CONF-901035--4

UCRL-JC--103668

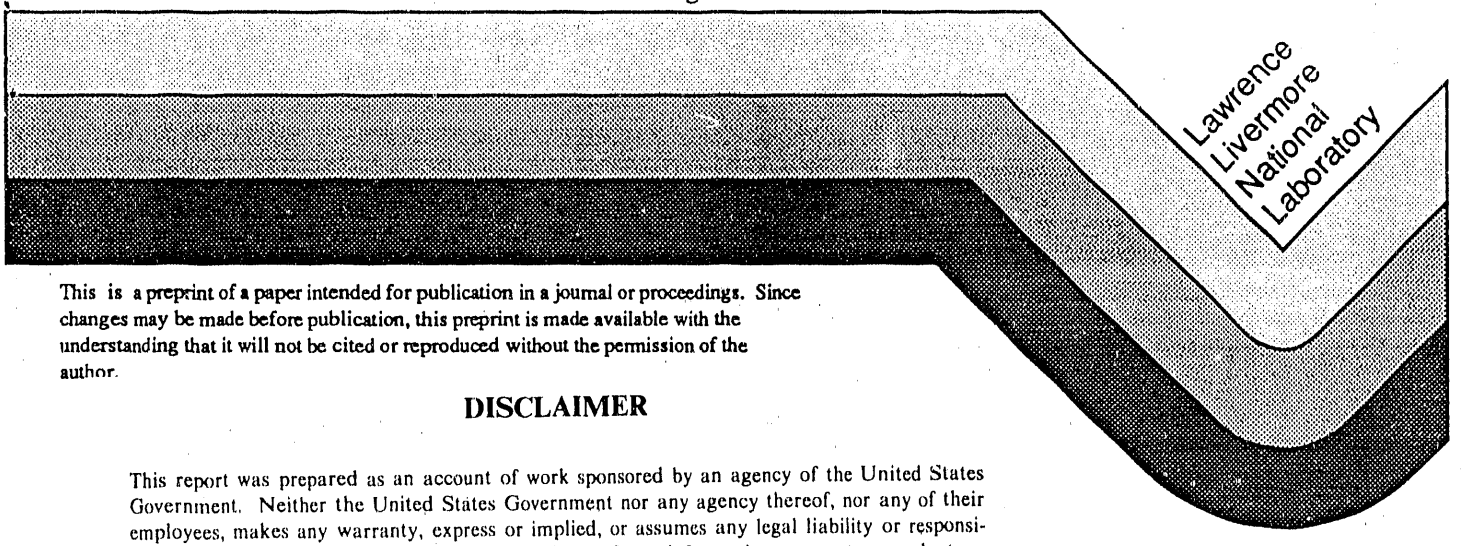
DE91 000939

REACTIVE SPUTTERING OF MOLYBDENUM-OXIDE GRADIENT-INDEX FILTERS

A. F. Jankowski
L. R. Schrawyer
P. L. Perry

This paper was prepared for submittal to
American Vacuum Society 37th Annual Symposium
and Topical Conferences
in Toronto, Canada on October 8-12, 1990.

August 1990



DISCLAIMER

REACTIVE SPUTTERING OF MOLYBDENUM-OXIDE GRADIENT-INDEX FILTERS

A.F. Jankowski, L.R. Schrawyer and P.L. Perry

Lawrence Livermore National Laboratory, Livermore, CA 94550

ABSTRACT

Molybdenum-oxide gradient-index films are produced by reactive sputter deposition. A molybdenum metal target is sputtered continuously with an argon-oxygen gas mixture. For each target power used, a reproducible oxide composition and corresponding refractve index result. Repetitive variation of applied target power is used to produce a structure composed of discrete layers of preselect stoichiometry. The systematic control of a single process parameter, target power, simplifies the fabrication of molybdenum-oxide rugate filters.

I. INTRODUCTION

Thin film structures with a continuous variation in refractive index enables the realization of complex filter structures.[1-3] Advantages of these gradient index optical coatings include flexibility in filter design and enhanced structural stability in adverse environments. Early production of simple refractive index profiles, for antireflection coatings, were produced using processes typified by multiple evaporative sources and rate monitor feedback systems. Thus, codeposition techniques often require ensuing compositional analysis to determine reproducibility. A straightforward deposition process to simplify fabrication of rugate filters, in simple form wherein a sinusoidal variation of the refractive index occurs, is clearly in demand. The sputtering of elemental molybdenum with an argon-oxygen gas mixture is developed for this purpose.

