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MAGNETRON SPUTTER DEPOSITION OF BORON AND BORON CARBIDE

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Abstract

The fabrication of x-ray optical coatings with greater reflectivity required the development of sputter deposition processes for boron and boron carbide. The use of high density boron and boron carbide and a vacuum brazed target design was required to achieve the required sputter process stability and resistance to the thermal stress created by high rate sputtering. Our results include a description of the target fabrication procedures and sputter process parameters necessary to fabricate B_4C[1] and B[2] modulated thin film structures.

Introduction

The very stable hard refractory compounds of boron and carbon are candidate materials for many engineering applications that are subjected to erosion, corrosion, and high temperatures. Films of these materials are often coated on high temperature substrates by chemical vapor deposition (CVD). Coatings of these materials are attractive as the low-Z non-absorbing layer in high-Z/low-Z multilayer mirrors offering enhanced reflectivity of 0.1 - 10 nm x rays from grazing to normal incident. However, the performance of multilayer coatings as x-ray optics requires precise control of layer thickness between 2 and 50 nm and chemically unrelated interfaces. This precludes the use of high temperature coating processes such as CVD. Consequently, a sputtering process with low substrate temperatures and excellent stability was developed that enabled the production of multilayer x-ray optics using boron and boron carbide as the transparent low-z layer material. The chemical stability, structureless morphology, and low absorption of sputtered films of boron and boron carbide resulted in the fabrication of Ti/B(1) and W/B_4C(2) multilayered x-ray optics with good reflectivities.

This paper addresses the development of high density boron and boron carbide sputter targets, sputter process parameters and characterization of films of these materials. The manufacture, structure, and performance of W/B_4C and Ti/B x-ray mirrors has been described in previous publications.(1,2)

Experimental

Boron sputter targets with sufficient density to allow reproducible control of the sputtering process were not available from the usual commercial sources. Consequently, a process was developed for fabricating pure dense boron sputter targets[3] using the hot isostatic press facility at Lawrence Livermore National Laboratory. Pure boron powder (99.9%) was vacuum sealed in a tantalum can by electron beam welding, and hot isostatically compacted at 1700°C in 0.21 GPa of Ar gas for 2 - 4 hrs.[3] The resulting monolithe of pure boron was fabricated into sputtering targets by standard ceramic machining techniques. The boron had an immersion density of 2.34 gm/cc and a porosity < 0.15%.

Boron films approximately 7 μm thick were deposited on a variety of substrates (i.e., fused silica, sapphire, silicon) by rf magnetron sputtering at 400 W in 2.1 Pa of Ar. A conducting silver paste was used to attach the substrates to a water cooled Cu plate ~7 cm from the sputter source. Boron film deposition rates of 0.2 nm/s were achieved with these process parameters and a magnetron sputtering source with a 6.35 cm diameter target.

Boron carbide sputter targets were fabricated from fully dense, high purity (99.9%) material acquired from various commercial sources. High deposition states and current densities required the use of a laminated target design to prevent catastrophic failure of the boron carbide target because of thermal stress created by large temperature gradients on the target surface resulting from the non-uniform ion bombardment associated with magnetron sputtering sources. The target design consisted of two 6.35 cm diameter boron carbide discs approximately 0.6 cm thick brazed together with a 1 mm Al shim at 300°C (Fig. 1). This laminated design enabled normal sputter deposition at powers above 1 kW where thermal stress reduced fractures routinely occurred. Boron carbide films over 50 μm thick were deposited on room temperature substrates by DC magnetron sputtering at 1200 W and 2.0 Pa of Ar. Deposition rates of 4.0 nm/s were possible with a 5 cm source to substrate separation.

The boron and boron carbide films were produced in cryogenic or turbo-molecular pumped sputtering systems with base pressures of at least 1.3 x 10^{-5} Pa. The systems were equipped with multiple 6.35 cm magnetron sputtering sources arranged along a circular path with a water cooled rotating substrate table to facilitate the deposition of multilayered coatings. Argon gas pressure (0.6 - 2.1 Pa) and flow rates (18 - 28 sccm) were maintained by an automatic flow control system consisting of an piezoelectric valve and a capacitance manometer. Depositions rates were controlled by quartz crystal monitors calibrated with thickness measurements determined by stylus profilometry.

