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E. J. Hsieh, C. W. Price, E. L. Pierce,
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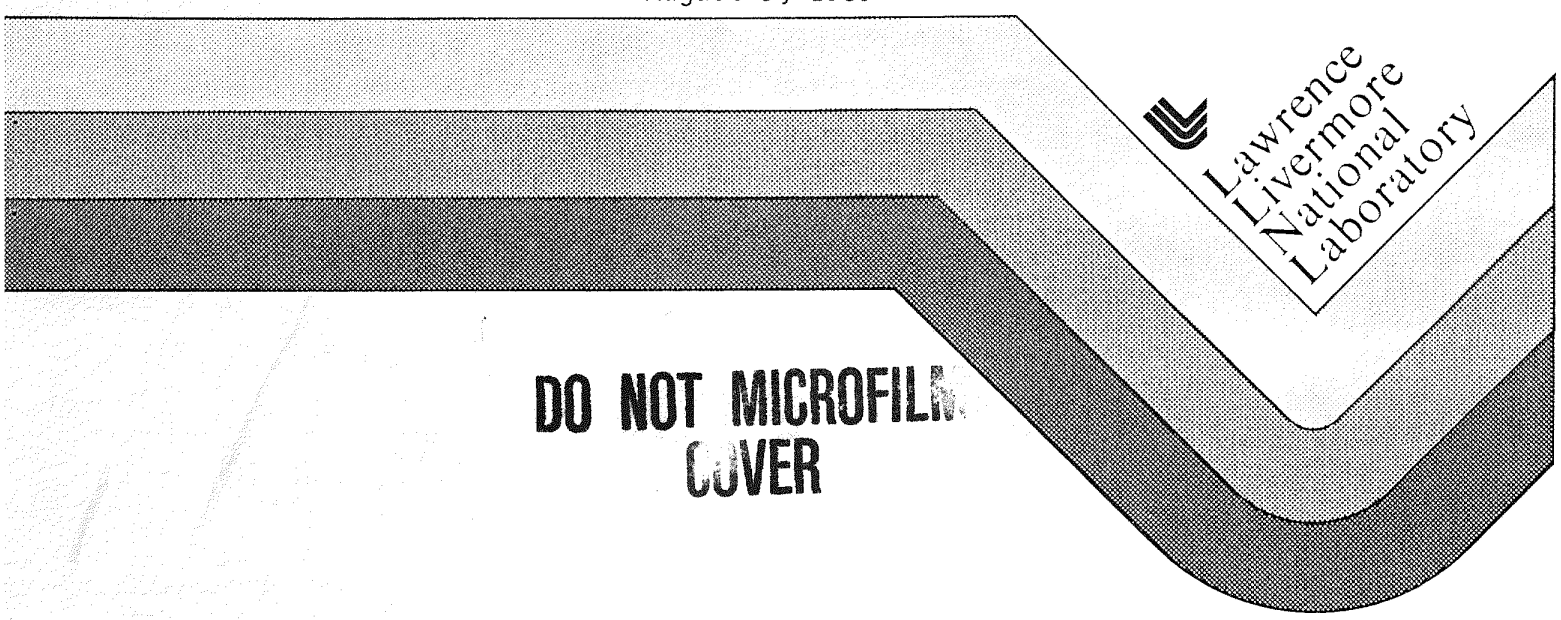

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EFFECTS OF NITROGEN PULSING ON SPUTTER-DEPOSITED BERYLLIUM FILMS

E. J. Hsieh, C. W. Price, E. L. Pierce, and R. G. Wirtenson

University of California
Lawrence Livermore National Laboratory
P. O. Box 5808, Livermore, California 94550

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ABSTRACT

Beryllium films have been used as a "heat sink" layer between the reflective coating of a mirror and its glass substrate to improve the mirror's radiation resistance to prompt deposition of x-rays. Under x-ray irradiation, the beryllium "heat sink" layer is subjected to tensile stresses caused by differences in thermal expansion coefficients. Test results indicated that the predominant failure mode was the film's crazing under tensile stress. The inherent columnar structure of the beryllium films deposited under normal conditions is detrimental to the tensile strength of the films and may be responsible for this type of failure.