The molybdenum-oxygen system is one in which it is feasible to produce, through magnetron sputter deposition, a composition continuous series of oxide structures.[4] This is accomplished through a systematic variation in the single deposition parameter - applied target power. This technique is unlike most other single process parameterization which involve working gas pressure cycling. Metastable oxide compounds are currently produced with refractive indices ranging from 1.5 to 2.9. Alternating between set target power(s) therefore produces multilayered structures in which the refractive index, by design, alternates. This result gives promise to the practical use of the molybdenum-oxide system in gradient-index filter technology.

II. EXPERIMENTALS

The molybdenum oxide films are produced using reactive d.c. planar magnetron sputtering wherein the film composition is continuously and reproducibly controlled with the power applied to the magnetron source.[4] Concurrently, the Ar-20%O_2 gas mixture, 5 mTorr working pressure and 21.5 sccm flow rate remain constant for all depositions. Under these pressure and flow conditions, it can be shown[5,6] and was found[4] that the formation of the oxide compound occurs at the substrate rather than at the target. A 0.99994 pure molybdenum target is reactively sputtered following a 250 °C high vacuum system bake-out for 4h at which point the system base pressure is better than 1 x 10^{-7} Torr. The substrates (which include cleaved muscovite, polished silicon and glass slides) are situated 8.9 cm from the deposition source, clamped to an aluminum substrate platen whose temperature remains between 60-85 °C during deposition.

A series of molybdenum-oxide films 1-2 μm thick are produced as a function of applied target power, ranging from 75 to 175 Watts. For each molybdenum oxide film the refractive index, n_c, is measured using the red hydrogen line, at a wavelength of 656.3 nm. A gradient index filter, i.e. a multilayer structure, is then sputtered on a (111) Si wafer by alternating between two preselected target power levels, 95 Watts (to produce a deposition rate of 0.34 nm/s and a 13.6 nm thick layer) and 125 Watts (to produce a 0.7nm/s rate and 14.0 nm thick layer). The change in target power levels is linearly ramped over 1 second. The 40 layer pair filter, with a design layer repeat period of 27.6 nm, is examined compositionally using Auger depth profiling and structurally using transmission electron microscopy.

III. RESULTS

The atomic concentration profiles of the molybdenum-oxide films are determined using depth profiling in combination with Auger Electron Spectroscopy. A 3 KeV, 10 μA electron beam is used to generate the Auger electrons. The measured intensities of the 186eV molybdenum, 272eV carbon and 503 eV oxygen peak, from data accumulated in the derivative mode, are used to compute the atomic concentrations. A 5 KeV, 2.2 μA argon ion beam is used to sputter etch a 25 mm^2 area of the sample surface for each individual oxide film composition, whereas a 2 KeV, 0.710 μA argon ion beam is used to sputter etch the multilayer. The sputter etch gas pressure is 3×10^{-5} Torr while the Auger system base pressure is 5×10^{-10} Torr. The measured refractive index is plotted in Fig.1 as a function of the applied target power and measured composition. (The Auger data was shown to be in quantitative agreement with Scanning Transmission Electron Microscopy microanalysis using an energy dispersive spectrometer.[4]) Auger data was unattainable for samples deposited below 100 Watts, since these samples periodically discharge upon electrron bombardment, producing unreliable quantitative results.

The atomic concentration profile of the last five layer pairs (N=36 to 40) in the molybdenum oxide gradient index filter is shown in Fig.2. By design, the 95 Watt - 125 Watt layering should produce alternate layers of 25 at.pct. molybdenum and 40 at.pct. molybdenum. Although the surface molybdenum concentration is 25 at.pct., the depth profiling reveals only a 5 at.pct. sinusoidal variation in the molybdenum concentration about an average layer value of 33 at.pct. The small amplitude to the concentration variation is most likely attributable to interfacial broadening as a result of sputter induced roughness the 25 mm^2 sampled area.

