Diffuse Absorbing Beryllium Coatings Produced by Magnetron Sputtering

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Abstract

Beryllium coatings with varying thicknesses and columnar grain sizes were deposited by low temperature magnetron sputtering and then wet chemically etched to enhance diffuse absorption of light. After etching these coatings exhibited a matte black surface finish and low specular reflectance (below 2%) in the IR up to a critical wavelength dependent upon the original grain size of the coating. Extremely thick coatings (300 um) with original grain sizes of 10 to 12 um have been produced which exhibited specular reflectances below 0.5% up to 50 um wavelength and a Lambertian BRDF at 10.6 um averaging 4.3×10^{-3} $ster^{-1}$. Scanning electron microscopy results are presented for etched and unetched beryllium coatings which showed the etching process produces roughness and porosity over several size scales simultaneously with the maximum size scale limited by the initial coating grain size. This technique for producing diffuse absorbing baffle materials has great versatility in choice of coating material and substrate and can be expected to provide optical system designers with a variety of material options for stray light management.

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Introduction

Existing diffuse absorbing baffle materials or paints used for stray light management are made from materials which are not resistant to x-ray radiation. X-ray radiation resistance requires a low atomic number, high melting point material of which beryllium is a good example. We report here the development of a diffuse absorptive beryllium coating by a process consisting of two major steps: Low temperature sputter deposition of a columnar beryllium coating, followed by a wet chemical etching to further enhance porosity and increase diffuse scatter and absorption of incident light. While this approach is general and can be used with most any material which can be sputtered and chemically etched, only diffuse absorbing beryllium coatings are discussed here.

Most diffuse absorptive materials use surface roughness or porosity to trap, scatter, and absorb incident light. This process is most effective when the surface features have a size comparable to or slightly larger than the wavelength of the incident light. It has long been recognized that deposition processes such as sputtering produce columnar surface features with some porosity. The size of these columns and the existence of porosity depends primarily on the deposition conditions such as temperature and pressure, but also on overall coating thickness. Generally low temperature deposition enhances the formation of gross columnar structures and increasing thickness results in increasing column size. For example, studies of beryllium coating structure produced at low temperatures by magnetron sputtering indicate a linear relationship between column size and coating thickness.[1] It is this feature of low temperature sputter deposition that is taken advantage of here to produce diffuse absorbing coatings.

Experimental Details

Beryllium coatings were produced on 5 cm diameter beryllium substrates by low temperature sputter deposition using a dedicated sputtering system shown schematically in figure 1. A 15 cm diameter magnetron sputtering gun was located within a 30 cm diameter stainless steel vacuum chamber. The system was rough pumped by two cryosorption pumps operated in series. After the crossover pressure was reached, a gate valve was opened and a cryopump continued evacuating of the system. Sputter deposition was started when the base pressure in the chamber was in the low 10^{-5} torr range. Beryllium coatings were produced by magnetron sputtering at 10 mtorr argon pressure. Deposition rates varied from 5 Å/s to 65 Å/s depending on the coating thickness required, as did the source substrate separation which varied from 20 cm to 8 cm. The temperature of the substrates being coated was allowed to float during deposition, but did not exceed 150°C. A variety of coatings with different thicknesses were produced for this study and are listed in table 1.

Initially a set of three coating runs were made at different thicknesses with three beryllium substrates per run. Each coated sample was divided into two halves and etched for different times as indicated in table 1 to produce diffuse absorptive surfaces. These coating runs are denoted in the sample number by the prefaces B1, B2, and B3. Individual samples in a particular run are identified by a letter and number following the run number. Finally the side of the sample is denoted by a 1 or 2 after the sample number. Only two sample were etched from each coating run. The third sample from each run was not etched, but used as a control. Following this first set of experiments a group of beryllium substrates were coated with an extremely thick layer of beryllium. These runs are denoted by the preface BQ followed by a sample number.

Four different wet chemical etching treatments were investigated to enhance porosity of the deposited beryllium coatings. While several etchants were found to successfully enhance the diffuse absorbing properties of the coatings, the most successful was a found to be a mixture of HF and ethanol. This solution was used for the subsequent experiments reported here. Coated samples were etched for pre-determined period of time depending on coating thickness, typically between 45 s and 180 s. After etching the samples were immediately rinsed in deionized water, followed by an ethanol rinse before being dried by a stream of pressurized dry air. An uncoated beryllium sample was also etched as a control.

Table 1. Summary of Beryllium Coatings Used in Baffle Development

Sample Number	Thickness (um)	Etch Time (sec)	Notes
1-B2	1	60	
1-C	1	0	control
2-B2	5	90	
2-C	5	0	control
3-A1	25	180	

3-A2	25	120	
3-B1	25	65	
3-B2	25	30	
3-C	25	0	control
BQ-4	350	180	
BQ-6	350	0	control

Following treatment coated samples were evaluated for optical performance by measuring IR reflectance and BRDF. IR reflectance was obtained at near normal incidence and wavelengths between 2 and 50 µm. BRDF scatter measurements were made at 10.6 µum wavelength and an angle of incidence of 30°. Coated, but unetched beryllium was also evaluated optically as a control. Etched beryllium coatings were also evaluated by scanning electron microscopy to determine the nature of surface features and porosity.

Optical Properties of Diffuse Absorbing Beryllium Coatings

Coated samples were visually examined prior to etching and appeared, at near normal incidence, to be a uniformly dull gray color typical of relatively thick beryllium coatings. As the sample was rotated away from normal the coating appeared shinier, while rotation in the opposite direction made the coating appear darker. This behavior is expected for a coating consisting of columnar grains with an highly oriented and faceted surface morphology. After etching the coatings appeared to be much darker than before. Rotation of the sample away from normal resulted in an slight increase in brightness for short etch times. Increasing etching time usually resulted in darker appearance; while still further etching resulted in complete removal of the coating. The best etched diffuse absorptive samples had a "black velvet" appearance after etching.

Specular IR reflectance measurements are presented in figures 2 through 4. Figures 2 and 3 are reflectance plots for the best three etched coatings from runs 1, 2, and 3 respectively. Figure 2a presents the IR reflectance for sample 2-C, an unetched beryllium coating. This sample reflectance is similar to polished beryllium, except at wavelengths below 10 um were the natural surface roughness of the coating resulted in considerable scatter. Unetched control regions from runs 1 and 3 are similar to that presented in figure 2a. Figures 2b, 3a and 3b are reflectance plots for increasing thickness (sample 1-B2, 2-B2, and 3-A1 respectively) representing the best etching results from each coating run. Note that increasing coating thickness from 1 um to 25 um resulted in lower reflectance at larger wavelengths. The etched samples generally exhibited a flat, minimum reflectance region below a critical wavelength. Thicker coatings had larger minimum reflectance regions extending to longer wavelengths. For example, sample 1-B2 had reflectance below 2% at wavelengths less than 2.7 µm, 2-B2 at wavelengths less than 17 µm, and 3-A1 at wavelengths less than 21 µm. Finally the IR reflectance of the much thicker coating (sample BQ-4) is shown in figure 4. Reflectance for this sample is less than 1% from 2um out to 50 um, the limit of the spectrometer.

The effect of increasing etch time on reflectance is illustrated in figure 5 which is a plot of reflectance as a function of etch time for a constant thickness of 25 um at four IR wavelengths. The average column size in a sputtered beryllium coating of this thickness is expected to be 2 to 4 um in diameter. For smaller wavelengths (below 20 um) reflectance drops rapidly as a function of etch time. Larger wavelengths require longer etch time before reflectance is minimize. At 40 um wavelength, which much larger than the average column size in this coating, increasing etch time results in a slow, non-monotonic decrease in reflectance.

BRDF scatter measurements at 10.6 um are shown in figure 6 for the 350 um thick beryllium coating (sample BQ-04). Here BRDF is plotted as a function of angle measured from specular for two locations on the same sample. Also shown is the BRDF instrument background signal obtained without a sample present. This BRDF plot for BQ-4 shows the Lambertian character of the scatter signal from thick etched beryllium coatings. No statistically significant increase in signal was observed at 0°, the specular reflectance angle. The average BRDF from -30° to +30° was 4.5×10^{-3} ster^{-1}.

Scanning Electron Microscopy of Diffuse Absorbing Beryllium Coatings

A series of scanning electron micrographs taken of samples from run 3 is shown in figure 7 for different etch times. Figure 7a shows the coating surface at 10000x before etching. The coating has isotropic columnar grains with dimensions between 3 and 5 um. There is also evidence of some porosity between columns. Figures 7b, 7c, and 7d are successive micrographs of the coatings after etch times of 30s, 65s and 180 s, respectively. As etch time increases from figure 7b to 7d the amount of porosity between grains also increases due to a reduction in the size of the columnar grains. Simultaneously, the individual grains are also attacked during etching resulting in the evolution of a porous microstructure within the columnar grains themselves. It is this production of micro-roughness and porosity on different size scales within the same coating that results in the a diffuse absorbing material effective over a range of wavelengths. However, porosity cannot increase beyond the original grain size of the coating and thus there is a maximum feature size which is capable of diffusely scattering and absorbing light. Hence, the thin coatings (runs 1, 2, and 3) with relatively small grain sizes cannot be effective at longer wavelengths; while thicker coatings (BQ runs) with larger grain size can.

Similar scanning electron micrographs (at 2000x magnification) of the much thicker unetched and etched coatings are shown in figure 8. Figure 8a shows the unetched surface morphology of sample BQ-6. Here the columnar grains have anisotropic shapes approximately 10 um to 12 um along their major dimension. Again etching (figure 8b) creates porosity between columns while attacking individual grains creating roughness and porosity over a range of size scales. Because of the larger initial grain size excellent diffuse absorptive behavior is observed out to 50 um.