We successfully suppressed the inherent columnar growth in beryllium films by incorporating periodic N_2 pulses during sputter deposition. The traditional substrate biasing approach did not seem to be as effective in modifying the grain structure. The results showed that higher N_2 pulse rates during deposition were more effective in suppressing the columnar growth. However, we noticed that films deposited with nitrogen pulsing show higher secondary-electron emission in SEM micrographs, which indicates a significant incorporation of contaminants into the beryllium films.

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Quantitative analyses were conducted for nitrogen and oxygen contamination in the beryllium films using standards prepared by ion implantation. Secondary ion mass spectroscopy (SIMS) depth profiles were obtained for oxygen and nitrogen using mass isotopes ^{16}O and $23(^{9}Be + ^{14}N)$. More than two percent of contaminants was observed in beryllium films at the higher pulse rates that were used. Thus, a minimum pulsing frequency and duration should be selected that provides grain refinement with a minimum amount of contamination.

INTRODUCTION

Requirements for hardening satellite components led to the development of an enhanced energy sharing concept for optical mirror coatings.[1, 2] This concept was developed to increase the survivability of aluminum-coated, fused-silica mirrors to prompt-energy deposition by interposing a thick layer of beryllium between the aluminum and the substrate. The separation of the high-Z materials by the low-Z beryllium film redistributes the deposited heat load over a larger volume and reduces the maximum temperature in the aluminum film. The beryllium "heat sink" layer was subjected to tensile stresses that were proportional to the fluence of x-rays. The predominant failure mode was crazing of the film under the tensile stresses generated by differential thermal expansion. The inherent columnar structure of Be films deposited under normal conditions is detrimental to the tensile strength of the film. In order to achieve a higher tolerance to x-ray irradiation, the columnar growth in the beryllium film must be modified or suppressed.

Previous work indicated that substrate biasing during sputter deposition of beryllium films promoted finer grain structure.[3] The negative bias on the substrate draws ionic particles to impinge on the growing film. Ion bombardment tends to modify the preferential columnar growth by resputtering the deposited atoms and introducing new nucleation centers for new grain growth. An even more powerful method to suppress the columnar growth is to introduce a reactive gas periodically during film growth. This method, known as the "pulsed-gas process"[4], interrupts the columnar growth presumably by the formation of a compound on the growing layer.

We tried both RF substrate biasing and the pulsed-gas process to deposit our beryllium films. Although it is important to minimize the columnar structure in the film, our special application can not tolerate large amounts of contaminants, including the reactive gas used in the deposition. As a first step, we need to quantitatively determine the amount of nitrogen and other contaminants that are introduced into the beryllium films during sputtering.

EXPERIMENTAL PROCEDURE

The beryllium films were deposited onto fused-silica substrates by DC magnetron sputtering in 12 milli-torr of argon at a deposition rate of one micron per hour. A RF power supply equipped with auto tuning permitted RF bias to be applied to the substrate stage during sputter deposition. The RF bias was 30 watts. Nitrogen pulses were introduced through an electrically controlled on/off valve which could be programmed for different pulse frequency and duration. The nitrogen-pulse duration for this experiment was

approximately 100 milli-seconds. In principle, the pulse duration should be just long enough to supply sufficient reactive gas to form a compound layer in the growing film, but not too long to introduce unnecessary contaminant into the resultant film. We observed an increase in sputtering pressure from 12 to 15 milli-torr at the initiation of a nitrogen pulse; return to the steady-state pressure occurred within five seconds after the pulse. Based on the deposition rate of one micron per hour, we estimated that an equivalent of 15 angstroms of compound was formed per nitrogen pulse. We tried three pulse intervals: one pulse every 2.5-, 5- and 10-minutes. The general guideline for effective modification of the growth morphology was to form a compound layer at every 1000 angstroms of the base material.[5] Our medium pulse interval of 5 minutes was chosen on this basis.

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.[6] 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. 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.