Structural characterization of the gradient-index molybdenum-oxide coating is made with transmission electron microscopy. When viewed in cross-section on the Si substrate, the layering which results from the alternate deposition between 95 and 125 Watts is clearly smooth and discrete (as seen in Fig.3) with a measured layer pair spacing average of 28 nm. High resolution imaging (as shown for the two layer pairs of Fig.4) reveals microcrystallinity within each layer. The dark layers (with higher molybdenum concentration than the light) account for half the layer pair thickness. The transition in amplitude contrast between the layers suggests a composition gradient through the interfaces, hence a gradient in the refractive index through the interface. Digitization of the image intensity profile through a typical interface (along line $\overline{nm}$ in Fig.4) is shown in Fig.5, supporting the finding of a gradient refractive index through the (95 to 125 Watt) interfaces. The baseline intensity of the trace increases with the thickness of the wedge shaped sample area under examination. The electron diffraction pattern of the molybdenum-oxide structure is superimposed on the $[\bar{1}12]$ pole projection of the silicon substrate in Fig.6. The polycrystalline ring pattern corresponds with measured d-spacings of 0.344, 0.244, 0.218, 0.171 and 0.142 nm. These planar spacings fit the previous diffraction analysis[4] of films produced at 95 and 125 Watts, except for the 0.218nm spacing. A orthorhombic MoO_3 phase was found for the 95 Watt film and a previously unreported hexagonal Mo_2O_3 phase for the 125 Watt deposit. It is possible that a monoclinic MoO_2 compound has formed in the interface, accounting for the 0.218 nm spacing. This intermediate composition phase appears at the positions of the interface plateaus in the image intensity digitization of Fig.5, at distances between 10 to 12.5 nm and 18 to 20.5 nm along line $\overline{nm}$.

IV. DISCUSSION

The fabrication of gradient-index filters through the use of a single target source and single process parameter is an advantageous process. The variation of target power alone, while reactively sputtering molybdenum in a partial pressure of oxygen is shown viable. The question of environmental and structural stability, is however, critical for successful use. The limitations of the 'power variation' synthesis approach are intrinsic to the stability of the oxide compound being formed, in this case the molybdenum-oxides. The Mo-O binary system contains five reported stable oxide phases and many metastable (between $MoO_{1.75}$ and $MoO_{1.92}$) in the assessed phase diagram.[7] The reactive sputtering process has been recently used[4] to produce additional stable molybdenum-oxide phases above 33 at.pct. molybdeum, both a hexagonal Mo_2O_3 phase and a cubic Mo_2O phase. The stability of a layered molybdenum-oxide structure, in which the composition varies between layers therefore depends on the concentrations sought. In the present work, an apparent interface phase (MoO_2) forms between the desired layering of 25 and 40 at.pct. molybdenum. Whereas the individual oxide compounds are structurally stable to moderate temperatures (> 800°C), regions with compositions intermediate to these stable oxides are (presentally shown) metastable. This prevents an unavoidable design limitation to the range of compositions available for use in the molybdenum-oxide system.

V. CONCLUSIONS

A molybdenum-oxide gradient-index filter is made using reactive sputter deposition. A single process parameter (applied target power) is used to control the composition of the growing deposit from an elemental molybdenum metal target in a Ar-20%O_2 working gas mixture. The structure of the coating is examined using Auger electron spectroscopy and transmission electron microscopy. The layered structure is microcrystalline and the composition varies within a layer pair in a graded transition, from 25 to 40 at.pct. molybdenum. The feasibility of using applied target power variation to produce rugate filters is presented for the case of the molybdenum-oxide binary system.

ACKNOWLEDGMENTS

We would like to acknowledge the National Center for Electron Microscopy at Lawrence Berkeley Laboratory for use of the JEOL 200 CX top-entry electron microscope. We also thank N.L. Thomas for the refractive index measurements. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract #W-7405-Eng-48

REFERENCES

[1]V.N. Yadava, S.K. Sharma and K.L. Chopra, Thin Solid Films **21**, 297 (1974).

[2]W.H. Southwell, Appl. Opt. **24**, 457 (1985).

[3]W. Gunning, in *Thin Film Technologies III*, SPIE Vol. **1019**, 204 (1988).

[4]A.F. Jankowski and L.R. Schrawyer, Thin Solid Films **193**, in press (1990).

