Residual stress and nanomechanical properties of sonoelectrodeposited Cu films

A. Mallik* and B. C. Ray

Knowledge of internal stresses in thin copper film structures is essential in understanding the film properties, such as stress migration, adhesion, hardness and elasticity. Internal stresses and nanomechanical properties in thin copper films were investigated by the curvature method, nanoindentation and atomic force microscope. Variations in the abovementioned parameters were studied with decreasing deposition temperature for the films. Irrespective of deposition temperature, the stress was observed to be compressive and increased at low electrolyte temperatures. Hardness and elasticity of the films were found to be increased with reduced deposition temperature. With increasing compressive stress, the hardness of the films increased. The surface adhesion of the film deposited at 5°C was minimum, indicating increased cleanliness and chemical stability with low deposition temperatures.

Keywords: Stress, Hardness, Sonoelectrodeposition, Profilometry, Copper

Introduction

Films or coatings on a substrate that are usually in a stressed state are addressed as residual stress. The film 'wants' to be smaller or larger than the substrate allows it to be. Hence, the film is in tensile stress (film 'wants' to shrink) or compressive stress (film 'wants' to expand). Residual stresses are basically caused by interface coherency, thermal cycling and/or change in deposition parameters and applications of films.[1–4] These stresses play a significant role in the mechanical performance and reliability of thin films. Large tensile and compressive stresses may lead to cracking and buckling of the film respectively.[5–8] Therefore, measuring the residual stresses and its effects on thin film mechanical properties is especially important. However, the conventional wisdom is to strive for a compressive stress of a few hundred megapascals, as it will make the film adhere to the substrate.

The application of ultrasound during electrodeposition is believed to affect the film synthesis in terms of good adhesion, surface coverage, compactness and brightness.[9–11] However, the impact of the parameter on the residual stress and the mechanical properties of the films has rarely been studied. Hence, this study addresses the important issue of residual stresses in sonoelectroplated films using well established techniques. Most importantly, this study clarifies the variation in residual stress and mechanical properties with variation in film morphology by alterations in the deposition temperature in the presence of ultrasound. Furthermore, knowledge of stress in thin films can be obtained in two ways: by directly measuring the crystal lattice strain in the film using X-ray diffraction (XRD)[12,13] and by measuring the elastic deformation of the substrate.[13,14] The second method has been used in this investigation to study the state and intensity of residual stress.

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Experimental

Graphite substrates (Asbury, USA) of 0·25 cm^2 surface area were used to electrodeposit the copper films. All the experiments were carried out on fresh graphite electrodes. The bath composition was 0·1M Cu(II) sulphate+0·02M sulphuric acid. The chemicals were purchased from Merck Chemical Co. and used without further purification. Double distilled water was used throughout. A three-electrode open cell with an Ag/AgCl reference electrode (Eco Chemie, The Netherlands) and a platinum counter electrode (surface area of 3·14 cm^2) were used for the deposition. The depositions were carried out at temperatures of 25, 20, 15, 10 and 5°C. A high density ultrasonic probe (Sonics and Materials, VCF1500) equipped with titanium oscillator (horn) 12·5 mm in diameter, operating at 20 kHz with a 20% output, was used for ultrasonic irradiation. The intrinsic stress of copper supporters was measured using a surface profilometer (Veeco Dektak 150) equipped with stress analysis software, which calculated the stress based on the substrate's radius of curvature before and after copper electrodeposition. The mechanical properties of Cu films were measured by a UMIS nanoindenter (Based Model, CSIRO) with a Berkovich diamond indenter (tip radius of $\sim$100 nm). During each test, the load was applied to a maximum value of 10 mN. The surface adhesion study was carried out in atomic force microscopy (AFM) by analysing the force–displacement curve in contact mode. The tip

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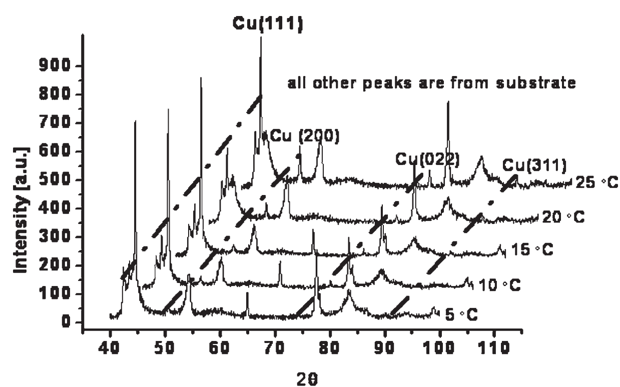


1 **Pattern (XRD) of sonoelectrodeposited Cu thin films at different temperatures**

details are *P*(*n*) doped silicon nitride with a spring constant of 0·9 N m^{-1}.