Grain structure in beryllium films can be analyzed conveniently by fracturing the films intact on the fused-silica substrates and examining the fractured beryllium surfaces in an SEM. Because of the problems in obtaining high-resolution SEM images, we developed an improved technique consisting of carbon coating both sides of the specimen before fracturing it and then examining the uncoated fracture surface at low voltage.[7] This technique permitted uncoated fracture surfaces of beryllium films to be examined at 2.5 KV in a field-emission SEM equipped with a field-emission gun.

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.[7, 8] Depth profiles were obtained for oxygen and nitrogen using mass isotopes, ^{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 homogenous compositions are not available, standards were prepared by the widely accepted technique of ion implantation. Oxygen standards were prepared by using 150-keV O^{+} implants in polycrystalline beryllium;[9] nitrogen standards were prepared for this study using 200-keV N^{+} implants in similar material.[7] The lower limits of detectability in the implanted specimens were 11 ± 2 appm (atomic parts per million) oxygen and 210 ± 70 appb (atomic parts per billion) nitrogen. Studies using a SiN^{-} signal to analyze for nitrogen in silicon also yielded reliable analyses in

the appb range.[10] The accuracy of the quantitative analyses in the beryllium films is estimated to be of the order of ± 25 per cent.

RESULTS & DISCUSSION

A composite film formed by overlaying three different deposits is shown in Fig. 1. 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 results in Fig. 1 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 interval nitrogen pulsing had slightly modified structure. Notice that the top layer (c) had slightly brighter secondary-electron emission which may indicate that a higher degree of contaminant was introduced into the beryllium film during the nitrogen gas pulsing process.

Structures in composite nitrogen-pulsed/unbiased films are shown in Figs. 2a, 2b, and 2c for pulse intervals of 2.5-, 5- and 10-minutes, respectively. The 2.5- and 5-minute interval nitrogen gas pulses did suppress the columnar structure and produce what appears to be a very fine, equiaxed grain structure. The 10-minute interval gas pulse, Fig. 2c, 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 when the general guideline on effective gas pulse intervals is observed.

SIMS depth profiles obtained from the nitrogen-pulsed specimens are shown for the 2.5-, 5- and 10-minute pulsing intervals in Figs. 3a, 3b, and 3c, respectively. The sputtering rate of 60 angstroms per second was used to obtain reasonable profiling rates and sensitivity, and also to match the sputtering rates on the implanted standards. Quantitative analyses were performed for nitrogen and oxygen in these specimens. 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.) These profiles show the increase in nitrogen that occurred at the inception of pulsing along with simultaneous and somewhat unexpected increases in the oxygen concentrations. The purity of the nitrogen gas used may be a contributing factor.

Quantitative analyses are indicated at various points in the profiles. As indicated previously, the accuracy of these analyses is of the order of $\pm$ 25 per cent. The profiles indicate that a significant amount of contamination was present at the start of the unbiased coating. This contamination was probably related to both gaseous contaminations introduced with the argon sputtering gas and surface-adsorbed contamination on the subtrate. The contamination 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. 3b is caused by partial resolution of individual pulses). Nitrogen varied from about 280 to 2400 appm (Fig. 3c) in the 10-minute pulsed film and 1300 to 3500 appm (Fig. 3b) in the 5.0-minute

pulsed film, but it fluctuated only slightly, about 3200 appm in the 2.5-minute pulsed film (Fig. 3a). Figure 3 also indicates that the total nitrogen content introduced by nitrogen pulsing, as indicated by the areas under the profiles, did increase as the pulsing rate increased.

SUMMARY

We found that nitrogen pulsing is an effective way to suppress the inherent columnar growth in the sputter-deposited beryllium films when proper gas pulse intervals are used. By comparison, the substrate biasing technique did not seem to be as effective in modifying the grain structure. However, a significant amount of contaminant was introduced into the film by the pulsed-gas process, as indicated by our data. 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. Since the 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. We are confident that this type of information will result in significant improvements in the quality of sputtered beryllium films.

ACKNOWLEDGEMENTS

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(a) 2.5-minute interval.
(b) 5-minute interval.
(c) 10-minute interval.

