Variation in stress with background pressure in sputtered Mo/Si multilayer films

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We have measured the stress in Mo/Si multilayer films deposited by magnetron sputtering, using the wafer-curvature technique, and find a strong dependence on background pressure. We find that for multilayers containing 40 bilayers of ~4.3 nm Si layers and ~2.6 nm Mo layers, the stress increases from approximately -280 MPa (compressive) to -450 MPa as the background pressure in the deposition chamber (i.e., measured just prior to deposition) decreases from 1.0×10^{-5} to 6.0×10^{-8} Torr. For multilayers of the same period but with thicker Mo layers, the dependence on background pressure is even stronger. X-ray (λ =0.154 nm) diffraction measurements reveal only a slight increase in interfacial roughness for films deposited at high background pressure, but no evidence was found for any differences in the microstructure of the polycrystalline Mo layers that comprise these structures. The peak soft x-ray (λ =13 nm) reflectance, which is sensitive to interfacial roughness at longer spatial wavelengths, also shows no correlation with background pressure or stress. Atomic concentrations of incorporated oxygen and carbon, measured with Auger electron spectroscopy, were found to be less than ~ 0.5 at. % for all samples. However, the average hydrogen concentration, as determined from forward-recoil-scattering measurements made using a 2.6 MeV He beam, was found to increase linearly with background pressure. We discuss possible mechanisms for the observed dependence of film stress on background pressure, including gas incorporation and the affect of residual gas atoms on adatom mobility. © 1995 American Institute of Physics.

I. INTRODUCTION

Periodic thin-film multilayer (ML) structures are interesting subjects for the study of film growth and interface formation.^{1,2} MLs are also being used for a variety of technological applications which take advantage of their unique optical, magnetic, electrical, and/or mechanical properties.³⁻⁷ For many of these applications, the film stress is an important parameter that must be characterized and ultimately controlled. For instance, stress affects the adhesion of the film to the substrate, and also causes the substrate to deform, which may be of critical importance for certain applications, e.g., diffraction-limited x-ray imaging using reflective ML coatings, for which the surface figure of the ML-coated optics must be controlled to ~1 nm.³ Excessive stress will further limit our ability to produce flat, free-standing thin-film MLs, as for x-ray beamsplitters, for example.

The stress in a ML film is determined by the stresses in the individual layers that comprise the ML, and by any interfacial stresses that may be present. The deposition stresses in the individual layers, i.e., the stresses resulting from nonequilibrium growth conditions, are highly dependent on the details of the deposition conditions. Thus, the stress in a ML film, as in a single-layer film, is process dependent, in general. For example, it is by now well known that the stress in single-layer films prepared by magnetron sputtering can be adjusted from tensile to compressive simply by decreasing the pressure of the working gas,⁸ and the same effect was reported recently for ML films.⁹ In order to control precisely the stress in ML films, we must, therefore, first characterize any dependencies of ML stress on deposition conditions. In this paper we report the results of an investigation of the stress dependence on background pressure in ML films composed of molybdenum and silicon layers prepared by magnetron sputtering. The stress in Mo/Si MLs has been reported previously.¹⁰ However, the dependence on stress with background pressure in these, or in any other ML structures has not, to our knowledge, been reported previously.

Previous investigations have shown that the highest quality Mo/Si MLs (i.e., those having well-defined layers with the smoothest interfaces, and consequently the highest peak soft x-ray reflectance) are prepared by ion-beam sputtering or by magnetron sputtering at low Ar pressure.¹¹ Using both x-ray diffraction and transmission electron microscopy, MLs prepared under these conditions are known to be composed of amorphous Si layers and polycrystalline Mo layers, separated by amorphous interlayer regions of mixed composition. The bcc Mo crystallites show a preferred {110} orientation, which places the most densely populated planes parallel to the substrate. The interfacial roughness in these structures is small, nominally 0.1-0.2 nm; the predominant interface imperfection is the diffuseness associated with the interlayers.

II. BACKGROUND

Before we describe the experimental details and the results of our investigation, which we present in Secs. III and IV, respectively, it will be useful to review briefly the subject of thin-film stress, with particular emphasis on the current understanding of the origins of deposition stresses in sputtered films. This background material will also aid in our analysis of the data, and in the discussion of our results in Sec. V.

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The total stress in a ML film results from the stresses in the individual layers that comprise the ML, and from any interfacial stresses that may be present. The interfacial stress f is equal to the work required to deform elastically by a unit strain a unit area of interface.¹² For the case of a periodic ML film consisting of alternating layers of materials A and B, having thicknesses d_A and d_B , and biaxial stresses σ_A and σ_B , respectively, the total biaxial stress σ_{ML} in the film is independent of the number of periods, and is given by¹³

$$\sigma_{\text{ML}} = (d_A \sigma_A + d_B \sigma_B + 2f)/(d_A + d_B). \tag{1}$$

Several assumptions are implicit in this expression, including (a) that the ML consists of many periods, so that one may neglect both the interfacial stress term associated with the film-substrate interface, and the surface stress term associated with the top layer, (b) that the layers are isotropic in the plane of the film, and (c) that the interfaces between the layers are sharp, i.e., there is no intermixing between the A and B layers, so that the interfaces and thus the interfacial stresses are well defined.

