Intrinsic residual stresses in metal films synthesized by energetic particle deposition

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Abstract

Residual stresses are intrinsic to all physical vapor deposited coatings. Bombardment with energetic particles (ions or neutrals) has a strong influence on both the sign and the magnitude of intrinsic stresses. For example, stresses can change from large tensile to large compressive with increasing particle bombardment. We develop a model for the evolution of tensile residual stress with increasing bombardment based on the hypothesis that the tensile stresses originate due to the attractive interatomic forces between the coalescing crystallites. The model predictions are shown to compare favorably with experimental results. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Physical vapor deposition (PVD) methods such as balanced or unbalanced magnetron sputtering, ion-beam assisted deposition, etc. are used for the synthesis of metallic and non-metallic coatings for a wide range of applications. Residual stresses arising from the growth process are intrinsic to these coatings and may lead to film cracking or delamination or undesired modifications of electrical, optical or magnetic properties [1]. Bombardment of the film during growth with energetic particles (ions or neutrals) with energies in the few

tens to a few hundred eV is inherent to most PVD processes, and these are referred to as ion-beam synthesis here. It is well known that in ion-beam synthesis both the magnitude and sign of the residual stress of the coating depends on the bombarding ion energy and flux [1–4]. Hence, synthesis may be performed under a chosen ion energy and flux condition so as to the tailor the stress in the coating for optimum performance. However, the fundamental mechanisms of stress evolution during ion-beam synthesis are not well understood.

The tensile residual stress evolution in thin films is usually attributed to an island coalescence mechanism [5,6] with the stress scaling inversely with the size of the coalescing islands. While order-of-magnitude estimates indicate that very large tensile stresses may result due to island coalescence [6], the evolution of tensile stress with increasing

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bombardment has not been modeled. The compressive stress is usually interpreted in a phenomenological way as an "atomic-peening" effect [1]. In the present investigation, we develop an interatomic force model to interpret the evolution of tensile stress with increasing ion energy in ion-beam synthesized metal thin films.

2. Experimental procedures

Cr films, with ∼150 nm nominal thickness, deposited by dc magnetron sputtering on {1 0 0} Si wafers using 300 W power to a 10 cm diameter target were used as a model system in this study. The target-to-substrate distance was ∼10 cm and the deposition rate was ∼0.6 nm/s. In the experiments described here, negative substrate bias was used to provide particle bombardment during synthesis. In one set of experiments, substrate bias was varied from 0 to 500 V at a fixed Ar gas pressure of 5 mTorr. These data are used to interpret the compressive stress evolution. In another experiment, substrate bias was varied from 0 to 250 V at a fixed Ar gas pressure of 6 mTorr, and Cr films capped with a thin layer of Al to protect from oxidation. These data are used to validate the tensile stress model. In a separate study, we have shown that adsorption of oxygen on the open columnar boundaries may affect the tensile residual stress [7]. Hence, the Al cap layer was used to study the tensile stress evolution in the Cr layer in the absence of oxygen adsorption. The residual stresses were measured after deposition using the wafer curvature technique. Transmission electron microscopy (TEM) was performed on a Philips CM 30 microscope at 300 keV. Rutherford back-scattering spectroscopy (RBS) was performed using 2 MeV He$^+$ ions.

3. Results

3.1. Stress evolution

The evolution of residual stress in Cr films with increasing substrate bias for 5 and 6 mTorr Ar pressures is shown in Fig. 1. For the 5 mTorr case,
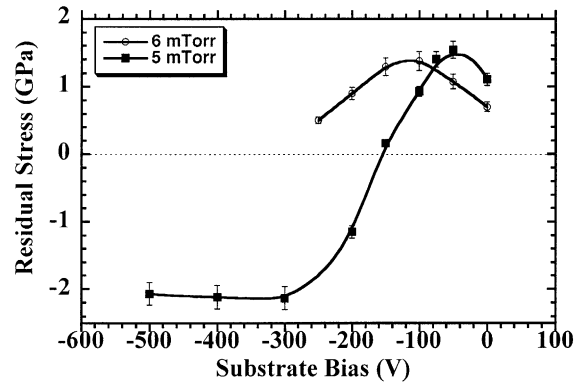

Fig. 1. Residual stress evolution in ∼150 nm thick Cr films as a function of negative substrate bias for sputter deposition under 5 and 6 mTorr argon pressures.

the stress evolution with increasing substrate bias voltage is as follows: initial increase of tensile stress to a peak of ∼1.5 GPa, relaxation of tensile stress, rapid build-up of compressive stress to a peak of ∼2 GPa and gradual decrease in compressive stress. The compressive stress evolution is interpreted as due to the extra volume added by the point defects induced during ion-beam synthesis [8], and is not discussed further in this article which is focused on modeling the tensile stress evolution.