Results

High angle $\theta/2\theta$ scans with a standard powder diffractometer and Cu $K\alpha$ x-ray radiation (8.0 keV) showed no evidence of crystallinity in either the boron or boron carbide films (Fig. 2).

Transmission electron microscopy on a 0.12 μm thick boron foil examined in plane-view confirmed the lack of any growth morphology or crystallinity. The accompanying selected area diffraction (SAD) pattern contained only a diffuse ring corresponding to the amorphous structure.

Auger electron spectroscopy (AES) was not obtained for the pure boron and boron carbide films. However, AES combined with ion beam etching generated an atomic concentration depth profile for the B/Ti and B_4C/W multilayer coatings prepared with identical sputter process parameters. Thus, analysis described in earlier publications[1,2] revealed only a small amount of oxygen (< 2 at %) in both the boron and boron carbide films.

Growth morphology of the films was investigated with optical and electron microscopy. Although TEM investigation of thin (< 1 μm) boron and boron carbide films revealed no crystallinity or columnar growth structure (Fig. 3), much thicker boron carbide films while still amorphorus show a columnar grains structure characteristic of films sputter deposited on low temperature substrates. The photo micrograph of the cross section of a film consisting of two layers of boron carbide and two layers of Al reveals columnar grains propagating through all layers in the film (Fig. 4).

The growth of columnar grains in the thick boron carbide layer appeared to have been accelerated by nucleatron sites on the initial Al layer and debri generated by the high rate sputtering process. Voids visible in the boron carbide layer (see Fig. 4) are the result of fractures along column boundaries occurring during metallographic sample preparation.

Scanning electron microscopy (SEM) of a fracture boron film 6.8 μm thick and a fractured boron carbide film 2.8 μm thick is shown in Fig. 5. Both films appear dense. The thicker boron film has a slightly rougher appearing surface and a submicron columnar morphology. The 2.8 μm thick boron carbide film is almost without distinguishable features at the same magnification.

Microhardness measurements were made on the 6.8 μm thick boron film (Fig. 5a) and on the 50 μm thick boron carbide layer (Fig. 4). Measurements were made with Leco model DM400 microhardness tester with a 50 gm load and a 5 μm indent. Microhardness measured on the surface of boron films deposited on sapphire had an average Vickers microhardness value of 2900 Kgm/mm^2 on the on the surface and 2750 Kgm/mm^2 measured normal to the film growth direction using a 10 gm load and a 2.5 μm indentor. The thick boron carbide film had an average microhardness of 1825 Kgm/mm^2 measured on a polished cross section of the film. This data should be viewed as qualitative because of the thickness of the boron film relative to indentor depth and presence of porosity in the thick boron carbide film.

Discussion

Sputtering processes for boron and boron carbide have been developed primarily to enable the fabrication of multilayer x-ray optics with enhanced reflectivity. Although fully dense high purity (99.9%) boron carbide sputter targets are available from several commercial sources, high density boron targets are not; therefore, a process for fabricating high density boron targets was developed. These dense high purity materials made it possible to sputter deposit high quality amorphous films of boron and boron carbide, and consequently to produce the first multilayer x-ray optics with boron and boron carbide as the low-Z transparent layer. Possibly the most significant result of this study was the development of a laminated sputtering target design which made it possible to sputter these brittle thermal-shock sensitive materials at power densities required for most practical coating applications. Fractures developing in the target during sputtering have only a minor impact on process performance and no affect on structural integrity of the target because of the strength of the high temperature Al braze (Fig. 6).

Conclusions

Amorphous films of boron and boron carbide have been prepared by magnetron sputter deposition on room temperature substrates. A process was developed for fabricating fully dense boron targets. A laminated target design was developed using an Al braze that allows full utilization of severely cracked sputtering targets. A consequence of these development efforts was the fabrication of quality multilayered x-ray optics using boron and boron carbide. The development of reliable and reproducible sputter processes for boron and boron carbide should facilitate the evaluation of their potential as engineering coating materials.

Acknowledgement

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References

1) A. Jankowski, D. Makowiecki, and M. McKernan, J. Appl. Physics 65(11) 4450 (1989).

2) D. Makowiecki, A. Jankowski, and R. Foreman, J. Vac. Science and Technology A, 8(6) 3910 (1990).

3) C. L. Hoenig, DOE Invention Case No. IL-8240, July 1988.

