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Evolution of nanoscale roughness in Cu/SiO₂ and Cu/Ta interfaces

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Synchrotron x-ray scattering was used to study the evolution of interface roughness with annealing for a series of Cu thin films. The films were encapsulated in SiO₂ or Ta/SiO₂ and prepared by sputter deposition. Specular x-ray reflectivity was used to determine the root mean square roughness for both the upper and the lower Cu/SiO₂ (or Cu/Ta) interfaces. The lateral roughness was studied by diffuse x-ray reflectivity. Annealing the films at 600 °C resulted in a smoothing of only the upper interface for the Cu/SiO₂ samples, while the lower Cu/SiO₂ interfaces and both interfaces for the Ta encapsulated films did not evolve significantly. This difference in kinetics is consistent with the lower diffusivity expected of Cu in a Cu/Ta interface (compared to a Cu/SiO₂ interface) and the mechanical rigidity of the lower Cu/SiO₂ interface. As a function of roughness wavelength, the upper Cu/SiO₂ interfaces exhibited a roughness decay with annealing that was only 12.5% of that expected for classical capillarity driven smoothing of a free surface. © 2012 American Institute of Physics. [doi:10.1063/1.3675611]

The morphological evolution of chemically stable metal/air or metal/vacuum interfaces (i.e., free surfaces) with annealing temperature and/or time has been explored in the past. Most notable is the classical model developed by Mullins¹ and subsequent experimental works,^{2–4} in which the tendency of a non-planar surface to reduce its total area and interface energy (capillarity) is the driving force for mass transport (diffusion) within the interface that results in evolution of the interface morphology. These works consider sinusoidal surface profiles and high temperature annealing. Much smaller scale sinusoidal perturbations and lower temperature anneals, however, have been demonstrated to evolve differently.^{5,6} In both classical and non-classical models, capillarity arises from the local variations in curvature and hence chemical potential of the rough surface. Investigations into solid/solid interfaces typically relate only to epitaxial interfaces,⁷ where misfit induced stress rather than capillarity is a driving force. Capillarity effects will play an important role in the evolution of solid/solid interfaces as they do for free surfaces. However, for buried interfaces, two solids are present and their morphology is mechanically coupled and diffusion potentials are therefore modified.⁸ The role of mechanical coupling to modify the evolution of buried interfaces is of significant interest to many nano-scaled systems and to semiconductor interconnections.^{9,10}

In the case of a free surface or a surface having a “capping material” that is unable to support mechanical stresses, capillarity driven smoothing by surface diffusion should occur relatively unimpeded. A classical theory for the smoothing of free interfaces has been developed^{1,11} which

predicts that the time dependent amplitude of a sinusoidal topography, $A(t)$, takes the following form:

$$A(t) = A_0 e^{-B(2\pi/\lambda)^4 t}, \quad (1)$$

where A_0 is the initial amplitude, t is time, and B is a kinetic coefficient given by $B = \Omega\gamma\delta D/kT$, where Ω is the atomic volume of the diffusing atoms, δ is the interface thickness, γ and D are the interfacial energy and an effective interface diffusivity, respectively, and kT is the usual product of Boltzmann’s constant and temperature. λ is the in-plane wavelength of the roughness.

If the capping material is a solid that is able to support mechanical stress, then the rates at which a buried interface evolve are expected to reflect interfacial diffusion of both solids present at the interface and to include their mechanical coupling. If the two solids have very different interfacial diffusivities, then mechanical stresses will be present. This should limit the effects of interfacial capillarity since interface curvature is no longer the only driving force for diffusion. There are however few quantitative reports on the evolution of roughness at buried interfaces.

In this work, the morphological evolution of Cu/Solid interfaces was studied by x-ray reflectivity. We show (1) the decay of interface roughness to be strongly correlated to the materials defining the interface and (2) the rate of roughness decay to be much lower than that expected for free surfaces.

X-ray reflectivity is a powerful technique for the study of surfaces and buried interfaces in thin film systems.^{12–16} There are two primary variations of this technique: specular and diffuse x-ray reflectivity. The former provides information regarding sample thickness, density, and the root mean square of the roughness amplitude ($\sigma = A_0/\sqrt{2}$). The latter

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FIG. 1. (Color online) (a) Experimental (filled circles and triangles) specular and diffuse (inset) x-ray reflectivity patterns and corresponding fits (solid lines) of nominally 35 nm thick, SiO₂ encapsulated, Cu thin films. Annealing at 600 °C (red circles) results in a smoother Cu/SiO₂ interface, as can be seen from the slower decay of specular intensity as compared to its 150 °C counterpart (blue triangles). Notable differences in the diffuse reflectivity patterns (inset) indicate differences in the lateral roughness character resulting from annealing. (b) Experimental (filled circles and triangles) specular and diffuse x-ray reflectivity (inset) patterns and fits (solid line) of nominally 35 nm thick encapsulated Cu thin films. Strong similarities between the two anneals in both the specular and diffuse reflectivity patterns (inset) indicate that no significant change in interface roughness takes place upon annealing.

yields information regarding the in plane structure of the sample: the lateral correlation length (ξ). Both specular and diffuse x-ray reflectivities are highly sensitive to surface and interfacial roughness and existing theories of x-ray scattering¹⁷ make these techniques highly quantitative. For isotropic surfaces, ξ is defined to be the value of r (lateral distance) for which the autocorrelation function, $C(r)$ drops to e^{-1} of its initial value.¹⁸ For random rough surfaces, the autocorrelation function proposed by Sinha *et al.*¹⁷ takes the form $C(r) = \sigma^2 \exp[-(r/\xi)^{2\alpha}]$, where the fractal or Hurst exponent, α , represents a smooth surface when approaching unity or a jagged surface as it approaches 0.

