

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF ELECTROPLATED Cu THIN FILMS

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ABSTRACT

Copper films of different thicknesses of 0.2, 0.5, 1 and 2 microns were electroplated on top of the adhesion-promoting barrier layers on <100> single crystal silicon wafers. Controlled Cu grain growth was achieved by annealing films in vacuum.

The Cu film microstructure was characterized using Atomic Force Microscopy and Focused Ion Beam Microscopy. Elastic modulus of 110 to 130 GPa and hardness of 1 to 1.6 GPa were measured using the continuous stiffness option (CSM) of the Nanoindenter XP. Thicker films appeared to be softer in terms of the lower modulus and hardness, exhibiting a classical Hall-Petch relationship between the yield stress and grain size. Lower elastic modulus of thicker films is due to the higher porosity and partially due to the surface roughness. Comparison between the mechanical properties of films on the substrates obtained by nanoindentation and tensile tests of the freestanding Cu films is made.

INTRODUCTION

With the rapid change of materials systems and decreased feature size, thin film microstructure and mechanical properties have become critical parameters for microelectronics reliability. Thorough reliability and compatibility tests are required to integrate new low-K dielectric materials and novel interconnects (Cu). For most reliability tests, knowledge of the thin film constitutive mechanical behavior is required. Mechanical properties of thin films often differ from those of the bulk materials. This can be partially explained by the nanocrystalline structure of thin films and the fact that these films are attached to a substrate. Due to typically high yield strengths thin films can support very high residual stresses. This residual stress can be relieved later during processing or in the actual device operation through either thin film plastic deformation or interfacial delamination. Thermal expansion coefficient and elastic modulus mismatch are typically the properties that cause these device failures.

Both elastic and plastic properties are important for thin film characterization. Thin film mechanical properties can be measured by tensile testing of freestanding films [1] and by the microbeam cantilever deflection technique [2-4], but the easiest way is by means of nanoindentation, since no special sample preparation is required and tests can be performed quickly and inexpensively.

Nanoindentation is similar to conventional hardness tests, but is performed on a much smaller scale using very sensitive load and displacement sensing equipment. The force required to press a sharp diamond indenter into tested material is recorded as a function of indentation depth. Since the depth resolution is on the order of nanometers, it is possible to indent even very thin (100 nm) films. The nanoindentation load-displacement curve provides a “mechanical fingerprint” of the material’s response to contact deformation. Elastic modulus and hardness are the two parameters that can be readily extracted from the nanoindentation curve [5-7].

In the case of a thin film, the yield stress is typically much higher than for a bulk material. Since thin films are typically nanocrystalline, this is explained by the Hall-Petch type relationship between the film yield stress and its grain size, d :

$$\sigma_{YS} = \sigma_i + kd^{-n} \quad (1),$$

where σ_i is some intrinsic stress, independent of the grain size d , and n is typically between 0.5 and 1. The classic $1/d^{0.5}$ Hall-Petch relationship is not typically observed for thin films due to the substrate effect, limiting thin film plasticity, or due to the dislocation looping along the metal/oxide interface [8]. Similar effects are observed in different nanocrystalline bulk materials and thin films [9, 10]. If the grain size of a thin film scales with the film thickness, h , the film thickness can be used instead of the grain size as the scaling parameter [11]:

$$\sigma_{YS} = \alpha \left[1 + \beta h^{-1/2} \right] \quad (2),$$

where α and β are the fitting parameters, and are 400 MPa and $0.287 \mu\text{m}^{-1/2}$ for evaporated Cu films [11]. A similar approach, based on the film thickness is used by Nix [8] to predict Cu flow stress behavior.

For a metal film the yield stress can be taken as the 1/3 of the hardness [12] measured by nanoindentation, or more accurately it can be extracted from the extent of the plastic zone size around the indenter, c , measured by AFM, using Johnson's spherical cavity model approach [13]:

$$\sigma_{YS} = \frac{3P_{\max}}{2\pi c^2} \quad (3),$$

where P_{\max} is the maximum indentation load. Although this was originally applied for the bulk materials, it was also shown to be applicable in the case of thin films [14].