Results and discussion

Residual stress

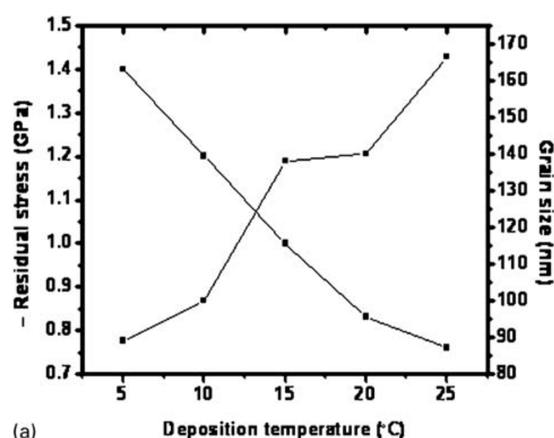
The XRD pattern of the films deposited at various temperatures are shown in Fig. 1. The sharp peaks show the crystallinity of the copper deposits. The diffraction peaks at $2\theta=43{\cdot}27$, 50·34 74·132 and 89·934 can be indexed as the (111), (200), (220) and (311) planes of copper with cubic symmetry respectively.[15] The intensity of peaks decreases with decreasing bath temperature. This is attributed to the formation of smaller sized grains at the lower bath temperature compared to the higher one. The measured residual stresses in the as deposited copper films as a function of deposition temperature and calculated grain size (by XRD) are shown in Fig. 2*a*. The film thickness was varying between 750 nm and 3 μm for deposition temperatures of 5–25°C respectively. The residual stress in the copper films was always compressive regardless of the film deposition temperature. The nature of the stress may vary with material systems, deposition methods, thickness of deposit and deposition temperature. It has been reported by other researchers that they can possess different internal stresses of various magnitude when the copper films were produced by different methods. Okolo[16] and Yu *et al.*[17] have shown compressive stresses in Cu films, while Hanabusaa *et al.*[18] and Kima *et al.*[19] have observed tensile residual stresses in sputtered and electrodeposited Cu films respectively. All these variations were explained on the relief of stress due to the coalescence of individual islands in the due process of film formation. Other parameters, e.g. volumetric distortion, thermal stress and presence of impurity atoms, have also been mentioned as reasons for these stress variations. In view of these many parameter affected alterations in stress, the explanation in this work is given in the following lines. The film growth process can be divided into three stages:

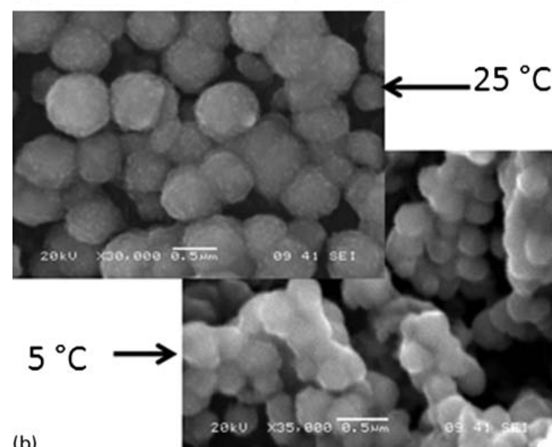
(i) island growth before coalescence
(ii) island coalescence
(iii) film growth after coalescence.

