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A Transmission Electron-Microscopy Study of RF-Magnetron-Sputtered and DC-Magnetron-Sputtered Thin-Film Chromium and Chromium Platinum Coatings

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A transmission electron microscopy study of rf- and dc-magnetron-sputtered thin film chromium and chromium-platinum coatings

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Microstructural features of sputtered chromium and chromium-50 wt.% platinum thin films on carbon substrates are presented. Films produced by rf sputtering and dc magnetron sputtering are compared using analytical electron microscopy techniques. All rf-sputtered films are uniform in chemistry and thickness and are amorphous. The chromium film became crystalline with a grain size of less than 100 Å after a 320 °C heat treatment for 1 h. The chromium-50 wt. % platinum film remained amorphous after the same heat treatment. The as-sputtered dc magnetron chromium film was crystalline.

I. INTRODUCTION

The microstructure of sputtered metal films depends in a complex manner on many factors. Included are the nature of the metals or alloys being deposited, the characteristics of the substrate and the specific method of deposition.^{1,2-4} Metastable phases have also been observed to form during deposition of the thin film and during low temperature annealing.⁵ In this study, pure chromium and a 50% chromium-platinum alloy were rf sputtered perpendicularly onto unheated thin film amorphous carbon substrates to evaluate the effects of alloying on the microstructure of the film. As-deposited films were subsequently heat treated at 360 °C in a protective nitrogen atmosphere to evaluate microstructural stability. A comparison of rf- and dc-magnetron sputtered chromium films was also undertaken to determine effects related to the rate of sputtering for the same substrate and alloy conditions. The usual dc magnetron sputtering rate is over 10 times the rf sputtering rate.

II. EXPERIMENTAL PROCEDURES

Amorphous carbon films approximately 750 Å in thickness were prepared by vapor deposition of carbon onto Bioten in a vacuum of 1×10^{-5} Torr. The carbon films were stripped from the plastic in acetone and floated onto 3 mm electron microscope specimen grids. Sputtering of the appropriate alloy under the desired conditions was performed onto carbon films to a thickness of approximately 600 Å. Metallographic examination was performed in a JEOL 100C analytical electron microscope with a Kevex 7000 energy dispersive x-ray analyzer attached.

For rf sputtering, the chamber was evacuated to 3×10^{-6} Torr and back filled with argon to 4×10^{-3} Torr. Both pure chromium and 50% chromium-50% platinum targets were used in this study. The power to the plasma was 1.5-2.0 kW. Radio frequency sputtering rates ranged between 17-25 Å/min. For the dc-magnetron experiments, a pure chromium target was used with a planar magnetron. The background pressure was 3×10^{-6} Torr with an argon operating pressure of 2×10^{-3} Torr. The net power was 5 kW and the deposition rate was 320 Å/min. Under all experimental con-

ditions the desired final film thickness was maintained at approximately 600 Å.

III. RESULTS AND DISCUSSION

Transmission electron photomicrographs for the as-fabricated carbon substrate, the as-deposited rf sputtered chromium film, the as-deposited rf-sputtered 50% chromium-50% platinum alloy film, and the as-deposited dc magnetron chromium film along with their respective selected area diffraction patterns are presented in Figs. 1-4. In Fig. 1 the amorphous carbon substrate is presented. In Fig. 1 the features that are seen are due to the replication of Bioten. The amorphous character of the carbon substrate is clearly depicted in its electron diffraction pattern which shows only two diffuse rings indicative of short range order. The prepared substrate was featureless only occasionally showing a bump or rift associated with the replication of the Bioten polymer substrate from which it was made. The features that are seen in Figs. 2 and 3 are due to the replication of the Bioten. The as-deposited rf-sputtered chromium film was also essentially amorphous although the selected area diffraction pattern is somewhat more sharply defined. The strongest of the two diffuse rings was positioned at the location of the (110) ring for crystalline chromium. No microstructural features were observed in this film at magnifications up to $(2.5 \times 10^6) \times$. The film was essentially continuous but with no evidence of crystallinity. Similarly, the rf-sputtered 50% chromium-50% platinum alloy was amorphous. Its diffraction pattern was somewhat more diffuse than that for the pure chromium film indicating a finer more random deposition. The microstructure for this alloy was featureless and energy dispersive x-ray analysis showed a uniform deposition within 5% of the chemistry of the target. The dc magnetron as-deposited chromium film was clearly crystalline. Both the microstructure and the electron diffraction pattern showed evidence of crystallinity. The spotty character of the rings in the diffraction pattern is a result of the limited field viewed indicating a much coarser microstructure than that achieved by rf sputtering of films to a similar thickness. The lattice parameter for this film is 3.00 Å which is 4% higher

