

Low-stress W/Cr films for SCALPEL[®] mask scattering layers

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I describe the development of low-stress W/Cr bilayer films, for use as SCALPEL[®] mask scattering layers. These films are produced by dc magnetron sputtering in argon, and consist of 25–50-nm-thick W layers deposited onto 5–10-nm-thick Cr layers. X-ray reflectance analysis is used to measure the thicknesses of the individual W and Cr layers with subangstrom precision; surface and interface roughnesses, film densities, and also the thickness of the tungsten–oxide overlayer which forms after exposure to air are determined by this technique as well. Film stress, which is measured using the wafer curvature technique, is controlled by adjusting the deposition conditions such that the Cr layers are in tension while the W layers are in compression (and thus have high density and low surface roughness), so that the net stress in the bilayer is balanced near zero. I present data that illustrates how the net stress in these films varies with argon pressure, background pressure (i.e., partial pressure of residual gases present in the vacuum chamber), and Cr layer thickness. I also show how the stress depends on the composition of the substrate: i.e., stresses measured in films deposited onto Si wafers are systematically higher (by several hundred MPa) than the stresses measured for the same films deposited onto silicon–nitride-coated Si wafers. I discuss the implication of these results with regard to the production of high-quality SCALPEL[®] mask blanks for sub 0.12 μm lithography. © 1999 American Vacuum Society. [S0734-211X(99)07604-0]

I. INTRODUCTION

The SCALPEL^{®1} electron beam projection lithography system requires masks consisting of a patterned “scattering” layer, i.e., composed of material having a relatively large scattering cross section for 100 keV electrons (e.g., W) formed on a supporting membrane composed of material having a relatively small scattering cross section for electrons (e.g., silicon–nitride.) The supporting silicon–nitride membrane is in slight tension, in order to maintain flatness, and the stress in the W scattering layer must be minimized as much as possible in order to reduce pattern-placement errors. The polycrystalline W layers should ideally consist of small columnar grains, in order to minimize line-edge roughness, and should have a high density, in order to minimize voids, and also to minimize the film thickness (and thus the aspect ratio of patterned features) required for high electron contrast.

Previous efforts to produce low-stress W films, for use in masks for x-ray lithography,² for instance, attempted to exploit the widely known dependence of stress with sputter-gas (e.g., argon, typically) pressure observed in metal films prepared by sputtering.³ However, this approach proved unsatisfactory, for the following reasons. First, the variation in stress with argon pressure is quite large near the zero stress point, and so it is difficult to control the pressure with sufficient accuracy. Second, the microstructure of the film also varies strongly with argon pressure,⁴ essentially for the same reasons that the stress does: at low argon pressure, because of the large amount of kinetic energy (~ 100 eV/Ar atom) delivered to the surface of the growing film by neutral argon atoms reflected from the sputtering target, through the so-

called “atomic peening” effect,⁵ the film consists of tightly packed columnar grains, with high density and low surface roughness, and consequently has a large compressive stress; at higher pressure, the reflected neutral argon atoms suffer more collisions in the gas phase and thus deliver less kinetic energy to the surface of the growing film, which is thus more porous, consisting of loosely packed grains and a large number of voids, with low density and high surface roughness, and consequently has a large tensile stress. Because of this variation in stress and microstructure with argon pressure, the sputter-gas pressure for which the stress is close to zero results in films having a microstructure that is somewhere between the two extreme cases just described, which is undesirable with regard to the requirement of minimal line-edge roughness in the finely patterned features needed for sub 0.12 μm lithography.