Direct measurements of the interfacial stresses in ML films have been reported by Ruud et al.13 for the case of Ag/Ni MLs, and by Bain et al.¹⁴ for Mo/Ni MLs. In the former case, where the mutual solubility of Ag and Ni is small, and the Ag-Ni interfaces sharp, the interfacial stress was found to be -2.27 ± 0.67 J/m². In the Mo/Ni system, on the other hand, where the mutual solubilities of Mo and Ni are substantial and the interfaces are likely diffuse, no evidence for interfacial stresses was found. A measurement of the interfacial stress in Mo/Si MLs has not, to our knowledge, been reported; considering that the interfaces in these structures show considerable diffuseness, and in light of the results for Ag/Ni and Mo/Ni MLs, interfacial stresses in the Mo/Si system may be absent. We thus adopt the simplest view and assume that the interfacial stress term in Eq. (1)may be neglected.

Stresses in the individual layers of the ML, as in the case of a single-layer film, can arise by several different mechanisms.¹⁵ Thermal stress will result from a difference $\Delta \alpha$ in the thermal expansion coefficient of the film relative to the substrate, according to

$$\sigma_{\text{thermal}} = Y_f \Delta \alpha (T_D - T_M) \tag{2}$$

(for the case of a single film on a substrate), where Y_f is the biaxial elastic modulus of the film, and T_D and T_M are the film deposition and stress measurement temperatures, respectively. Epitaxial or coherency stress will result from the strain associated with a mismatch in lattice parameters in the case of heteroepitaxial multilayer films. Stress can also arise from interface reactions leading to, e.g., density and/or bond configuration changes resulting from phase formation. And finally, so-called growth or deposition stresses can result from the nonequilibrium growth conditions associated with various deposition techniques. That is, nonequilibrium growth conditions may lead to density changes, the formation of voids, gas incorporation, etc., and these aspects of the microstructure and composition will determine the stress state of the film. In this last case, the resulting stress is highly dependent on the details of the deposition process. Deposition stresses are also dependent on the film thickness, in general, so the σ 's in Eq. (1) can be thickness dependent as well.

The relationship between the deposition stress, the microstructure and composition, and the deposition conditions of thin films deposited by physical vapor deposition (i.e., evaporation or sputtering) has been the subject of active investigation for many years. In the case of films prepared by sputtering, a number of authors have reported on the effect of such parameters as substrate temperature, working gas pressure, working gas composition, source-to-substrate distance, substrate bias, and angular distribution of adatoms. Though a complete fundamental understanding of the physical mechanisms involved is still lacking, a large body of knowledge has been assembled, some of which was summarized recently by Windischmann.¹⁶ By an analysis of results presented in the literature, he suggests that for low substrate temperatures, where the effects of bulk diffusion are negligible, so that the dynamics of the growth process are dominated by adatom surface mobility, the microstructure and deposition stress in a thin film prepared by sputtering or by ion-assisted deposition is determined chiefly by the normalized momentum delivered to the growing film. $P_n^* = \gamma(ME)^{1/2}$, where M is the mass, E is the energy, and γ is the energetic particle/adatom flux ratio; P_n^* is a function of several deposition parameters.

At low P_n^* (as in the case of sputtering at high gas pressure, for example, in which case the gas is thermalized)¹⁷ the surface mobility of adatoms is small, so films are characterized by a porous columnar microstructure having large surface roughness¹⁸ (i.e., zone 1 microstructure, according to the structure zone model described by Thornton)¹⁹ and a tensile stress state resulting from the interatomic forces exerted across the gaps between columnar grains.²⁰ At higher P_n^* values, the surface mobility of adatoms increases, due to collisions with energetic particles striking the film, and by the fact that arriving adatoms have larger kinetic energies to begin with. With greater adatom mobility, voids collapse to dimensions comparable to the range of interatomic forces and the tensile stress thus reaches a maximum. This is followed by a sharp transition from tensile to compressive stress, which is accompanied by a zone T-type microstructure consisting of tightly packed columns. At these high P_n^* values, as the size and number of voids decreases further as the result of large adatom mobility, interatomic forces which would otherwise lead to tensile stress are reduced. Compressive stress results as the film becomes overdense by the socalled atomic peening effect.²¹ Compressive stress may also be due to implanted working gas atoms,²² though conclusive evidence for this latter effect has not been reported.

The effect of gas impurities on the stress in sputtered films was also first reported some years ago, by Stuart,²³ who investigated a variety of metal films deposited by triode sputtering. For example, he reported that the stress state in tantalum films changed from compressive to tensile by the introduction of oxygen during sputtering. Subsequent studies (Refs. 24–28, for example) of the effect of gas impurities on film stress for both sputtered and evaporated films focused mainly on the properties of relatively thick films of otherwise

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pure materials, and generally involved the deliberate introduction of reactive gas species (e.g., H_2O , H_2 , O_2) into the vacuum system during deposition. Nonetheless, in all of these investigations the film stress was found to (a) depend strongly on the partial pressure of the impurity gases, and (b) be correlated with the amount of impurity atoms incorporated into the film. However, there remains some discrepancy among the various results, and although several possibilities have been proposed (e.g., lattice distortions due to interstitial impurity atoms, the effect of impurity atoms on adatom mobility), a clear explanation of the mechanism by which impurity atoms affect film stress has not yet emerged.