For the 6 mTorr, only the tensile stress part was investigated, and stress in the Cr layer only (minus the stress in the Al-capped films, as shown in [7]) is reported. However, the tensile stress evolution is similar: increase to a peak followed by relaxation. The bias voltage (which roughly scales with the bombarding ion energy) at which the peak in tensile stress is observed is shifted to higher values as the Ar pressure is increased. The peak in tensile stress for the 6 mTorr deposition is of the same order as that for 5 mTorr.

3.2. Film microstructures and density

Cross-section TEM was done to correlate the film microstructure evolution with increasing ion bombardment. A typical microstructure is shown in Fig. 2 that is a bright field under-focused image from a film deposited at 6 mTorr argon pressure and no bias. For the film shown in Fig. 2, the Al
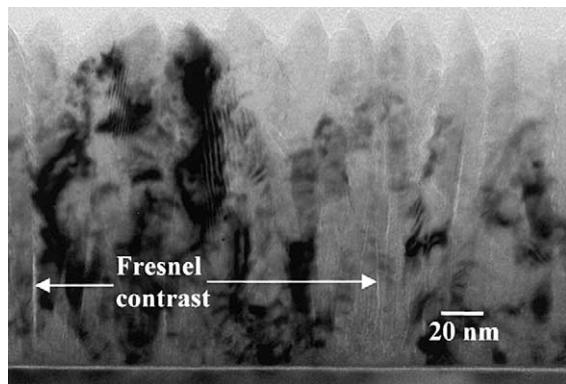
Fig. 2. Cross-section of the TEM micrograph of a 6 mTorr, no bias deposited Cr film showing Fresnel contrast at columnar boundaries in under-focused bright field images.

cap layer was not deposited. The microstructure is columnar with an average in-plane grain size (d) of $\sim 19 \pm 1$ nm for the 6 mTorr films, with no significant change as a function of bias. The under-focused bright field TEM images revealed bright fringes at the columnar boundaries as shown in Fig. 2. This Fresnel contrast is due to a phase shift in electrons transmitted through the boundary region as compared to that within the grains, and is consistent with a lower atomic number in the boundary regions. An incomplete coalescence of these nanocrystalline columns may lead to porous inter-columnar regions where oxygen may adsorb on the free surfaces and, hence, the Fresnel contrast as shown in Fig. 2. As the ion bombardment energy is increased, the intercolumnar gaps gradually close up and no Fresnel contrast is observed when the tensile stress starts decreasing (bias voltage being more negative than 100 V in Fig. 1 for 6 mTorr deposited films). Similar observations have been made for tensile stress evolution with decreasing argon pressure in the absence of substrate bias [9].

The atomic density of the films (N_{film}) was obtained by dividing the number of Cr atoms/cm^2 (obtained by RBS) by the film thickness as measured by TEM. In the absence of any inter-columnar voids, N_{film} is equal to N_{ideal} which for Cr is 8.33×10^{22} atoms/cm^3. The inter-columnar voids add extra volume and result in $N_{film} < N_{ideal}$. Mathematically,

$$N_{film}/N_{ideal} = V_{ideal}/V_{film} = d^2 h/(d + \Delta)^2 h, \qquad (1)$$

where V_{ideal} is the volume in the absence of voids, V_{film} the volume in voided film and h is the column height that remains same for both cases. Eq. (1) may be simplified to express Δ in terms of d and the density ratio as follows:

$$\Delta = d[(N_{ideal}/N_{film})^{1/2} - 1]. \qquad (2)$$

These results are presented later when comparing the experimental data with the model predictions.

4. Discussion

We hypothesize that the tensile stress evolution is due to the attractive interatomic interaction between the coalescing nanocrystallites. The interatomic force (F) between two atoms separated by a distance (a) may be obtained from a functional description of dE/da versus a, where E is the interatomic potential energy. We use the universal binding energy relation by Smith et al. [10] as an approximation to the interatomic potential for Cr. The interatomic mean stress is given as dE/dV, where V is the atomic volume. A calculated plot of σ versus a is shown in Fig. 3. This interatomic stress may be correlated with the experimental stress and microstructure evolution by
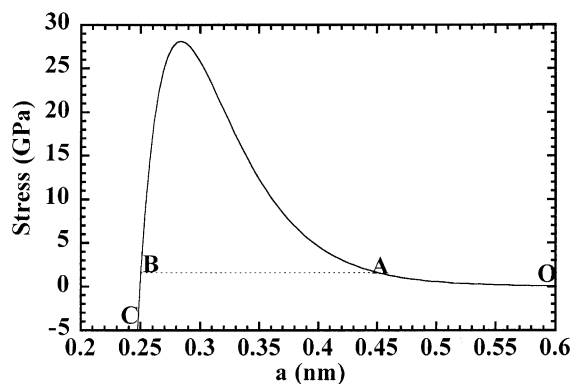