Figure Captions

1) Sketch of laminated target design attached to cathode assembly of the magnetron sputter source.

2) The CuKα high angle $\theta/2\theta$ scan of (a) 0.12 μm thick boron film, and (b) 2.8 μm thick boron carbide film.

3) TEM images of the 0.12 μm thick boron film; (a) bright field, (b) dark field, and (c) selected area diffraction.

4) Optical micrograph of polished cross section of a thick Al/B_4C multilayered film.

5) SEM micrographs of a fractured boron film 6.8 μm thick (a), and a fractured boron carbide film 2.8 μm thick (b).

6) Boron carbide sputter target severly fractured by thermal stress, but still fractional.

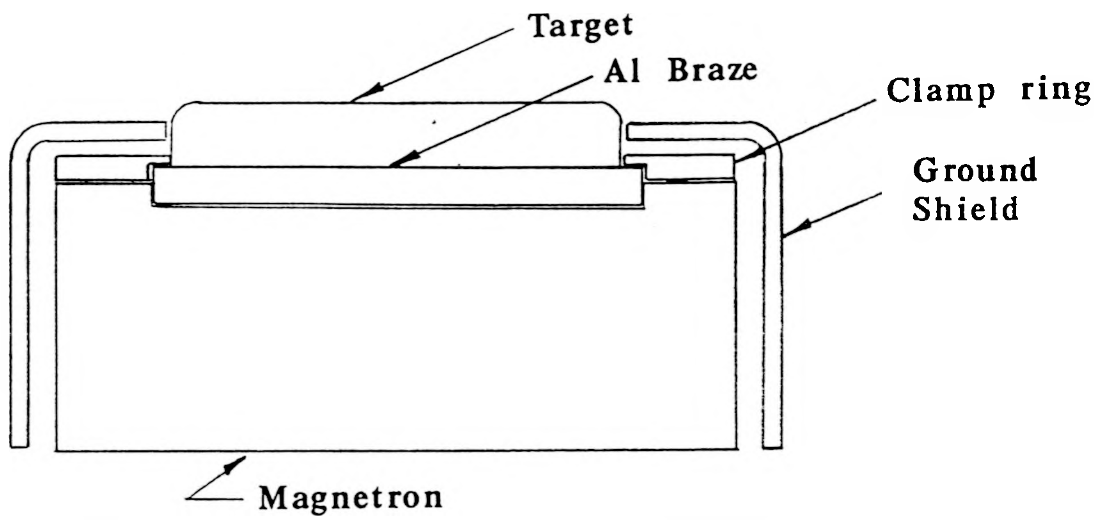

Figure 1

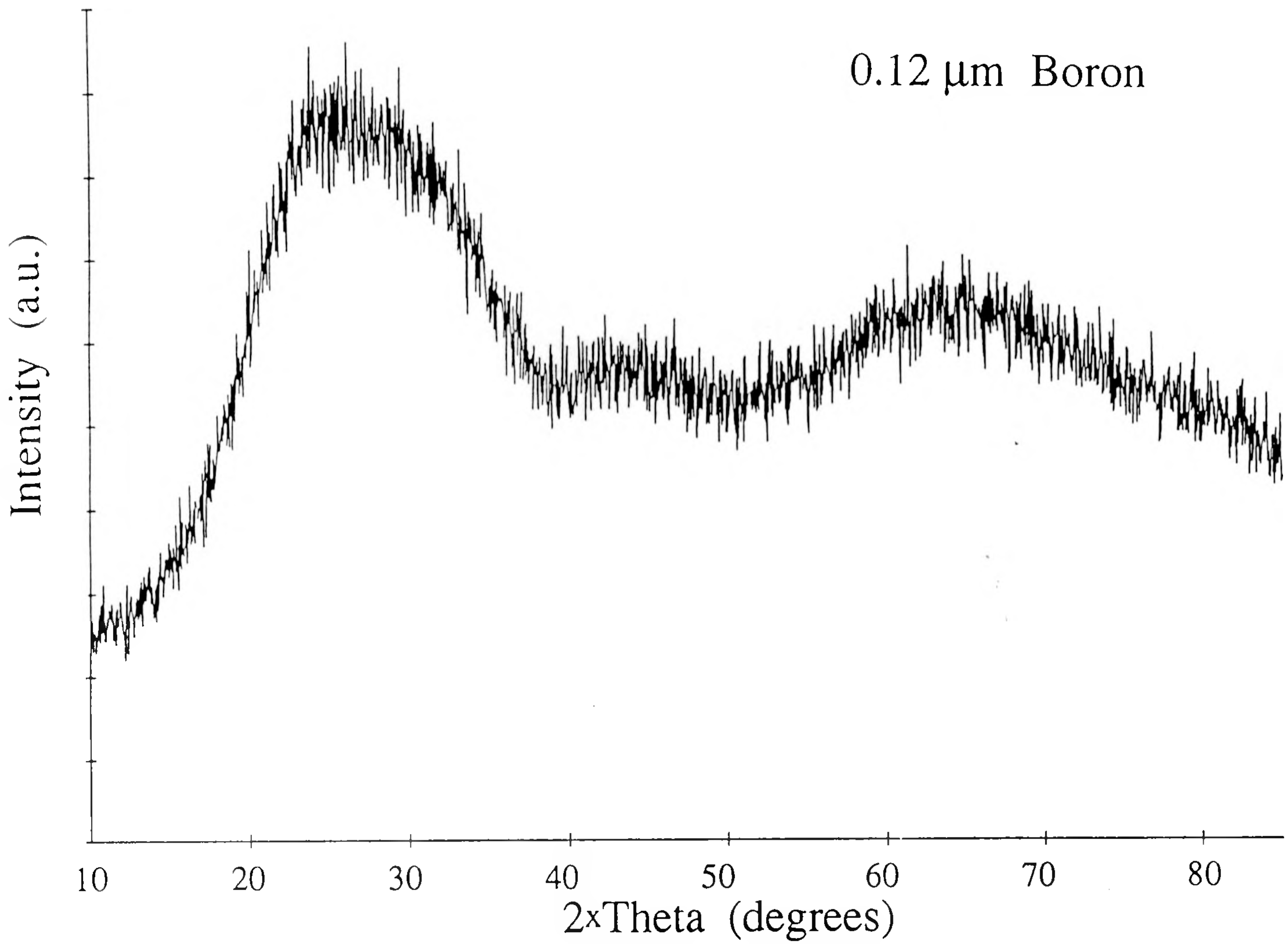
0.12 µm Boron
Intensity (a.u.)
10
20
30
40
50
60
70
80
2xTheta (degrees)