The general trend of stress development during the three phases follows the generation of an early compressive stress during the first stage island growth.[20,21] This established observation needs no further explanation at this juncture. In the second stage, as the growing crystallites contact each other at their bases, the sidewalls zip together, and the tradeoff between surface and grain boundary energies can drive crystallite coalescence and generate tensile stresses.[22–24] The corresponding microstructures of the deposits at the early stage of deposition are shown in Fig. 2*b*. The extent of coalescence of the grains at the highest and lowest temperatures of deposition in the present investigation can clearly be observed from the figures. Hence, a net tensile stress should be expected instead of the observed compressive stress. This may be due to the fact that if the metal being deposited has high adatom mobility, the post-coalescence intrinsic stress may decrease with further film growth. In many cases, particularly face centred cubic metals with lower melting temperatures, the stress eventually becomes compressive. Another factor that may contribute to the evolution of compressive stress is the surface stress. In addition to a change in surface energy, island coalescence will lead to a change in surface stress equal to $h_{gb}/2-h$, where h is the surface stress of the free surface, and h_{gb} is the interface stress associated with the grain boundary. This change in surface stress will lead to an instantaneous change in the intrinsic stress of[20]

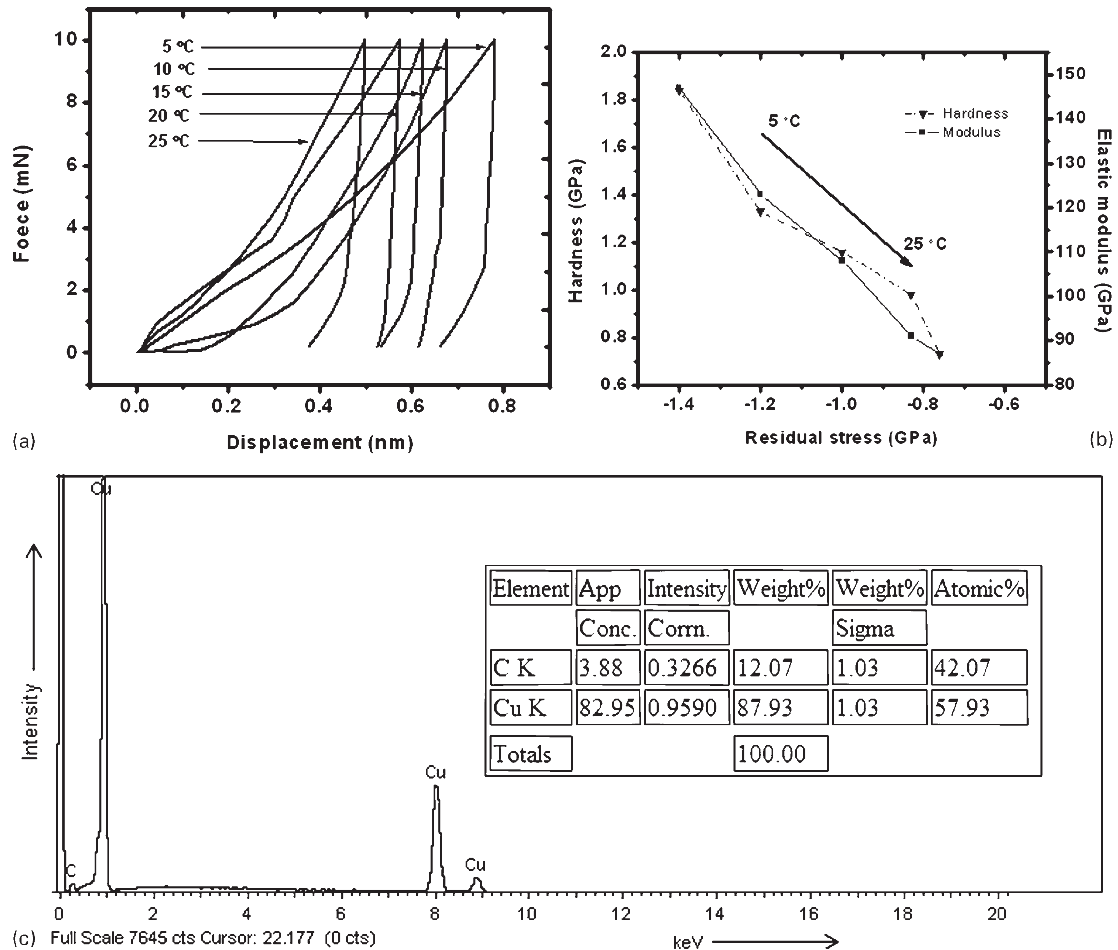
$$\Delta\sigma_{t,imp}=\beta(h_{gb}-h)/d_{imp} \quad (1)$$

where β is a constant, and d_{imp} is the grain size of the deposited film. As can be observed from equation (1), the stress can only be negative (compressive) if the free surface stress is higher than the grain boundary stress. In