Since σ is a measure of the amplitude of the roughness, from Eq. (1) it is expected that σ will decrease with annealing as atoms become mobile at elevated temperatures. Additionally, although ξ and λ are not equivalent, high frequency (small λ) surface perturbations are nonetheless expected to decrease more quickly, leading to an effective increase in ξ . It should be noted that independent values for σ corresponding to the upper and lower Cu interfaces may be obtained from the x-ray reflectivity experiments. Independent values of ξ , however, are more difficult to measure; the generalization will therefore be made that the values of ξ represent a combined effect of the upper and lower Cu interfaces.

SiO₂ and Ta/SiO₂ encapsulated Cu thin films were prepared by magnetron sputtering onto thermally oxidized Si(100) substrates. The films were annealed at 150 °C and at 600 °C in Ar + 4% H₂. Further details regarding sample processing have been reported previously.^{19,20}

X-ray scattering experiments were performed at the stanford synchrotron radiation lightsource (SSRL). Data were collected on thin-film diffraction beam line 2-1. X-rays with a wavelength of 1.549 Å were monochromated with a double bounce Si(111) crystal. To determine film thickness and RMS roughness (σ_{upper} and σ_{lower}) specular and offspecular scans were collected: For specular scans $\omega = 2\theta/2 = \theta$ whereas for off specular scans $\omega = 2\theta/2 = \pm 0.15^\circ$. The off specular scans were used to subtract the contribution of diffusely scattered x-rays to the specular reflection. To determine the lateral correlation length, rocking curves were collected by fixing the detector at approximately $2\theta = 3^\circ$, and rocking the sample through $\omega = \pm 1.5^\circ$. A 2θ of 3° was

chosen to obtain diffuse scattering that was sufficiently strong. The x-ray data was analyzed using Bede REFS software.²¹ While no dominant wavelength is present, as is evident from the absence of a characteristic peak in the diffuse reflectivity patterns (insets in Fig. 1), the lateral correlation length is used as a single parameter related to λ to simplify the discussion of the results.

X-ray scattering techniques reveal significant differences in the interfacial evolution of Cu thin films encapsulated by SiO₂ as compared to those encapsulated by Ta/SiO₂. Qualitative conclusions can be drawn by inspection of the specular patterns which are shown in Fig. 1. Annealing SiO₂ encapsulated films at 600 °C results in a smoother Cu/SiO₂ interface, as can be seen from the slower decay of specular intensity as compared to its 150 °C counterpart (Fig. 1(a)). Ta/SiO₂ encapsulated films change little upon annealing (Fig. 1(b)).

The specular intensity profiles seen in Fig. 1 were modeled to determine quantitative values of σ_{upper} and σ_{lower} of the Cu interface. The diffuse scattering intensity profiles are shown in the insets to Fig. 1 and were modeled to determine values of ξ and α that are representative of the combined scattering of upper and lower interfaces. Results of modeling can be found in Table I. Each entry represents an average of six sister samples (i.e., a total of 24 samples are represented) whose thicknesses were in the range of 27 nm to 158 nm. For SiO₂ encapsulated films, significant changes upon annealing

TABLE I. Average values of upper and lower interface roughness (σ_{upper} and σ_{lower}), in plane correlation length (ξ), and the fractal exponent (α) for SiO₂ and Ta/SiO₂ encapsulated Cu films. Each entry represents an average of six sister samples (i.e., a total of 24 samples are represented) with thicknesses in the range of 27 nm to 158 nm. Errors were calculated at a 90% confidence level; those values reported represent the average error of the corresponding six samples.

	SiO ₂ /Cu/SiO ₂		Ta/Cu/Ta	
	150 °C	600 °C	150 °C	600 °C
$\langle \sigma_{\text{upper}} \rangle$ [nm]	1.0 ± 0.1	0.3 ± 0.1	1.4 ± 0.2	1.1 ± 0.2
$\langle \sigma_{\text{lower}} \rangle$ [nm]	1.2 ± 0.1	0.9 ± 0.1	1.4 ± 0.2	1.2 ± 0.2
$\langle \xi \rangle$ [nm]	$38.3\% \pm 10\%$	$53.3\% \pm 10\%$	$52.3\% \pm 10\%$	$58.8\% \pm 10\%$
$\langle \alpha \rangle$	0.9 ± 0.1	0.7 ± 0.3	0.5 ± 0.2	0.7 ± 0.2

at 600 °C are observed. Firstly, σ_{upper} decreases significantly in comparison to σ_{lower} . This is attributed to the fact that the bottom Cu/SiO₂ interface, although chemically identical to the top, is attached to a rigid substrate which mechanically hinders changes in interfacial topography. For Ta/SiO₂ encapsulated films, σ_{upper} and σ_{lower} are not only comparable to one another, but also do not evolve significantly upon annealing. These observations indicate that either a sufficiently rigid adjacent material or the presence of a Ta layer in the interface can significantly inhibit the morphology evolution of the interface. We note that the thickness of the Ta layer is sufficiently thin (2 nm) that we may neglect its mechanical stiffening effect and attribute its effect solely to the chemical or microstructural changes that it has on diffusivity within the interface.