Figure 2a

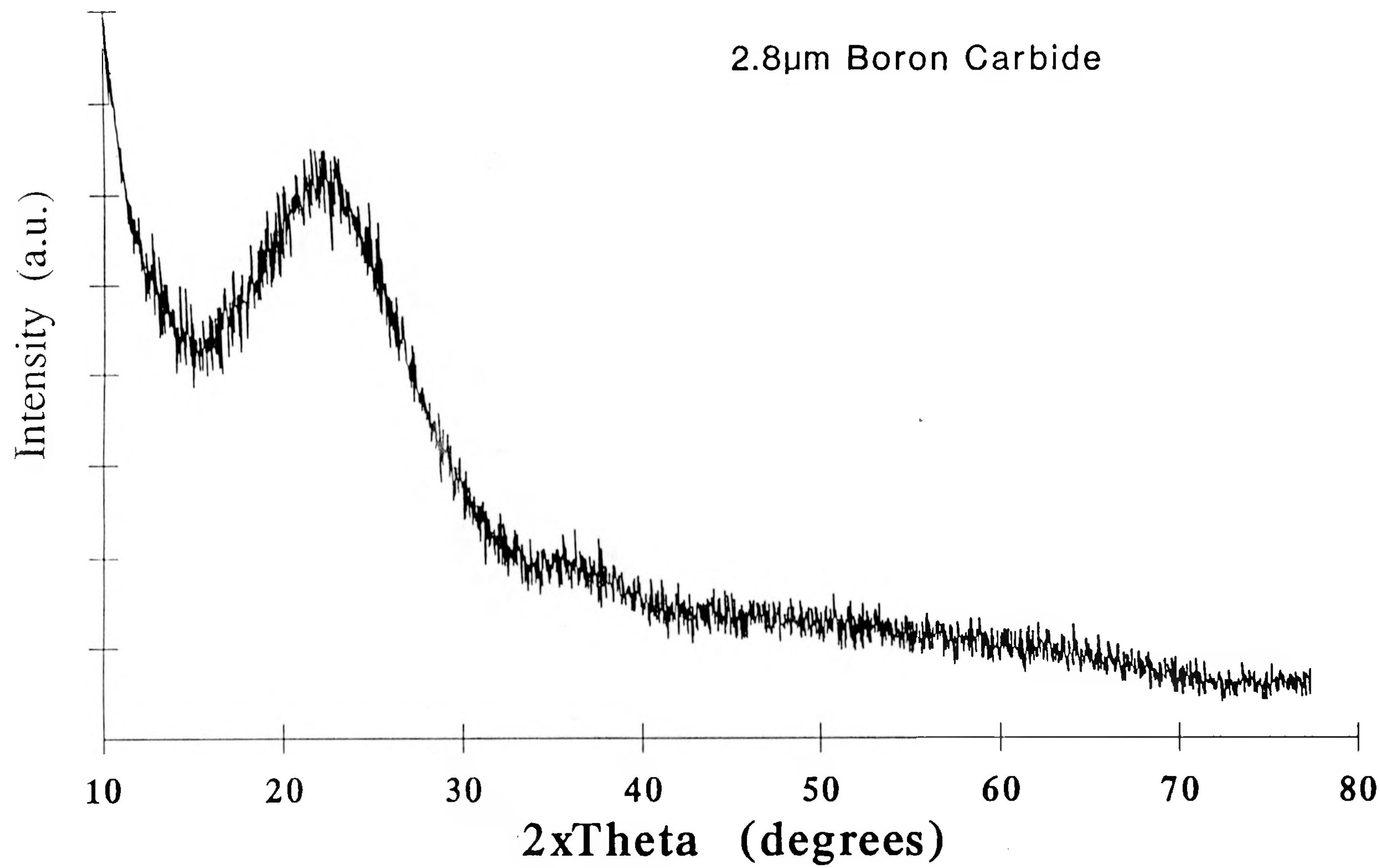
2.8μm Boron Carbide
Intensity (a.u.)
10
20
30
40
50
60
70
80
2xTheta (degrees)