III. EXPERIMENT

A. Film growth

ML films were deposited by dc magnetron sputtering, using argon as the working gas. Planar targets, measuring $50.8 \times 8.9 \times 0.6$ cm, were used, containing either solid Si of 99.999% purity or Mo of 99.9% purity. In this system, which has been described previously,²⁹ the magnetrons (VacTec, Inc.) are mounted along the diagonal of a square, stainlesssteel vacuum chamber, and face upward. The substrate is mounted facing downward on a platen that spins as it rotates over each magnetron source (vertical target to substrate distance is 90 mm), thereby building up the multilayer one layer per pass. The spin motion, which is used to enhance coating uniformity, is driven by a dc motor, and operates at approximately 235 rpm, whereas the rotation motion is driven by a computer-controlled stepper motor with great reduction, and operates at any desired rotation rate between 0.00003 and 5.5 rpm. The individual layer thicknesses in the multilayer are thus adjusted by controlling the rotation speed independently over each source, while keeping the intrinsic source deposition rates constant by maintaining constant source power and gas pressure. Stainless-steel shielding is used to limit the angular range of deposition, and also serves to minimize cross contamination between the two sources. The temperature of the substrate was not controlled during deposition.

The deposition chamber was evacuated to a pressure of 0.4 Torr with a rotary piston pump. High vacuum was then achieved using a cryopump (CTI model CT-10; pumping speed =3000 ℓ /s for air, 9000 ℓ /s for water). The pressure in the chamber was measured using a Bayard-Alpert type ionization gauge (Granville-Phillips model 274 gauge and model 307 controller); the composition of the background gas was also measured during a separate run with a residual gas analyzer (RGA) (Leybold Quadrex 200 with electron multiplier). Accurate partial pressures of background gas components were determined by calibrating the RGA using a controlled leak of N₂. Figure 1(a) shows the RGA spectra versus time; Fig. 1(b) shows the partial pressures of the predominant residual gas components versus time computed from these data, as well as the total pressure computed from the sum of the partial pressures. The apparent total pressure measured with the ion gauge is also shown in Fig. 1(b); the pressure measured with the ion gauge is generally lower than the true pressure (sum of the partial pressures) because the ion gauge controller is calibrated for N2, whereas the pre-



FIG. 1. (a) Residual gas analyzer (RGA) spectra vs pumpdown time. The predominant features correspond to water (OH⁺ and H₂O⁺; masses 17 and 18, respectively), hydrogen (H⁺ and H₂⁺; masses 1 and 2, respectively), nitrogen/carbon monoxide (N₂⁺/CO⁺; mass 28), and oxygen (O⁺ and O₂⁺; masses 16 and 32, respectively). (b) Partial pressures of major background gas species vs pumpdown time, computed from the data in (a). The total pressure (dotted), equal to the sum of the partial pressures, and the apparent total pressure measured with an ionization gauge (dashed) are indicated.

dominant component of the background gas is water vapor, as indicated in the RGA spectra. The RGA spectra reveal that lesser quantities of hydrogen, nitrogen and/or carbon monoxide, and oxygen are present in the background gas as well.

We maintained precisely the argon pressure during deposition with a closed-loop feedback system consisting of a mass-flow controller (MKS model 2259C) and a capacitance manometer (MKS model 390HA), using Ar of 99.998% purity. The Ar pressure was thus maintained at 1.5 mTorr (0.2 Pa) during deposition (Ar flow rate of \sim 230 sccm). Power to each magnetron source was supplied by a 1 kW power supply (Advanced Energy model 2011), operated in the regulated power mode at 200 W; typical voltages were \sim 300 V. The power supplies were ramped to full power over a period of 2 min, with an additional 20 min warm-up period prior to film growth. The substrate was electrically grounded.

Under the conditions just described, the deposition rates for Mo and Si were measured to be 0.25 and 0.18 nm/s, respectively. ML films containing 40 periods of ~6.9-nmthick Mo/Si bilayers were deposited onto Si(100) wafer sections measuring ~16×16 mm², of nominal 100 μ m thickness. The native SiO₂ layer was not removed from the wafers. Three different combinations of individual Mo and Si layer thicknesses were chosen: $(d_{Si}, d_{Mo}) = (4.3, 2.6 \text{ nm})$, i.e., $\Gamma = 0.625$; (3.5 nm, 3.5 nm), i.e., $\Gamma = 0.5$; and (2.6, 4.3), i.e., $\Gamma = 0.375$, where $\Gamma \equiv d_{Si}/(d_{Mo} + d_{Si})$. The first layer deposited was Mo and the last Si. The deposition times were of order 40 min, depending on the Γ value.

