-mm thick) that were mirror-polished on one side, were cut into rectangular pieces having a length and width of 1.3 cm and 2 cm, respectively. These substrates were rinsed with ethanol in an ultrasonic bath, and organic contamination was chemically removed using a mixed solution of H_2SO_4 and H_2O_2 . Finally, the surfaces of the Si substrates were terminated by hydrogen using a dilute HF solution.

Deposition of Ta and Cu was carried out using DC magnetron sputtering equipment (ULVAC MPS-2000) under 1.3×10^{-1} Pa Ar at ambient temperatures. The nominal purity of Ar was 99.9999%. The distance between the substrate and the target was 200 mm. We applied 50 W each of rf and dc power to the coil for helicon wave generation and to the target (Ta (99.95%) or Cu (99.999%), $\phi = 2$ in.), respectively. The film growth rates of Ta and Cu were approximately 2 and 5 nm/min, respectively. The thicknesses of the deposited Ta and Cu were determined based on the weight change of an Al foil located near the substrate. For Ta/Cu, a 35-nm-thick Ta barrier layer was deposited on the Si substrate, and a Cu film with the desired thickness was subsequently deposited on the Ta barrier layer without breaking the Ar atmosphere. For Ta/Cu/Ta, a 5-nm-thick Ta capping layer was further deposited on the Cu film without breaking the Ar atmosphere. To examine the morphology of the Ta barrier layer, a 35-nm-thick Ta barrier layer was deposited on the Si substrate (Ta barrier alone). A single Cu (111) crystal with a diameter of 10 mm and thickness of 0.5 mm was used as a model sample with a fully preferred oriented state. Cu pellets were prepared by compacting Cu powder (10- μm grains) for reference samples of polycrystalline bulk Cu with fully random textures. The porosity of the Cu pellets was determined from their weight and dimensions.

XRD measurements in the 2θ - θ scan mode were performed with Cu-K α radiation (40 keV, 30 mA, Rigaku RINT 2100). The scattering vector was normal to the film. The axes of 2θ and θ were adjusted according to the maximum Cu 111 reflection intensity prior to the 2θ - θ scan, and a 1° divergence slit was used. The 111 reflection from the Cu single crystal was used as the instrumental line broadening for an estimation of the mean grain size. Reflections from Si powders placed on the film surface were used as references for the 2θ scale. XRD measurements in the ω scan mode (2θ scan with θ at the Bragg position of the Cu 111 reflection) were also conducted for several samples.

Fig. 1 X-ray diffraction patterns for Ta/Cu (dashed lines) and Ta/Cu/Ta (solid lines) for Cu film thicknesses of (a) 17 nm, (b) 33 nm, and (c) 500 nm. In (b), the pattern for the Ta barrier alone (35 nm) is also shown (dotted/dashed line). The broad peak at $\sim 2\theta = 69.2^\circ$ is the Si 400 reflection from the substrate (the Si (100) direction is off from the scattering vector by $\sim 1^\circ$).

3. Results and Discussion

Figures 1(a)–(c) show example XRD spectra for the Ta/Cu and Ta/Cu/Ta samples deposited on mirror Si substrates with t_{Cu} of 17, 33, and 500 nm, respectively. The spectrum for the sample composed of the Ta barrier alone is also shown in Fig. 1(b). There were no reflections of α -Ta; only the 002 and 004 reflections of β -Ta were observed, indicating that the 35-nm-thick Ta barrier layer consisted of β -Ta with a highly preferred (001) texture, in which the (001) planes of most crystallites were parallel to the flat surface of the film. In the XRD spectra for Ta in Ta/Cu and Ta/Cu/Ta, only the 002 and 004 reflections of β -Ta were observed for all Ta/Cu and Ta/Cu/Ta samples with t_{Cu} between 5 and 500 nm. This indicates that the 35-nm-thick Ta barrier layers remained as β -Ta with the highly preferred (001) texture after Cu film deposition and that the 5-nm Ta capping layers also had the same texture. Figures 1(a) and (b) show that the base of the β -Ta 002 reflection for Ta/Cu/Ta with t_{Cu} of 17 or 33 nm was broader than that for Ta/Cu because of the overlap of the additional reflection from the 5-nm Ta capping layer. In contrast, Fig. 1(c) shows that the base of the β -Ta 002 reflection due to the 5-nm-thick Ta capping layer was smeared by increased background scattering from the 500-nm-thick Cu film.