The approach presented here to produce low-stress scattering layers for SCALPEL[®] masks also makes use of the variation in film stress with argon pressure just described, but with one crucial difference: rather than attempting to find the deposition conditions (i.e., argon pressure) that give rise to near-zero stress in the W layer, instead we attempt to balance the stress in the W layer with the stress in an underlying layer of Cr (which also serves as a dual purpose as an etch stop layer, and acts to mitigate membrane charging during e-beam exposure). This technique takes advantage of the fact that the “transition pressure,” i.e., the pressure at which the stress in a sputtered film changes from compressive to tensile, also depends on the atomic mass of the adatom relative to the atomic mass of the working gas.³ Specifically, in the case of W and Cr films sputtered in argon, this transition pressure is larger for W than it is for Cr, and thus there exists (in general) a range of argon pressures for which the W is in

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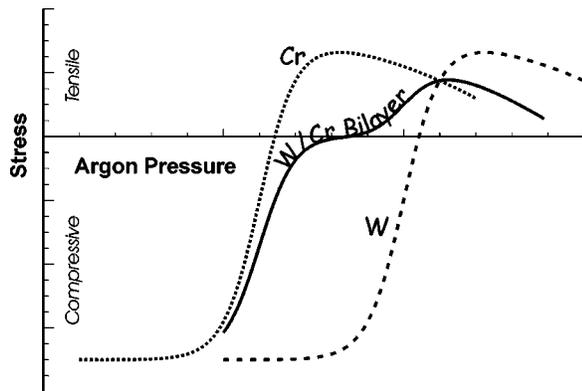


FIG. 1. Diagram showing conceptually how the stress varies with argon pressure in single-layer W and Cr layer films, and in a W/Cr bilayer film.

compression while the Cr is in tension; with a suitable choice of W and Cr layer thicknesses (consistent with the requirements on electron contrast¹), the net stress in the bilayer can be made to balance. Although the bilayer stress still depends strongly on the argon pressure, the variation in stress with pressure is much less sensitive than in the case of a single-layer film, as illustrated schematically in Fig. 1. Furthermore, the W layer remains in compression and thus consists of the more desirable fine-grained, high-density, low-roughness material.

In Sec. II, I describe the preparation of such low-stress W/Cr bilayer films, and the characterization of these films using x-ray reflectance analysis for the precise determination of layer thicknesses, roughnesses and densities. In Sec. III, I present experimental results illustrating the dependence of film stress on argon pressure, Cr layer thickness, and background pressure (i.e., partial pressure of residual gases present in the vacuum system during deposition). I also present results showing that the stress in these films depends strongly on the composition of the substrate on which they are grown. Finally, in Sec. IV, I discuss the implications of these results with regard to the production of high-quality SCALPEL® mask blanks for sub μm lithography.

II. FILM PREPARATION AND CHARACTERIZATION

The films described here are grown by dc magnetron sputtering in argon of 99.999% purity, using a deposition system having sub-angstrom film thickness control for the production of multilayer x-ray optics that has been described previously.⁶ The system is cryo-pumped, and the argon pressure is maintained with a closed-loop gas-flow system using a capacitance manometer and a mass-flow controller. In all cases, the power to each of the two 50-cm-long \times 9-cm-wide planar magnetrons, i.e., one for W (99.95% purity), one for Cr (99.99% purity), is fixed at 200 W, and the individual film thicknesses are adjusted by varying the rotational velocity of the substrate (which faces downward) as it travels over the sources (which face upward, 10 cm below the plane of the substrate). The deposition rates are typically of order 0.18 nm/s for W and 0.24 nm/s for Cr (with a slight dependence on argon pressure), and are computed from the

film thicknesses determined by x-ray reflectance analysis, described below. Except where noted, the samples described here were grown on (unheated) 14 mm \times 14 mm, 100- μm -thick Si wafer substrates having a thin (\sim 2–3 nm) native oxide layer.

X-ray reflectance measurements are made as a function of grazing incidence angle at a fixed wavelength, using a four-circle diffractometer with a rotating anode x-ray source having a Cu target, and a pyrolytic graphite monochromator tuned to the $\text{CuK}\alpha$ line near 8 keV (1.54 \AA). Reflectance measurements are typically made for incidence angles in the range $0^\circ < \theta < 4^\circ$, which in most cases discussed here corresponds to a span of roughly seven orders of magnitude in reflected intensity. The angular resolution of the diffractometer is \sim 0.02°, and measurements are typically made every 0.01°, conditions that are just sufficient to resolve the thickness fringes for the thickest films (\sim 50 nm W/10 nm Cr) discussed here.