MLs were deposited at various background pressures by varying the pumpdown time, i.e., the elapsed time between the opening of the gate valve isolating the cryopump and the start of the magnetron source warm-up period and subsequent film growth. The pumpdown time was thus varied from \sim 30 min for films deposited at an apparent pressure of $\sim 1.0 \times 10^{-5}$ Torr, up to a period of several days for films deposited at the lowest background pressures. For most samples, the ionization gauge was turned on during the entire pumpdown period (and turned off during deposition). However, one set of MLs was prepared for which the ion gauge was intentionally left off during pumpdown, except during a 3 min period just prior to the magnetron source warmup (so that the background pressure could be measured). We note that for films deposited at the highest pressures, the deposition time is comparable to the pumpdown time; considering the data of Fig. 1(b), it is clear that the partial pressures of the background gases must have dropped significantly during the course of the deposition for these samples. Unfortunately, due to the configuration of the system, it was not possible to obtain RGA data during deposition.

B. Film characterization

If a film of thickness t_f having a biaxial stress σ is attached to a substrate of thickness t_s , it will cause the substrate to deform, as required by the condition of static equilibrium. If the substrate is very much thicker than the film, the deformation will be spherical, having a radius of curvature R. The relationship between σ and R is given by the well-known Stoney equation:³⁰

$$\sigma = \frac{Y_s}{6} \frac{t_s^2}{t_f} \frac{1}{R},\tag{3}$$

where Y_s is the biaxial elastic modulus of the substrate [which is related by $Y_s = E_s / (1 - v_s)$ to E_s , Young's modulus, and v_s , Poisson's ratio for the substrate]. A measurement of the radius of curvature R can thus be used to infer the stress in the film, assuming that the elastic properties of the substrate and the thicknesses are known. By convention, positive σ refers to a tensile stress state, in which the substrate is bowed towards the film (concave), while negative σ corresponds to a compressive stress state, in which the substrate is bowed away from the film (convex).

ML stress was thus measured using the wafer curvature technique, with a laser-scanning apparatus that has been described previously.³¹ With this apparatus, wafer curvature is determined by measuring the deflection of a HeNe laser beam as it scans along the surface of the sample. The curvature resulting from the stress in the film is computed by measuring the wafer curvature before and after deposition. From the measured curvature, the film stress is computed using Eq. (3). Substrate thicknesses were measured with a

micrometer, and film thicknesses determined from x-ray diffraction (described below). A value of 180 GPa for Y_s was used.³² We estimate that the stress measurements are accurate to $\pm 5\%$.

In addition to the wafer curvature measurements, the microstructure of selected samples was characterized using a variety of x-ray techniques, and film composition was investigated by both Auger electron spectroscopy (AES) and forward-recoil scattering (FRS). Characterization was limited to selected Γ =0.625 ML films.

X-ray diffraction measurements were made at a wavelength of 0.154 nm (Cu $K\alpha$) using a four-circle diffractometer fitted with a rotating anode source and a pyrolytic graphite crystal monochromator. Small-angle measurements (from 0° to 8° grazing) in the θ -2 θ geometry were used to measure the Bragg peaks resulting from the ML periodicity (i.e., $d \sim 6.9$ nm), while large-angle measurements (from 2θ =30° to 50°), also in the θ -2 θ geometry, were used to examine the Mo(110) diffraction peaks. From the small-angle measurements, the individual layer thicknesses (and therefore the deposition rates) were determined with high precision, by fitting the measured data with calculations based on recursive application of the Fresnel equations.³³ Nonspecular x-ray scattering measurements were also made, in this case by varying the detector angle (2θ) while maintaining a fixed incidence angle (corresponding to the first Bragg peak, i.e., θ =0.73°), in order to measure any intensity variations in the Yoneda peaks that would result from different amounts of correlated interfacial roughness.34

The absolute soft x-ray reflectance was measured using a laser-plasma-based reflectometer system that has been described previously.³³ The reflectance was measured versus wavelength from 12 to 15.5 nm, in 0.5 nm increments, at a fixed incidence angle of 3° from normal.

Oxygen and carbon concentrations were determined from AES measurements made with a PHI595 system (Perkin-Elmer). Depth profiling was achieved by sputtering with a 4 keV argon beam. Hydrogen concentrations were determined from FRS measurements using a 2.6 MeV He beam, at 15° grazing incidence on the samples with the H recoil at 30° to the incident beam direction.³⁵ He atoms were removed from the forward scattered beam using an $11.8 - \mu m$ thick Mylar foil, and recoil H atoms were measured with a silicon surface barrier detector. The average concentration of hydrogen in selected ML samples was determined by taking the ratio of the number of forward recoil H events measured for each sample, at a fixed dose of 40 μ C of beam, to the number of counts obtained from a calibration sample of Si containing 5×10^{15} atoms/cm² of implanted hydrogen. As a result of the uncertainty associated with the application of the pure Si calibration sample to a ML film, we estimate that the hydrogen concentrations reported in the next section are only accurate to $\pm 10\%$. However, the precision of these measurements (i.e., resulting from the uncertainty associated with the H counting statistics) is much better, in the range of $\pm 1\%$ –2%, depending on the sample.



FIG. 2. Measured stress vs background pressure in ~6.9 nm period multilayer films, with Γ =0.375 (squares), Γ =0.5 (diamonds), and Γ =0.625 (open triangles). Also shown are the data for Γ =0.625 ML films for which the ion gauge remained off during pumpdown (filled triangles). The dashed lines are least-squares fits to these datasets.