The XRD spectra for Cu in Ta/Cu with t_{Cu} of 17 and 33 nm (Figs. 1(a) and (b)) show that only the 111 reflection of fcc Cu was seen in the 2θ range shown here, and only the Cu 222 reflection was seen in the 2θ range of $76\text{--}100^\circ$ (not shown here). For Ta/Cu with t_{Cu} of 500 nm, minor Cu 200 and 220 reflections were observed in addition to the major Cu 111 reflection (Fig. 1(c)). The Cu 200 and 220 reflections were detected for $t_{\text{Cu}} > 200$ nm. At t_{Cu} of 17 nm, the profile of the Cu 111 reflection in Ta/Cu/Ta was almost the same as that in Ta/Cu (Fig. 1(a)). However, the peak intensity of the Cu 111 reflection was higher in Ta/Cu/Ta than in Ta/Cu. The latter feature suggests that the 5-nm-thick Ta capping caused some modification of the crystallographic texture in the already-deposited Cu film. In contrast, at t_{Cu} of 33 nm, both the profile and intensity of the Cu 111 reflection showed good agreement between Ta/Cu and Ta/Cu/Ta (Fig. 1(b)), i.e., there was no modification of the crystallographic texture in the already-deposited Cu film by the 5-nm-thick Ta capping layer. At t_{Cu} of 500 nm, the major Cu 111 reflection and the minor Cu 200 and 220 reflections in Ta/Cu/Ta were in good agreement with those in Ta/Cu (Fig. 1(c)).

The XRD results above indicate that the present Cu films sputter-deposited on the β -Ta barrier layer had the highly preferred (111) texture, in which the (111) planes of most crystallites were parallel to the flat surface of the specimen. Furthermore, the degree of alignment in the preferred (111) texture of the already-deposited Cu films with t_{Cu} between 10 and 30 nm was modified by capping with the 5-nm-thick Ta layer. Figure 2 shows the dependence of the integral intensity of the Cu 111 reflection (I_{111}) for Ta/Cu and Ta/Cu/Ta on the value of t_{Cu} . From the mass absorption of the X-ray, the dependence of I_{111} on t_{Cu} can be expressed by the following equation:²³⁾

$$I = I_0 \exp(-2\mu t_{\text{Cu}} / \sin \theta_{111}). \quad (1)$$

where I_0 is the intensity of the incident X-ray; μ , the mass absorption coefficient of Cu- $K\alpha$ radiation for Cu; and θ_{111} , the Bragg angle for the Cu 111 reflection. The intensity of the XRD reflection depends on the dimensions as well as on the crystallinity of a sample. The t_{Cu} dependence of I_{111} for the (111) single crystalline state was estimated from the I_{111} measured for the Cu (111) single crystal sample ($\phi = 10$ mm, 0.5-mm thick) under the same measurement conditions, based on eq. (1). Figure 2 shows the result as a solid line as a guide for the fully preferred (111) texture state. The dotted/dashed line shown in Fig. 2 denotes the dependence of I_{111} on t_{Cu} for the fully random-oriented polycrystalline state, in which I_{111} for Cu pellets was measured under the same conditions, and the t_{Cu} dependence was estimated based on eq. (1) as well as the influence of porosity on intensity.

For Ta/Cu samples shown in Fig. 2, all of the I_{111} data are between the values expected for the fully (111) textured and fully random states. The slope of the t_{Cu} dependence of I_{111} in Ta/Cu at t_{Cu} between 33 and 100 nm agreed well with that expected from eq. (1). The I_{111} value observed at t_{Cu} of 500 nm exhibited a downward deviation from the line extrapolating the t_{Cu} dependence of I_{111} between 33 and 100 nm in Fig. 2. This was associated with the appearance and increase in the Cu 200 and 220 reflections at $t_{\text{Cu}} > 200$ nm, as mentioned previously. For $t_{\text{Cu}} > 22$ nm, the slope

Fig. 2 t_{Cu} dependencies for I_{111} . The solid line and dotted/dashed lines show the t_{Cu} dependence expected for the Cu (111) single crystalline state and the fully random-oriented polycrystalline state, respectively. The dashed line shows the results of fitting eq. (1) using the observed data at t_{Cu} between 33 and 100 nm.

