CONF-8810401--1

UCRL- 99314
PREPRINT

UCRL--99314

DE89 015727

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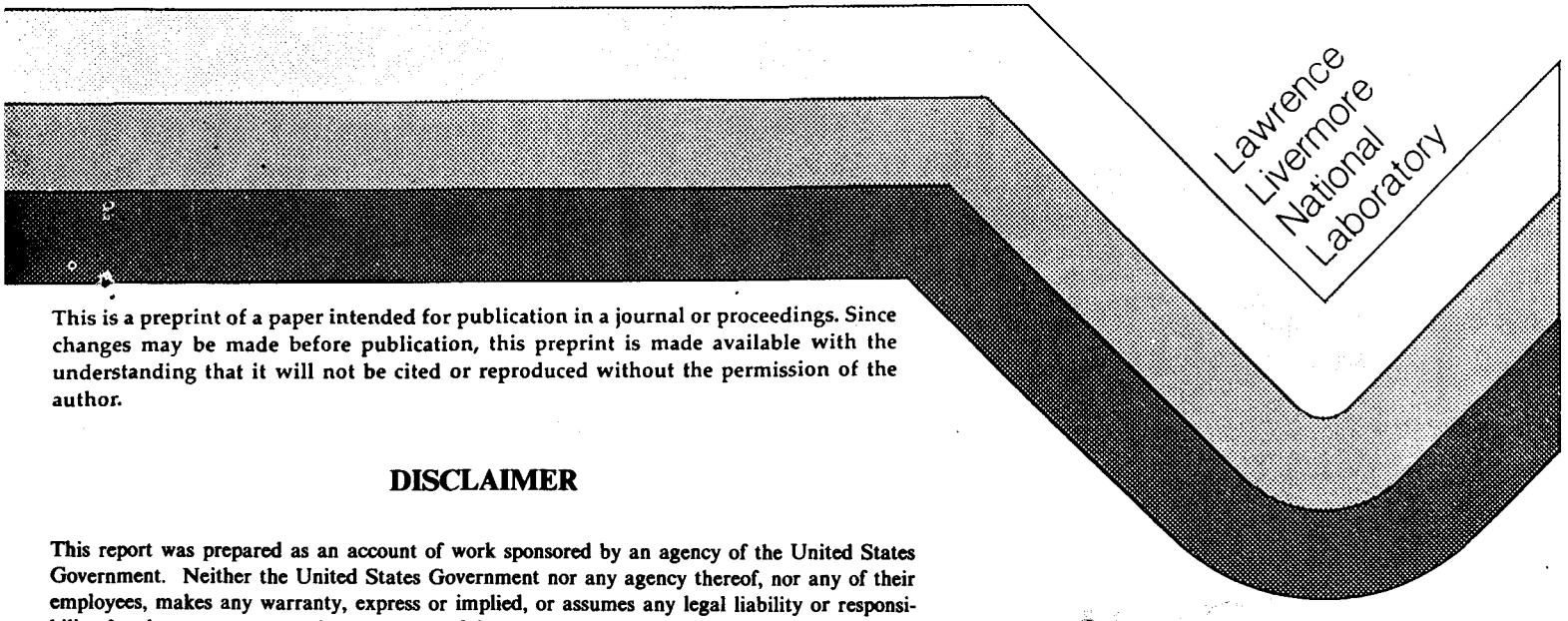
THIS PAPER WAS PREPARED FOR SUBMITTAL TO
HIGH POWER LASER OPTICAL COMPONENTS
TOPICAL MEETING
BOULDER, COLORADO
OCTOBER 24-25, 1988

OCTOBER 1988



DISCLAIMER

ANALYSIS OF DC MAGNETRON SPUTTERED BERYLLIUM FILMS*

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Abstract

We are evaluating techniques that alter the columnar grain structure in sputtered beryllium films on fused silica substrates. The films are formed by DC magnetron sputtering, and the columnar structure, which is characteristic of this and most other deposition techniques, is highly detrimental to the tensile strength of the films. Attempts to modify the columnar structure by using RF-biased sputtering combined with nitrogen pulsing have been successful, and this paper describes the analyses of these films. Sputtered beryllium films are quite brittle, and the columnar structure in particular tends to form a distinct intergranular fracture; therefore, the grain structure was analyzed in fractured specimens using the high-resolution capability of a scanning electron microscope (SEM) equipped with a field emission gun (FESEM). Ion microanalysis using secondary-ion mass spectroscopy (SIMS) was conducted on some specimens to determine relative contamination levels introduced by nitrogen pulsing. The capability to perform quantitative SIMS analyses using ion-implanted specimens as standards also is being developed. This work confirms that the structure of DC magnetron sputtered beryllium can be improved significantly with combined nitrogen pulsing and RF-biased sputtering.

*Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

Introduction

DC magnetron sputtering is an excellent technique for the deposition of mirror-quality beryllium films on fused silica substrates.[1] However, a major problem characteristic of this and most other deposition techniques is the development of columnar grain structures that can be highly detrimental to the tensile strength and other physical properties of the films. Columnar structures produced during sputtering can be modified by using RF-biased sputtering, periodic nitrogen pulsing, or combined nitrogen pulsing and RF-biased sputtering,[2] and these techniques are being evaluated to refine the grain structure of the beryllium films. This paper describes the analysis of beryllium films produced by these techniques.

Fine structure in beryllium is difficult to image in a scanning electron microscope (SEM) because of both the low atomic number and the low secondary-electron emission coefficient of beryllium. The low atomic number permits excessive electron-beam penetration, and the low secondary-electron coefficient produces a very low signal-to-noise ratio. These effects seriously degrade the contrast of secondary-electron images, and resolution also is compromised when the electron-beam diameter and current are increased to obtain reasonable contrast. Application of a conductive coating improves image contrast, but the coating structure obliterates much of the fine structure in the beryllium films. Efforts to improve SEM imaging of the beryllium films by using an SEM equipped with a field-emission electron gun (FESEM) will be described.

Previous experience has shown that deposition of beryllium can be affected by environmental contamination in the deposition chamber.[3] In addition, information also was required on the amount of contamination that may be introduced by nitrogen pulsing. Therefore, ion microanalysis was performed on selected specimens for carbon, nitrogen, and oxygen.

Experimental Procedure

The DC magnetron sputtering system and the technique for depositing beryllium films has been described elsewhere.[1] A RF power supply equipped with auto tuning permitted RF bias to be applied to the substrate stage during sputtering. The RF bias created a dense plasma around the substrate

with an intensity that was proportional to the RF power. Nitrogen pulses also could be introduced into the vacuum chamber by an electronically controlled on/off valve that also controlled the pulsing frequency. These techniques could be used either individually or in combination.

Because of initial difficulties and inconsistent results in the analysis of the grain structure of the beryllium films in the SEM, composite films were prepared to permit direct comparisons of structures produced by the RF-bias and nitrogen-pulsing grain-refinement techniques with the unmodified DC magnetron sputtering. The use of composite films also facilitated optimization of the controlling parameters of the grain-refinement techniques.

Beryllium is brittle, and fractures in sputtered beryllium films, particularly those films with columnar grain structures, tend to be intergranular; therefore, a convenient technique to analyze grain structure in beryllium films is to fracture the beryllium film intact on the fused-silica substrate and examine the fractured beryllium surface in an SEM. Because of the aforementioned problems in obtaining high-resolution SEM images from beryllium, many workers deposit a thin conductive coating of Au or Au-Pd[4] on beryllium to improve the secondary electron emission. A conductive coating also was required to reduce severe electron charging of the fused silica substrate, even at low electron-beam voltages. Therefore, coatings of Au-Pd deposited by conventional sputtering, Au deposited by ion-beam coating, and carbon deposited by thermal evaporation were evaluated.[5] As will be shown, however, coatings obliterate much of the fine structure on the films.

An improved technique was developed that consists of carbon coating both sides of the specimen before fracturing it and then examining the uncoated fracture surface at low voltage. The proximity of conductive surface coatings to the fracture surface tends to bleed off the charge on the silica fracture surface and also minimizes adverse edge effects on the beryllium. This technique permits uncoated fracture surfaces of beryllium films to be examined at 2.5 kV in an Hitachi S-800 FESEM. The field-emission electron gun is superior to conventional electron guns for low-voltage imaging. The FESEM used for this work also was equipped with a cryogenic vacuum pumping system that significantly reduces the electron-beam induced contamination film that forms over the rastered area of a specimen during examination in

an SEM.

To determine the extent of contamination that formed in the beryllium films during sputtering, secondary ion mass spectroscopy (SIMS) was performed with a CAMECA IMS-3f ion microanalyzer using a $^{133}Cs^{+}$ primary ion beam. The primary-beam acceleration potential was 10 kV and the specimen was maintained at -4.5 kV to yield a bombardment potential of 14.5 kV. Primary-beam currents of either 6 or 10 μA yielded sputtering rates of about 1 or 6 nm/s, respectively. Depth profiles were obtained for carbon, oxygen, and nitrogen using mass isotopes ^{12}C, ^{16}O, and $23(^{9}Be + {}^{14}N)$; mass isotope 23 was used to analyze the BeN^{-} signal because nitrogen has a low electron affinity and yields a low N^{-} signal.