Fits to the x-ray reflectance data, performed with the IMD software package,⁷ are used to determine film thicknesses, densities and roughnesses, for both the W and Cr layers, as well as for the tungsten-oxide overlayer (assumed to be WO_3) that apparently forms on these films after exposure to air. With this technique, the measured reflectance versus incidence angle data are compared with a theoretical reflectance curve computed using an algorithm based on recursive application of the Fresnel equations; the formalism described by Stearns⁸ is used to account for the effects of interfacial roughness (or diffuseness). Nonlinear, least-squares curve fitting can be used to fit the data, but in many cases simply taking advantage of IMD's ability to "manually" vary several adjustable parameters simultaneously is a more efficient approach, particularly for the highly oscillatory reflectance data typical of these films. The effect on the resultant reflectance curve is significantly different for each of the adjustable parameters (i.e., film thicknesses, roughnesses, and densities) used to fit the data, and so each of these parameters can be determined uniquely, in general. The sensitivity of the x-ray reflectance analysis technique to layer thicknesses and roughnesses is particularly high—typically these parameters can be determined with a precision of better than 0.1 nm—but the sensitivity to film density is much worse: the precision with film density can be determined is generally no better than about 10%.

To illustrate, shown in Fig. 2 is the measured x-ray reflectance for a W(\sim 20 nm)/Cr(\sim 4.5 nm) bilayer film. The best-fit curve (labeled " $\sigma=3.5 \text{ \AA}$," i.e., corresponding to a WO_3/W interface roughness of 3.5 \AA) was obtained by fitting eight adjustable parameters: the densities, layer thicknesses, and interface roughnesses of both the W and Cr layers, as well as the thickness and roughness of the WO_3 overlayer; the best-fit parameters are indicated. Also shown are curves computed using other WO_3/W interface roughness values, illustrating the strong effect of this particular parameter on the computed reflectance. The high-frequency and low-frequency modulations in the reflectance data (having periods of \sim 0.18° and \sim 1.0°) correspond to interfer-

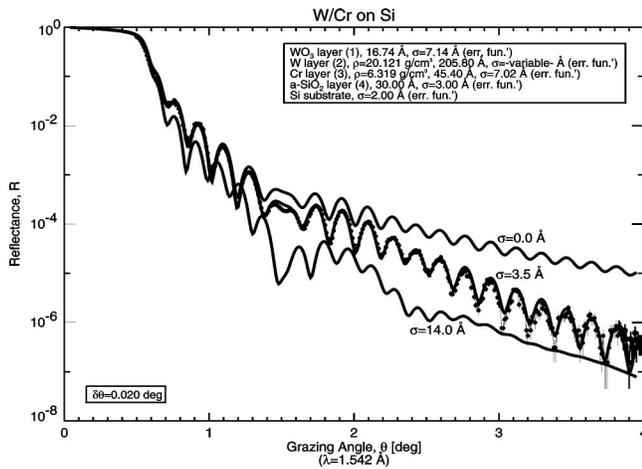


FIG. 2. Typical x-ray reflectance-vs-incidence-angle data for a W/Cr bilayer film. Calculated reflectance curves for three values of the WO_3/W interfacial roughness are shown; the best-fit curve (labeled “ $\sigma=3.5 \text{ \AA}$ ”) to the measured data (filled circles) was obtained using nonlinear, least-squares curve fitting, with eight adjustable parameters as indicated.

ence due to the total film thickness (i.e., $\text{WO}_3 + \text{W} + \text{Cr}$ layer thicknesses) and the Cr layer thickness, respectively. But note that these thickness modulations shift measurably with WO_3/W interface roughness; in general, although each of the fit parameters can ultimately be determined uniquely, the fact that many parameters are often coupled adds to the complexity of finding the best-fit parameters.