Fig. 3. Calculated plot of the interatomic mean stress for Cr using the universal binding energy potential [11] as an approximation. The experimentally observed trend is shown schematically as the curve marked by points $OABC$, where the dotted line AB represents the film yield strength.

putting the interatomic distance (*a*) in Fig. 3 equal to the inter-columnar gap distance (*Δ*). Note the qualitative similarity between Figs. 1 and 3. This is consistent with our hypothesis that with increasing ion bombardment during synthesis the intercolumnar gaps gradually close up, thereby reducing *a* and building up tensile stress to a maximum. Further decreases in *a* result in tensile stress relaxation, and when $a = a_0$ (a_0 is the equilibrium interatomic distance for which the potential energy is minimum), the stress is zero. For films with maximum tensile stress, *Δ* was calculated using Eq. (2) to be ∼0.48 nm. Applying this distance to Fig. 3, gives a tensile stress of ∼0.9 GPa, of the same order as the ∼1.5 GPa maximum stress experimentally measured for the 6 mTorr deposited films. Interestingly, *Δ* of 0.48 nm does not correspond to the maximum stress in Fig. 3.

Examining Fig. 3, we see that the stress values predicted in the region between points *O* to *A* correspond to the experimental stresses in Cr films made at 6 mTorr in the energy range between 0 and −100 V. The experimental saturation stress value is point *A* in Fig. 3. We hypothesize that the stress level shown by a dotted line in Fig. 3 represents the yield strength of the film and sets a limit to the maximum elastic residual stress possible in our films (in the region from *A* to *B* in Fig. 3). From points *B* to *C* in Fig. 3, as the gap distance approaches a_0, the tensile stress quickly decreases to zero consistent with the data of Fig. 1. Two additional issues arise from the above discussion and these are discussed below.

First, we note that the calculation of d*E*/d*V* (Fig. 3) gives the mean hydrostatic pressure when the interatomic distance changes between all atoms in the solid. To accurately evaluate the tensile stress in our films, we sum up the interatomic forces exerted on one crystallite by the adjoining crystallite. Our approach is schematically illustrated in Fig. 4, which shows two adjoining crystallites X and Y separated by a distance *Δ*. Consider the interatomic force on an atom labeled 1 in crystallite X (atom 1X). A lower bound estimate of the stress on atom 1X (σ_1) can be made by considering only the force from the atom 1 in crystallite Y (atom 1Y) at a distance *Δ*. There

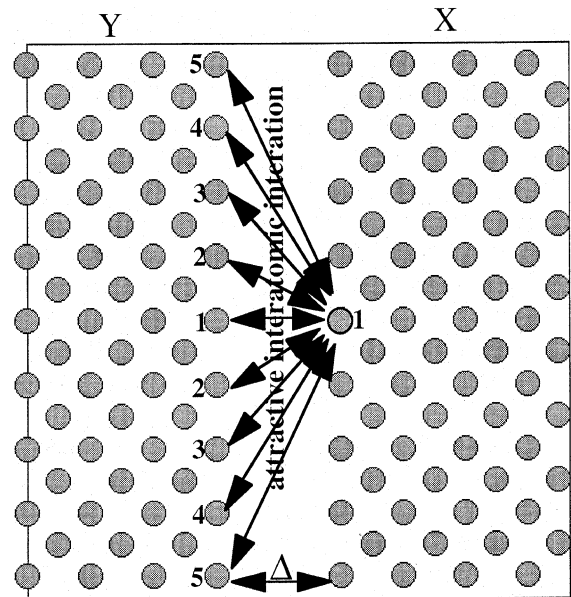
Fig. 4. Schematic of the attractive interatomic forces between two adjoining grains labeled X and Y separated by a distance *Δ*. Each atom (e.g., labeled 1 in grain X) experiences a net attractive force in tensile stressed films that is given by the sum of forces from atoms 1Y, 2Y, 3Y, etc. in the surface layer of the adjoining island. The tensile stress in the film is the net force on each atom times the number of atoms per unit area.