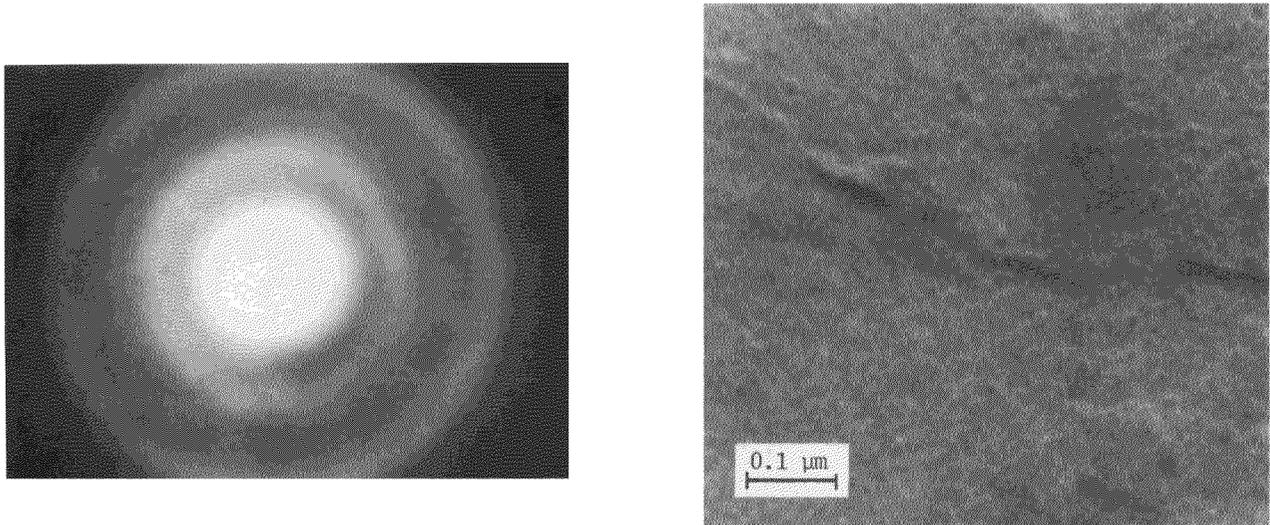


FIG. 1. As-fabricated carbon substrate and corresponding selected area diffraction pattern.