2 ***a*** **residual stress of Cu thin films at various deposition temperatures and** ***b*** **SEM images of deposits at 25 and 5°C**



Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	3.88	0.3266	12.07	1.03	42.07
Cu K	82.95	0.9590	87.93	1.03	57.93
Totals			100.00		

3 ***a*** **load–displacement curves of Cu films at various deposition temperatures,** ***b*** **variation of hardness and elasticity of Cu films with residual stress and** ***c*** **EDS plot of Cu deposit at 25°C**

addition, the magnitude of this stress will, in part, be determined by how strongly attached the island to the substrate.[20,21] Ultrasound increases both the parameters, i.e. adatom mobility,[25] and the attachment of the islands with the substrate.[9,10] Furthermore, the level of compressive stress will be additionally high with decreasing grain size, as can be depicted from the equation. Hence, the smaller the grain size, the higher the compressive stress.

Hardness and elasticity

Figure 3*a* shows the typical load–penetration depth curves of nanoindentation tests of Cu deposited at different bath temperatures. The maximum load used was 10 mN. No evidence of substrate effects in the form of either kickback or elbows in the unloading curves can be observed. It was found that the mechanical properties obviously varied with temperature of deposition. The deposition at 5°C is the hardest as the depth of penetration of the indenter is less. By the Oliver–Pharr relation,[26] the hardness and the elastic modulus of the Cu films were obtained, as plotted in Fig. 2*b*. The hardness values observed are in the range from 0·78 to 1·86 GPa. The copper films at temperatures below 15°C have hardness above the hardness values for pure crystalline copper (1–1·5 GPa).[27] This can be attributed both to grain size strengthening (small grains compared to the grain size of pure crystalline copper) and/or strain hardening. The grain size strengthening is determined by the strength of Cu grains H_0 and the average grain size d of Cu according to the Hall–Petch relation $H=H_o+kd^{-1/2}$, where k is the Hall–Petch coefficient accounting for the grain boundary resistance to dislocation movement. Thus, the increased dislocation piled up with decreasing size has resulted such high strength in films. The determined Young's modulus values range from 87 to 147 GPa. The variation in these parameters with compressive stress is also given in Fig. 3*b*. With increasing compressive stress, the hardness and modulus increased from 0·78 and 87 GPa to 1·86 and 147 GPa respectively. During the nanoindentation tests, it was known that both normal compressive stresses and radial shear stresses were mainly applied to the films. Basically, the radial shear stresses were much easier to induce cracking of the films. Residual compressive stresses in the films would retard the work of applied shear stresses, thus inhibiting crack initiation and propagation. Therefore, the highest mechanical properties were measured for the film containing the largest compressive stress. In addition, the intrinsic properties of thin films, such as microstructure and chemical composition, are believed to affect their mechanical properties. However, in this study, all the deposited Cu films containing different residual stresses had no special structures like textures or preferred orientations from XRD analyses and SEM observations. In addition, by SEM/EDS analyses, all the Cu films were identified to be of 100 at-%Cu (Fig. 3*c*). Therefore, all the Cu films