The objective of this study is to correlate thin film mechanical properties to the microstructure employing each of the above mentioned approaches.

EXPERIMENT

Copper films of different thicknesses of 0.2, 0.5, 1 and 2 microns were electroplated on top of the Cu seed layer on adhesion-promoting Ta or TiW barrier layers on <100> single crystal silicon wafers using copper sulfate bath with proprietary additives. Typically grain growth is observed in electroplated Cu films at room temperature (self-anneal process), so films were annealed at 350 °C for 3 minutes in high vacuum in order to enhance Cu grain growth. Electroplated Cu film mechanical properties were evaluated with the Nanoindenter XPTM, using a sharp (< 100 nm tip radius) Berkovich tip and the continuous stiffness modulation (CSM) option. Thicker 6 μm free-standing Cu samples were prepared through standard lithographic processes and substrate etching. These were tensile tested using special equipment, providing stress-strain curves [1].

Cu FILM MICROSTRUCTURE

It is important to measure thin film grain size, since it affects the mechanical properties, specifically yield stress. In the case of a nanocrystalline columnar grain Cu film its grain size can be measured by means of Atomic Force Microscopy (AFM), where grains can be resolved on the surface. Measurements from the AFM section analysis provide the average grain size. Surfaces of a 200 nm and 2 μm thick electroplated Cu films annealed in vacuum at 350 °C for three minutes are shown in Figure 1. Grains about 350 nm in diameter in the plane are distinguishable in a 200 nm thick Cu film; however their profile is obscured by smaller oxide particles.

The grains of the 2 μm thick Cu films are barely distinguishable even when the section analysis is used due to the higher surface roughness and oxide particle growth. Annealing causes grain coalescence through the film thickness, but not necessarily surface reconstruction that would replicate the new bigger grain size. Focused Ion Beam machining (FIB) is a more suitable technique for allowing measurement of the thin film grain size. It is similar to the Scanning Electron Microscopy (SEM), except instead of the electron beam, a focused ion beam of Ga is used to raster along the sample surface. FIB can also be used to clean the surface from an oxide by sputtering the film material away. The image is constructed by collecting secondary ions, which produce a contrast according to the grain orientation. FIB image of a 200 nm and a 2 μm thick electroplated Cu films are presented in Figure 2. It is clearly seen that the grain size increases with the film thickness. The sample is tilted 45° to the ion beam, so all grains appear contracted in the vertical direction. Grain size can be directly measured from the images in Figure 2, where intragranular contrast is Cu twinning.