Discussion and Summary

We have shown that it is possible to produce diffuse absorbing surfaces by sputter deposition of beryllium at low temperatures followed by wet chemical etching to enhance diffuse scatter and absorption. The wavelength range over which these coatings are effective was shown to be dependent on columnar grain size of the original material. Thicker coatings which have larger columnar grains are diffuse absorbing out to longer wavelengths after etching than thin coatings with smaller column sizes. Attack within the columnar grains by wet chemical etching produces porosity over a variety of size scales which diffusely scatter and absorb light at a variety of wavelengths.

There are several advantages to the approach described here to make diffuse absorptive baffle materials. First, use of a low temperature sputter deposition process allows a wide variety of materials to be used as substrates. Many currently available baffle materials require specialized surface treatment of a particular substrate material; for example, Martin Black requires an aluminum substrate. In this study we have applied diffuse absorptive beryllium coatings to a variety of substrates including aluminum, fused silica, and SiC. This versatility allows choice of a substrate material based on other important design criteria such as cost, weight, or strength. Finally, sputter deposition of beryllium makes available in a baffle coating with greater resistance to x-ray radiation than other, currently available baffle materials or paints.

References

1. C. M. Egert and J. G. Gooch, *Hardened Passive Optical Components Monthly Report* , June 1988, MMES/USASDC-88-6.

Figure Captions

1. Schematic diagram of the beryllium coating system.

2. Reflectance as a function of wavelength from 2 um to 50 um for etched beryllium coatings from run 1: a) sample 2-C, 5 um thick and unetched; b) sample 1-B2, 1 um thick with 60 s etch.

3. Reflectance as a function of wavelength from 2 um to 50 um for etched beryllium coatings from runs 2 and 3: a) sample 2-B2, 5 um thick with 90 s etch; b) sample 3-A1, 25 um thick with a 180 s etch.

4. Reflectance as a function of wavelength from 2 um to 50 um for sample BQ-4, 350 um thick and etched for 180 s.

5. Reflectance at four wavelengths as a function of etch time for sample from run 3 with a constant thickness of 25 um.

6. BRDF plot for thick coated sample BQ-4 measured at two locations on the sample also showing the background signal of the scatterometer.

7. Scanning electron micrograph of beryllium coating samples from run 3 which were etched for different times: a) 3-C, no etch; b) 3-B2, 30 s etch; c) 3-B1, 65 s etch; d) 3-A1, 180 s etch.

8. Scanning electron micrograph of thick (350 um) beryllium coatings a) unetched sample BQ-6 and b) etched for 180 s, sample BQ-4.

