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Final Report on this project summarizing the principle results, publications and personnel.

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GROWTH AND CHARACTERIZATION OF REFRACTORY METAL MULTILAYERS:POTENTIAL ULTRA-HIGH STRENGTH-HIGH TEMPERATURE SURFACE COATINGS

FINAL REPORT:

December 31, 1996

by

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GROWTH AND CHARACTERIZATION OF REFRACTORY METAL MULTILAYERS: POTENTIAL ULTRA-HIGH STRENGTH-HIGH TEMPERATURE SURFACE COATINGS

Brief Outline of Research Findings:

A Detailed reports of the findings of this project will be found in the various publications, reports, and Thesis documents written as a result of this research. Two important fundamental results have been achieved which have broad application to the whole field of thin films and multilayer coatings.

1) **Residual Stress**: The first is that residual stress plays a key role in determining the ultimate properties of any coating. The synchrotron has proven valuable in determining residual stresses for films as thin as 2.5nm and as thick as 60μm. New techniques have been developed to achieve these results and to extend the measurements of residual stresses to buried layers.

2) **Texture:** The second key finding is the ability to control texture both out-of-plane and in-plane has been demonstrated for a variety of refractory metal films and multilayer combinations. The texture work has likewise been able to show the evolution of complex textures via a combination of high resolution synchrotron grazing angle incident (GIXS) scattering and high resolution electron microscopy (HREM).

A description of the synchrotron GIXS type of analysis that has been pioneered for studies of texture evolution follows.

Experiments have shown that the degree of *in-plane* texturing during thin film deposition scales with the film's thickness [1]. Further experimentation on thin films deposited onto purposely anisotropically roughened surfaces shows that the rate of *in-plane* texturing is dependent upon the roughened surface's orientation with respect to deposition chamber geometry [2]. A novel method for quantifying these effects uses grazing incidence x-ray scattering (GIXS). In GIXS mode, the phenomenon of total external reflection of the incident monochromatic x-ray beam is used to control its penetration depth

Data collected using the symmetric GIXS geometry can be analyzed to determine both the preferred orientation (*out-of-plane* and *in-plane*) and the textured volume fraction of thin films at various film thicknesses and as a function of penetration depth [3].

Experiment:

All GIXS experiments were conducted on the eight-pole focused wiggler station on beamline 7-2 (BL 7-2) of the Stanford Synchrotron Radiation Laboratory (3 GeV and 100 mA at fill). A Si (111) double-crystal monochromator was used to select the wavelength of the x-ray beam, 0.124 nm (10 keV) in focused mode. The diffracted x-rays were detected using a sold-state Ge detector, cooled with liquid nitrogen. Samples were mounted onto an automated Hüber 5020 four-circle diffractometer. All experiments were conducted in "dose" mode, in order to eliminate the effects of beam instabilities and beam decay as a function of time. Appropriate photon doses were measured with a scintillation detector, which was placed upstream of the incident beam slits. Samples were placed in a He gas-filled enclosure to minimize air scattering.

A GIXS Bragg geometry was used to collect diffraction information from planes nearly perpendicular to the film surface. For each sample, the Bragg conditions for Mo (110), Mo (200) and Mo (211) peaks were identified, $2\theta \approx 32.38°$, $2\theta \approx 46.53°$ and $2\theta \approx 57.78°$, respectively. Once these diffraction conditions were established, each sample was rotated about its surface normal (through ϕ) to collect information about the *in-plane* distribution of Mo {110}, {200} and {211} planes. Penetration depths were controlled by varying the incident angle of the x-ray beam close to the angle for total external reflection. The penetration depths were determined to an accuracy of ≈ 10 nm, except very near the critical angle where the accuracy was ≈ 15 nm. A total of 14 Mo films were analyzed: 1 film 40 nm thick, 3 films 80 nm thick, 3 films 200 nm thick, 2 films 500 nm thick, 3 films 1 μm thick and 2 films 2 μm thick. Diffraction data was collected for Mo (110), (200) and (211) peaks at five different penetrations (3).