Fig. 3 (a) t_{Cu} dependencies of I_{111} normalized by t_{Cu} (open symbols) and those revised by accounting for differences in the preferred texture (filled symbols, see text for details). (b) t_{Cu} dependence of the full width at half maximum for the peak in Fig. 4 ($\Gamma_{\omega 111}$).

of the t_{Cu} dependence of I_{111} for Ta/Cu exhibits good agreement with that for t_{Cu} between 33 and 100 nm. However, the I_{111} values for $t_{\text{Cu}} < 22$ nm were about one-half of those expected from the t_{Cu} dependence of I_{111} between 33 and 100 nm. Figure 3(a) shows I_{111} normalized by t_{Cu} (I_{111}/t_{Cu}), and a step-like decrease at t_{Cu} between 22 and 33 nm is clearly seen for Ta/Cu. The data for Ta/Cu/Ta exhibit a gradual increase in I_{111}/t_{Cu} at t_{Cu} between 10 and 30 nm because of the 5-nm-thick Ta capping.

Figure 4 shows the XRD spectra for the Cu 111 reflection in the ω scan mode. The integrated intensity was normalized

Fig. 4 Profiles of X-ray diffraction peaks in the ω -scan mode for the Cu 111 reflection of Ta/Cu (dashed lines) and Ta/Cu/Ta (solid lines) at t_{Cu} of (a) 5 nm, (b) 17 nm, and (c) 33 nm.

for all peaks. A broader peak in the ω scan mode indicates weaker alignment in the preferred (111) orientation of the crystallites. At t_{Cu} of 5 nm, the peak profiles for Ta/Cu and Ta/Cu/Ta were broad and nearly identical. At t_{Cu} of 17 nm, the peak profiles for both Ta/Cu and Ta/Cu/Ta were sharper than their counterparts at t_{Cu} of 5 nm, and the peak of Ta/Cu/Ta with the 5-nm-thick Ta capping was sharper than that of Ta/Cu. At t_{Cu} of 33 nm, the peak profiles for both Ta/Cu and Ta/Cu/Ta were sharper than their counterparts at t_{Cu} of 17 nm, but further sharpening due to the 5-nm-thick Ta capping was not observed. To evaluate the degree of alignment in the preferred (111) texture, the full width at half maximum ($\Gamma_{\omega 111}$) was determined by assuming that the peak profile was approximated by a Gaussian function. The t_{Cu} dependence of $\Gamma_{\omega 111}$ is shown in Fig. 3(b). As t_{Cu} increased, $\Gamma_{\omega 111}$ for Ta/Cu exhibited a gradual decline for $t_{\text{Cu}} < 22$ nm, a step-like decrease at t_{Cu} between 22 and 33 nm, and then saturation at $\sim 3^\circ$ for larger t_{Cu} . After the 5-nm-thick Ta capping, $\Gamma_{\omega 111}$ for Ta/Cu/Ta exhibited a gradual decrease to $\sim 3^\circ$ with increasing t_{Cu} . In other words, peak sharpening in the ω scan mode occurred at t_{Cu} between 10 and 30 nm after the 5-nm-thick Ta capping. Apparently, the lack of Ta capping effects on $\Gamma_{\omega 111}$ at $t_{\text{Cu}} > 30$ nm was associated with saturation of the $\Gamma_{\omega 111}$ sharpening at $\sim 3^\circ$ for both Ta/Cu and Ta/Cu/Ta.