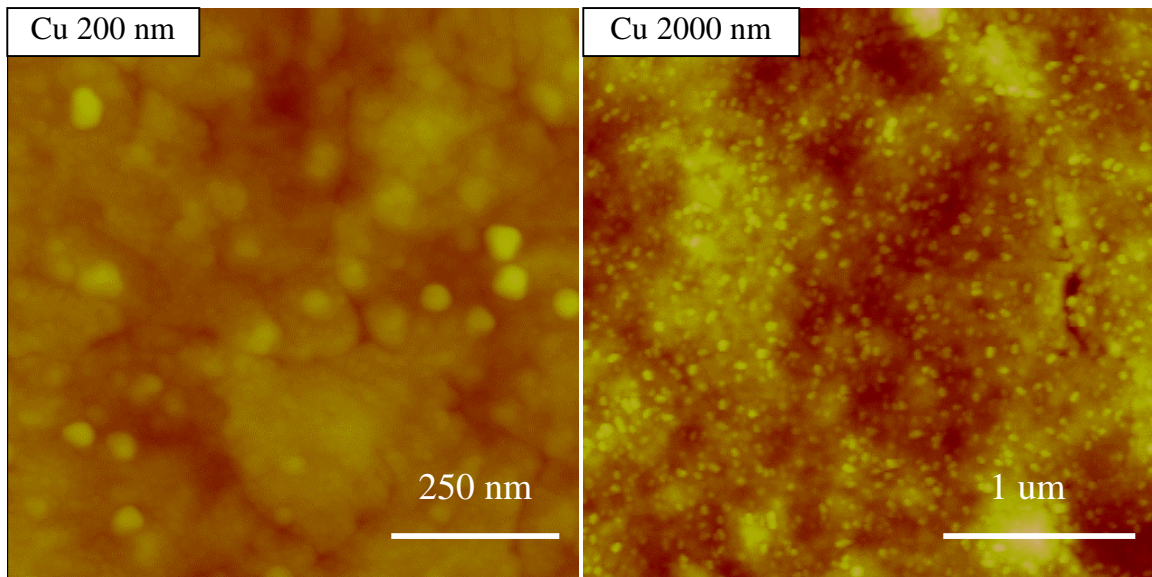


Figure 1. Height AFM images of electroplated Cu films (100 nm Z range).

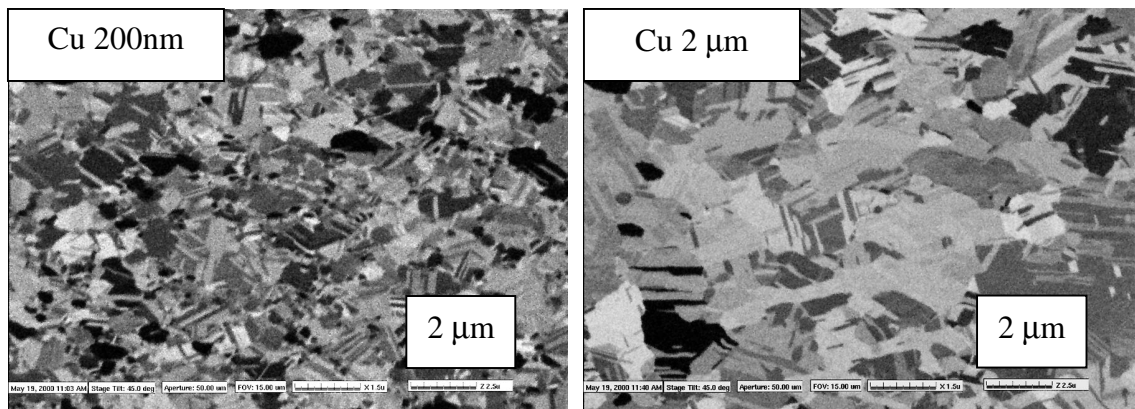
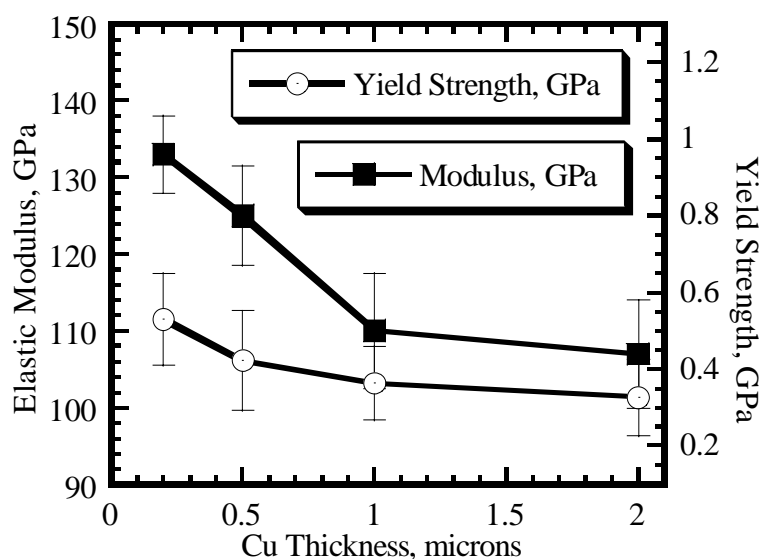


Figure 2. Focused Ion Beam image of a 2 μm thick electroplated Cu films of different thickness (45° tilt).