Analysis

Thickness dependent texturing of films

For films with well defined *in-plane* textures, the texture orientation can be assessed by noting the symmetry and position of different {hkl} peaks in the diffraction patterns. The diffraction patterns in figure 1 shows a two-fold *in-plane* symmetry, with the {110} peaks positioned 90° apart from one another. This particular distribution of peaks at the zone edge corresponds to a (110) texture (i.e. both *out-of-plane* and *in-plane* textures are present). Data obtained from the GIXS experiments provided information concerning the azimuthal distribution of Mo {110}, Mo {200} and Mo {211} planes nearly perpendicular to the film surface. Representative data, collected from the top ≈100 nm of films 80 nm, 200 nm, 500 nm and 1 μm in thickness, is shown in figure 2.

Data obtained from the GIXS experiments provided information concerning the azimuthal distribution of Mo {110}, Mo {200} and Mo {211} planes nearly perpendicular to the film surface. Representative data, collected from the top ≈100 nm of films 80 nm, 200 nm, 500 nm and 1 μm in thickness, is shown in figure 2.

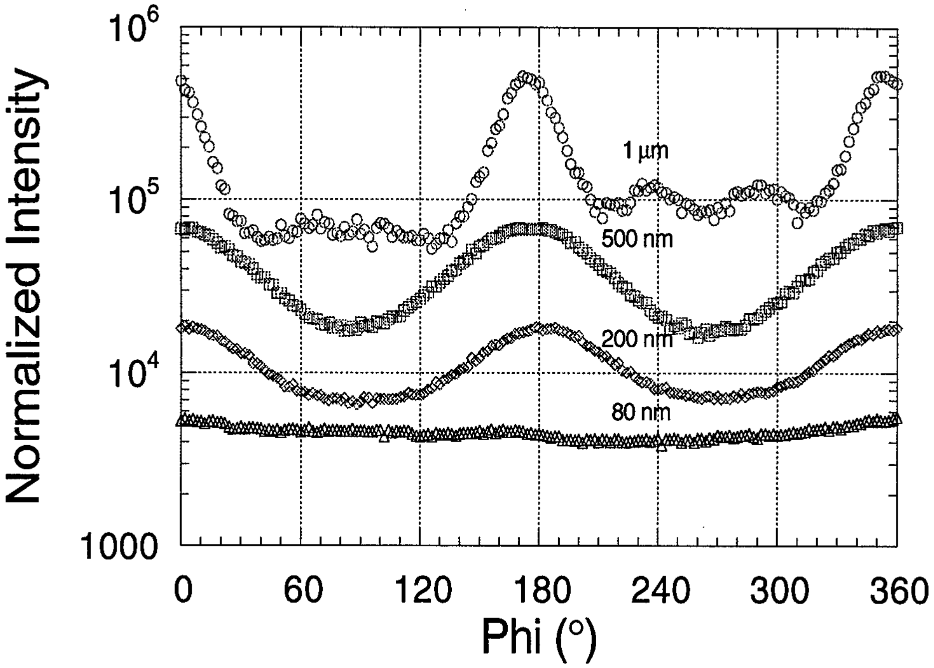

Figure 1: Plot showing the detected diffraction intensity in a Mo (110) diffraction pattern, as a function of azimuthal angle. Diffraction patterns collected from Mo films of thickness 80 nm, 200 nm, 500 nm and 1 µm at an x-ray penetration depth of ≈ 100 nm are displayed [3]. Similar data was obtained for the (200) and (211) diffraction planes.

Data obtained from the GIXS experiments provided information concerning the azimuthal distribution of Mo {110}, Mo {200} and Mo {211} planes nearly perpendicular to the film surface. Representative data, collected from the top ≈100 nm of films 80 nm, 200 nm, 500 nm and 1 µm in thickness, is shown in figure 1.