Because a divergence slit of 1° was used in the present XRD measurements, the crystallites involved in the 111 reflection peak in the 2θ - θ scan mode were those whose $\langle 111 \rangle$ directions were within 0.5° from the scattering vector. That

is, the area fraction within 0.5° from the top of the peak in the ω scan peak (R) is the fractional ratio of the crystallites contributing to $I_{\text{Cu}111}$ in the present 2θ - θ scan mode. In Fig. 3(a), the filled symbols for $t_{\text{Cu}} < 33$ nm are the I_{111}/t_{Cu} values calibrated using R at a given t_{Cu} and normalized by R_{33} at t_{Cu} of 33 nm as a reference, $(I_{111}/t_{\text{Cu}})/(R/R_{33})$. The $(I_{111}/t_{\text{Cu}})/(R/R_{33})$ data for both Ta/Cu and Ta/Cu/Ta exhibited good agreement with the mean value for $(I_{111}/t_{\text{Cu}})/(R/R_{33})$ in Ta/Cu between 33 and 100 nm. The reduced I_{111}/t_{Cu} in Ta/Cu at $t_{\text{Cu}} < 33$ nm was associated with weaker alignment in the preferred (111) texture. In other words, alignment of the preferred (111) texture in the already-deposited Cu film spontaneously improved as a result of capping with the Cu overlayers (Cu self-capping effect) at t_{Cu} between 22 and 33 nm. The data for Ta/Cu/Ta in Fig. 3(a) indicate that the spontaneous improvement of the preferred (111) texture in the already-deposited Cu film by the 5-nm-thick Ta capping (Ta capping effect) also occurred at t_{Cu} between 10 and 30 nm.

The spontaneous improvement in the alignment of the preferred (111) texture in the already-deposited Cu films was attributed to rotation of the crystallites. In this case, the mean rotated angle was expected to be a few degrees based on the $\Gamma_{\omega 111}$ data shown in Fig. 3(b). Spontaneous grain rotation of constituent nanocrystallites without grain growth has been reported for nanocrystalline (n -) Au during plastic creep deformation under applied stress > 30 MPa at room temperature.²⁴⁾ A close similarity in the mechanisms of plastic creep deformation was reported between n -Au and n -Cu.²⁵⁾ These phenomena also suggest that for the present Cu films in Ta/Cu and Ta/Cu/Ta, both the Cu self-capping and the Ta capping effects were associated with spontaneous grain rotations in the already-deposited Cu films. For the Cu self-capping, the driving force for spontaneous rotation was attributed to the self-adjustment of the crystallographic directions in the already-deposited film induced by lateral growth of the crystallites in the capping layer. When a new crystallite formed on the polycrystalline film, nucleation at the triple junctions most likely occurred. The $\langle 111 \rangle$ orientations of the new crystallite formed at the triple junctions, as well as the crystallites beneath it, adjusted in one direction to reduce the mismatch between their interfaces. For the Ta capping effect, the strong interaction between Cu and Ta was attributed to the driving force (see below). There were no Ta capping effects at $t_{\text{Cu}} < 10$ nm; thus, t_{Cu} of ~ 10 nm corresponded to the transitional thickness for initially formed islands that transitioned to a continuous film. Below t_{Cu} of ~ 10 nm, the interfacial interaction between the Cu films and the Ta barrier was larger than that between the Cu films and the Ta capping. The gradual Ta capping effect observed for Ta/Cu/Ta at t_{Cu} between 10 and 30 nm indicates that the β -Ta barrier effects on the microstructure of deposited Cu crystallites ceased at t_{Cu} of 30 nm. The effects of the mixed Ta barrier composed of α -Ta and β -Ta on the microstructure of deposited Cu crystallites continued up to t_{Cu} of 80 nm, as previously mentioned.^{4,15)}

Figure 5(a) shows the t_{Cu} dependence of the interlayer distance for Cu (111) ($d_{\text{Cu}111}$) normal to the film surface, as determined from their respective XRD peak positions. Successive alternations in the in-plane stress from compres-