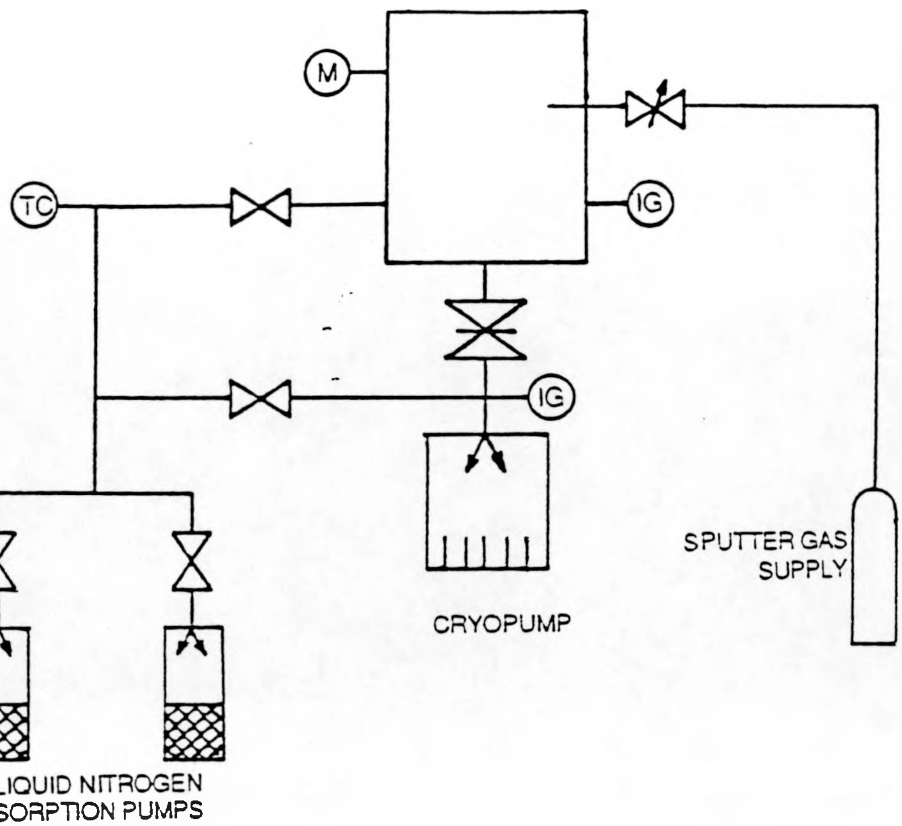

M
TC
IG
IG
SPUTTER GAS
SUPPLY
CRYOPUMP
LIQUID NITROGEN
SORPTION PUMPS

Figure 1

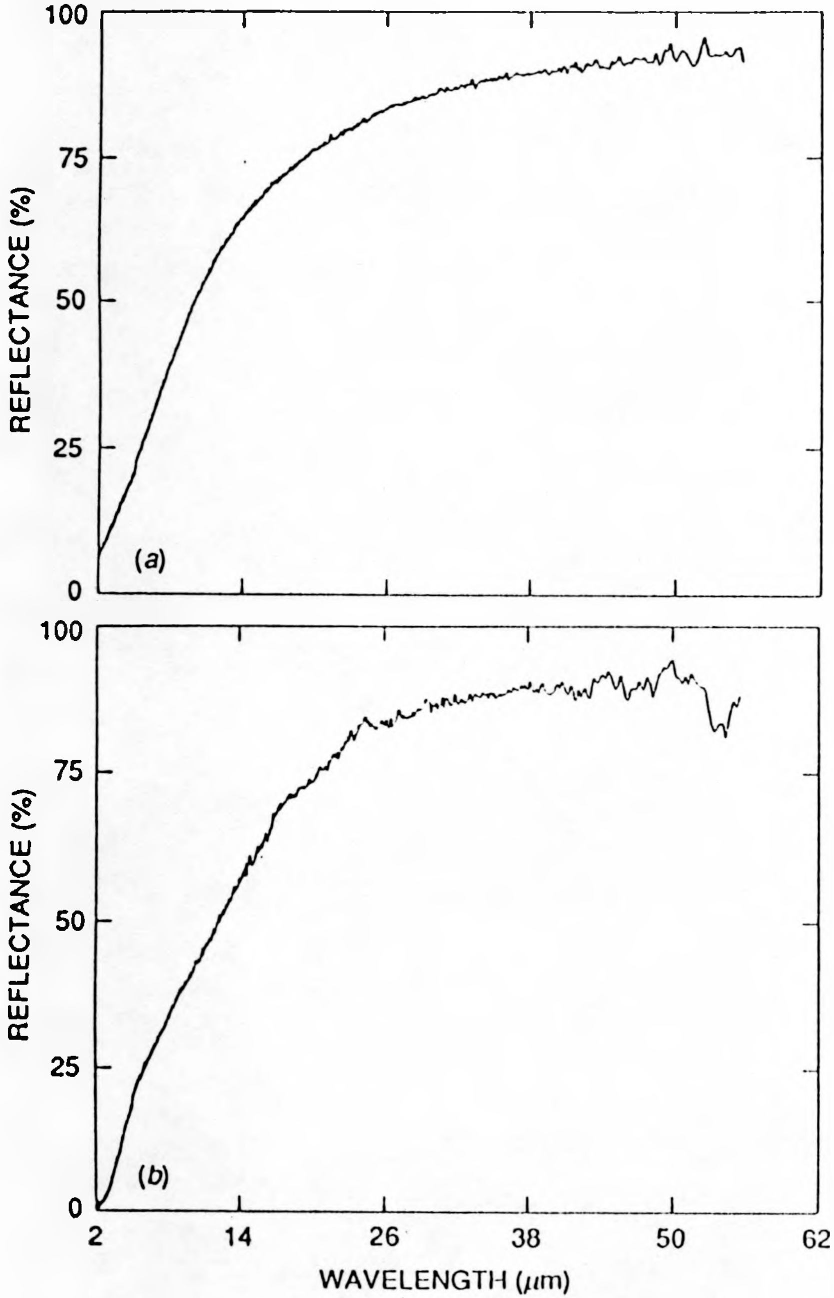


Figure 2

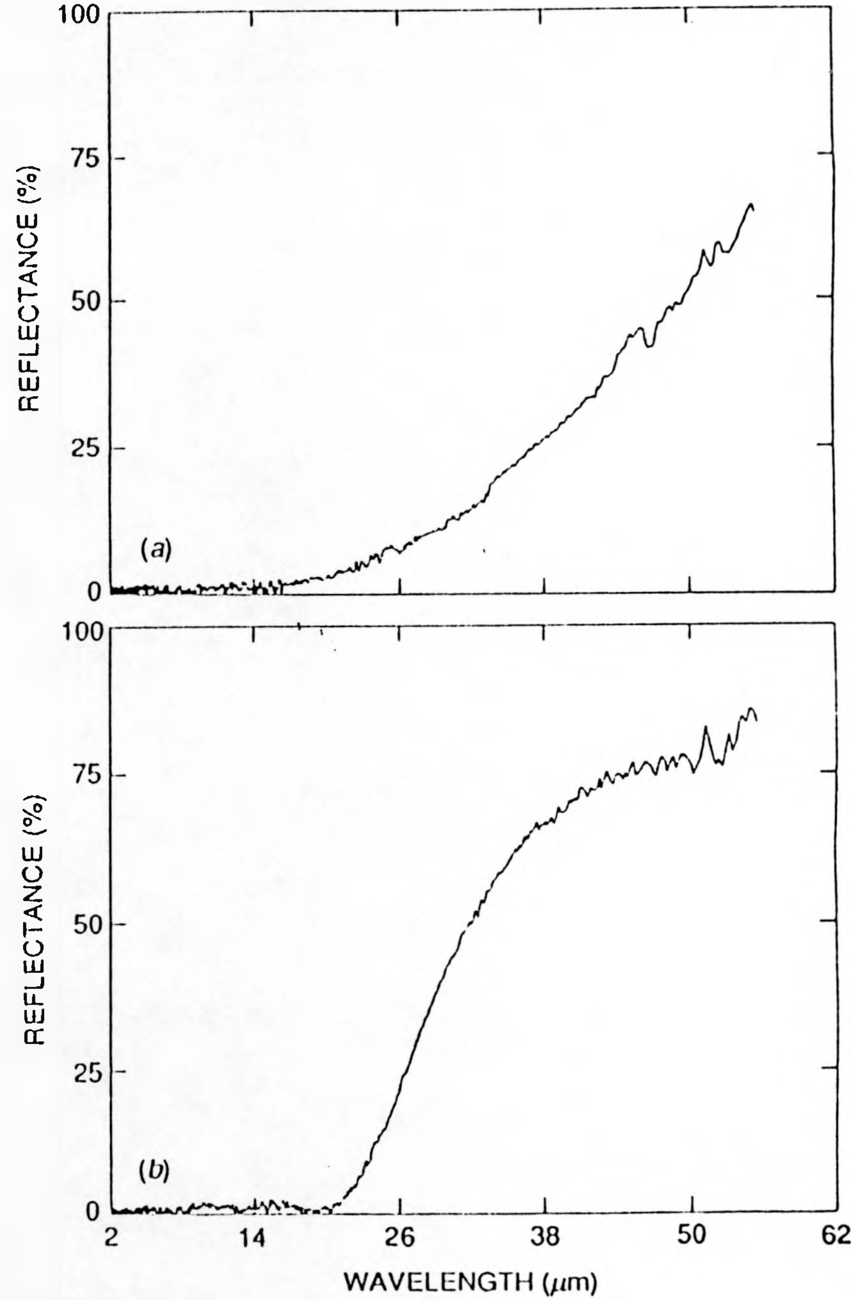


Figure 3

SPECULAR REFLECTANCE OF ORNL ETCHED Be

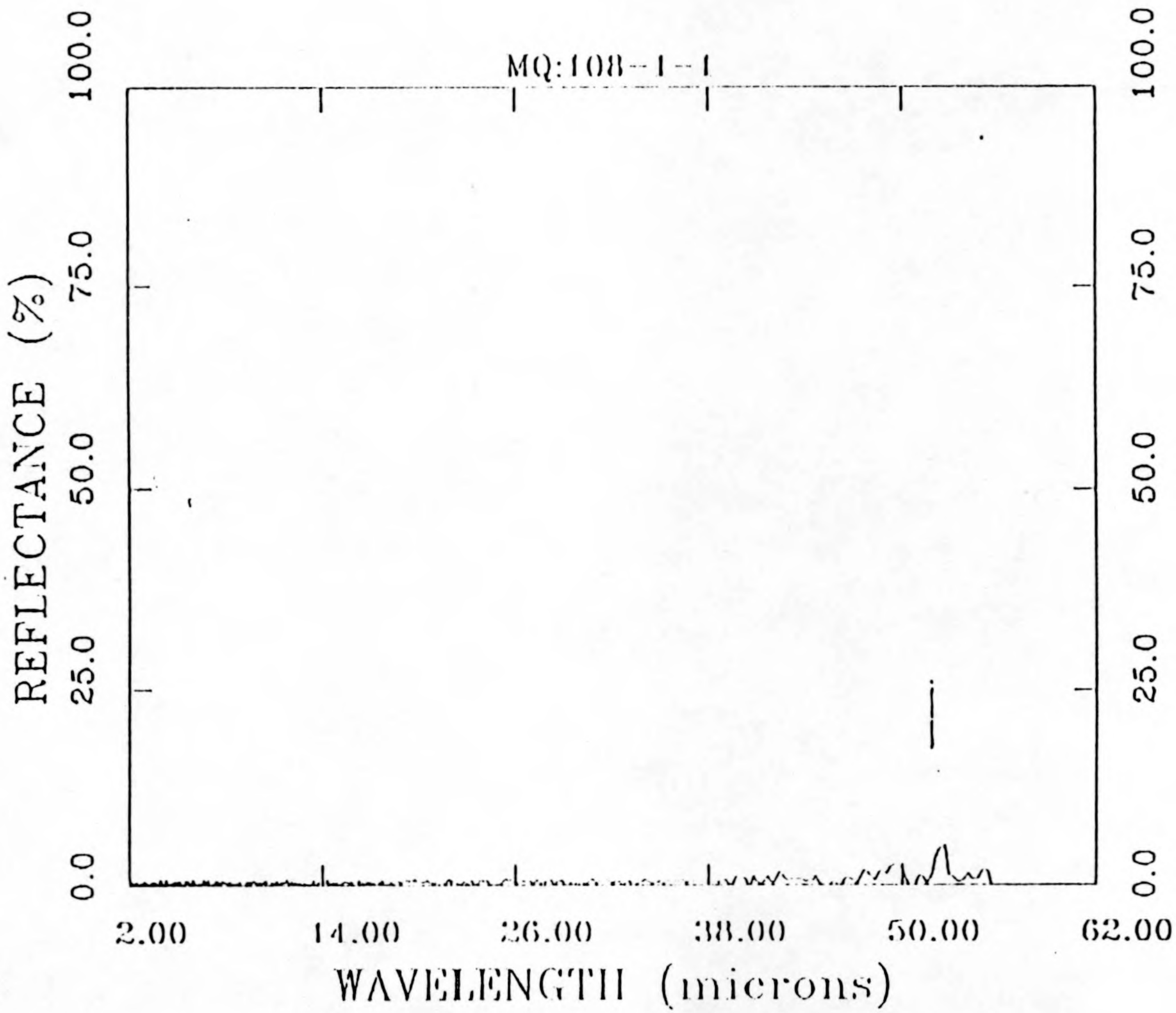


Figure 4

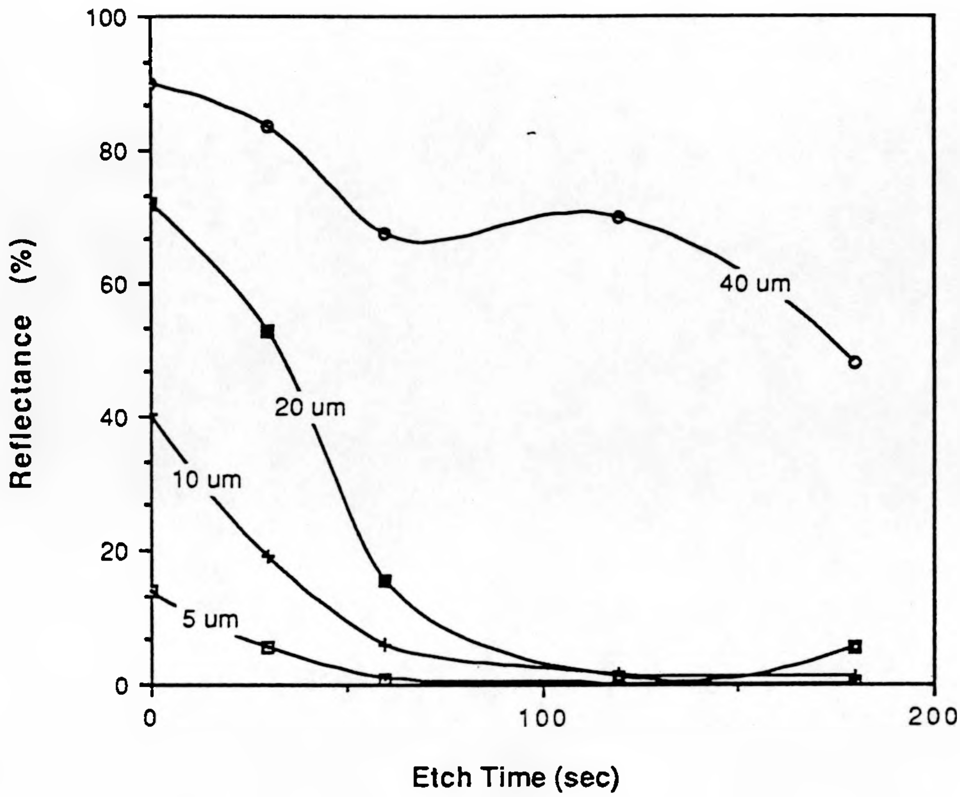

100
80
60
40
20
0
Reflectance (%)
40 um
20 um
10 um
5 um
0
100
200
Etch Time (sec)