III. FILM STRESS

Film stress is measured using the wafer curvature technique, with an instrument that has been described previously.⁹ With this technique, the net film stress is determined using Stoney’s equation¹⁰ from the measured change in radius of curvature of the thin substrate; the radius of curvature of the substrate is determined by measuring precisely the deflection of a laser beam as it is scanned along the length of the sample. The experimental uncertainty in the measured film stress is larger on the small wafer sections used here (relative to measurements on full-sized wafers) as a result of the larger relative uncertainty in the substrate thickness, and also because of the larger uncertainty in the determination of the change in radius of curvature of these samples associated with the smaller scan lengths. In all cases presented below, scans were made at several positions on the substrate, resulting in scatter in the data between different measurements for a given sample.

Shown in Fig. 3 is the stress in sputtered W(50 nm)/Cr(25 nm) films as a function of argon pressure, in the range $P_{\text{Ar}}=2.1\text{--}2.8$ mTorr. In this case, the background pressure in the vacuum chamber prior to film deposition was $5.0\pm 0.1\times 10^{-6}$ Torr for all samples. The variation in stress with pressure is approximately linear, ranging from ~ 200 MPa compressive for $P_{\text{Ar}}=2.10\pm 0.01$ mTorr, to ~ 350 MPa tensile for $P_{\text{Ar}}=2.80\pm 0.01$ mTorr, and the films having the lowest stress were grown at an argon pressure of 2.35 ± 0.01 mTorr. The scatter in the stress data for multiple mea-

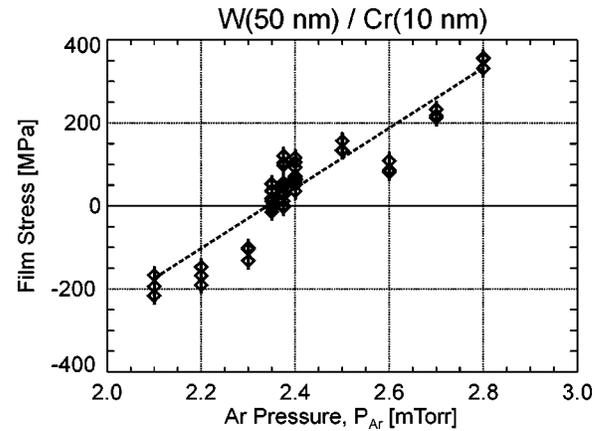


FIG. 3. Measured stress in W(50 nm)/Cr(25 nm) films as a function of argon pressure. The dashed line is a linear fit to the data.

surements made on multiple samples is roughly ± 40 MPa. We note that, although the sputter target voltages can vary with argon pressure, in principle, and the voltages can in turn affect the amount of energy delivered by argon ions to the surface of the growing film (which can thus affect the film stress and microstructure), in this case the target voltages varied by less than ~ 5 out of ~ 340 V (i.e., $\sim 1.5\%$) over this range of argon pressures; given the large amount of energy delivered to the surface of the growing film by reflected neutral argon atoms (i.e., ~ 100 eV/atom), the variation with argon pressure in energy delivered by argon ions is thus negligible.

In a previous investigation,¹¹ the stress in Mo/Si x-ray multilayer films were found to depend strongly on the background pressure of the vacuum system. We find a similar result for W/Cr bilayer films, as indicated in Fig. 4, which shows the stresses measured as a function of background pressure for W(50 nm)/Cr(10 nm) films deposited at an argon pressure of $P_{\text{Ar}}=2.40\pm 0.01$ mTorr. The background pressure was measured with an ionization gauge just prior to film deposition, and was adjusted by varying the pumpdown time of the vacuum system: the pumpdown time ranged from ~ 90 min for samples grown at $P_{\text{background}}=5.0\times 10^{-6}$ Torr,