Cu FILM MECHANICAL PROPERTIES

Modulus and hardness data for electroplated Cu films of different thickness is presented in Figure 3. Unlike the sputtered Cu films, where the modulus is independent of thin film thickness, the elastic modulus drops from about 133 GPa for a 200 nm thick film down to 110 GPa for a 2 μm thick Cu film. Theoretically, the elastic modulus should not be affected by the film grain size or thickness. In this case the modulus reduction can be partially explained by the fact that thicker films are less dense, so a lower modulus reading may be expected. Also the surface roughness increases significantly with the film thickness (Figure 1), which affects the contact area determination in the indentation analysis. The effect of surface roughness on thin film modulus measurements by nanoindentation is discussed in [15] and in [16].

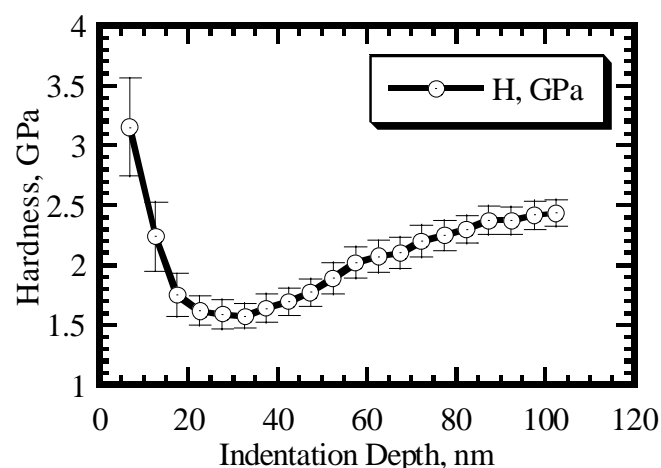
The yield stress of electroplated Cu was calculated from hardness, measured as a function of indentation depth with the CSM option of the Nanoindenter XPTM (Figure 4). Increased hardness at low indentation depth (< 20 nm) is due to a surface oxide and/or indentation size effect [17]. The hardness minimum at a depth of 25 nm for a 200 nm thick film, just over 10% of the film thickness is assumed to be the intrinsic film hardness of 1.6 GPa. At a depth of 40 nm



the tip starts to sense the hard Si substrate, with the hardness elevating accordingly. For each indent the curve minimum (e.g. Figure 4) was taken as the measure of the thin film hardness. Since Cu films have been annealed during processing, and the grain size is large, electroplated Cu films appear to be quite ductile.

Figure 3. Electroplated Cu elastic modulus and yield stress as a function of film thickness.

As expected, the yield strength (taken as 1/3 of the hardness and confirmed by the inverse method for one film thickness, equation (3)) drops with an increase in film thickness (Figure 3).



The grain size of electroplated Cu was measured using AFM and FIB as described in the previous section.

Figure 4. Electroplated 200 nm Cu film hardness as a function of the indentation depth.