[5]E. Hollands and D.S. Campbell, J. Mater. Sci. **3**, 544 (1968).

[6]T. Abe and T. Yamashina, Thin Solid Films **30**, 19 (1975).

[7]L. Brewer and R.H. Lamoreaux, Bull. Alloy Phase Diagrams **1** (2), (1980).

FIGURE CAPTIONS

Fig.1. The refractive index n_c variation with composition and applied target power used in the reactive sputter deposition of molybdenum-oxide coatings on glass.

Fig.2. The Auger electron spectroscopy determined atomic concentration profile of a molybdenum-oxide gradient-index coating produced by sequential layering at target powers of 95 and 125 Watts.

Fig.3. The transmission electron microscopy bright field image of the molybdenum-oxide gradient-index coating, as viewed in cross-section, reveals the distinct layering of the structure.

Fig.4. A high resolution electron micrograph of the two layer pairs shows microcrystalline molybdenum-oxide regions and a composition graded transition through the layer pair interfaces.

Fig.5. An image intensity digitization along the line $\overline{nm}$ of Fig.4 reveals an intermediate phase at the 95-125 interface regions. The discontinuous slope and plateaued regions are found at distances 10-12.5 nm and 18-20.5 nm.

Fig.6. The electron diffraction pattern (corresponding with the area of Fig.3) of the molybdenum-oxide multilayer coating on the (111) Si substrate shows the superposition of the $[\bar{1}12]$ pole projection of the substrate and the polycrystalline ring pattern from the multiple phases within the oxide coating.