Fig. 5 (a) Dependence of the Cu (111) interlayer distance (d_{Cu111}) on t_{Cu} . The dashed line indicates the d_{Cu111} value reported for bulk Cu. (b) Dependence of the β -Ta (002) interlayer distance ($d_{\beta\text{Ta002}}$) on t_{Cu} . The dotted/dashed line indicates the mean value for three samples of the 35-nm-thick Ta barrier alone. The dashed lines indicate the $d_{\beta\text{Ta002}}$ values reported for a 30- μm -thick β -Ta film deposited on an AISI4340 steel substrate (266.4 pm)²¹⁾ and for a ~ 20 - μm -thick β -Ta single crystal (265.32 pm).³¹⁾ The ordinate on the right-hand side shows the scale converted to the in-plane strain, where the $d_{\beta\text{Ta002}}$ reported for the β -Ta single crystal is considered as the bulk value. (c) Dependence of the mean grain size of the Cu film (D_{Cu111}) on t_{Cu} . The dashed line indicates the relationship of $D_{\text{Cu111}} = t_{\text{Cu}}$.

sive to tensile and back to compressive with increasing t_{Cu} were reported for the three-dimensional island growth mode.^{26,27)} Quantitatively, d_{Cu111} in Ta/Cu at t_{Cu} of 5 nm was $\sim 0.2\%$ larger than the bulk Cu value, indicating that the in-plane compressive strain (or stress) in a 5-nm-thick Cu film on a 35-nm-thick Ta barrier layer was $\sim 0.25\%$ (or 0.5 GPa) (see the right-hand side vertical axis in Fig. 5(a)), assuming a mean Poisson ratio of 0.343 and a mean Young's modulus of 130 GPa²⁸⁾ along the direction of the film. As t_{Cu} increased above 5 nm, d_{Cu111} in Ta/Cu decreased to a slightly smaller value than the bulk Cu value, exhibited a local minimum at t_{Cu} of ~ 10 nm, and then increased slightly above the bulk Cu value at t_{Cu} above ~ 30 nm. The t_{Cu} values of the crossover points for these successive changes exhibited good agreement with those reported (i.e., the first crossover from compressive to tensile states at t_{Cu} between 1 and 20 nm, and again to the compressive state at t_{Cu} between 4 and 40 nm, respectively).²⁶⁾ The first crossover from compressive to tensile states was observed when the initially formed islands transitioned to a continuous film. That is, when the reduction in the total surface and interface energies by contacting neighboring islands was larger than the increase in the strain energy of the resultant continuous film, the isolated islands

coalesced and formed a continuous film (the zipping effect).²⁹⁾ A tensile stress of ~ 1 GPa in the continuous film was estimated from model calculations for the zipping effect.³⁰⁾ In Fig. 5(a), the compressive stress of ~ 0.5 GPa for Cu at t_{Cu} of 5 nm became nearly zero or slightly tensile for t_{Cu} between 10 and 30 nm, indicating that the island-like film transitioned to a continuous film at t_{Cu} of ~ 10 nm in the present Ta/Cu films. d_{Cu111} exhibited a local maximum at t_{Cu} of ~ 30 nm that was slightly larger than the bulk value. Because the spontaneous improvement of the preferred (111) texture caused by the Cu self-capping was seen for t_{Cu} between 22 and 33 nm (Fig. 3(a)), the in-plane compressive stress may have been induced by the Cu self-capping effect. At t_{Cu} above 30 nm, d_{Cu111} first exhibited a slight decline to the bulk value at t_{Cu} of ~ 100 nm and then increased slightly at t_{Cu} above 200 nm. As mentioned above, the 200 and 220 reflections appeared at $t_{\text{Cu}} > 200$ nm. These changes in both d_{Cu111} and the XRD spectra suggest that the growth mode of the Cu films further changed at t_{Cu} between 100 and 200 nm. For Ta/Cu/Ta, d_{Cu111} was almost constant for t_{Cu} from 10 to 500 nm and larger by $\sim 0.3\%$ than that of the bulk value. The values of d_{Cu111} in Ta/Cu/Ta were slightly larger than those in Ta/Cu at t_{Cu} between 10 and 30 nm, at which the spontaneous improvement of the preferred (111) texture by the 5-nm-thick Ta capping was observed (Fig. 3(a)). The spontaneous improvement of the preferred (111) texture may have been responsible for the slightly larger d_{Cu111} values in Ta/Cu/Ta at t_{Cu} between 10 and 30 nm. In contrast, the increase in d_{Cu111} by the 5-nm-thick Ta capping was observed up to t_{Cu} of ~ 80 nm in our previous studies^{4,15)} and indicates that the effects of the mixed Ta barrier composed of α -Ta and β -Ta on the deposited Cu microstructures continued up to t_{Cu} of 80 nm, as previously mentioned.