IV. RESULTS

Shown in Fig. 2 are the stresses measured in Mo/Si ML films as a function of background pressure. As can be seen from this plot, the compressive stress in these films varies \sim linearly with the log of the background pressure: for the

 Γ =0.625 films, the compressive stress decreases from approximately -450 to -250 MPa as the apparent background pressure in the deposition chamber (measured with the ion gauge just prior to deposition) increases from 6.0×10^{-8} to 1.0×10^{-5} Torr. For the Γ =0.5 and Γ =0.375 samples, the stress variation is even more strongly dependent on background pressure. (We note that for a given background pressure, the stress becomes more tensile with decreasing Γ , i.e., with increasing Mo layer thickness; evidently the Mo layers are in tension, and the Si layers in compression.) Also shown in Fig. 2 are the stress-vs-background pressure data for the (Γ =0.625) samples deposited with the ion gauge off during pumpdown. The stresses for these samples are approximately 30 MPa more compressive than for the equivalent samples deposited with the ion gauge turned on during pumpdown.

Figure 3 shows representative x-ray and soft x-ray data, comparing the results obtained for high background pressure/ low compressive stress versus low background pressure/high compressive stress Γ =0.625 MLs. The only significant difference in these data between the low-stress and high-stress films is in the appearance of the three ML diffraction peaks [Fig. 3(a)] measured at the largest angles, i.e., between 5.5° and 7.5°: these peaks are sharper, and more intense for the high-compressive-stress sample. By fitting these curves, we attribute this to a difference of ~0.2 nm in interfacial roughness between these two films. In contrast, the peak soft x-ray



FIG. 3. X-ray characterization results for Γ =0.625 MLs, comparing high-background pressure/low-stress (solid) vs low-background pressure/high-stress (dashed) multilayer films. (a) Small-angle, specular x-ray (λ =0.154 nm) reflectance measured in the θ -2 θ geometry. The Bragg peaks correspond to the multilayer period $d\sim$ 6.9 nm. (b) Soft x-ray reflectance measured near normal incidence (3°) vs wavelength. (c) Nonspecular x-ray (λ =0.154 nm) reflectance measured by varying 2 θ at a constant incidence angle θ =0.73°. (d) Large-angle x-ray (λ =0.154 nm) scattering, also in the θ -2 θ geometry, comparing the Mo(110) diffraction peaks.

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reflectances [Fig. 3(b)] of the two samples are identical within experimental uncertainty, aside from a slight wavelength shift resulting from a small difference in ML period. (This difference in ML period is due to a drift in the deposition rate from run to run, and was determined to be uncorrelated with background pressure.) The nonspecular scattering curves [Fig. 3(c)] indicate that there are no significant differences in the amount of light scattered into the Yoneda peaks,³⁶ suggesting no differences in the correlated interfacial roughness in these structures. The widths of the Mo(110)peaks in the large-angle x-ray diffraction data [Fig. 3(d)] are also identical for the two samples, indicating no differences in the average grain size along the growth direction of the Mo crystallites in these films, which we infer from these widths to be $\sim 2.9 \pm 0.2$ nm³⁷ (i.e., comparable to the thickness of the Mo layers in these samples). From the location of these peaks (i.e., $2\theta = 40.54^{\circ}$) we can discern no differences in the average out-of-plane {110} interplanar spacing between the two films. However, the sensitivity of these measurements to variations in the in-plane stress is not great: assuming that the relative locations of the (110) peaks can be determined with a precision of 0.05°, corresponding to an uncertainty in the average (out-of-plane) interplanar spacing of 0.0005 nm, the smallest strain that can be measured is thus $\sim 2.3 \times 10^{-3}$. Using the elastic constants for bulk Mo from Ref. 38, this corresponds to an in-plane biaxial stress of \sim 900 MPa, larger than any of the stresses we have measured.

The small-angle x-ray scattering measurements, the nonspecular x-ray scattering measurements, and the soft x-ray reflectance measurements are each sensitive to particular aspects of the interface morphology of the MLs studied here. The soft x-ray reflectance measurements are sensitive to both interfacial diffuseness and to interfacial roughness over spatial wavelengths from about 1 μ m to 10 nm.³⁹ The smallangle x-ray data are also sensitive to diffuseness, and to roughness over a larger range of spatial wavelengths, from about 5 μ m to 0.15 nm, though the effect of interfacial roughness on the x-ray reflectance [Fig. 3(a)] is greatest at the largest grazing angles. The heights of Yoneda peaks evident in the nonspecular scattering data, on the other hand, are sensitive only to correlated interfacial roughness at short spatial wavelengths (from 0.15 nm to 0.15 μ m, depending on 2θ). Therefore, because the only significant difference between the high-compressive-stress and low-compressivestress MLs evident in the x-ray data is the sharper and more intense ML Bragg peaks observed in the low-angle x-ray data, we conclude that the high-compressive-stress MLs have slightly reduced uncorrelated, high-frequency (i.e., spatial wavelengths between 0.15 and 10 nm) interfacial roughness.