Quantitative analyses can be generated from measured SIMS ion currents if adequate standards are available to determine the necessary conversion factors. Since reliable beryllium standards with truly homogeneous compositions are not available, standards were prepared by the widely accepted technique of ion implantation. Oxygen standards were prepared in previous work using 150-keV O^{+} implants in polycrystalline beryllium;[6] nitrogen standards were prepared for this study using 200-keV N^{+} implants in similar material. The lower limit of detectability of oxygen in the implanted specimens was 11 ± 2 appm (atomic parts per million), which was primarily limited by residual gaseous contamination in the specimen chamber. The lower limit of detectability of nitrogen in the implanted specimens was 220 ± 80 appm; roughly half of this limit was matrix nitrogen in the beryllium, and the remainder was residual gaseous contamination. Studies using the SiN^{-} signal to analyze for nitrogen in silicon also yielded reliable analyses in the appb (atomic parts per billion) range.[7] Because of the usual fluctuations of instrument conditions coupled with the relatively high impurity levels in the beryllium that was available for implantation, the accuracy of the quantitative analyses is of the order of ± 25 per cent.

Results

A composite film formed by overlaying three different deposits is shown in Fig. 1a. The bottom layer (a) was deposited with the RF-bias technique, the middle layer (b) with no bias, and the top layer (c) with nitrogen

pulsing at 10-minute intervals. The specimen was coated with about 15 nm Au-Pd using conventional sputtering. The structure of the Au-Pd coating is prominent in Fig. 1a. It does not obscure the columnar beryllium structure and may even enhance it, and the three layers are visible; however, the structure of the Au-Pd coating does prevent observation of fine structure that may exist within the columnar structure. Figure 1b shows the composite film after ion-beam coating with about 10 nm Au. Ion-beam coating produces much finer coating structure than sputtering,[8] as is evident in Fig. 1b, and some of the ambiguity caused by the coarse Au-Pd structure in Fig. 1a is removed. However, delineation of the sharp structural features associated with the columnar structure has diminished. The results in Fig. 1b indicate that the columnar structure in the bottom layer deposited with the RF-bias technique had broken up to some extent, the middle layer with no bias had normal, nearly continuous columnar structure, and the top layer with 10-minute nitrogen pulsing had only slightly modified structure.

Figures 2a and 2b compare Au-Pd and carbon coatings on a fractured surface in a film deposited with RF bias. The specimen was sputter coated with about 15 nm Au-Pd for Fig. 2a, and about 10 nm of carbon for Fig. 3b. Fine structure in Fig. 2a is again obliterated by the relatively coarse structure of the Au-Pd coating. Carbon yielded slightly better structure delineation but less contrast than ion-beam coating with Au. Faint evidence of fine structure can be detected in the carbon-coated specimen in Fig. 2b, but delineation of the structure still is not satisfactory. Figure 2b does indicate, however, that the RF bias can alter the columnar structure.

Structures in composite nitrogen-pulsed/unbiased films are shown in Figs. 3a, 3b, and 3c for pulse intervals of 2.5, 5.0, and 10.0 minutes, respectively. These specimens were carbon coated on both the beryllium and the glass sides of the specimen before they were fractured, and the fractured beryllium surfaces were examined at 2.5 kV in the uncoated condition. Figures 3a through 3b demonstrate that significantly better structure delineation is obtained with this technique than with conductive coatings deposited on the fracture surfaces (Figs. 1 and 2). The 2.5- and 5.0-minute intervals, Figs. 3a and 3b, respectively, did dissociate the columnar structure and produce what appears to be a very fine, equiaxed grain structure, but the 10.0-minute interval (Fig. 3c) produced only slight modification of the columnar structure. These results confirm that the

microstructure of DC magnetron sputtered beryllium can be improved significantly with nitrogen pulsing, but for the conditions used in this experiment, the pulsing interval must be 5.0 minutes or less.

SIMS depth profiles obtained from the nitrogen-pulsed specimens are shown for the 2.5-, 5.0- and 10.0-minute nitrogen pulsing intervals in Figs. 4a, 4b, and 4c, respectively. As discussed in the section on "Experimental Procedure," profiles for carbon, nitrogen, and oxygen were obtained from each specimen using mass isotopes ^{12}C, ^{16}O, and $23(^{9}Be + {}^{14}N)$ respectively. The slower sputtering rate of 1 nm/s was used to generate these profiles to resolve the individual pulses; sympathetic oscillations of the carbon and oxygen profiles also are evident. The numbers of oscillations in Figs. 4b and 4c coincide with the numbers of pulses that were used for each film (26 pulses for the 5.0-minute interval in Fig. 4b and 14 pulses for the 10.0-minute interval in Fig. 4c); individual pulses become difficult to resolve in Fig. 4a as the profile approaches the beryllium/glass interface.