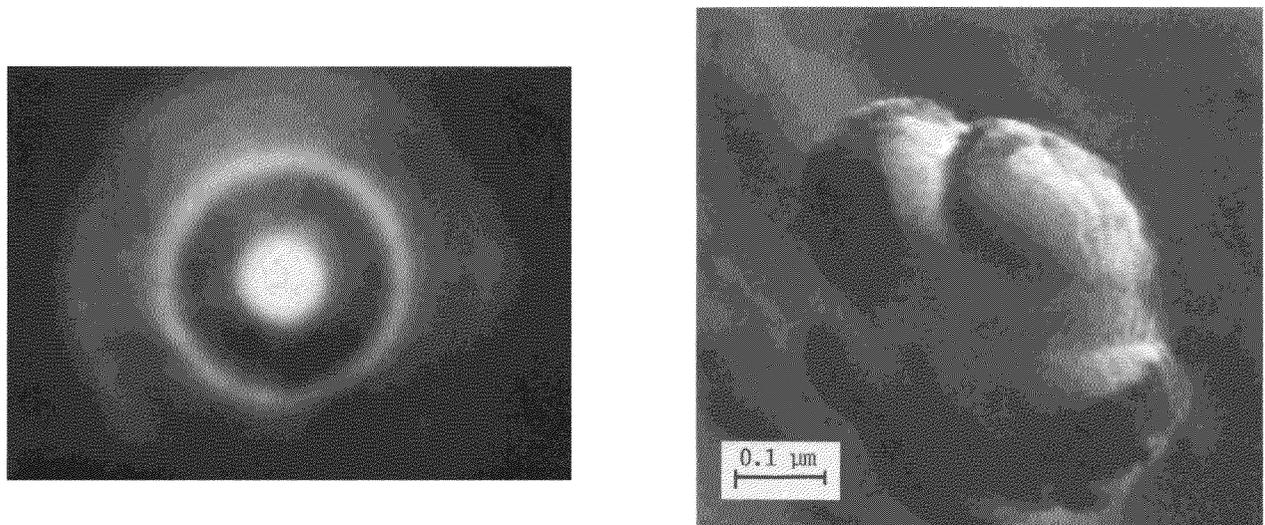


FIG. 2. As-deposited rf-sputtered chromium film and corresponding selected area diffraction pattern.

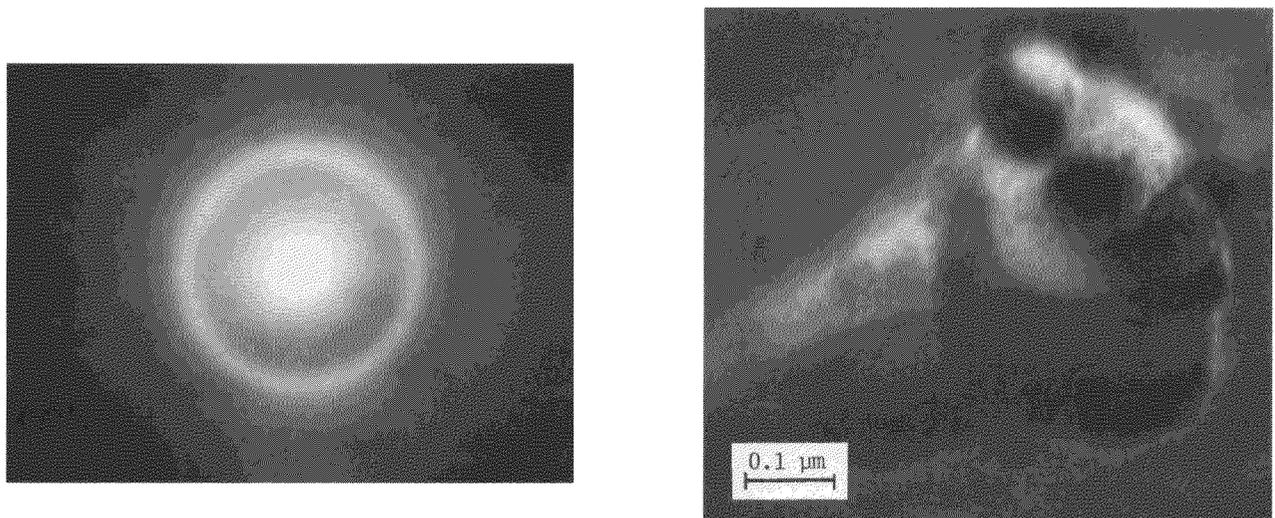


FIG. 3. As-deposited rf-sputtered 50% chromium-50% platinum alloy and selected area diffraction pattern.