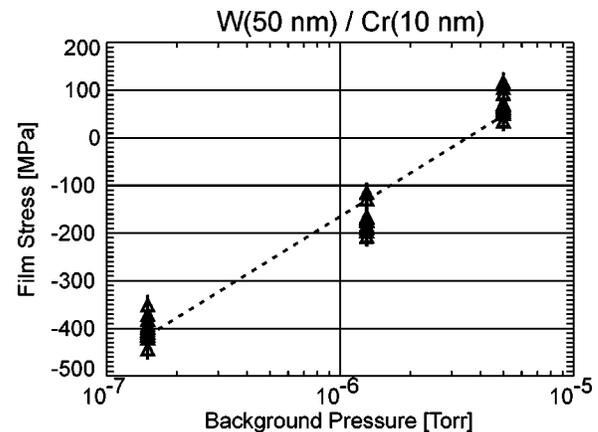


FIG. 4. Measured stress in W(50 nm)/Cr(25 nm) films as a function of background pressure. The argon pressure was fixed at 2.4 mTorr in this case. The dashed line is a linear fit to the data.

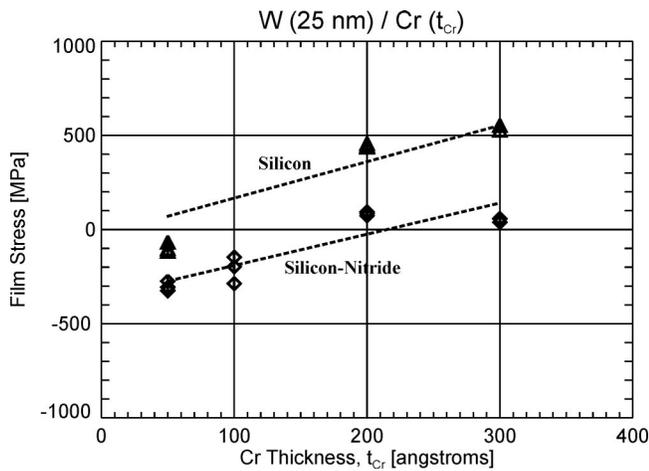


FIG. 5. Measured stress in W/Cr films containing 25-nm-thick W layers, as a function of Cr layer thickness. Stresses are shown for films deposited onto both bare and silicon-nitride-coated silicon substrates, as labeled. The dashed lines are linear fits to the data.

to ~ 24 h for samples grown at $P_{\text{background}} = 1.5 \times 10^{-7}$ Torr. As in the case of the Mo/Si multilayer films reported previously, the stress is highly compressive in W/Cr bilayer films prepared at low background pressure (~ -400 MPa), and is tensile ($\sim +60$ MPa) for those grown at high background pressure. In the case of Mo/Si multilayers, x-ray diffraction measurements revealed no observable microstructural changes, but forward recoil scattering measurements indicated that the concentration of hydrogen in films varied from ~ 0.5 at. % for films grown at low background pressure to ~ 2.0 at. % for those grown at high background pressure; the variation in stress with background pressure was thus attributed to this measured variation in hydrogen concentration, although the precise mechanisms responsible for the stress variations were not identified conclusively. In the case of the W/Cr films shown in Fig. 4, x-ray diffraction also reveals no microstructural variations. Forward recoil scattering measurements were not performed on any of the W/Cr samples discussed here, but it is possible that a similar systematic variation in hydrogen concentration might be found. As in the case of the stress-versus-argon-pressure data shown in Fig. 3, the small ($\sim 3\%$) variation in target voltage with background pressure for the data in Fig. 4 is unlikely to have a significant affect on the bilayer stress.

The variation in stress in W/Cr bilayer films containing 25-nm-thick W layers as a function of Cr layer thickness is shown in Fig. 5, for films deposited onto Si wafer substrates. The stress increases by several hundred MPa as the Cr layer thickness is increased from 5 to 30 nm. Because the net stress in the bilayer depends on the stresses in W and Cr layers, weighted by the respective W and Cr layer thicknesses, this result clearly indicates that the Cr layers are in tension, as thicker Cr layers result in more tensile films. Also shown in Fig. 5 are the stresses measured in identical films (i.e., grown during the same deposition cycle) but deposited onto 100- μm -thick Si wafers that were coated [by chemical vapor deposition (CVD)] with ~ 120 nm of silicon-nitride.