Figure 5

ORNL Etched Be on Be

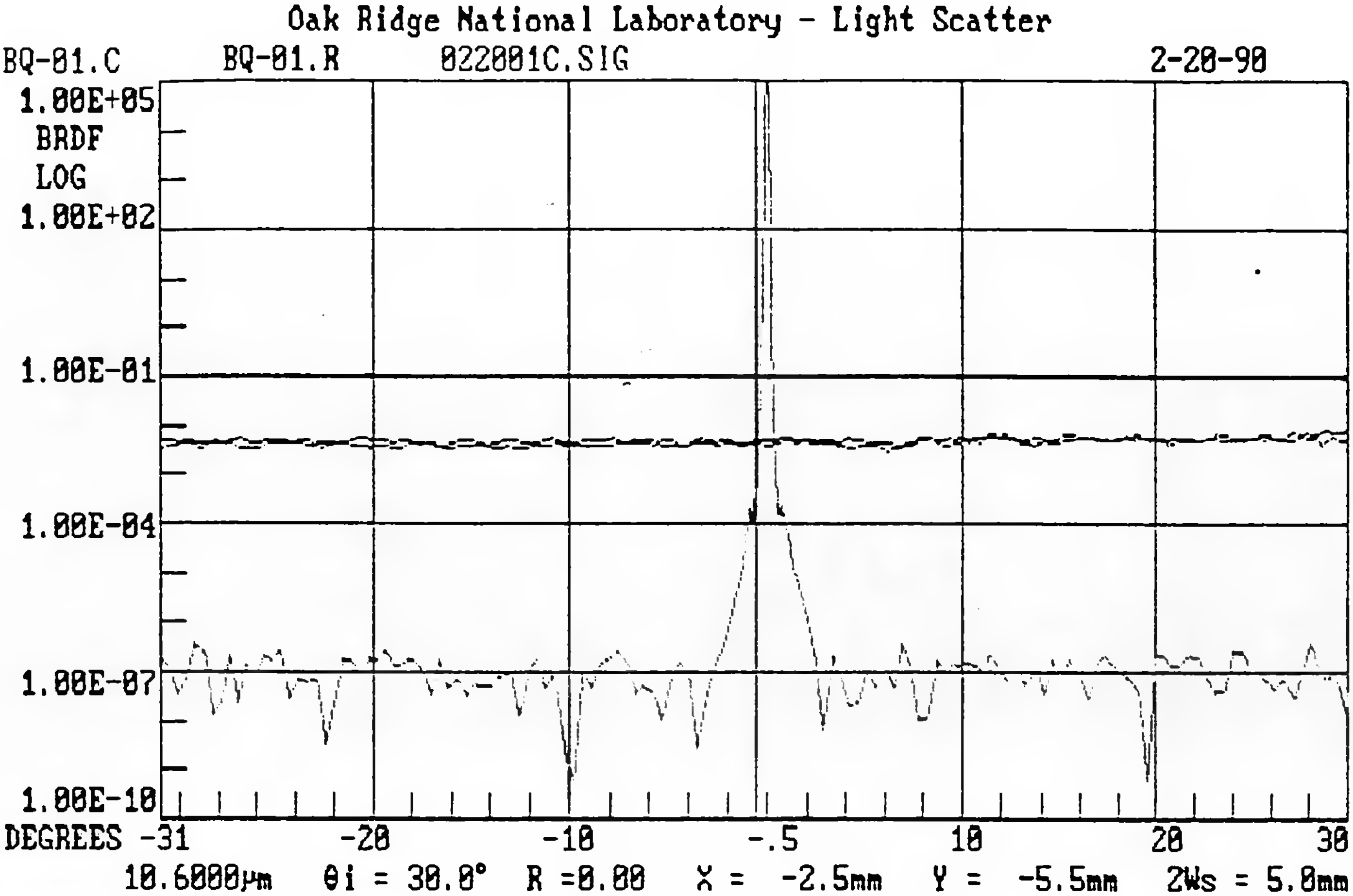
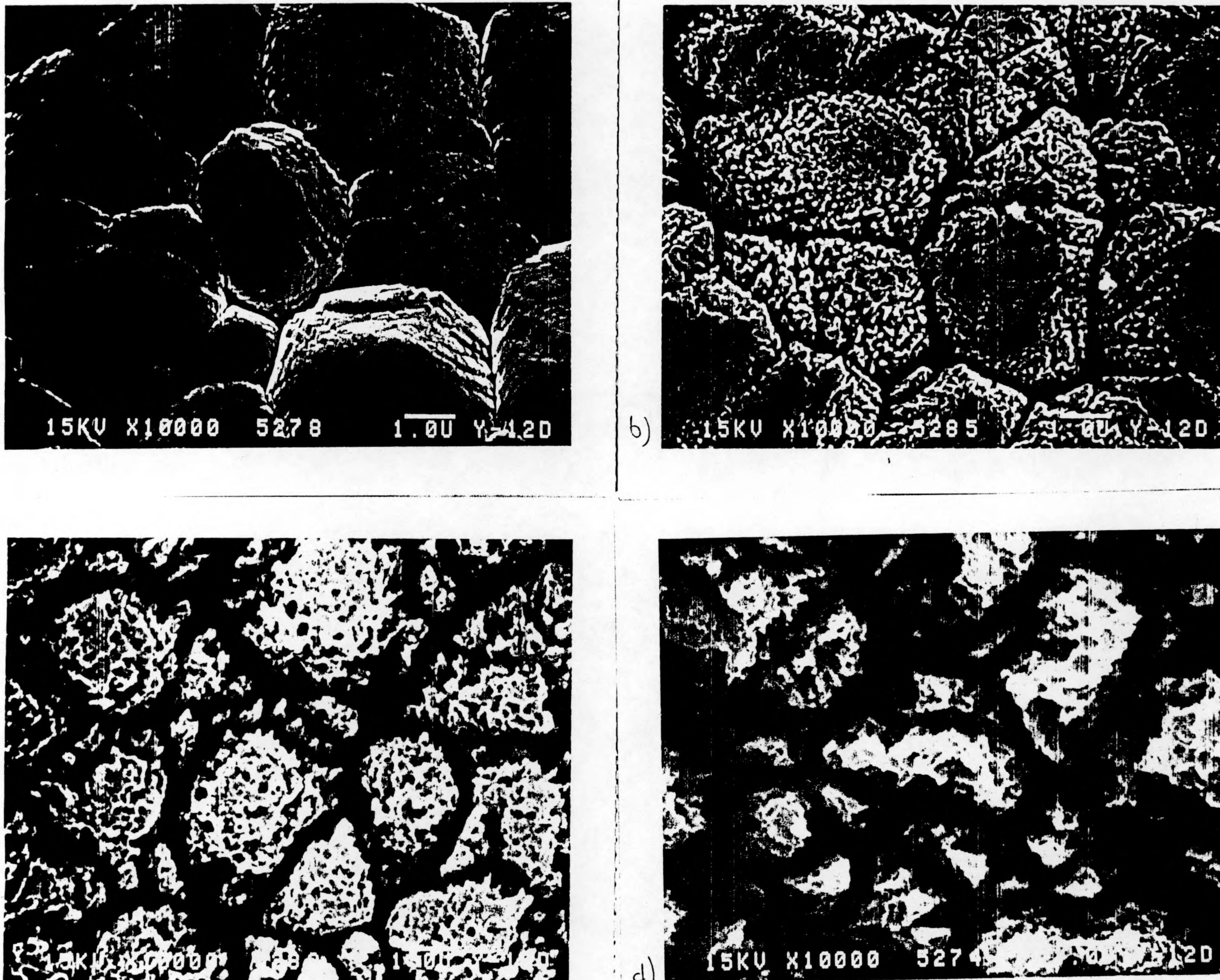


Figure 6

File 1: C:\SCATTER\BAFFLE\MQPASS\BQ-01.C
File 2: C:\SCATTER\BAFFLE\MQPASS\BQ-01.R
File 3: C:\SCATTER\BAFFLE\MQPASS\022001C.SIG

	BRDF		
DEGREES	File 1	File 2	File 3
-30.000	4.041E-03	4.356E-03	4.535E-08
-20.000	3.535E-03	5.177E-03	1.841E-07
-10.000	3.839E-03	4.368E-03	1.211E-09
-5.000	3.810E-03	5.208E-03	7.492E-08
-4.000	3.753E-03	4.103E-03	8.582E-08
-3.000	4.267E-03	5.171E-03	4.890E-08
-2.000	4.341E-03	4.793E-03	1.006E-06
-1.000	3.922E-03	4.460E-03	7.172E-05
0.000	4.079E-03	5.277E-03	1.359E+05
1.000	4.851E-03	5.582E-03	6.014E-05
2.000	4.906E-03	4.835E-03	1.388E-06
3.000	5.017E-03	4.665E-03	8.191E-08
4.000	3.886E-03	4.881E-03	3.899E-08
5.000	3.713E-03	4.889E-03	1.010E-07
10.000	4.544E-03	5.594E-03	1.380E-07
20.000	5.860E-03	5.663E-03	1.872E-07
30.000	4.912E-03	8.061E-03	9.272E-08

Figure 7



a) b) c) d)

a)
b)


Figure 8

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Diffuse-Absorbing Beryllium Coatings Produced by Magnetron Sputtering