Quantitative analyses were performed for nitrogen and oxygen in the same specimens shown in Fig. 4. The faster sputtering rate of 6 nm/s was used to obtain reasonable profiling rates and sensitivity and also to correspond with the sputtering rates used on the implanted standards. The profiles penetrated through both the nitrogen-pulsed and the unbiased layers. (Please note that the interface between the beryllium and the fused silica is on the right side of the profiles.) Figures 5a, 5b, and 5c are for the 2.5-, 5.0-, and 10.0-minute pulses, respectively. Individual pulses are not resolved for the faster pulsing rates in Figs. 5a and 5b, and they are only partially resolved in Fig. 5c for the 10.0-minute pulse rate. These profiles show the increase in nitrogen that occurred at the inception of pulsing along with simultaneous and somewhat unexpected increases in the carbon and oxygen concentrations.

Quantitative analyses are indicated at various points in the profiles. As discussed previously, the accuracy of these analyses is of the order of ± 25 per cent. The profiles indicate that a significant amount of contamination present at the start of the unbiased coating -- probably gaseous contamination introduced with the argon sputtering gas as well as surface-adsorbed contamination on the substrate -- dropped off rapidly to a steady-state level of about 100-200 appm nitrogen and 3000-4000 appm

oxygen. At the inception of nitrogen pulsing, the nitrogen levels increased to the range of 2000-3000 appm and the oxygen levels to 1.5-2.5 atomic per cent. As nitrogen pulsing progressed, the oxygen level recovered somewhat to about 5000-9000 appm, but the nitrogen level remained reasonably constant (the irregular nitrogen profile in the pulsed region of Fig. 5b is caused by partial resolution of individual pulses). Nitrogen varied from about 280 to 2400 appm (Fig. 5c) in the 10-minute pulsed film and 1300 to 3500 appm (Fig. 5b) in the 5.0-minute pulsed film, but it fluctuated only slightly, about 3200 appm in the 2.5-minute pulsed film (Fig. 5a). Because of depth-resolution problems to be discussed in the next section these values do not necessarily reflect the absolute minimum and maximum values of individual pulses. Figure 5 also indicates that the total nitrogen contents introduced by nitrogen pulsing, as indicated by the areas under the profiles, did increase as the pulsing rate increased.

Discussion

Use of the FESEM at low voltage to examine fracture surfaces through the beryllium films provides effective analyses of the microstructure in the films. Application of conductive coatings to the fracture surface, which normally is required for most SEM examinations of beryllium, obliterates much of the fine microstructural features, but the technique of coating both the beryllium and the glass sides of a specimen before it is fractured permits the beryllium fracture to be examined without coating. This technique has proven to be necessary to resolve the fine structure in the films. This work also demonstrates that the ion microanalyzer is an effective tool to analyze the composition of the films and determine the microstructural distribution of elements within the films.

Several observations that may be made from the depth profiles in Fig. 4 are worthy of discussion. The SIMS signal is plotted on a linear scale in these figures to compare the relative amplitudes of the oscillations; the scale for the nitrogen profile was shifted upward so that the amplitude of the oscillations could be emphasized (the scale for carbon and oxygen is on the left, and the scale for nitrogen is on the right in each figure). The average amplitude of the oscillations decreases from Fig. 4a to Fig. 4c as the pulse interval decreases; the amplitude also decays with depth into the

specimen. Both effects are associated with depth resolution.

Two major factors that affect depth resolution are the analysis time required to obtain appropriate counting statistics for each point in a profile and the geometry of the sputtered craters that are formed by the primary ion beam. The analysis time (1.0 s) causes the concentration to be averaged over the total depth of sputtering that occurs during the analysis time. Therefore, as the depth of a concentration oscillation corresponding to a single nitrogen-pulse approaches the depth that is sampled during the analysis time, depth averaging smooths out the oscillation and reduces its apparent amplitude. Depth averaging also occurs over the portion of the sputtered crater that is analyzed. Both the curvature and the surface roughness of the crater bottom increase as the depth of the crater increases; consequently, the depth sampled over the area that is being analyzed in the crater also increases. This increased depth of averaging causes an apparent decay in the amplitude of the oscillations as the depth profile progresses to the beryllium/glass interface. This decay is particularly noticeable in Figs. 4a and 4b. Obviously, care must be exercised in attaching significance to differences in the amplitudes and shapes of the oscillations because of the depth averaging. However, relative differences among the nitrogen, carbon and oxygen profiles are considered to be of significance.