Figure 5(b) shows the t_{Cu} dependence of the interlayer distance for β -Ta (002) ($d_{\beta\text{Ta002}}$) normal to the film surface, as determined from their respective XRD peak positions. The dotted/dashed line in Fig. 5(a) denotes a $d_{\beta\text{Ta002}}$ of 268.65 pm in the 35-nm-thick Ta barrier alone. For the bulk value, a $d_{\beta\text{Ta002}}$ of 266.4 pm was reported for a 30- μm -thick β -Ta film deposited on an AISI4340 steel substrate,²¹⁾ whereas a value of 265.32 pm was reported for a ~ 20 - μm -thick β -Ta single crystal.³¹⁾ The larger $d_{\beta\text{Ta002}}$ as compared to the bulk values indicates that the present 35-nm-thick β -Ta films sputter-deposited on Si(100) were in a compressed state along the surface of the film. The in-plane compressive strain (or stress) estimated for the 35-nm-thick β -Ta barrier alone ranged from 0.7 to 1.2% (or 1.3–2 GPa) using the bulk values of $d_{\beta\text{Ta002}}$ mentioned above, a biaxial modulus of 175 GPa for the β -Ta film along the (001) plane,³²⁾ and a Poisson ratio of 0.3. In Cr films (but not in β -Ta films) on Si, the compressive stress was reported to have increased with decreasing film thickness (t_f).³³⁾ Application of the film-thickness dependence of the internal stress reported in Cr films to the present case gave a compressive stress of 2.0 GPa at a thickness of 35 nm, exhibiting good agreement with the estimated compressive stress in the 35-nm-thick Ta barrier layer. On the other hand, the $d_{\beta\text{Ta002}}$ values of both Ta/Cu and Ta/Cu/Ta decreased as compared to that of the Ta barrier alone (Fig. 5(b)). The in-plane compressive strain (or stress) of the barrier decreased to 0.4–0.7% (or 0.7–

1.3 GPa) after deposition of a Cu film, suggesting that there was a strong elastic interaction at the interface between the Cu film and the Ta barrier. The fcc Cu (111) plane has been reportedly grown heteroepitaxially on the β -Ta (002) plane with a lattice mismatch of 7.6%,³⁴⁾ and the interface between fcc Cu and β -Ta exhibited high thermal stability.¹⁸⁾ As previously mentioned for the SK growth mode of the Cu films on β -Ta, the formation of one conformal monolayer of Cu can decrease the in-plane compressive strain (or stress) in the Ta barrier and weaken the Cu-thickness dependence of the $d_{\beta\text{Ta}002}$ values of both Ta/Cu and Ta/Cu/Ta, as shown in Fig. 5(b). A small local minimum observed at $t_{\text{Cu}} \sim 100$ nm for the Cu-thickness dependence of the $d_{\beta\text{Ta}002}$ values may have been associated with a change in the growth mode of the Cu films (i.e., the transition from the (111) textured structure to the randomly textured structure began at t_{Cu} between 100 and 200 nm).