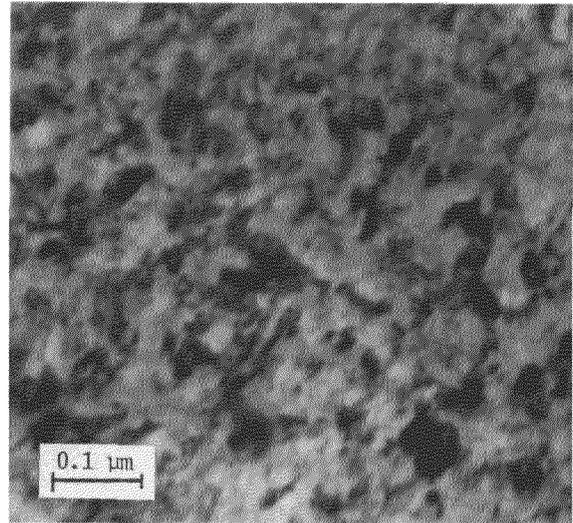
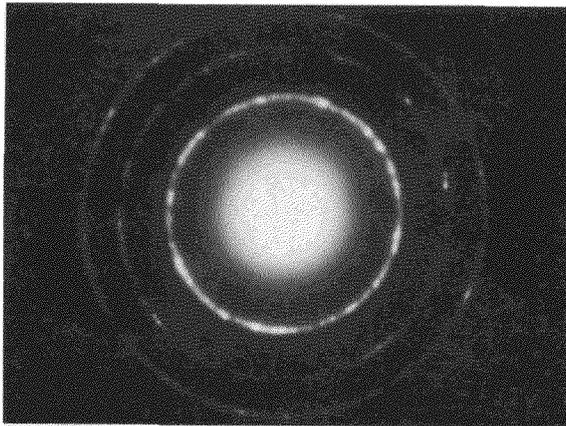


FIG. 4. As-deposited dc-magnetron sputtered film and selected area diffraction pattern.

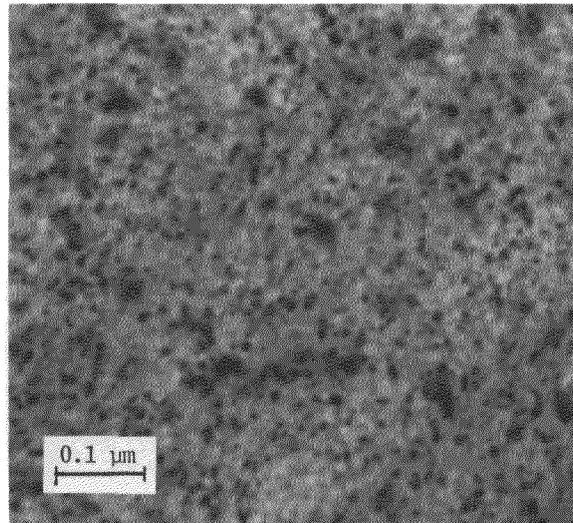
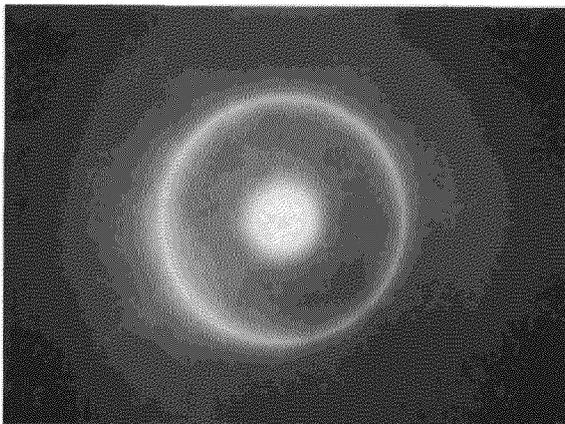


FIG. 5. Heat treated rf-sputtered chromium film and selected area diffraction pattern (1 h in nitrogen at 360 °C).