The most significant observation of the amount and distribution of contamination that is introduced during pulsing is the noticeable increase in both carbon and oxygen concentrations at the inception of nitrogen pulsing. This increase does tend to recover as the nitrogen pulsing continues, but the carbon and oxygen contents level off to a higher level than the prepulsing concentrations. Carbon also shows a slightly greater proportional increase than oxygen during nitrogen pulsing. Another subtle observation is that the nitrogen and oxygen oscillations are in phase, but the carbon oscillations appear to be nearly 180 degrees out of phase. This could indicate that partial pressures of contaminant gases introduced during pulsing favor dissociation of carbides (Be_2C hydrolyzes in moist air, and the nitrogen gas was found to have substantial water vapor), but as the vacuum recovers prior to the next pulse, carbides become stable. The profiles also show a few secondary fluctuations that extend over several pulses. These secondary fluctuations are particularly noticeable in Fig. 4a

for the 2.5-minute interval pulses; the oscillations associated with nitrogen pulsing shift slightly downward during a fluctuation, and the amplitude of the oscillations also decreases. These fluctuations probably are related to processing fluctuations that cause changes in the partial pressures of the sputtering-chamber gases.

The analytical techniques described in this paper are now capable of generating the type and quality of data that is required to optimize the DC magnetron sputtering technique. So far, these techniques have revealed that the somewhat surprisingly high contamination level within the beryllium films increases as the pulsing interval decreases; therefore, the optimum pulsing interval is the longest interval that reliably produces the desired structure. Clearly, the sources of contamination also must be identified so that they can either be eliminated or neutralized to the greatest extent possible. We are confident that this type of information will result in significant improvements in the quality of the sputtered beryllium films.

Conclusions

The structure of DC magnetron sputtered beryllium can be improved significantly by the use of nitrogen pulsing combined with RF-biased sputtering.

Nitrogen pulsing intervals of five minutes or less are required to significantly alter the columnar structure for the specific sputtering conditions that were used.

The contamination level within the film increases as the pulsing interval decreases (i.e., as the pulsing frequency increases), so the longest interval that produces the desired structure should be used.

Sources of contamination should be identified and neutralized.

The analytical techniques described in this paper are now capable of generating the type and quality of information that is required to significantly improve the quality of the beryllium films.

Acknowledgments

The authors gratefully acknowledge the collaboration of R. G. Musket and R. G. Patterson, who performed the ion implantation, and the support and guidance of G. R. Wirtenson.

References

1. E. J. Hsieh, C. H. Gillispie, E. L. Pierce, and C. W. Hatcher, J. Vac. Sci. Technol., A6, 1893 (1988).

2. R. W. Springer, B. L. Barthell, and D. Rohr, J. Vac. Sci. Technol., 17, (Jan/Feb 1980).

3. C. W. Price and J. C. Norberg, to be published.

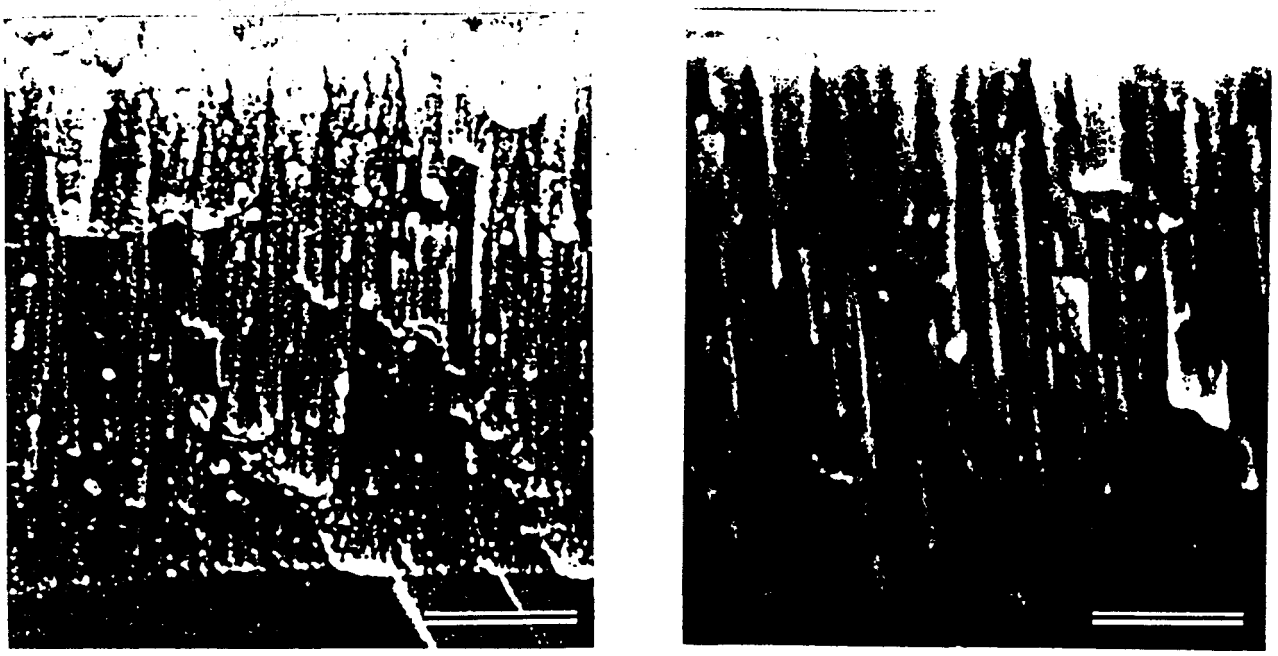
4. L. E. Murr and R. T. Payne, J. Appl. Phys., (1973)44, 1722.