Figure 2b

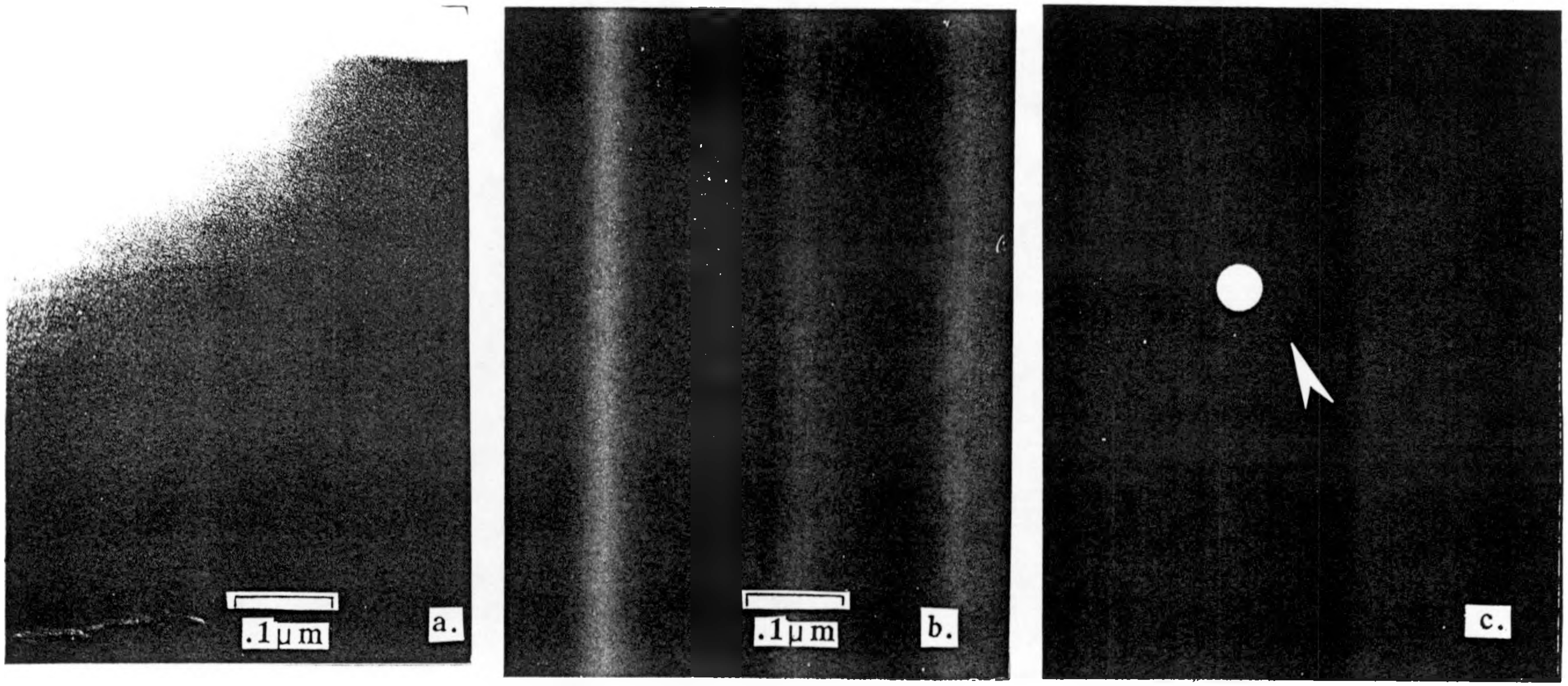

Figure 3

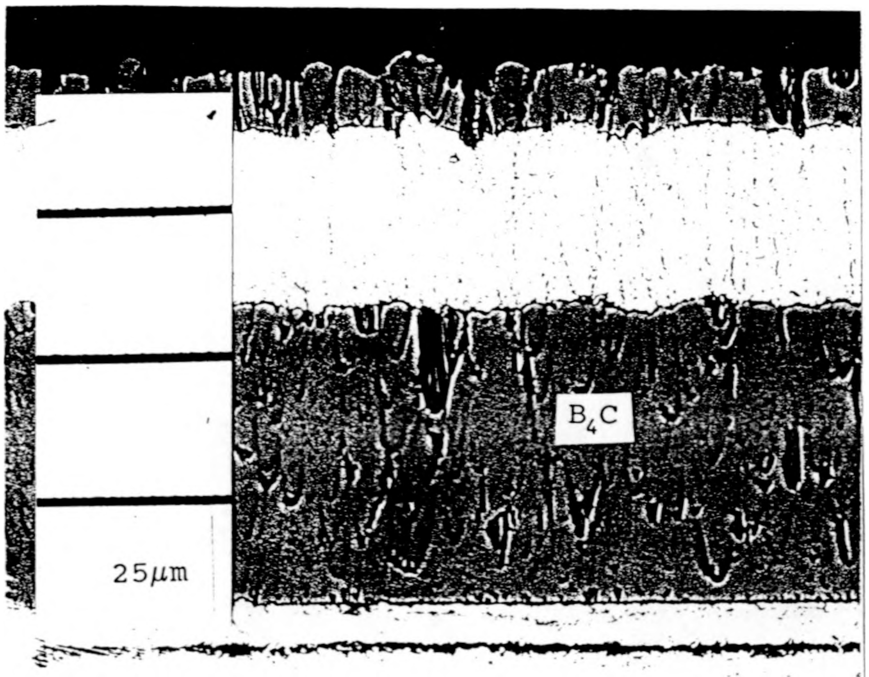