AES measurements detected only trace quantities (~ 0.5 at. %) of oxygen in both high-stress and low-stress MLs, with no measurable differences between the two. Furthermore, no carbon was detected (instrumental limit of ~ 0.1 at. %) in either film. However, as can be seen from the FRS data in Fig. 4, the hydrogen concentration was found to depend strongly on the background pressure.



FIG. 4. (a) FRS spectra for selected $\Gamma = 0.625$ ML samples: $P = 1.1 \times 10^{-7}$ Torr (solid), $P = 2.0 \times 10^{-6}$ Torr (dotted), $P = 1.0 \times 10^{-5}$ Torr (dashed). (b) Average hydrogen concentration as a function of background pressure for the three samples shown in (a). The dashed line in (b) is a least-squares fit to the data.

Shown in Fig. 4(a) are FRS spectra for three representative MLs, all having Γ =0.625, but each deposited at a different background pressure. For these spectra lower H energy corresponds to greater depth into the films. The peak at channel \sim 395 arises from H at the film surface, present as adsorbed gas or as hydrocarbons due to exposure to room air. The film-substrate interface is centered at approximately channel 250. As can be seen from these curves, the average H concentration increases with increasing background pressure (as indicated by the relative areas under the curves). We also note that the distribution of H is not uniform in the films, but increases with depth into the film, as indicated by the rise in counts from just below the surface H peak towards the film-substrate interface. Presumably the decrease in H concentration as the film is deposited is a result of the normal reduction in background pressure with time [Fig. 1(b)], enhanced by the gettering action of the Mo and Si deposited on the internal surfaces of the deposition system.

Shown in Fig. 4(b) are the average H concentrations (through the film thickness) $\langle n_{\rm H} \rangle$ deduced from the FRS spectra shown in Fig. 4(a). Since the FRS results indicate that the change in H concentration is linear with background pressure [at least for the Γ =0.625 MLs shown in Fig. 4(b)], it follows that the change in ML stress also scales linearly with the log of the H concentration.

Using the stress-vs-background pressure-vs- Γ results presented in Fig. 2, we can estimate the contribution from the individual layers to the total variation in stress with pressure. The variation in ML stress with background pressure is given by

$$\sigma'_{\rm ML}(\Gamma) = \Gamma \sigma'_{\rm SI} + (1 - \Gamma) \sigma'_{\rm Mo}, \tag{4}$$

obtained by differentiating Eq. (1) (and neglecting the interfacial stress term). In this expression we are using the abbreviated notation for the derivative of stress with respect to the log of the background pressure P, i.e., $\sigma' \equiv d\sigma(P)/d \log P$. Although the values for σ_{Si} and σ_{Mo} depend, in general, on $d_{\rm Si}$ and $d_{\rm Mo}$, respectively, it is reasonable to assume that the derivatives with respect to background pressure of these quantities, i.e., $\sigma'_{\rm Si}$ and $\sigma'_{\rm Mo}$, are independent of thickness over the range of layer thicknesses investigated here. Thus, using for σ'_{ML} the slopes of the three stress-vs-background pressure curves presented in Fig. 2, there are three ways we can solve this system of three equations for the two unknown quantities σ'_{Si} and σ'_{Mo} . We find that $\sigma'_{Si} = -220 \pm 11$ MPa/log(Torr) and $\sigma'_{Mo} = 560 \pm 11$ MPa/log(Torr), where the uncertainties in these values refer to the standard deviations about the mean values for the three sets of slope values. So, according to this analysis, the change in stress in the $\Gamma=0.5$ ML films, for example, associated with the increase in background pressure from 3.3×10^{-7} to 1.5×10^{-5} Torr would be the result of the Si layers becoming more compressive by \sim 340 MPa, and the Mo layers more tensile by \sim 850 MPa. Thus, the stresses in the tensile Mo layers and the compressive Si layers both increase with increasing background pressure, and the contribution of the Mo layers to the change in ML stress with background pressure is ~ 2.5 times greater than that of the Si layers.

V. DISCUSSION

The variation in ML stress with background pressure is most likely due in some way to the reactive gas species present in the background gas and observed with the RGA (Fig. 1), i.e., hydrogen, oxygen, water, etc., as an increase in the partial pressures of these gases is correlated with an increase in tensile stress in the MLs. Because of this correlation, we attribute our observation that the ML stress is more tensile when the ion gauge is turned on during pumpdown to an increase in the partial pressures of the residual gases that affect the film stress most strongly, as a result of enhanced electron and ion stimulated desorption from the walls of the vacuum chamber.⁴⁰

Therefore, and in light of the discussion of the origins of deposition stresses in sputtered films presented in Sec. II, the most likely explanations for the observed variation in ML stress with background pressure are: (1) adsorption of impurity atoms on the surface of the film affects a number of parameters that can influence the growth process, including the surface mobility of adatoms, the probability of adatom adsorption, and the density of available surface sites; and (2) the increase in tensile stress is due to an increase in impurity atom incorporation in the film. We discuss each of these possibilities in turn.