5. SEM Analysis of DC Magnetron Sputtered Beryllium Films, E. F. Lindsey, C. W. Price, E. L. Pierce, and E. J. Hsieh, (1988).

6. R. G. Musket, C. W. Price, and J. C. Norberg, "Implanted standards for Ion Microanalysis of Oxygen in Beryllium," Submitted to Nucl. Instr. and Math. Phys. Res.

7. R. S. Hockett, C. A. Evans, Jr., and P. K. Chu, SIMS VI, eds., , (1987), p. .

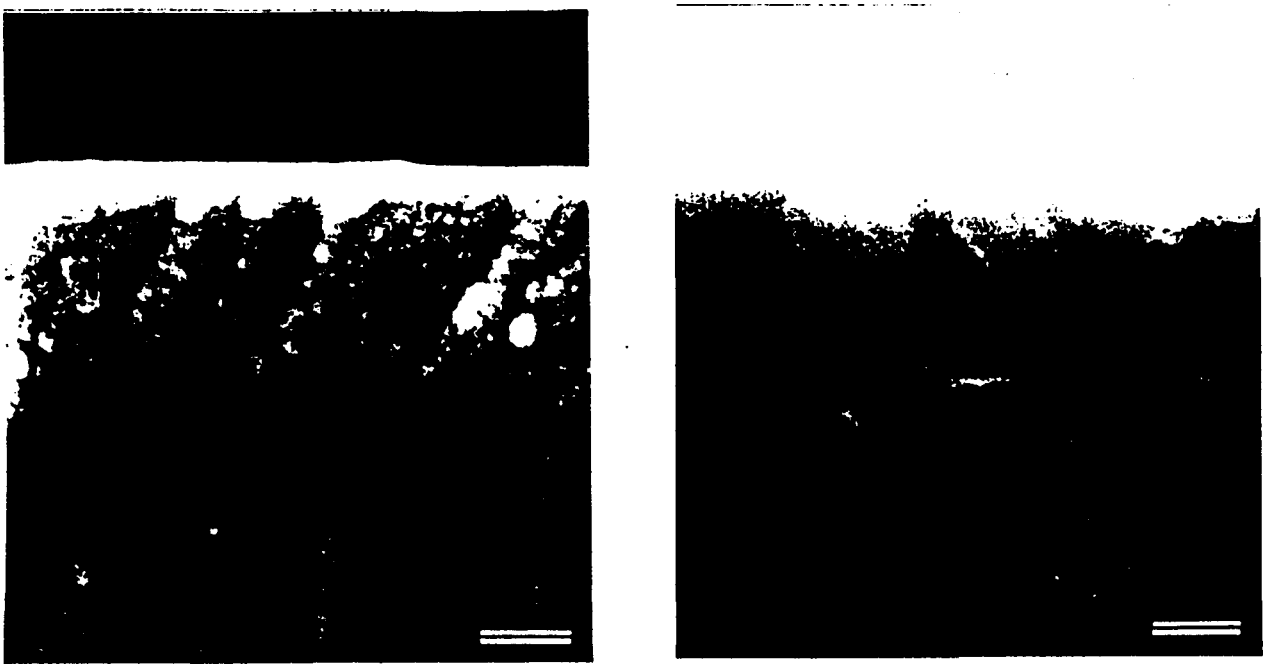
8. J. Franks, et al., SEM-1980 I, 155.



a. Au-Pd sputter coated.

b. Au ion-beam coated.