Figure 3 SIMS depth profiles through the composite nitrogen-pulsed/ unbiased films with a sputtering rate of 6 nm/s.
(a) 2.5-minute interval.
(b) 5-minute interval.
(c) 10-minute interval.

Fig. 1
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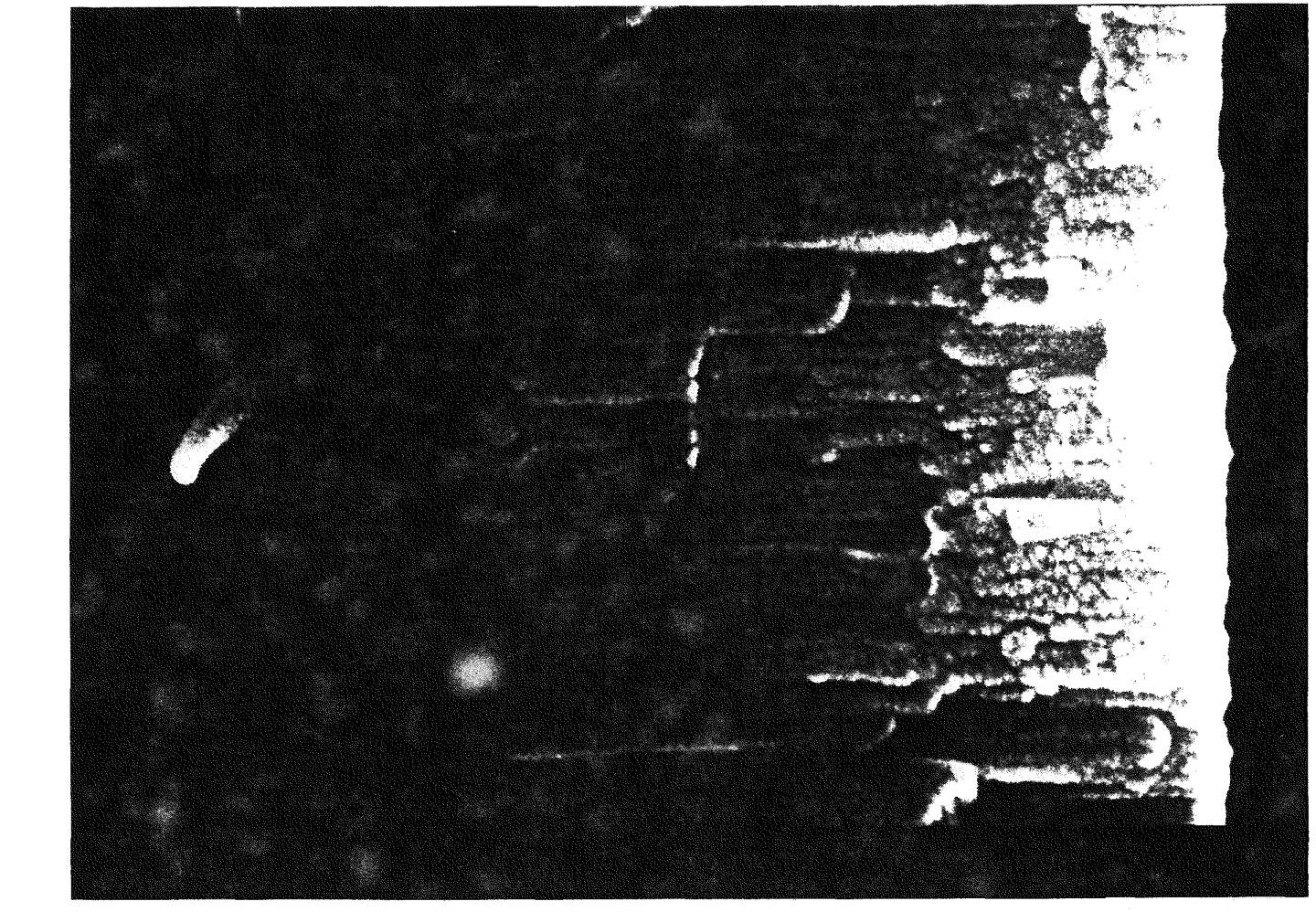