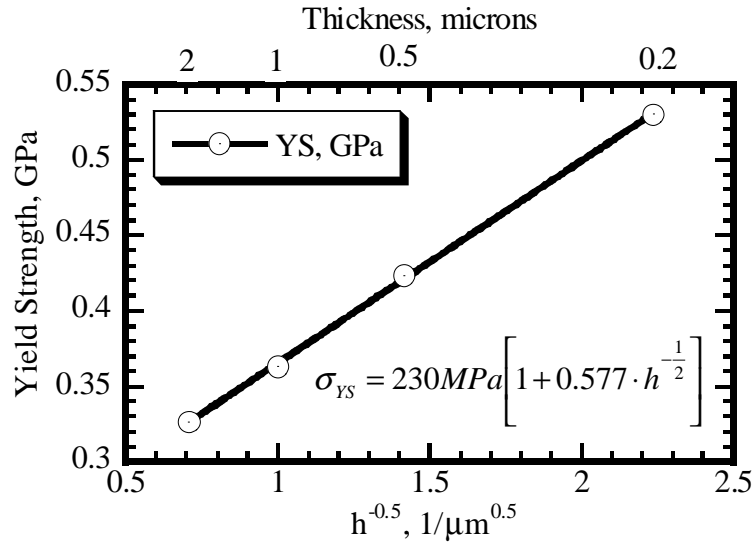
The yield stress of electroplated Cu films follows the classical Hall-Petch relationship $\sigma_{ys} = \sigma_i + kd^{-1/2}$, so for electroplated annealed Cu films the following dependence of yield stress on grain size may be used:

$$\sigma_{ys} = 180 \text{ MPa} + 0.262 d^{-1/2} \quad (4),$$

where d is the thin film grain size in microns. Also, the Wei and Hutchinson approach [11] can be used for these films to fit the yield stress data using the film thickness (Figure 5), following equation (2):

$$\sigma_{ys} = 230 \text{ MPa} \left[1 + 0.577 \cdot h^{-\frac{1}{2}} \right] \quad (5),$$

where h is the thin film thickness in microns. The electroplated films considered in this study are more ductile compared to the non-annealed evaporated Cu films, for which the equation (2) was originally applied. Thermal treatment may drastically affect plastic thin film properties through altering microstructure, so 400 °C annealed evaporated films [18] exhibit a similar plastic



behavior (Figure 6). Thicker 6 μm Cu freestanding films were also tested using a microtensile loading apparatus described elsewhere [19, 20], which provides a stress-strain curve similar to the standard tensile test. Strain is measured either directly or by employing a more accurate image correlation technique. Thinner films exhibited wrinkling upon substrate removal due to the residual stress relief, and were not tested.

Figure 5. Cu yield stress fit using film thickness.

From the microtensile evaluations, yield stress of 275 ± 25 MPa was taken at a 0.002 strain offset on the stress-strain curve. This appears to be compatible to the extrapolation fit using equation (5) (Figure 6). Note that the yield strength data obtained from the tensile experiments was not used in the fit, nevertheless, the average 275 MPa yield strength value nearly lies on the fit prediction of equation (5). Fracture surfaces of the freestanding films observed in SEM

exhibited the evidence of ductile intragranular fracture.

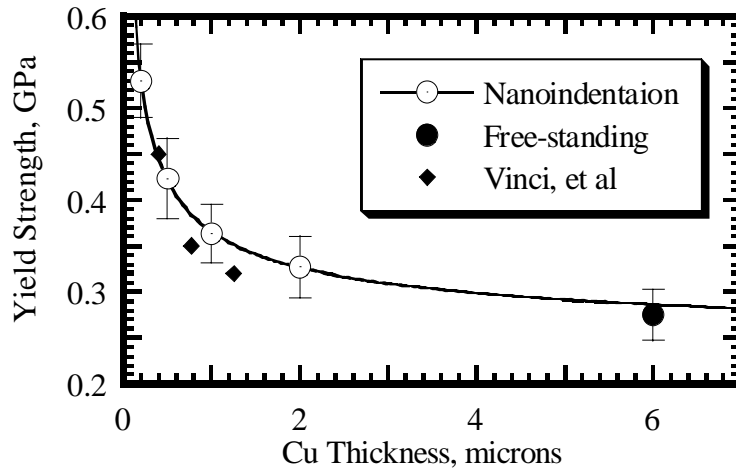


Figure 6. Electroplated Cu yield stress obtained by two different methods and compared to the annealed Cu yield stress from [18], and theoretical prediction from equations (4) and (5).