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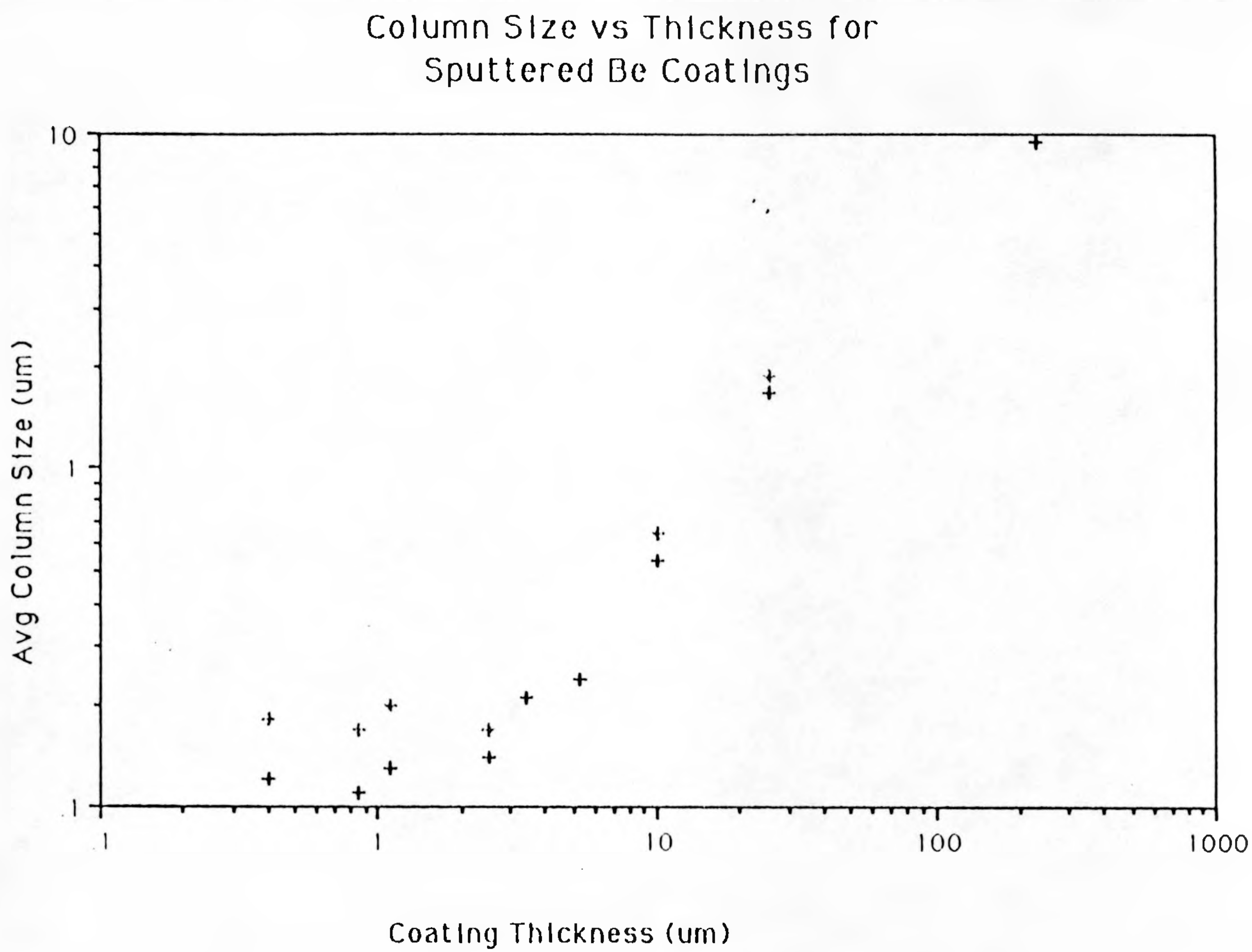
The Approach Used To Produce Baffle Materials

- It is well known that light is strongly absorbed when surface features (columnar grains) are approximately the same size as the wavelength of light.
- Coatings can be produced by low temperature sputtering with surface feautures of the desired size depending on thickness and other coating parameters.
- This columnar structure can then be chemically etched to enhance optical absorption in the wavelength region of interest.

Column Size Increases With Increasing Thickness



A least squares fit to the linear portion of this plot gives:

$$\text{Col. size} = 0.79 * \text{Thickness}^{0.9} \quad \text{(all dimensions in um)}$$

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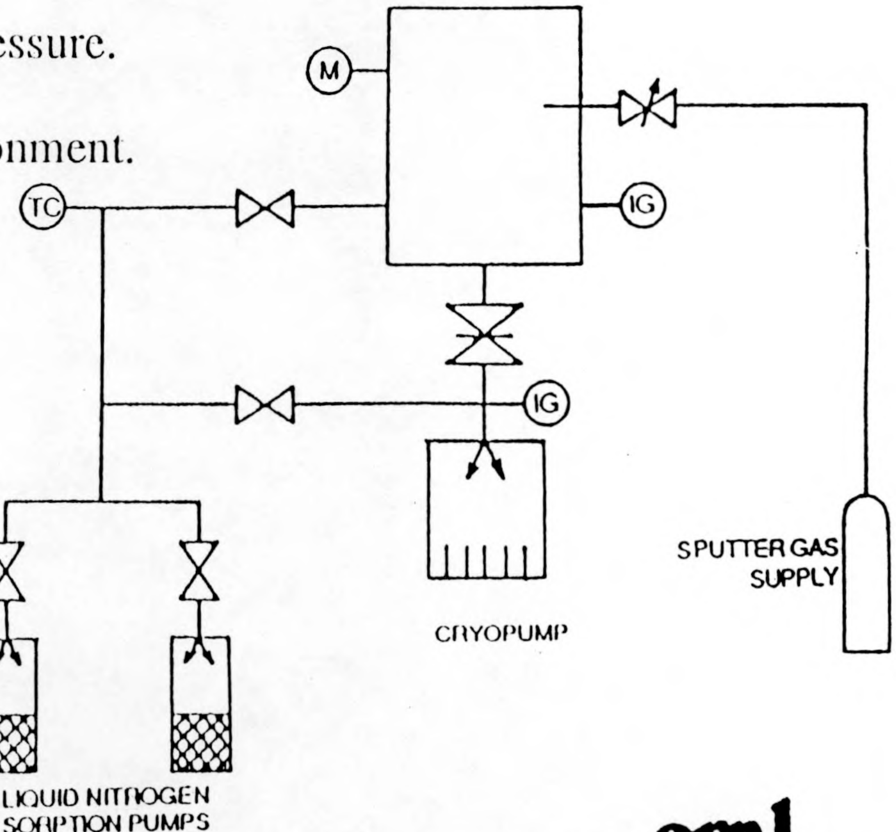
Experimental Details

Be coatings on various substrates were produced in a dedicated be coating system.

- LN_2 - sorption rough pumped.
- Cryopumped to mid 10^{-7} torr base pressure.
- No direct access to laboratory environment.

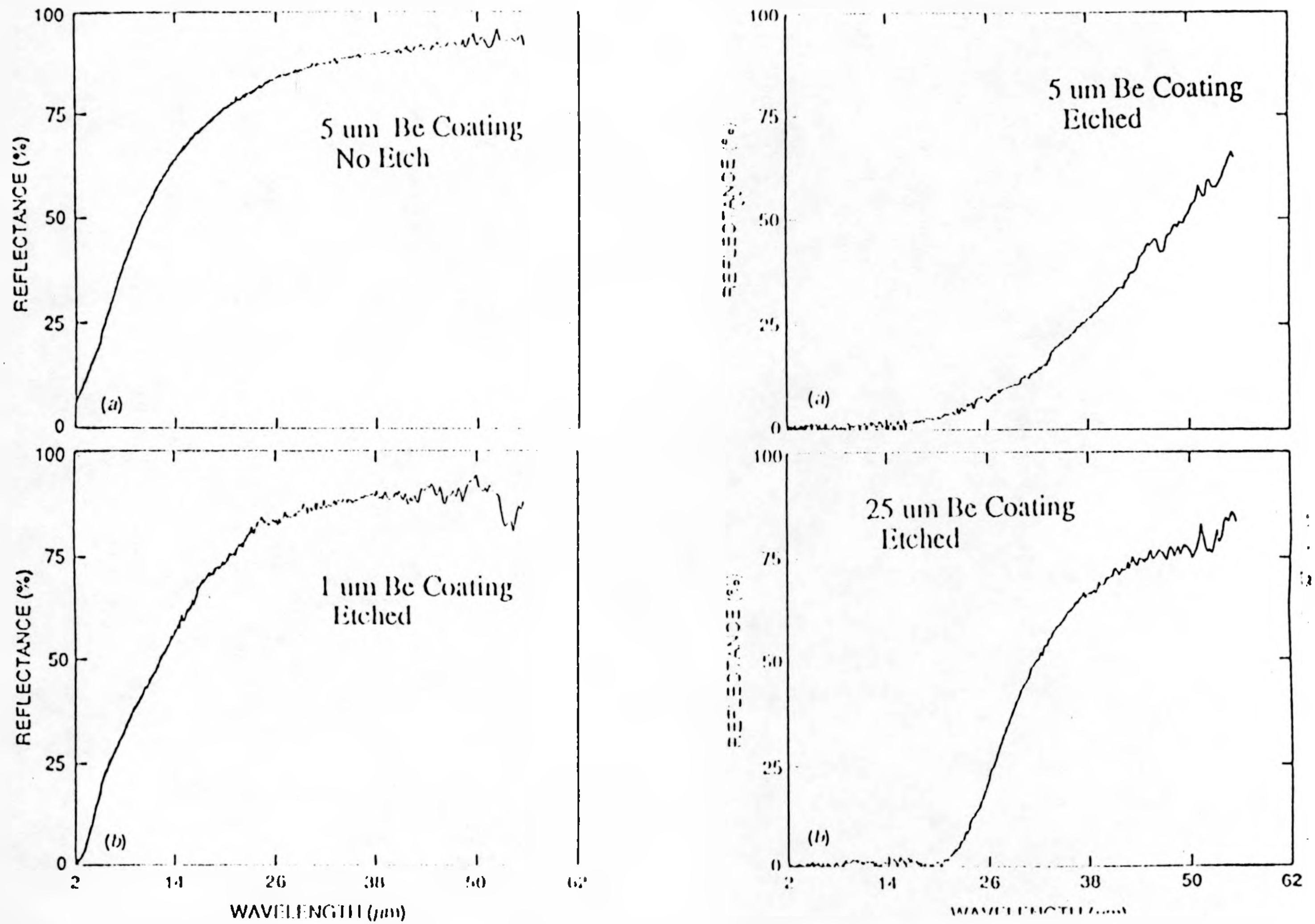
Schematic Diagram:



A Variety of Coating Thicknesses and Etch Times Were Tested

Thickness (μm)	Etch Times (sec)
1	0, 60
5	0, 90
25	0, 30, 65, 120, 180
350	0, 180

Etch Time And Coating Thickness Affect IR Optical Performance



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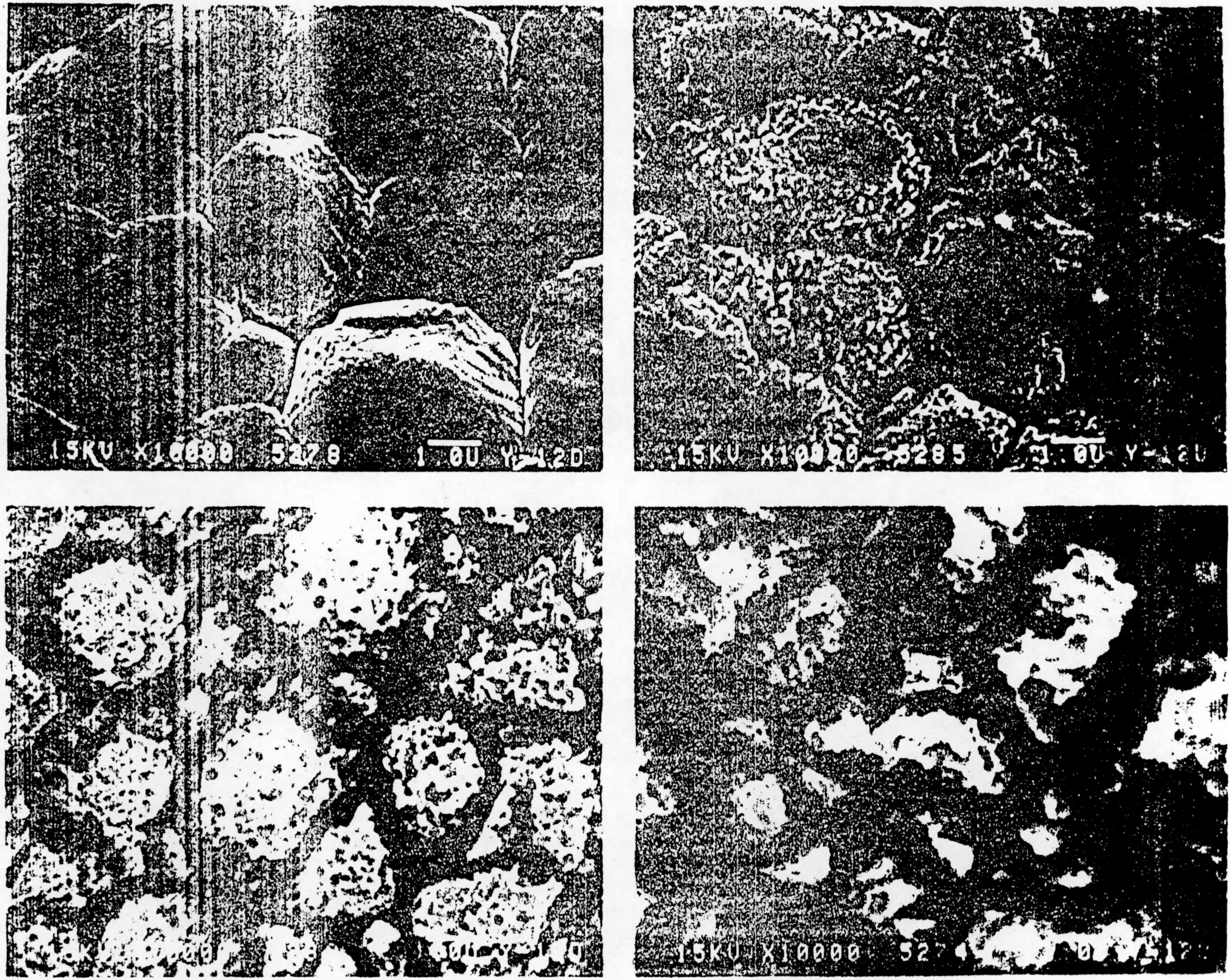
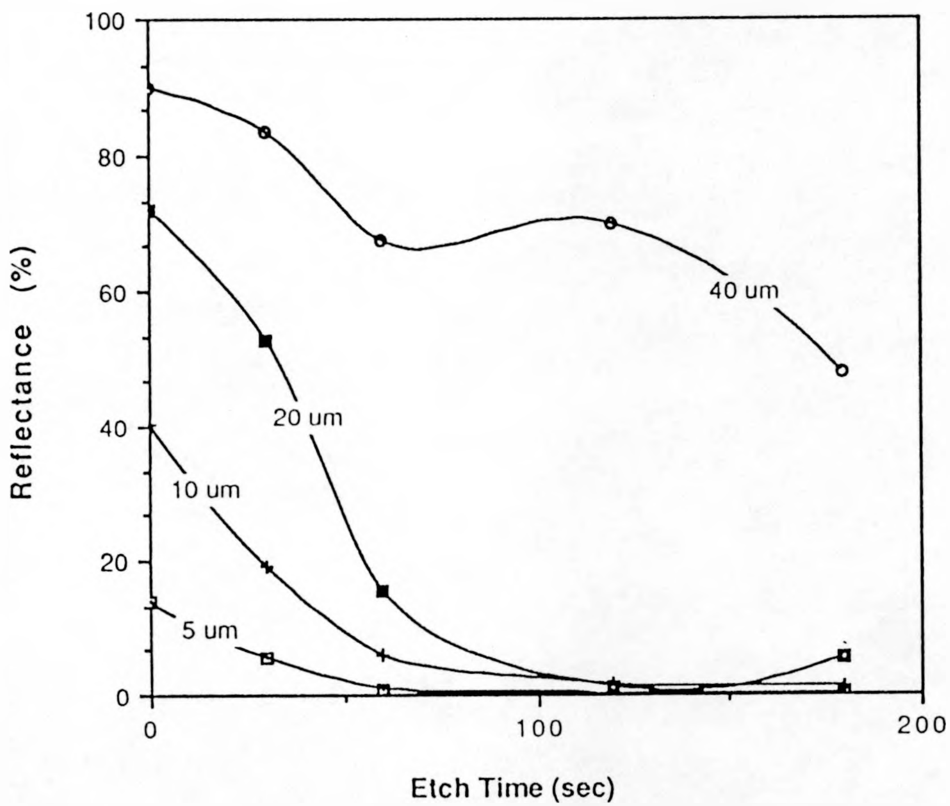
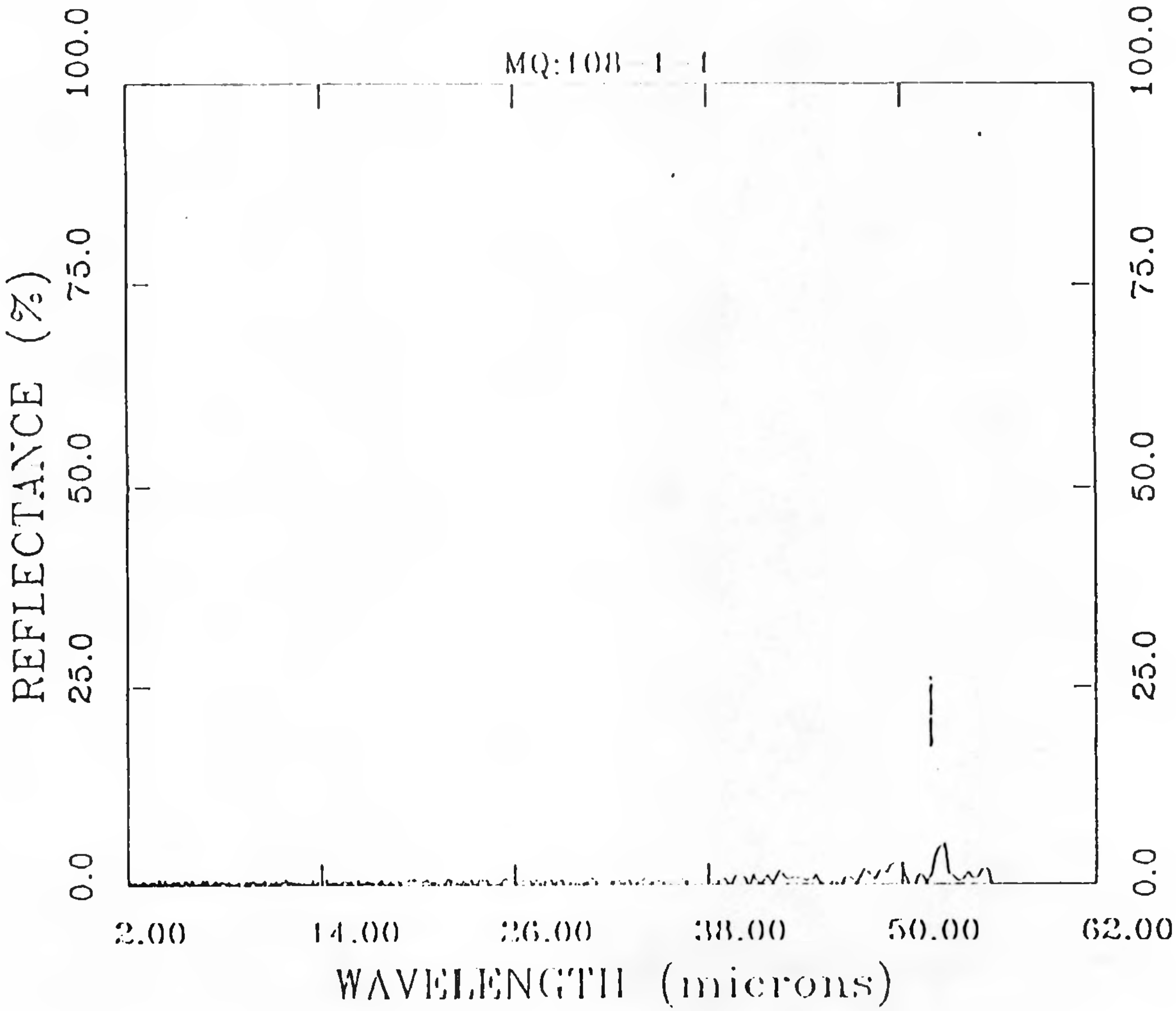