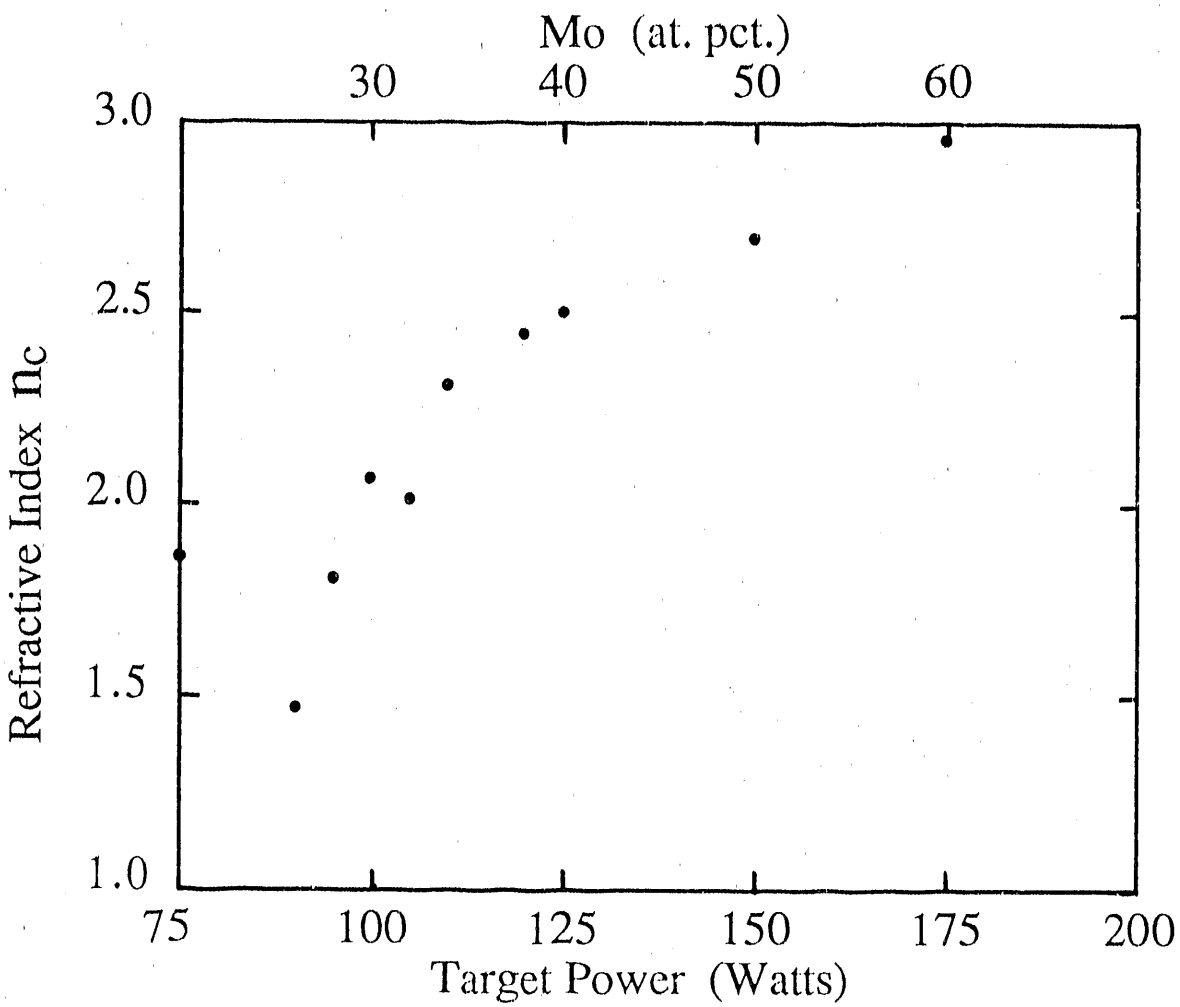

Mo (at. pct.)
30
40
50
60
3.0
2.5
2.0
1.5
1.0
Refractive Index n_c
75
100
125
150
175
200
Target Power (Watts)