The surface mobility of adatoms can be affected by adsorbed gas atoms, by a variety of possible mechanisms.^{19,28,41} Regardless of the details of the specific mechanisms that may be involved, we note that as the background gas partial pressure increases, the ratio of the number of residual gas atoms striking the film to the number of sputtered atoms being added to the film also increases; at the highest background gas pressures considered here, i.e., 1×10^{-5} Torr, this ratio is of order 5.⁴² It seems likely, therefore, that the observed variation in stress with background pressure is due, at least partially, to a chemically induced reduction in adatom surface mobility resulting from adsorbed residual gas atoms. We also note that our observation of increased interfacial roughness in films deposited at the highest background pressures is consistent with the tendency towards a zone 1 microstructure (and corresponding tensile stress state) associated with reduced adatom mobility.⁴¹ In particular, the increased roughness may be indicative of changes in the distribution or size of the Mo grains in the plane of the film (i.e., that were not detected by the x-ray diffraction measurements described above), which could be the cause of the change in stress.²⁰ It may also be possible that adsorbed residual gas atoms affect in some way the formation of the mixed Mo-Si interlayers in these films, thereby affecting any interfacial stresses that may be present. However, we have no evidence that there are any such stresses, so we cannot estimate quantitatively how the residual gas atoms might have an effect.

As described in Sec. II, incorporation of impurity atoms in sputtered films is known to affect film stress, though the exact mechanism by which this occurs has not been determined conclusively. In our case, we find very little incorporated oxygen and carbon; distortion of the Mo lattice, as was reported for the Mo films containing oxygen impurities investigated by Yamaguchi and Miyagawa,²⁷ was not observed in any of our films as well. We do, however, find a strong correlation between film stress and incorporated hydrogen: the ML stress varies as the log of the average hydrogen concentration; this functional dependence has not, to our knowledge, been reported previously. Our conclusion that the Si layers become more compressive with increasing background pressure is consistent with similar observation in a-Si:H films reported by Windischmann et al.²⁶ It seems likely, therefore, that the incorporated hydrogen is at least partly responsible for the observed variation of stress with background pressure.

VI. CONCLUSIONS

We have measured the stress in Mo/Si ML films deposited by magnetron sputtering and find that the stress in these films becomes increasingly tensile with increasing background pressure. The variation in the dependence of film stress with background pressure as a function of relative Mo layer thickness suggests that while the Mo layers become more tensile with increasing background pressure, the Si layers become more compressive. We find that the variation in ML stress correlates with the concentration of incorporated hydrogen in these films, i.e., increasing hydrogen concentrations correspond to more tensile films. The concentration of

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hydrogen varies linearly with background pressure. The concentrations of oxygen and carbon were found to be very small, and were uncorrelated with stress. The only evidence for microstructural variations in these films was a slight increase in the uncorrelated, high-frequency interfacial roughness with increasing background pressure (as determined from small-angle x-ray scattering,) suggesting a tendency towards tensile, zone 1-type microstructure with increasing background pressure.

The most likely explanations for the observed variation in ML stress with background pressure are first, that the stress is due to incorporation of hydrogen atoms, and second, that the surface mobility of adatoms is decreased with increasing background pressure, most likely due to the effect of adsorbed residual gas atoms. From our measurements alone we cannot provide any further information regarding the details of how these two possible mechanisms affect film stress.

We note that Mo/Si MLs (Γ =0.625, d=6.9 nm) deposited at high background pressure still show high soft x-ray reflectance. This implies that the stress in such films can and should be minimized by controlling the background pressure, or perhaps by the deliberate introduction of impurity gases, in order to reduce the deformation of the substrate in x-ray imaging applications such as projection lithography. Our results also indicate that the background pressure of the deposition system must be controlled in order to produce low-stress films with good repeatability. Indeed, the dependence of stress on background pressure may be the cause of the scatter in some of the stress data reported in the literature.^{43,44}

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¹B. M. Clemens and R. Sinclair, Mater. Res. Soc. Bull. XV, 19 (1990), and references therein.

- ²I. K. Schuller, J. Guimpel, and Y. Bruynseraede, Mater. Res. Soc. Bull. XV, 29 (1990), and references therein.
- ³J. E. Bjorkholm, J. Bokor, L. Eichner, R. R. Freeman, J. Gregus, T. E. Jewell, W. M. Mansfield, A. A. MacDowell, E. L. Raab, W. T. Silfvast, L. H. Szeto, D. M. Tennant, W. K. Waskiewicz, D. L. White, D. L. Windt, and O. R. Wood, II, J. Vac. Sci. Technol. B 8, 1509 (1990).
- ⁴J. B. Kortright and J. H. Underwood, Nuc. Instrum. Methods Phys. Res. A 291, 272 (1990).
- ⁵J. B. Kortright and R. S. DiGennaro, Rev. Sci. Instrum. **60**, 1995 (1989).
 ⁶C. M. Falco and I. K. Schuller, in *Synthetic Modulated Structures*, edited by L. L. Chang and B. C. Giessen (Academic, Orlando, FL, 1985), pp. 339-364.