Figure 4

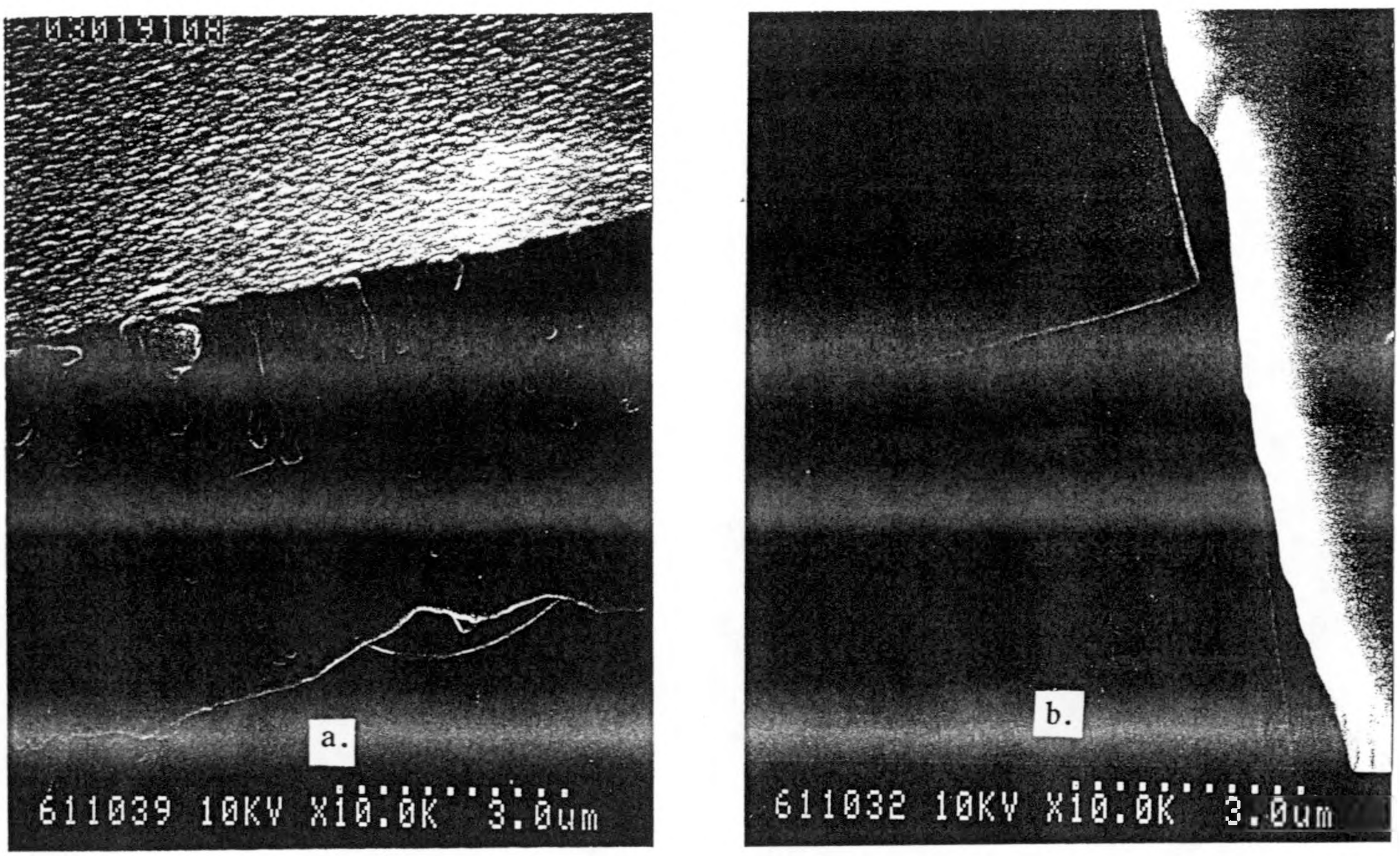

Figure 5

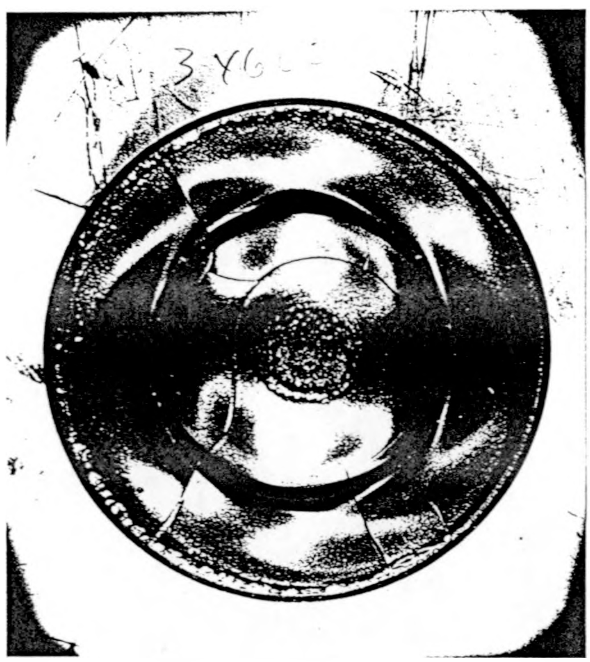

Figure 6