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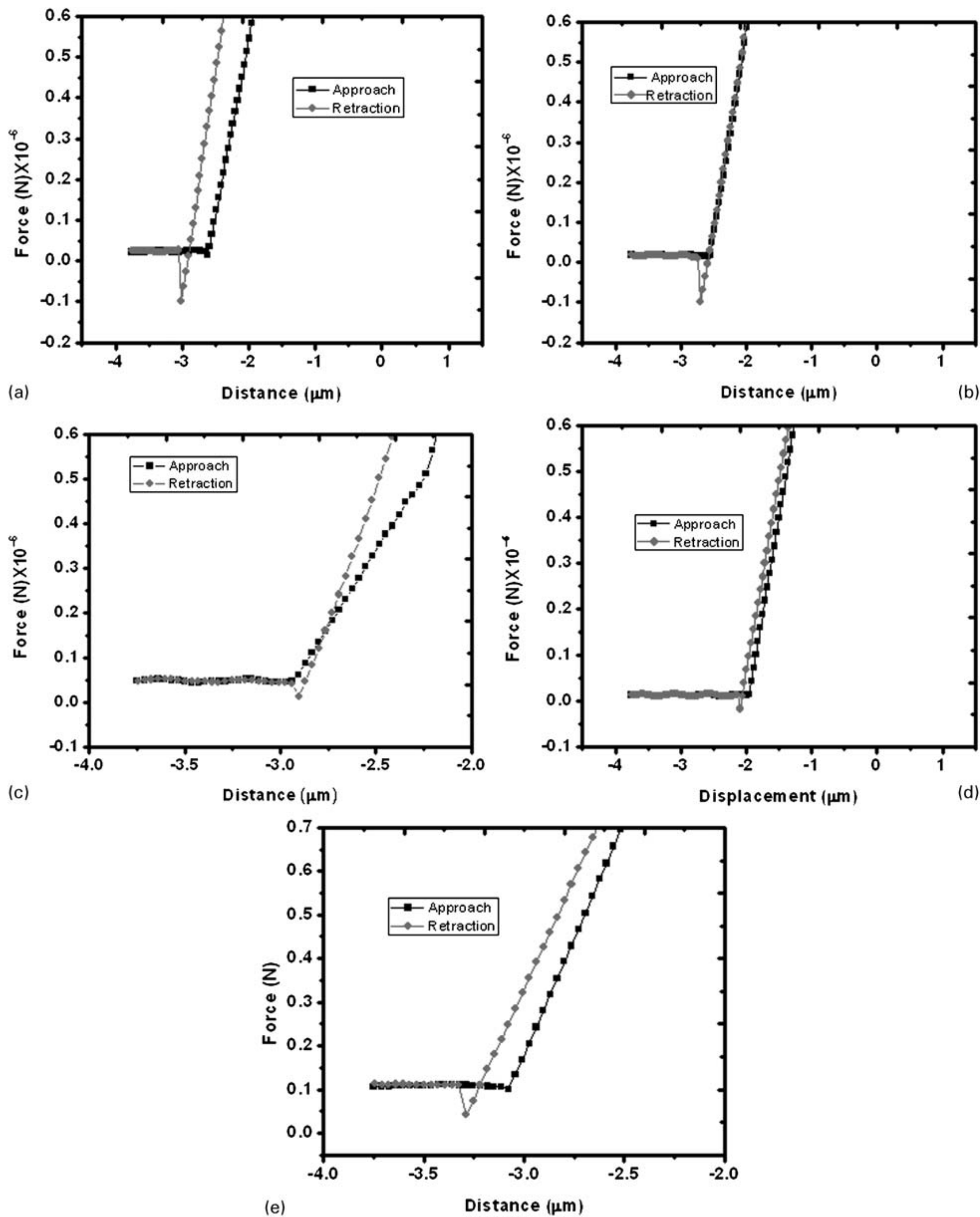

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4 Force–displacement curve at grain boundaries for Cu films deposited at *a* 25°C, *b* 20°C, *c* 15°C, *d* 10°C and *e* 5°C

investigated in this study are believed to be similar from the viewpoint of their intrinsic properties. A similar relation has also been observed by the other authors.[28] Moreover, the hardness and modulus of the Cu films prepared in this study were lower than the values of conventional Cu films, as reported in some literatures.[29]

From the viewpoint of atomic bonding force to interatomic spacing,[30] the difference in the mechanical properties of Cu films containing different residual stresses can be realised as well. It is known that atoms locate at a balanced interatomic separation r_0, and the spacing changes under a force. Ideally, atomic bonds will not break, and deformation will not initiate until the interatomic separation exceeds the maximum value r_{max} under a force over the maximum atomic bonding force F_{max}. Although the residual stresses in thin films will not affect the relation between the bonding force and the interatomic spacing, however, they change the spacing and hence the force required to break bonds. Under the effect of residual compressive stresses, the interatomic spacing is compressed, and a larger applied force is needed to break bonds. On the contrary, under residual tensile stresses, the spacing is enlarged, and the required force for plastic deformation may get lowered.