The azimuthal variation in diffracted intensity clearly shows an anisotropic distribution of {110} planes *in the plane* of growth. Similar effects are seen for {200} and {211} planes (3).

To quantify the *in-plane* texture as a function of film thickness, it is necessary to calculate the volume fraction of the film which is textured (V^{tex}) at each penetration depth (d). This can be accomplished by dividing the integrated "textured" intensity (I^{tex}) of the diffraction pattern, by the total integrated intensity (I^{tot}) of the diffraction pattern, $V^{tex} = I^{tex}/I^{tot}$. Similarly, the volume fraction of the film which is randomly oriented (V^{ran}), can be calculated by dividing the integrated "random" intensity (I^{ran}), by the total integrated intensity (I^{tot}) of the diffraction pattern, $V^{ran} = I^{ran}/I^{tot}$. For these expressions, I^{tex} and I^{ran} can be obtained by fitting individual diffraction peaks with Gaussian profiles. The results of this analysis on Mo (110) and (200) diffraction patterns for Mo films 80 nm to 2 μm thick are shown in figure 2.

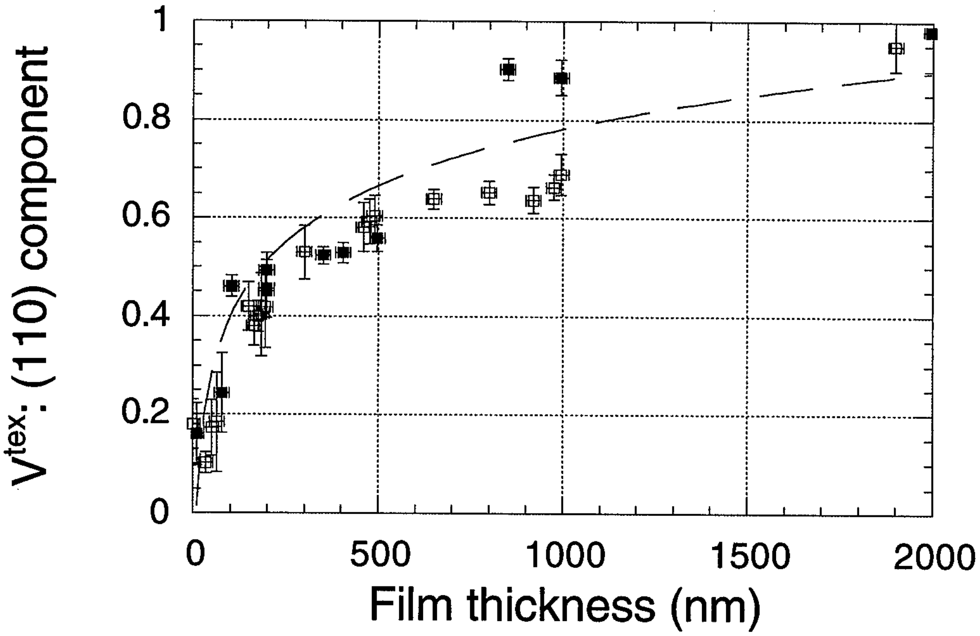

Figure 2: Plot showing variation in calculated values of V^{tex} as a function of film thickness. Values for V^{tex} were calculated from individual diffraction patterns collected at various x-ray penetration depths for films 80 nm, 200 nm, 500 nm, 1 μm and 2 μm thick [3].

Conclusions

Using a GIXS configuration on BL 7-2, the orientation of film texture (both *out-of-plane* and *in-plane*) can be determined by analyzing the distribution of diffraction intensities in diffraction patterns. Textures can be quantified by calculating textured and random volume fractions as a function of film thickness. This method was applied to the analysis of texturing in thin sputter deposited Mo films.

It is planned to extend this would to a more quantitative physical model which incorporates the atomistic mechanisms of growth. It is also planned to extend this to rough surfaces, which are germane to "real" film coating environments.

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Final Report

Appendix I

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Appendix II

Publications

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