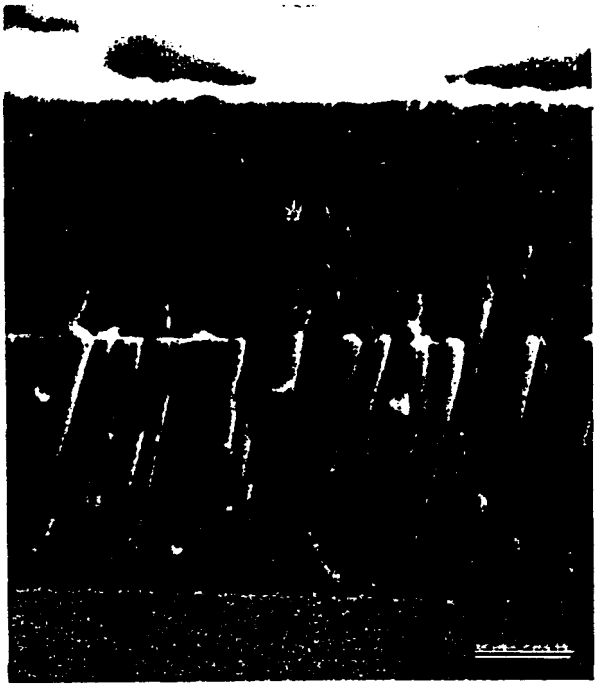
Fig. 1. Composite film comparing different coating techniques; (a) 20 kV, (b) 5 kV, bar = 0.5 μm.



a. Au-Pd sputter coated.

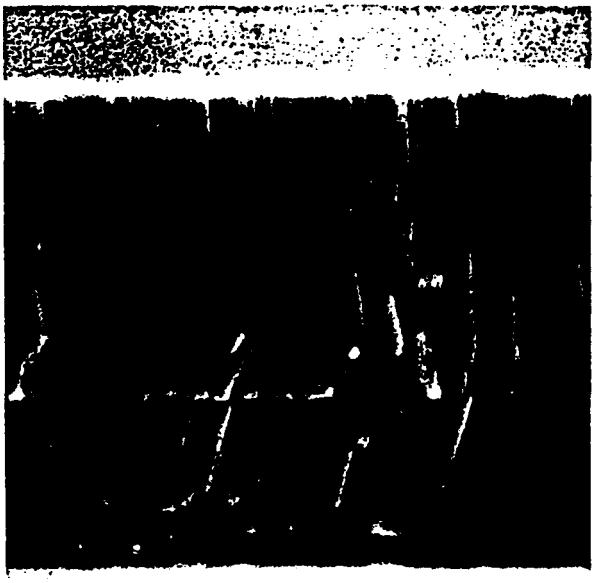
b. Carbon coated.

Fig. 2. RF-biased film comparing different coating techniques; (a) 20 kV, (b) 5 kV, bar = 0.2 μm.



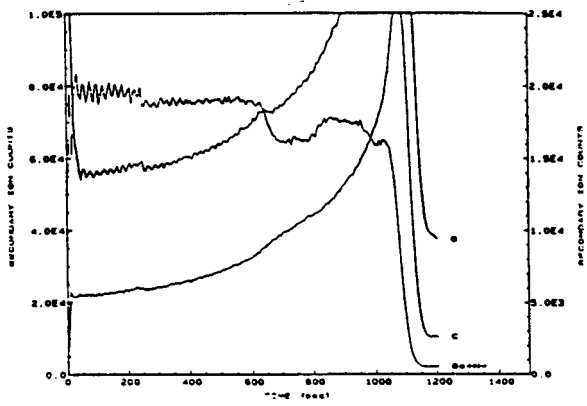
a. 2.5-minute pulses.

b. 5.0-minute pulses.

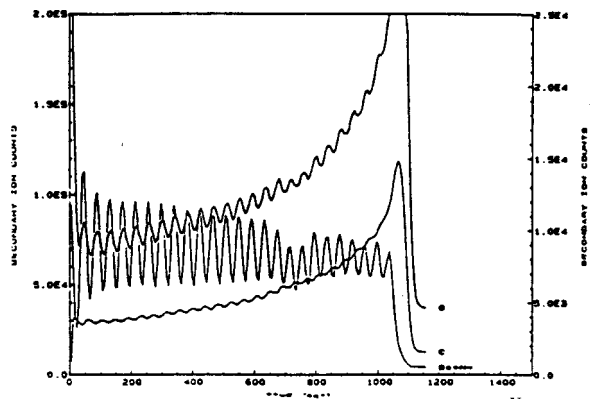


c. 10.0-minute pulses.

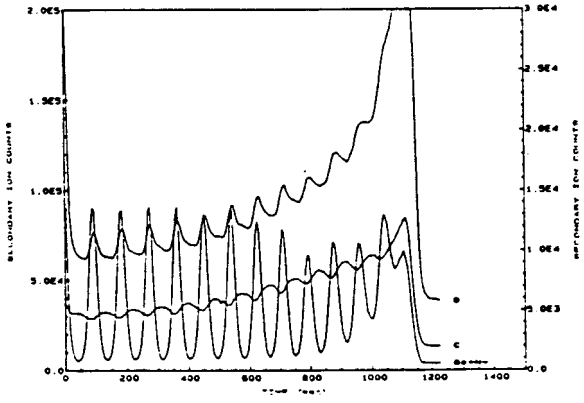
Fig. 3. Nitrogen-pulsed films deposited with different pulse intervals over unbiased films; uncoated, 2.5 kV, bar = 0.5 μm.



a. 2.5-minute pulses.