Figure 5(c) shows the Cu-thickness dependence of the mean grain size normal to the film surface ($D_{\text{Cu}111}$), estimated from the width of the Cu 111 reflection using the Scherrer equation. The instrumental line broadening was corrected from the 111 reflection observed for the Cu single crystal sample. The nearly identical Cu-thickness dependence of $D_{\text{Cu}111}$ between Ta/Cu and Ta/Cu/Ta supports the conclusion that the 5-nm-thick Ta capping did not cause grain growth but may have improved the alignment in the preferred (111) texture in Cu films by spontaneous rotational motion of the crystallites. As shown in Fig. 5(c), $D_{\text{Cu}111}$ was nearly identical to the Cu film thickness for t_{Cu} below ~ 10 nm, at which island-like Cu film growth following coverage with one conformal monolayer was expected, as mentioned previously. For $t_{\text{Cu}} > 10$ nm, the increase in $D_{\text{Cu}111}$ exhibited saturation at ~ 30 nm for $t_{\text{Cu}} > 100$ nm (Fig. 5(c)). At this t_{Cu} , continuous Cu film growth in the SK mode and cessation of the effect of β -Ta barrier on the Cu film growth were likely. Then, the saturation of $D_{\text{Cu}111}$ at ~ 30 nm for $t_{\text{Cu}} > 100$ nm (Fig. 5(c)) suggests that the ~ 30 nm crystallites were thermally stable in the present Cu films. The mean grain size in nanocrystalline Cu with the preferred (111) texture prepared by various methods have been commonly reported at 25–30 nm.^{25,35)} That is, constituent nanocrystallites with grain sizes of 25–30 nm were in a quasi-stable state in nanocrystalline Cu with the preferred (111) texture. Very similar results for the grain size stabilization in nanostructured fcc metals with the preferred (111) texture have been found in n -Au.^{24,36)} In contrast, in the nanocrystalline Cu films deposited on the mixed Ta barrier composed of α -Ta and β -Ta, the mean grain size increased beyond 30 nm and exhibited a poorly preferred (111) texture.^{4,15)} This again suggests that the effects of the mixed Ta barrier composed of α -Ta and β -Ta on the deposited Cu crystallites continued up to t_{Cu} of 80 nm.

4. Conclusion

Cu films were sputter-deposited on 35-nm-thick β -Ta barrier films, and changes in their texture as a function of Cu thickness and by 5-nm-thick Ta capping were investigated. For the Cu-thickness (t_{Cu}) < 100 nm, all Cu films exhibited a highly preferred (111) texture in which the (111) planes

of most crystallites were parallel to the flat surface of the sample. For Cu films without Ta capping (Ta/Cu), the Cu-thickness dependence of the integral intensity of the 111 reflection exhibited a step-like increase at t_{Cu} between 22 and 33 nm, indicating spontaneous improvement of the preferred (111) texture in the already-deposited Cu films by subsequent deposition of Cu (Cu self-capping effect). For Cu films with the 5-nm-thick Ta capping (Ta/Cu/Ta), the spontaneous improvement of the preferred (111) texture in the already-deposited Cu films by 5-nm-thick Ta capping occurred at t_{Cu} between 10 and 30 nm (Ta capping effect). Both these effects were associated with spontaneous rotational motion of the Cu crystallites. For creep deformations (but not for film deposition), such spontaneous rotational motion of the crystallites has been reported in nanocrystalline Cu and nanocrystalline Au. In the present study, reduction in the total surface and interface energies caused self-adjustment of the crystallographic directions in the already-deposited Cu films. The mean grain size in the Cu films with the preferred (111) texture deposited on β -Ta barrier films exhibited saturation at ~ 30 nm, whereas that in the Cu films with a poorly preferred (111) texture deposited on the mixed Ta barrier composed of α -Ta and β -Ta increased beyond 30 nm, as reported in previous works. These observations indicate that grain sizes of 25–30 nm were in a quasi-stable state in nanocrystalline Cu with the preferred (111) texture.

The present experimental results indicate the following model for the microstructural evolution of nanometer Cu films deposited on β -Ta barrier. At the initial stage of Cu deposition, one conformal Cu monolayer was formed on the β -Ta barrier, and it decreased the in-plane compressive strain (or stress) in the β -Ta barrier on the Si(100) substrate. Then, isolated island growth of Cu occurred with increasing deposited Cu thickness up to ~ 10 nm, where the degree of the preferred (111) texture in the Cu films remained poor, and neither Cu self-capping effects nor Ta capping effects were expected. Above a Cu thickness of ~ 10 nm, the isolated islands coalesced and formed a continuous film, where the degree of the preferred (111) texture in the Cu films improved, and both Cu self-capping effects and Ta capping effects were expected. After saturation of the enhanced preferred (111) texture in the Cu films for a Cu thickness of ~ 30 nm, both Cu self-capping effects and Ta capping effects disappeared. The present results reemphasize the technological scientific importance of a controlled interface and grain boundaries for nanometer-sized devices.

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