We now focus the discussion on the wavelength term in the exponent of Eq. (1) in the context of the upper Cu/SiO₂ interface which undergoes significant morphology evolution due to the higher temperature anneal. Because the classical model predicts that the decay of the amplitude exponent is proportional to the inverse of wavelength to the fourth power, λ^{-4} , short wavelength roughness is expected to smoothen more quickly than long wavelength roughness, leading to an increase in the in-plane correlation length of the roughness as the amplitude of the roughness decreases.

Our results are in agreement with equation (1), in that we see a significant increase in the correlation length (Table I) for Cu/SiO₂. Further, our quantitative analysis of the diffusely scattered intensity over values of Q_x for which the kinematical scattering approximation is valid (0.0006 Å⁻¹ to 0.005 Å⁻¹) shows a greater reduction in intensity at shorter wavelengths. These observations are qualitatively consistent with the trend expected from Eq. (1). However, we find our data are not consistent with the expected λ^{-4} dependence. We find instead our data to fit a much weaker wavelength dependence, decaying as $\lambda^{-1/2}$ for the evolution of this buried interface (Fig. 2).

Non-classical theories of smoothening of rough surfaces have been developed in the past⁵ and experimentally verified.⁶ The method of Ealenbacher *et al.*⁶ considered the free surface of single crystal Si whose height profile was intentionally modulated in a sinusoidal fashion. Subsequent heat treatments, below the roughening temperature, were reported to result in an inverse linear amplitude dependence on wavelength. Although the surface statistics of such a system differ from encapsulated, random-rough thin films, the Ealenbacher approach shows merit and should be investigated further.

The difference in wavelength dependence and the lack of significant change of the lower Cu/SiO₂ interface are clear indications that evolution of buried interfaces is more complex than that of free surfaces. We hypothesize that the mechanical constraints of the opposing layer material are significant and thus also warrants further investigation. The observed differences in smoothening between SiO₂ and Ta/SiO₂ encapsulated Cu films are consistent with the expectation that the diffusivity of Cu in a Cu/dielectric interface is higher than that in a Cu/metal interface.^{22,23} Hence, one might expect a reduced evolution of the Cu/Ta interface. Thus, we have identified two contributing factors to the morphological evolution of solid/solid interfaces: (1) The diffu-

FIG. 2. Plot of the log of the intensity ratio versus the log of Q_x from the diffuse reflectivity profile in the inset of Fig. 1(a), indicated as data (black circles). Data from nominally 50 nm and 80 nm thick, SiO₂ encapsulated, Cu films are represented as gray and white circles, respectively. Values for Q_x were chosen such that the kinematical scattering approximation is valid. Also shown is Eq. (1) (dashed line), which yields a slope much steeper than that of the experimental data. The solid line is an empirical fit to the data and corresponds to an exponent of $1/2$, rather than 4. A non-classical treatment of surface evolution (see Refs. 5 and 6) also shows merit and should be investigated further (short dashed line).

sivity within the buried interface and (2) the rigidity of the adjacent layer materials.

Specular and diffuse x-ray reflectivities were used to study the interfacial evolution of Cu thin films encapsulated by either SiO₂ or Ta/SiO₂. The tendencies of such buried interfaces to evolve with time and temperature will be crucial to the reliability of future nanoelectronic devices and are not yet well understood. The roughness of the lower interface was consistent amongst all SiO₂/Cu samples. By contrast, the roughness of the upper Cu/SiO₂ interfaces was very different for the two annealing conditions. The lateral correlation length is seen to increase upon annealing for Cu/SiO₂ interfaces, though, the effect is not distinguished between upper and lower interfaces. For the samples with Cu/Ta interfaces, a significant reduction in roughness with annealing was not observed for either upper or lower interfaces. Qualitatively, the interfaces evolve in a manner consistent with capillarity, albeit with some notable differences. Specifically, our data shows a $\lambda^{-1/2}$ dependence on roughness decay, rather than the λ^{-4} dependence expected for classically evolving free rough surfaces. In the case of a non-evolving bottom SiO₂/Cu interface, the deviation from capillarity is hypothesized to stem from the coupling of kinetic properties to mechanical properties. Whereas the lack of notable changes in either Cu/Ta interfaces is attributed to the lower diffusivity of Cu on Ta compared with Cu on SiO₂. Mechanical coupling would also be expected to play a role in Cu/Ta systems; however, the absence of a changing interface prevents this effect from being observed.

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