will be additional weaker attractive forces on atom 1X from atoms labeled 2–5, etc. in island Y and the upper bound estimate will involve summing up forces from all these atoms, including the ones in the out-of-plane direction in Fig. 4 at equivalent co-ordinates. The illustration in Fig. 4 is the (1 0 0) projection for Cr and hence, the interplanar distance (e.g., from atom 1Y to 2Y) is 0.288 nm. Knowing *Δ* from Eq. (1), we can calculate the distances 1X–2Y, 1X–3Y, etc. and obtain the corresponding interatomic forces, d*E*/d*a*, as a function of atom separation, *a*. These forces act in the respective directions 1X–2Y, 1X–3Y, etc. and only the resolved component along the horizontal direction in Fig. 4, i.e., along 1X–1Y is considered. Since the interatomic forces rapidly decrease with interaction distances above ∼0.5 nm, typically only the contributions from atoms at co-ordinates 2Y and 3Y count. The summed up net force (*F*) on atom 1X is the same force each surface atom in crystallite X

experiences from the surface layer of atoms in the adjoining island. The stress is then obtained as the net force on each atom times the number of atoms per unit area,

$$\sigma_u = F(N_{film})^{2/3}. \tag{3}$$

Eq. (3) gives an upper bound estimate of the interatomic stress, σ_u. For a range of Δ values that would roughly correspond to the region OA in Fig. 3, σ_u and σ_1 are calculated and shown in Fig. 5. The experimental stress values for bias voltages of -100, -50 and 0 V are also plotted in Fig. 5, and the predicted values of Δ that correspond to the measured stresses are obtained. These Δ values are used to predict the film density using Eq. (2) and the results are compared with the measured densities in Table 1. The measured densities compare reasonably well with the film densities calculated from the tensile stress
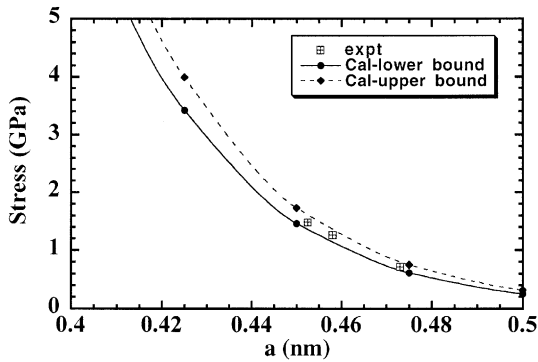

Fig. 5. Tensile stress in Cr films as a function of gap between the coalescing islands. The lower bound calculation only considers the interatomic forces from the nearest atoms across the intercolumnar gap, and the upper bound calculation follows the approach shown in Fig. 4.

model. The film thickness (and hence the density) measurements are not very precise due to the surface roughness of films (Fig. 2). Furthermore, the approximation that all grains are square in cross-section and of the same size adds to the error in the Δ estimates from the density measurements. Hence, we have back-calculated the film density by comparing the experimental stress values to the model predictions and compared to experimental density measurements. Finally, the interatomic potential used is an approximation, and so the model predictions and experimental data comparisons should only be regarded as approximate. Nevertheless, the trends in our experimental data are well described using the Smith potential and our estimates of Δ. It is expected that better absolute agreement could be obtained with a more accurate potential for Cr and more precise values for Δ.

Second, we need to estimate the yield strength of the film and compare with the experimentally measured maximum tensile residual stress. For grain size <20 nm, pile-up based Hall–Petch model may break down and yield strength may be estimated by the Orowan bowing stress for single dislocations [11],

$$\sigma_{Orowan} = M \frac{Gb}{4\pi(1-v)} d^{-1} \ln\left(\frac{d}{b}\right), \tag{4}$$

where M is the Taylor factor (≈ 2.75 for bcc metals), G the shear modulus (95 GPa for Cr films), v Poisson's ratio (0.21 for Cr) and b is the Burgers vector (0.249 nm for Cr). For grain size $\ll$ film thickness, only grain size may be considered as the obstacle spacing in the Orowan model [11]. For $d = 19 \pm 1$ nm, the calculated yield strength is 1.5 ± 0.06 GPa and this compares well with the

Table 1
Comparison of the calculated film density from the tensile stress model with the experimental measurements

Bias (V)	Stress (GPa)	Δ (nm)[a]	k (calculated)[b]	k (measured)[b]
-100	1.4800	0.452 ± 0.003	0.954 ± 0.003	0.951 ± 0.006
-50	1.2600	0.460 ± 0.003	0.953 ± 0.003	0.940 ± 0.006
0	0.71700	0.475 ± 0.003	0.951 ± 0.003	0.921 ± 0.006

[a] From Fig. 5.
[b] The density ratio N_{film}/N_{ideal}.

maximum tensile residual stress ($\sim$1.48 GPa), consistent with our hypothesis that residual stress may only be as high as the film yield strength.

5. Summary

A model has been developed that predicts the tensile stress evolution with increasing ion bombardment in ion-beam synthesized coatings. Tensile stress originates from the attractive interatomic interactions between coalescing crystallites as the ion bombardment is increased. We show that the inter-columnar gap distance may be estimated by measuring the film density and using interatomic potentials, the interatomic forces may be summed on the surface atoms of the coalescing crystallites and used to calculate the tensile stress. The model predictions are shown to compare well with the experimentally measured stresses in sputtered Cr coatings on biased substrates.

Acknowledgements

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