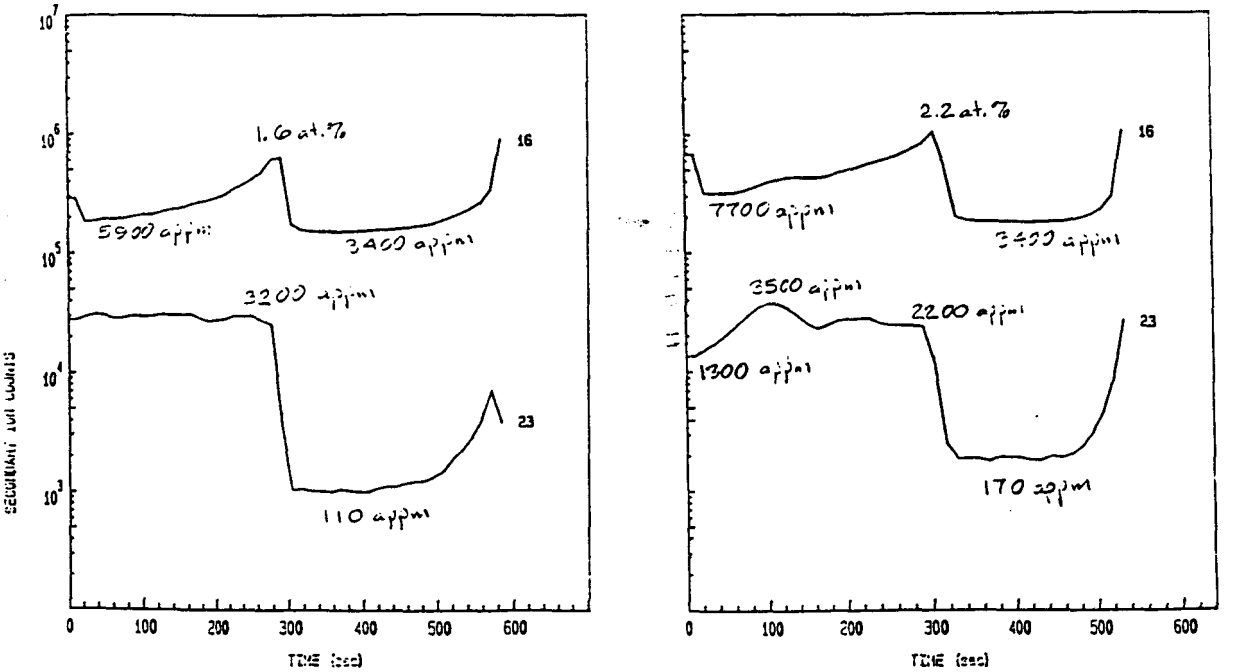


b. 5.0-minute pulses.



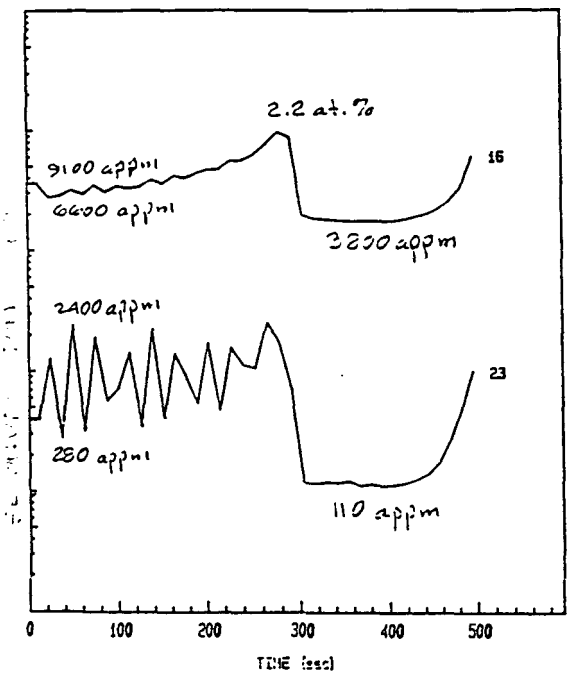
c. 10.0-minute pulses.

Fig. 4. SIMS depth profiles through the composite nitrogen-pulsed/unbiased films generated with the slow sputtering rate of 1 nm/s.



a. 2.5-minute pulses.

b. 5.0-minute pulses.



c. 10.0-minute pulses.

Fig. 5. SIMS depth profiles through the composite nitrogen-pulsed/unbiased films generated with the fast sputtering rate of 6 nm/s.