Figure 1

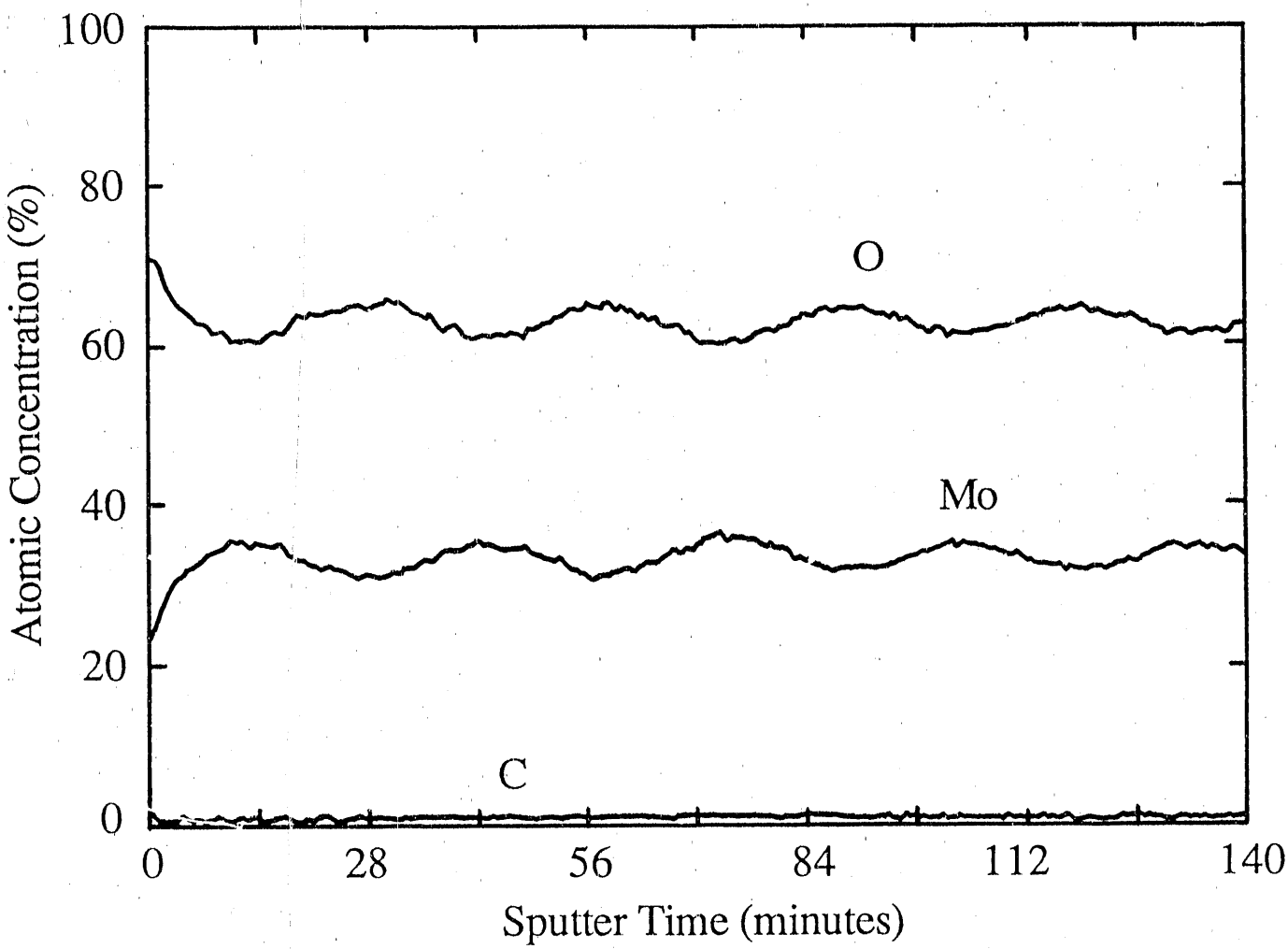

100
80
60
40
20
0
Atomic Concentration (%)
O
Mo
C
0
28
56
84
112
140
Sputter Time (minutes)