SUMMARY

Electroplated Cu films of varying thicknesses were characterized in terms of their mechanical properties using nanoindentation and microtensile testing. Microstructure was assessed by AFM and FIB, the latter providing more accurate grain size measurements. A decrease in elastic modulus as a function of increasing Cu film thickness was observed due to the higher porosity and surface roughness. As grain size increased with the film thickness, yield strength decreased due to the Hall-Petch effect. Based on this observation, phenomenological fits to the electroplated Cu yield strength are provided using either the grain size or film thickness. These fits allow one to predict thin film plastic properties for other Cu film thicknesses given the same processing conditions. Microtensile tests of thicker films provided results comparable to the fit.

ACKNOWLEDGEMENTS

Authors would like to acknowledge support for this research from Jaynal Molla, Jin-Wook Jang and Owen Fay from Interconnect Systems Labs, Atul Konkar, Himansu Yapa, Bob Carpenter, Lester Casoose, Michael Kottke, Larry Rice and Ha Le from Process and Materials Characterization Labs and John D'urso from Physical Science Research Labs at Motorola. One of us "WWG" would like to acknowledge support from Basic Energy Sciences, Department of Energy under grant DOE-DE-FG0296ER45774.

REFERENCES

1. D.T. Read, J.W. Dally, J. Mater. Res., 8(7), pp. 1542-1549, 1993
2. T.P. Weihs, S. Hong, J.C. Bravman, and W.D. Nix, J. Mater. Res. 3(5), pp. 931-942, 1988
3. S.P. Baker and W.D. Nix, J. Mater. Res. 9(12), pp. 3131-3144, 1994
4. S.P. Baker and W.D. Nix, J. Mater. Res. 9(12), pp. 3145-3152, 1994
5. M. Doerner and W. Nix, J. Mater. Res. 1, p. 601, 1986
6. G.M. Pharr, W.C. Oliver, F. Brotzen, J. Mater. Res., 7 (3), pp. 613-617, 1992
7. W.C. Oliver and G.M. Pharr, J. Mater. Res., 7, pp.1564-1583, 1992
8. W.D. Nix, Metallurgical Transactions A 20A, pp. 2217-2245, 1989
9. J.B.Savader, M.R.Scanlon, R.C.Camarata, D.T.Smith, and C.Hayzelden, Scripta Mater., pp. 29-34, 1997
10. L. Lu, L.B. Wang, B.Z. Ding, K. Lu, J. Mater. Res., 15 (2), pp. 270-273, 2000
11. Y. Wei and J.W. Hutchinson, J. Mech. Phys. Solids, 45 (7), pp. 1137-1159, 1997
12. D. Tabor, The Hardness of Metals, Claredon Press, United Kingdom, p. 174, 1951
13. D. Kramer, H. Huang, M. Kriese, J. Robach, J. Nelson, A. Wright, D. Bahr and W.W. Gerberich, Acta Mater. 47, p. 333, 1999
14. D.E. Kramer, A.A. Volinsky, W.W. Gerberich, submitted to J. Mater. Res., 2001
15. W.W. Gerberich, W. Yu, D. Kramer, A. Strojny, D. Bahr, E. Lilleodden, J. Nelson, J. Mater. Res., 13 (2), pp. 421-439, 1998
16. D.L. Joslin, W.C. Oliver, J. Mater. Res., 5(1), pp. 123-126, 1990
17. W.W. Gerberich, et al, Interpretations of Indentation Size Effects, submitted to J. Appl. Mech. "2000"
18. R.P. Vinci, E.M. Zielinski, J.C. Bravman, Thin Solid Films 262, pp. 142-153, 1995
19. D.T. Read, J.W. Dally, AMD Vol. 187, ASME 1994
20. D.T. Read, Tensile Testing of Thin Films: Technique and Results, NIST Technical Note 1500-1, Materials Reliability Series