Surface adhesion

In addition to topographical imaging, however, the AFM can also probe nanomechanical and other fundamental properties of sample surfaces, including their local adhesive or elastic (compliance) properties, by measuring the forces on the AFM probe tip as it approaches and retracts from the surface. Figure 4

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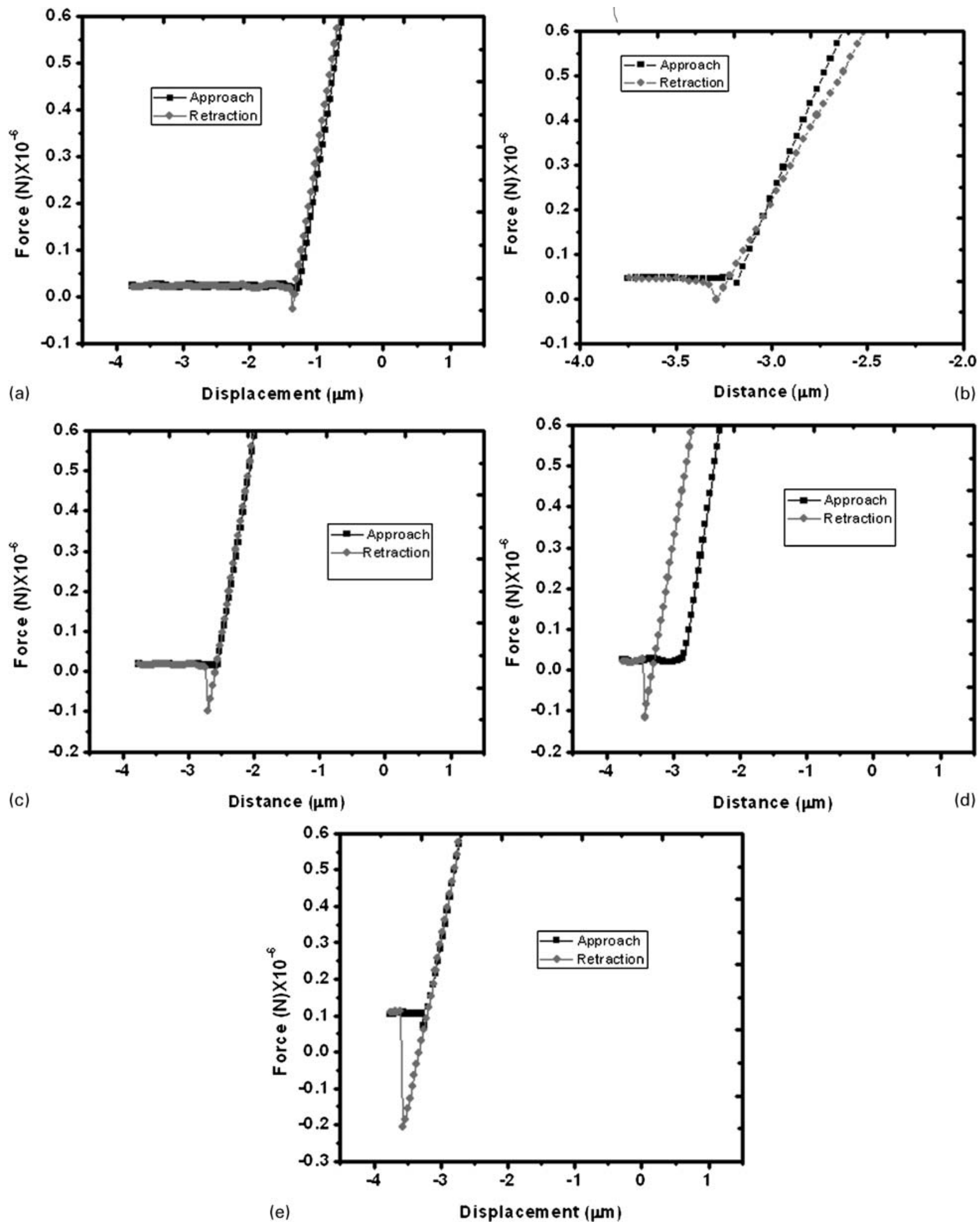