Figure 2

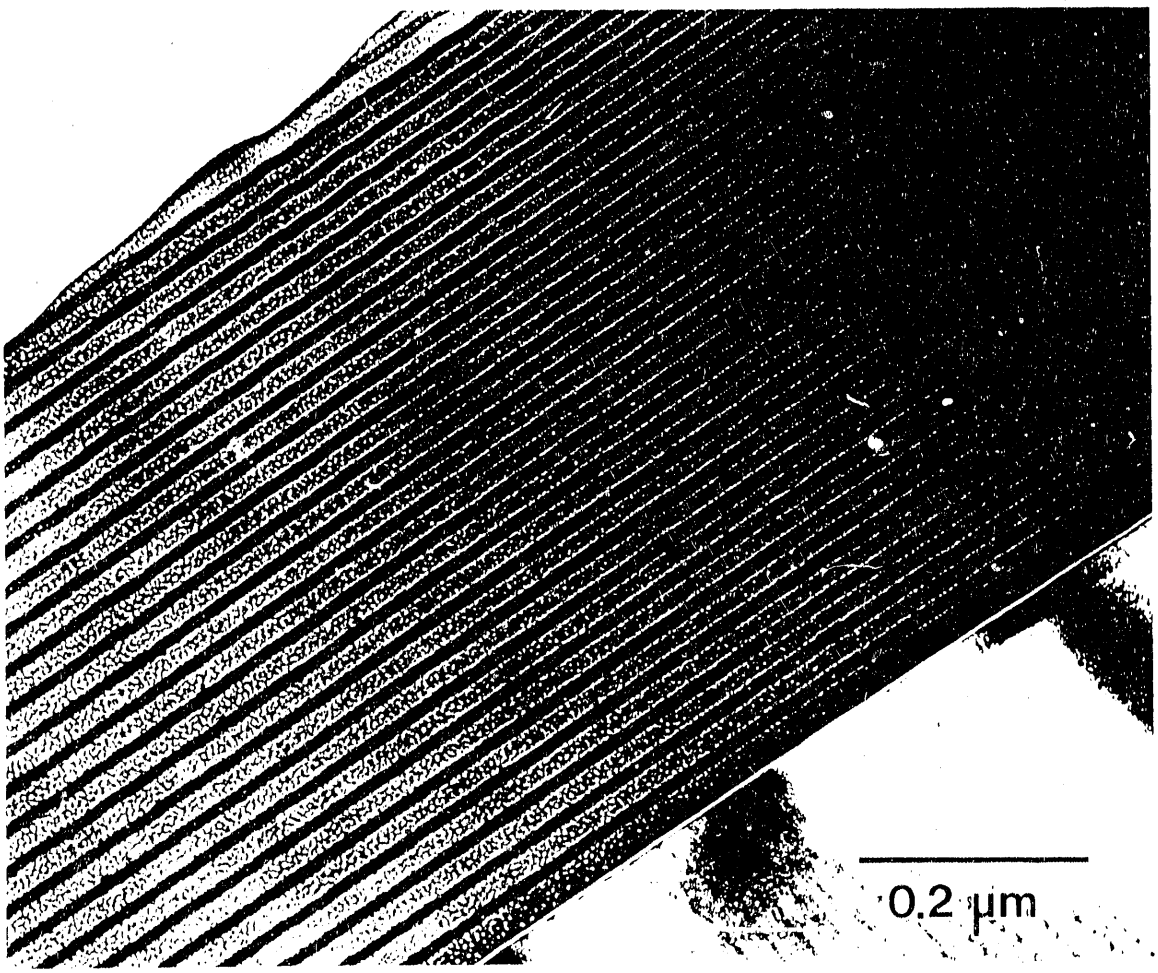


Figure 3

Figure 4

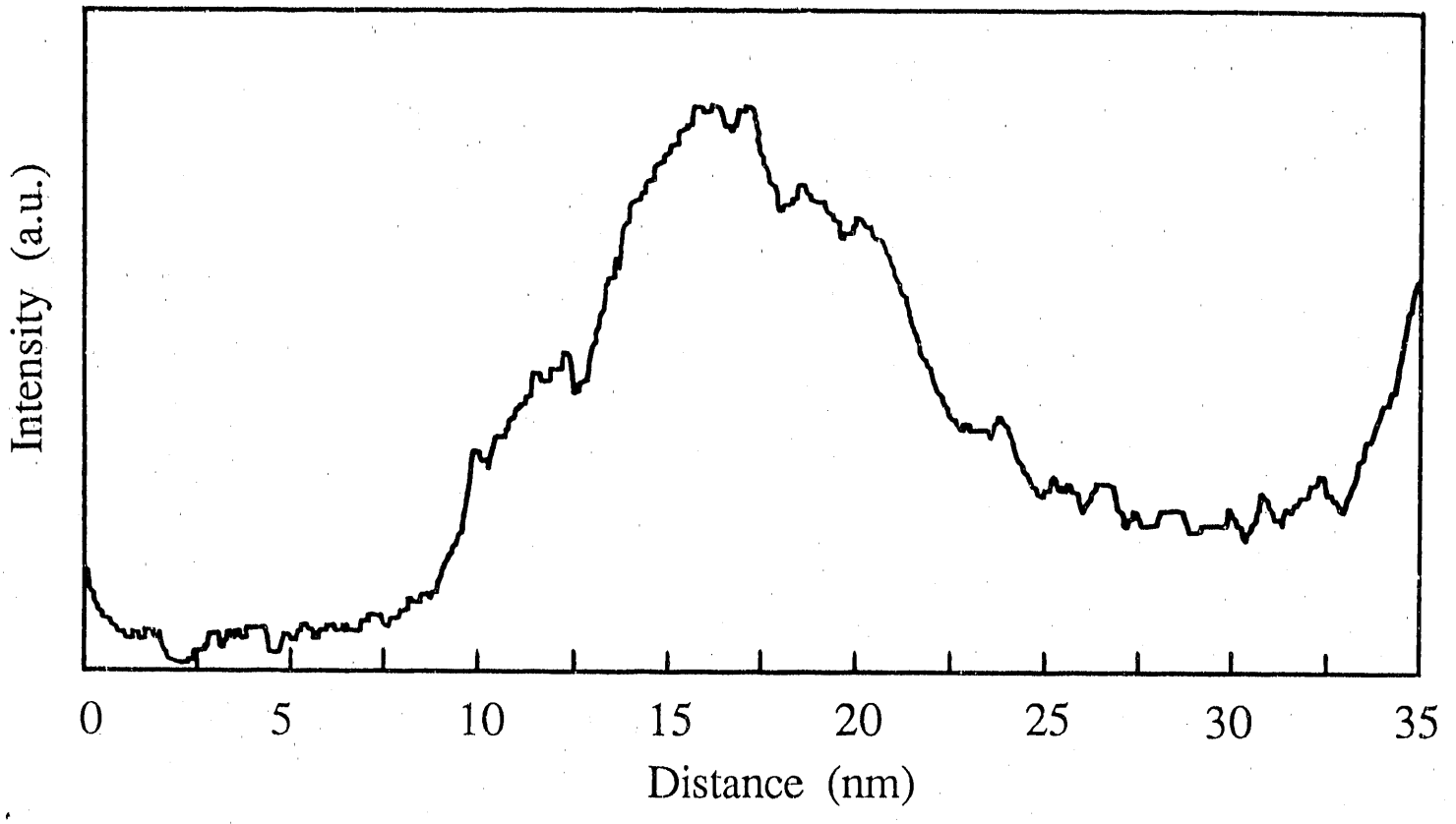