- ⁷T. W. Barbee, Mater. Res. Soc. Bull. XV, 37 (1990), and references therein.
- ⁸J. A. Thornton and D. W. Hoffman, J. Vac. Sci. Technol. 14, 164 (1977).
- ⁹D. L. Windt, R. R. Kola, W. K. Waskiewicz, R. Hull, J. Griffith, and D. A. Grigg, Tech. Dig. Opt. Soc. Am. 7, 12 (1992).
- ¹⁰ R. R. Kola, D. L. Windt, W. K. Waskiewicz, B. E. Wier, R. Hull, G. K. Celler, and C. A. Volkert, Appl. Phys. Lett. **60**, 3120 (1992).
- ¹¹A. K. Petford-Long, M. B. Stearns, C. H. Chang, S. R. Nutt, D. G. Stearns, N. M. Ceglio, and A. M. Hawryluk, J. Appl. Phys. **61**, 1422 (1987); K. Holloway, K. B. Do, and R. Sinclair, *ibid*. **65**, 474 (1989); D. G. Stearns, M. B. Stearns, Y. Cheng, J. H. Stith, and N. Ceglio, *ibid*. **67**, 2415 (1990); R. S. Rosen, M. A. Viliardos, D. G. Stearns, M. E. Kassner, and S. P. Vernon, Proc. SPIE **1547**, 212 (1991); D. L. Windt, R. Hull, and W. K. Waskiewicz, J. Appl. Phys. **71**, 2675 (1992).
- ¹² J. W. Cahn and F. Larche, Acta Metall. 30, 51 (1982).
- ¹³ J. A. Ruud, A. Witvrouw, and F. Spaepen, J. Appl. Phys. 74, 2517 (1993).
- ¹⁴J. A. Bain, L. J. Chyung, S. Brennan, and B. M. Clemens, Phys. Rev. B 44, 1184 (1991).
- ¹⁵W. D. Nix, Metal. Trans. A 20A, 2217 (1989).
- ¹⁶H. Windischmann, J. Vac. Sci. Technol. A 9, 2431 (1991).
- ¹⁷R. E. Somekh, J. Vac. Sci. Technol. A 2, 1285 (1984).
- ¹⁸G. S. Bales and A. Zangwill, J. Vac. Sci. Technol. A 9, 145 (1991).
- ¹⁹ J. A. Thornton, J. Vac. Sci. Technol. 11, 666 (1974).
- ²⁰F. A. Doljack and R. W. Hoffman, Thin Solid Films 12, 71 (1972).
- ²¹ F. M. D'Heurle, Metall. Trans. 1, 725 (1970).
- ²²C. C. Fang, F. Jones, and V. Prasad, J. Appl. Phys. 74, 4472 (1993).
- ²³ P. R. Stuart, Vacuum 19, 507 (1969).
- ²⁴ P. M. Alexander and R. W. Hoffman, J. Vac. Sci. Technol. 13, 96 (1976).
- ²⁵R. A. Roy and R. Messier, J. Vac. Sci. Technol. A 2, 312 (1984).
- ²⁶ H. Windischmann, R. W. Collins, and J. M. Cavese, J. Non-Cryst. Solids 85, 261 (1986).
- ²⁷ T. Yamaguchi and R. Miyagawa, Jpn. J. Appl. Phys. **30**, 2069 (1991).
- ²⁸ R. Abermann, Mater. Res. Soc. Symp. Proc. **239**, 25 (1992).
- ²⁹D. L. Windt and W. K. Waskiewicz, J. Vac. Sci. Technol. B **12**, 3826 (1994).
- ³⁰G. G. Stoney, Proc. R. Soc. London Ser. A **82**, 172 (1909).
- ³¹C. A. Volkert, J. Appl. Phys. **70**, 3251 (1991).
- ³²W. A. Brantley, J. Appl. Phys. **44**, 534 (1973).
- ³³D. L. Windt and W. K. Waskiewicz, Proc. SPIE 1547, 144 (1991).
- ³⁴D. G. Stearns, J. Appl. Phys. 71, 4286 (1992).
- ³⁵L. C. Feldman and J. W. Mayer, Fundamentals of Surface and Thin Film Analysis (Elsevier Science, New York, 1986).
- ³⁶ Yoneda, Phys. Rev. 131, 2010 (1963).
- ³⁷B. D. Cullity, *Elements of X-Ray Diffraction* (Addison-Wesley, Reading, MA, 1987), p. 284.
- ³⁸ Handbook of Tables For Applied Engineering Science, edited by R. E. Bolz and G. L. Tuve (CRC, Boca Raton, FL, 1991).
- ³⁹ D. L. Windt, W. K. Waskiewicz, and J. E. Griffith, Appl. Opt. **33**, 2025 (1994).
- ⁴⁰M. Andritschky, Vacuum 42, 753 (1991).
- ⁴¹ R. Messier, A. P. Giri, and R. A. Roy, J. Vac. Sci. Technol. A 2, 500 (1984).
- 42 C. M. Falco, J. Appl. Phys. 56, 1218 (1984).
- ⁴³T. D. Nguyen, X. Lu, and J. H. Underwood, *The Physics of X-Ray Multilayer Structures*, 1994 Technical Digest Series, Vol. 6 (Optical Society of America, Washington, DC, 1994), pp. 102-105.
- ⁴⁴R. R. Kola, G. K. Celler, J. Frackoviak, C. W. Jurgensen, and L. E. Trimble, J. Vac. Sci. Technol. B 9, 3301 (1991).