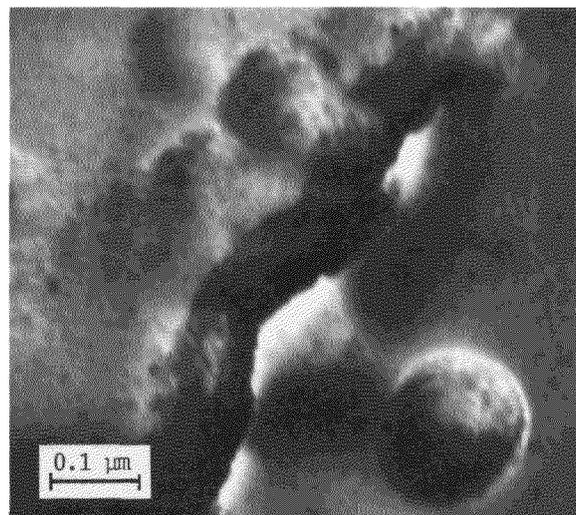
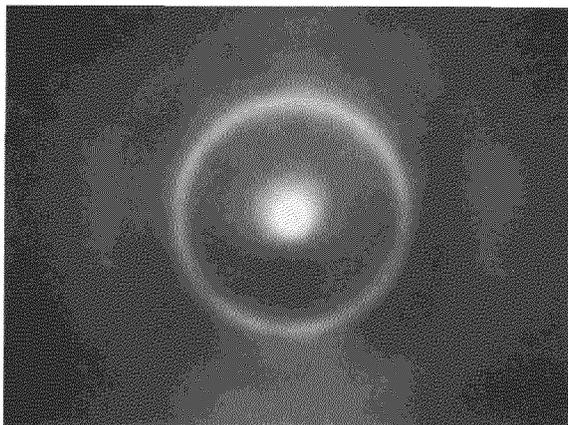


FIG. 6. Heat treated rf-sputtered 50% chromium–50% platinum alloy film and selected area diffraction pattern (1 h in nitrogen at 360 °C).

than the established value for high purity chromium.

Both rf-sputtered films were subjected to heat treatment to determine if these films could be crystallized. A 1 h hold at 360 °C produced the results shown in Figs. 5 and 6. The pure chromium film crystallized as evidenced by the fine ringed polycrystalline diffraction pattern. The platinum–chromium alloy did not. Its diffraction pattern was still highly diffuse. The microstructure of the chromium film shows evidence of very fine crystals while the 50% chromium–50% platinum alloy appears to be unchanged from the as-deposited condition indicating the more stable amorphous structure.

The discontinuous rings in the polycrystalline diffraction pattern of dc magnetron sputtered films are an indication of the relatively large crystallite size in this material. Larger crystals are usually formed when the deposition temperature is high. The temperature of the coating during deposition depends on four fundamental heating processes: (1) heat of condensation, (2) sputtered atom kinetic energy, (3) plasma radiation, and (4) ion neutralization and reflection at the cathode. For all of these processes, heating rate increases with the increase in the deposition rate. Therefore, the higher deposition rate of the dc magnetron sputtering as compared with the rf sputtering rate likely results in a higher

temperature of the film as it is being sputtered and, therefore, a greater tendency to crystallize and to have crystal growth during the sputtering process.

IV. SUMMARY AND CONCLUSIONS

As-deposited films produced by rf sputtering onto cold amorphous carbon substrates are uniform in chemistry and thickness and are amorphous. A low temperature heat treatment (360 °C for 1 h) crystallizes the chromium film but is insufficient to convert the 50% chromium–50% platinum alloy film. However, even in the annealed chromium films, the grain size was under 100 Å. Direct current magnetron sputtering resulted in a polycrystalline film in the as-sputtered condition. The grains in this film were equiaxed in shape with some as large as 400 Å.

¹J. A. Thornton, in *Deposition Technologies for Films and Coatings* (Noyes, Park Ridge, NJ, 1982), p. 212.

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⁵M. I. Birjega, C. A. Constantin, I. Th. Florescu, and C. Sarbu, *Thin Films* **92**, 315 (1982).