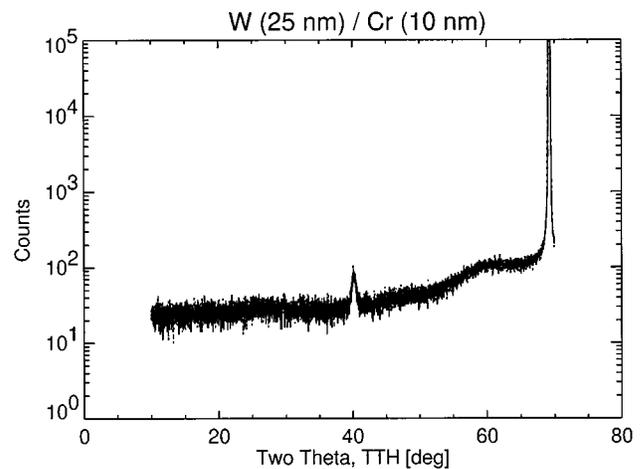


FIG. 6. Large-angle x-ray diffraction data (obtained in the θ - 2θ geometry) for W(25 nm)/Cr(10 nm) films grown on both bare (solid lines) and silicon-nitride-coated (dashed lines) silicon substrates. The curves are nearly indistinguishable. The peaks near $2\theta = 40.5^\circ$ are due to diffraction from the bcc W (110) lattice planes, while the sharp peaks near $2\theta = 69^\circ$ are due to diffraction from the silicon substrate. The broad peaks near $2\theta = 60^\circ$ are due to diffraction from the (amorphous) native silicon-oxide layer present on the silicon substrates prior to coating.

The stresses in the films grown on silicon-nitride are systematically lower—by several hundred MPa—than those grown on Si. The difference in the stresses for films grown on silicon versus silicon-nitride can be due to differences in the interfacial stresses present at the Cr-substrate interface, or possibly due to differences in the microstructure of the two films.¹² However, large-angle x-ray diffraction measurements made on these films reveal no microstructural differences, as shown in Fig. 6, for example, suggesting that the difference in stress is predominantly due to interfacial stress differences.

IV. CONCLUSIONS

I have described an approach to produce low-stress W/Cr bilayer films suitable for use as scattering layers in SCALPEL® masks for sub 0.12 μm lithography. The films are grown by magnetron sputtering in argon: the deposition conditions are adjusted so that the W layers are in compression and the Cr layers in tension, so that for a given set of layer thicknesses (as driven by the requirements on electron contrast), the net stress in the bilayer is minimized by balancing the stresses in the two metal layers, and yet the compressive W layer is composed of the more desirable fine-grained, high-density, low-roughness material. X-ray reflectance analysis can be used to determine with high precision layer thicknesses, roughnesses and densities.

I have shown that the stress in these films depends on the argon pressure, the background pressure, and the Cr layer thickness, and also depends on the composition of the substrate—stresses measured in W/Cr bilayers deposited onto Si wafers are systematically higher (by several hundred MPa) than the stresses measured for the same films deposited onto silicon-nitride-coated wafers; these results have the following implications for the production of high-quality

SCALPEL® mask blanks. First, to produce films with consistently low stress, it is clearly necessary to control precisely both the argon pressure and the background pressure of the vacuum system. Other deposition conditions that are known to affect films stress, such as magnetron power, source-to-substrate distance, etc., will almost certainly need to be controlled with high precision as well. Second, if such films are to be grown on silicon–nitride-coated substrates, then one must take into account the differences in the composition (and undoubtedly the cleanliness as well) of thin-wafer substrates (suitable for wafer-curvature measurements) that might be used to calibrate the dependence of stress with deposition conditions.

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¹²The stress difference could also be due, in principle, to the small difference in the coefficients of thermal expansion between silicon and silicon–nitride; but to explain the measured stress difference of several hundred MPa measured here would require a substrate temperature of roughly 5000 °C during deposition, which is completely unreasonable.