15KV X10000 5278
15KV X10000 5285
15KV X10000

Increasing Etch Time Results in Lower Reflectance in the IR

- Coating Thickness = 25 um
- Plot Reflectance as a function of etch time for different wavelengths:



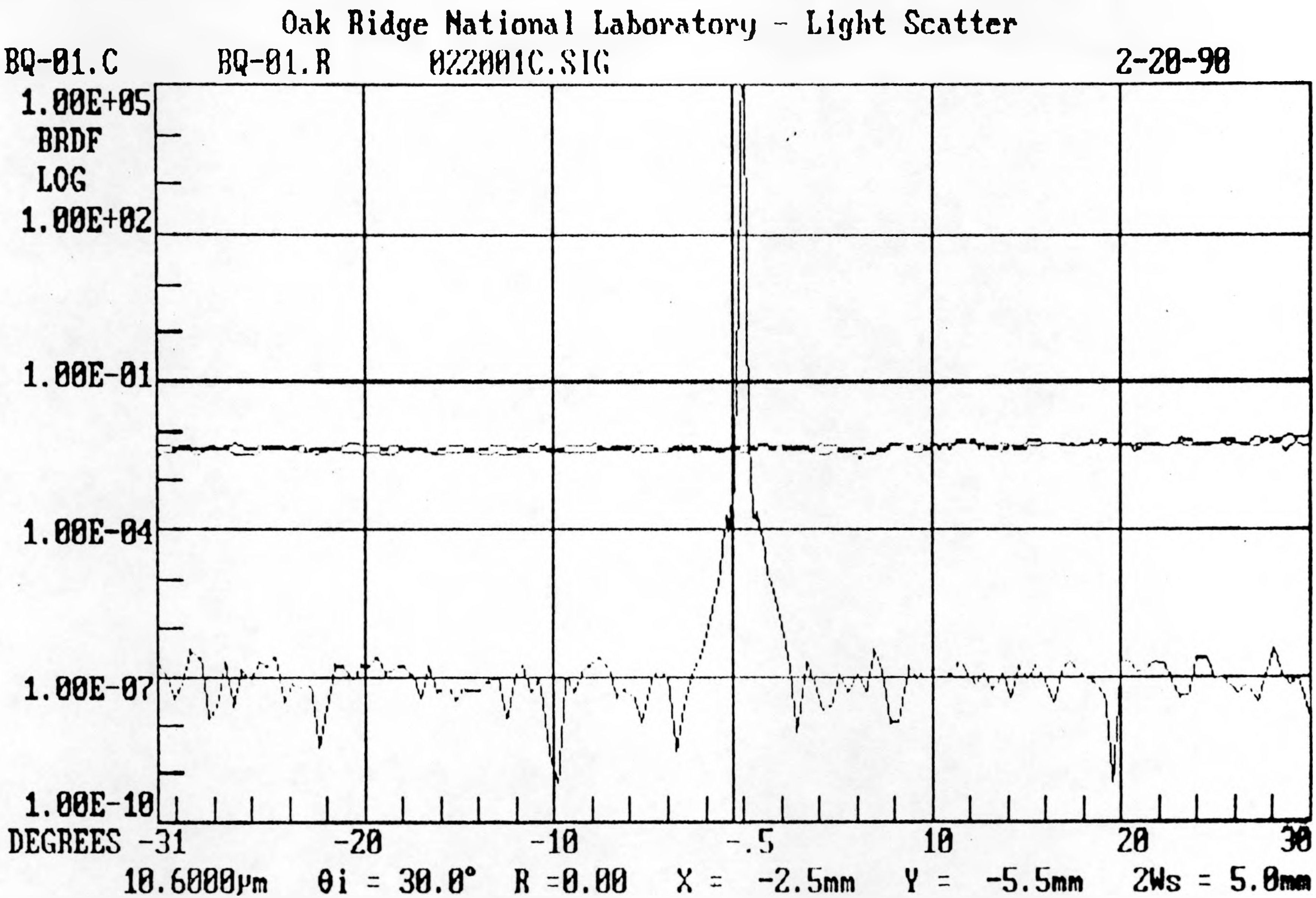
SPECULAR REFLECTANCE OF ORNL ETCHED Be

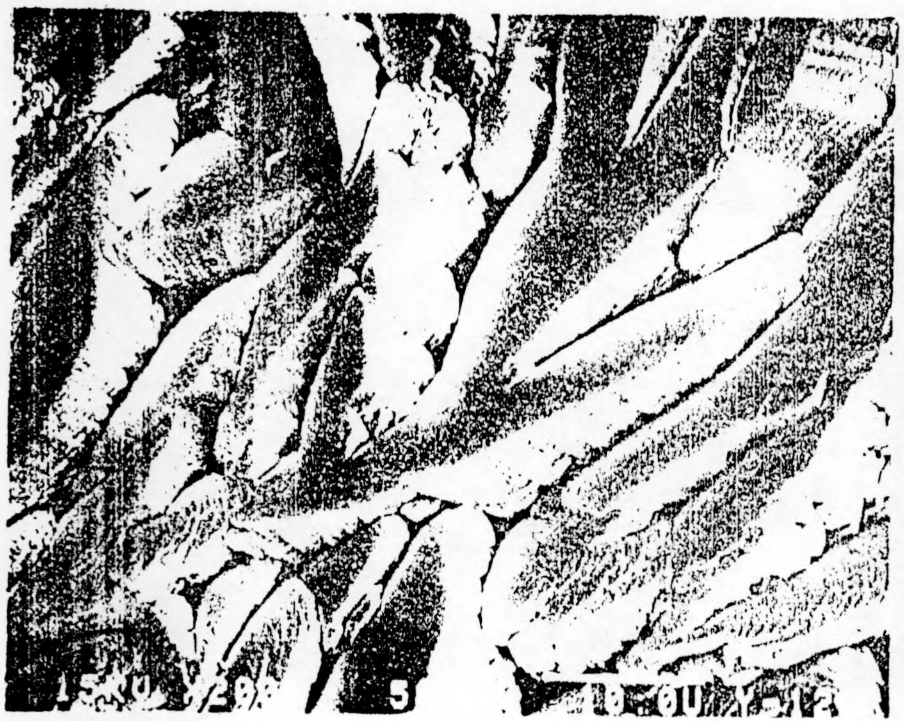


ornl

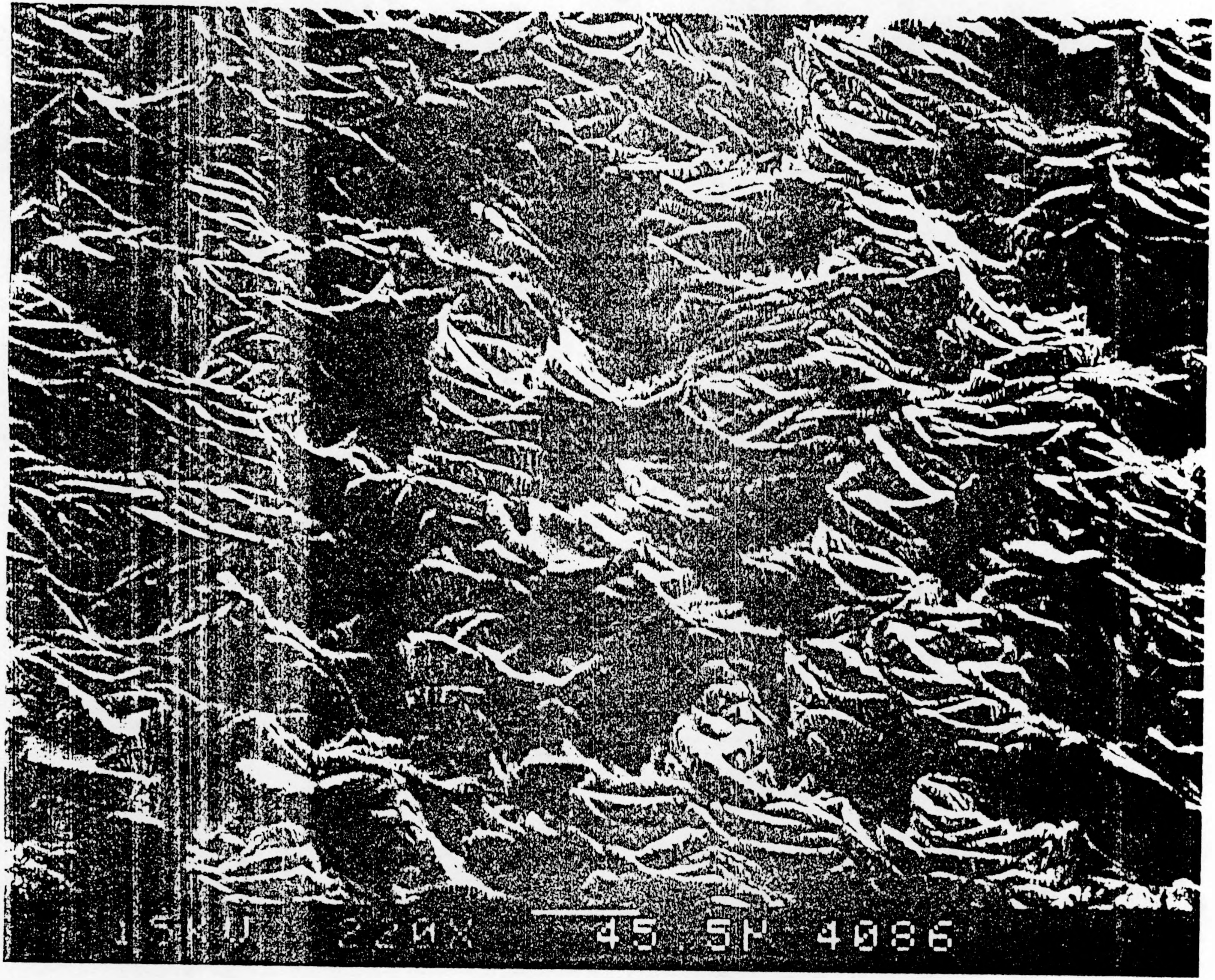
Figure 4

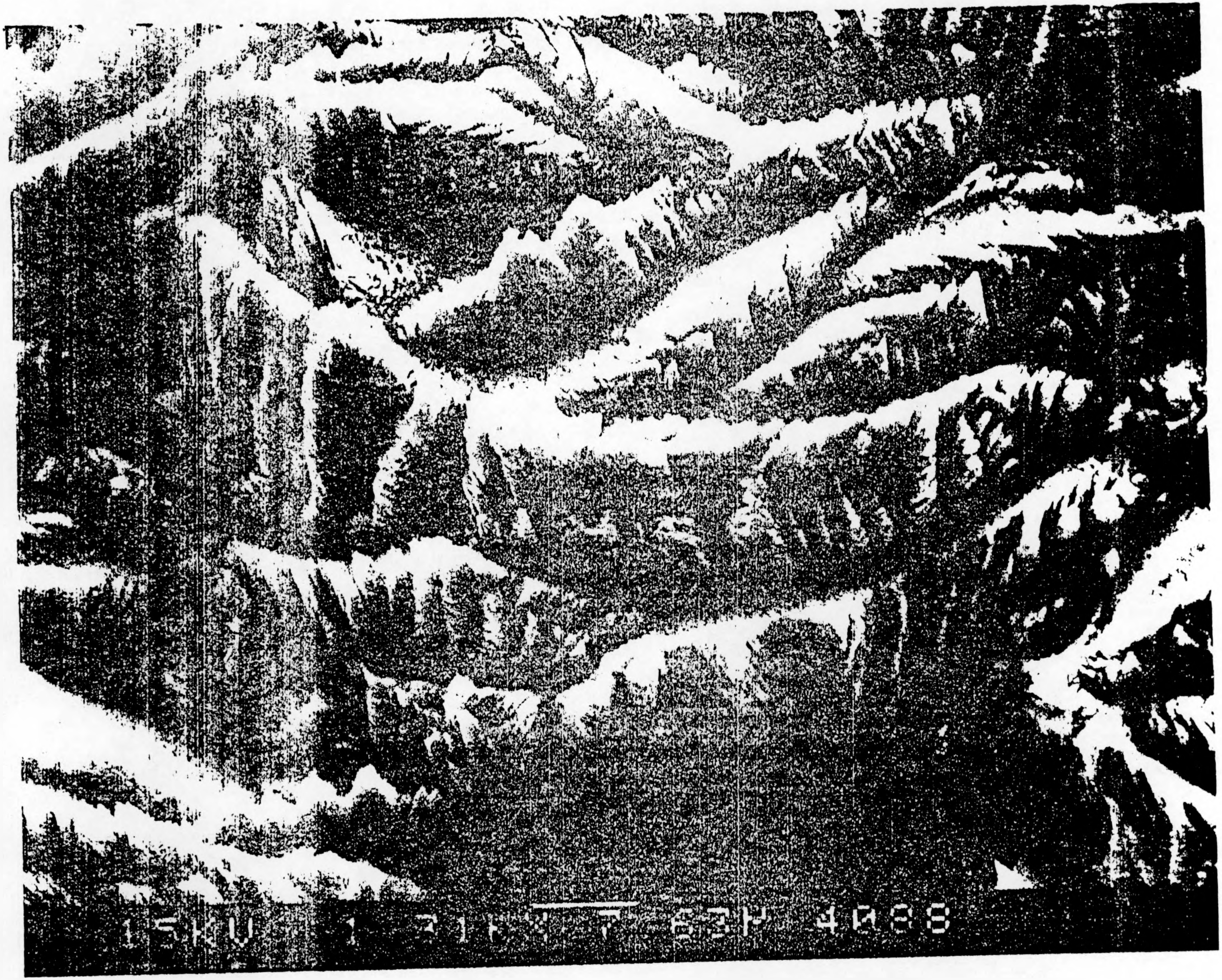
ORNL Etched Be on Be

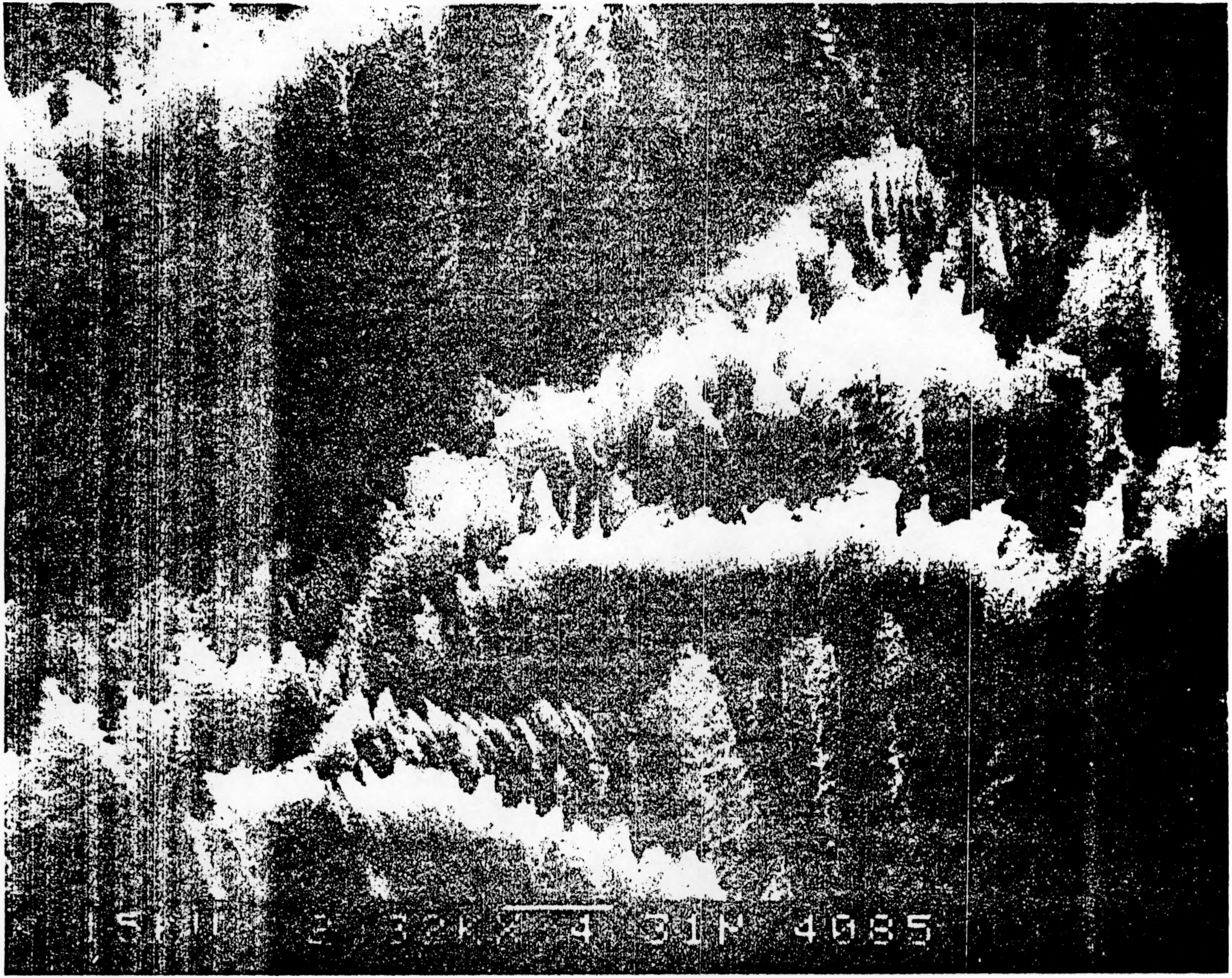





X2000
Y-120


15KU 220X 45.5U 4086


15KV


4085

Diffuse Absorptive Beryllium Coatings Can Be Applied To A Variety Of Substrate Materials.

- Beryllium
- Aluminum
- Silicon Carbide
- Fused Silica
- Plasma Sprayed Beryllium

Etched Beryllium Coatings Have Several Advantages As Diffuse Absorptive Baffle Materials

- Excellent optical performance throughout the IR.
- Uses existing readily available and well understood sputtering technology.
- Scaleable to large dimensions and complicated geometries.
- Is a versatile baffle material which can be applied to a variety of substrate materials.

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