Figure 5

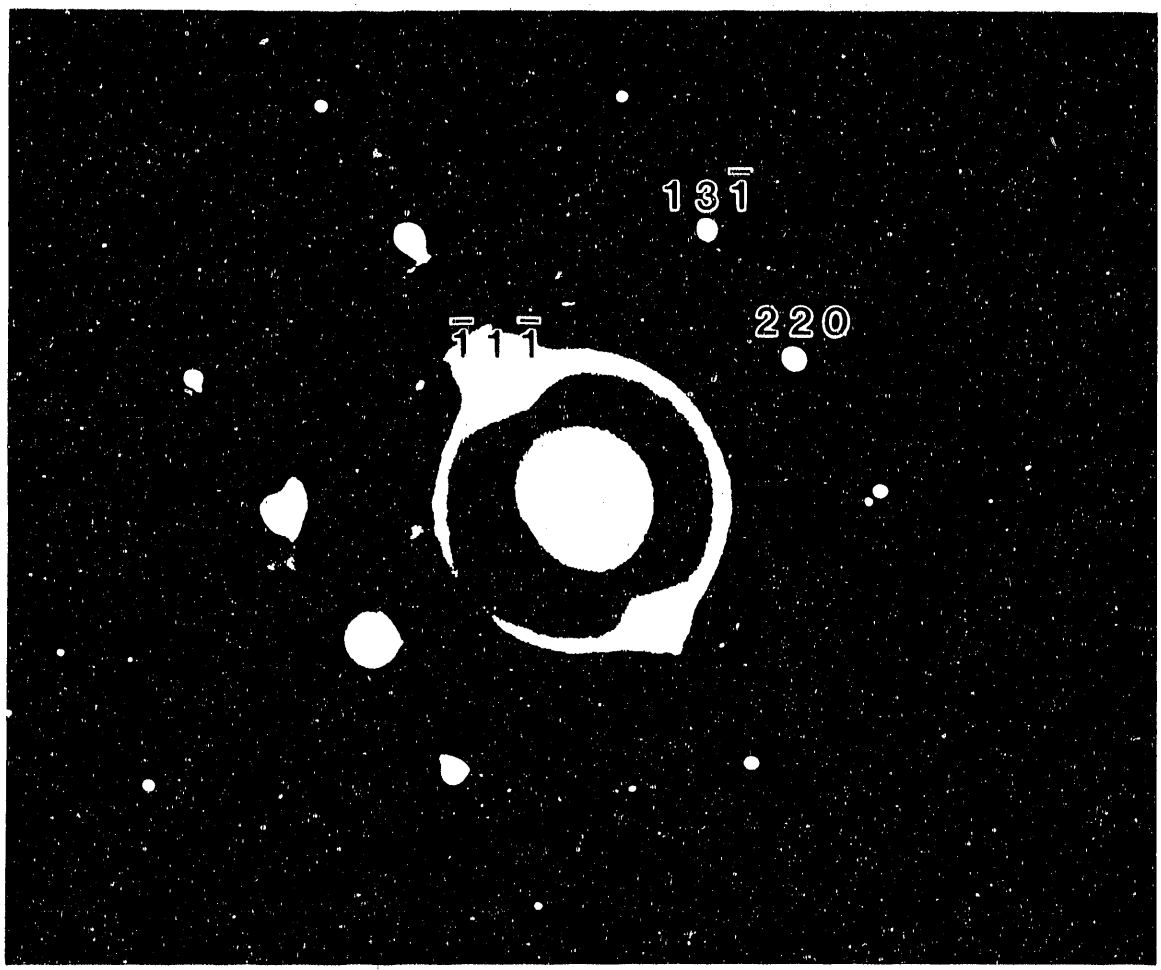


Figure 6

-END-

DATE FILMED

11 / 02 / 90