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5 Force–displacement curve at grains for Cu films deposited at *a* 25°C, *b* 20°C, *c* 15°C, *d* 10°C and *e* 5°C

shows a set of force–displacement curves for the grain boundary for all the deposition temperatures. The data in Fig. 4*a* show a typical force curve for the sample probed at the grain boundary of the deposit at 25°C. The results presented are an average of 20 readings. The approach curves show irregularities for the deposits at low temperatures. These may be due to the presence of long range force in the samples. The retraction curve estimates a rupture force of ~100 mN. Similar data were obtained for experiments performed at 20, 15, 10 and 5°C (data are shown in Fig. 4*b–e* respectively). Similar to Fig. 4*a*, the data accumulated for a set of approach–retraction cycles are measured at each deposit. The data indicate that the tip–sample interaction is relatively small at low temperatures (minimum of 54 mN at 5°C). Hence, a strong decrease in the rupture forces is observed and achieves a maximum at 25°C. The curves also indicate the formation of multiple interactions between the tip and the surface. The data for the surface's grain interaction with the AFM tip are shown in Fig. 5. Unlike the force at rupture for grain boundaries, the rupture force at grains increases monotonously with the decrease in deposition bath temperature. The above discrepancy may be due to the level of surface energy and interfacial tension present at the grains and grain boundaries of the deposit surface. However, the atoms present at the grain boundaries will contribute more to surface energies than the intergrain atoms. Figure 6*a* and *b* shows the contact angle of water on the deposited surface at 25 and 5°C respectively for surface energy measurements. The calculated values were found to vary between 34·28 and 59·92 mN m^{-1}

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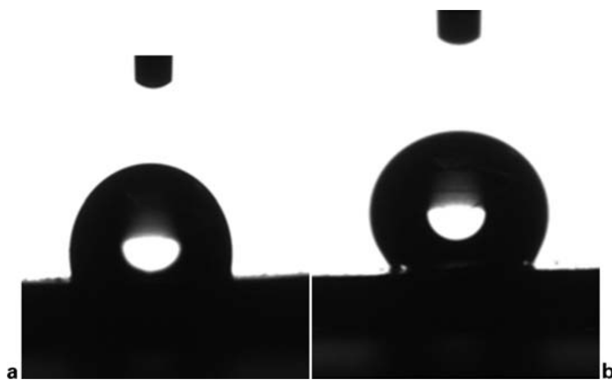

6 Contact angle measurement with water droplets for Cu films deposited at *a* 25°C and *b* 5°C

for films deposited at 25–5°C respectively. Hence, as the deposition temperature decreases, the amount of surface energy increases. If the surface energy is high, then each atom finds it favourable to cohere while in contact with a foreign atom. Accordingly, the maximum deflection of the tip/adhesion force at grains was for the deposit at 5°C. If this is true, then it follows that when the interfacial tension is high, the force of adhesion is weak, since each species does not find it favourable to bond to the other. As the AFM tip approaches the grain boundaries, the surfaces of the tip and film will experience interfacial tension. With the increase in approach of the tip, the interfacial tension increases. This tension may be maximum for the atoms at the finest grain boundaries as they possess the highest amount of surface energy. This argument can be extended to the idea that when a surface is in a medium with which binding is favourable, it will be less likely to adhere to another surface, since the medium is taking up the potential sites on the surface that would otherwise be available to adhere to another surface. The explanation may support the observations of increased deflections in the approaching curves for the grain boundaries. These data suggest that adhesion is more at grain boundaries for the deposit at 25°C and more at grains for 5°C depositions. Hence, as the volume fraction of grain boundaries increases for deposits obtained from low bath temperatures, the surfaces will be comparatively clean and chemically stable.

Summary

In this study, the effects of low deposition temperature on the state and level of residual stresses in sonoelectrochemically prepared copper thin films have been investigated. The mechanical properties, including hardness, elasticity and surface adhesion, and the relationship of residual stress with the mechanical properties in the deposited films have also been studied. The reduction in synthesis temperature reduces the grain size of the films. Irrespective of deposition temperature, the stress was observed to be compressive and increased at low deposition temperatures (maximum of 1·46 GPa at 5°C). The mechanical properties H and E show a reverse linear variation with the deposition temperature. The maximum hardness and elasticity, i.e. 1·86 and 147 GPa, occurs at 5°C. A strong dependence of hardness and elasticity with compressive residual stress exists, which can be ascribed to the effects of residual compressive stresses to blunt crack tips and suppress crack propagation. In addition to hardness and elasticity, the surface adhesion at the grain surfaces also increased with decreasing bath temperature. However, the adhesion at grain boundaries was decreased. The above discrepancy may be due to the variation in surface energy of the grains and grain boundaries and the interfacial tension between the AFM tip and the film's surface. Thus, a cleaner and chemically stable surface with good interface adherence may be expected for the films deposited at low bath temperatures.

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