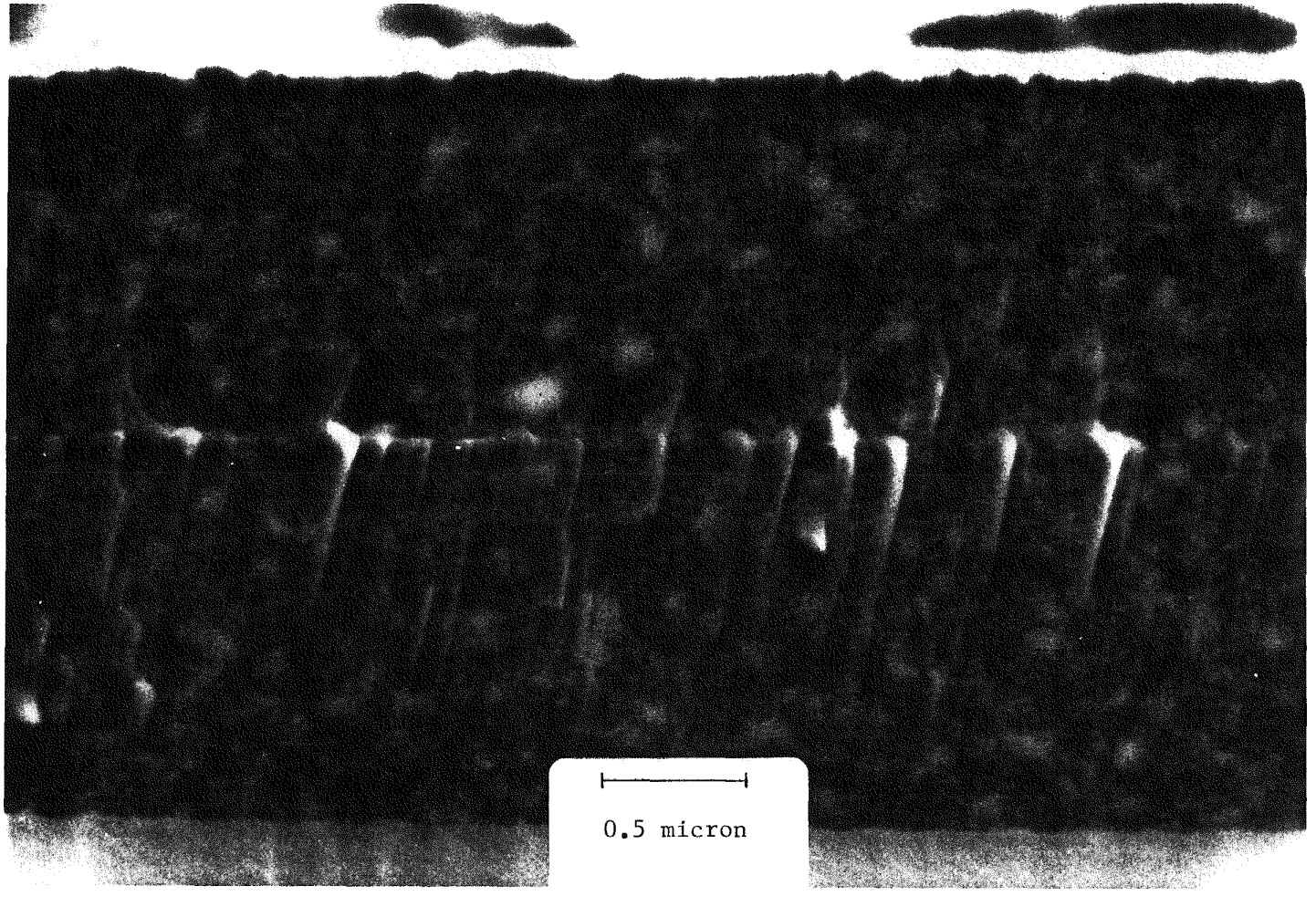

Fig. 2a
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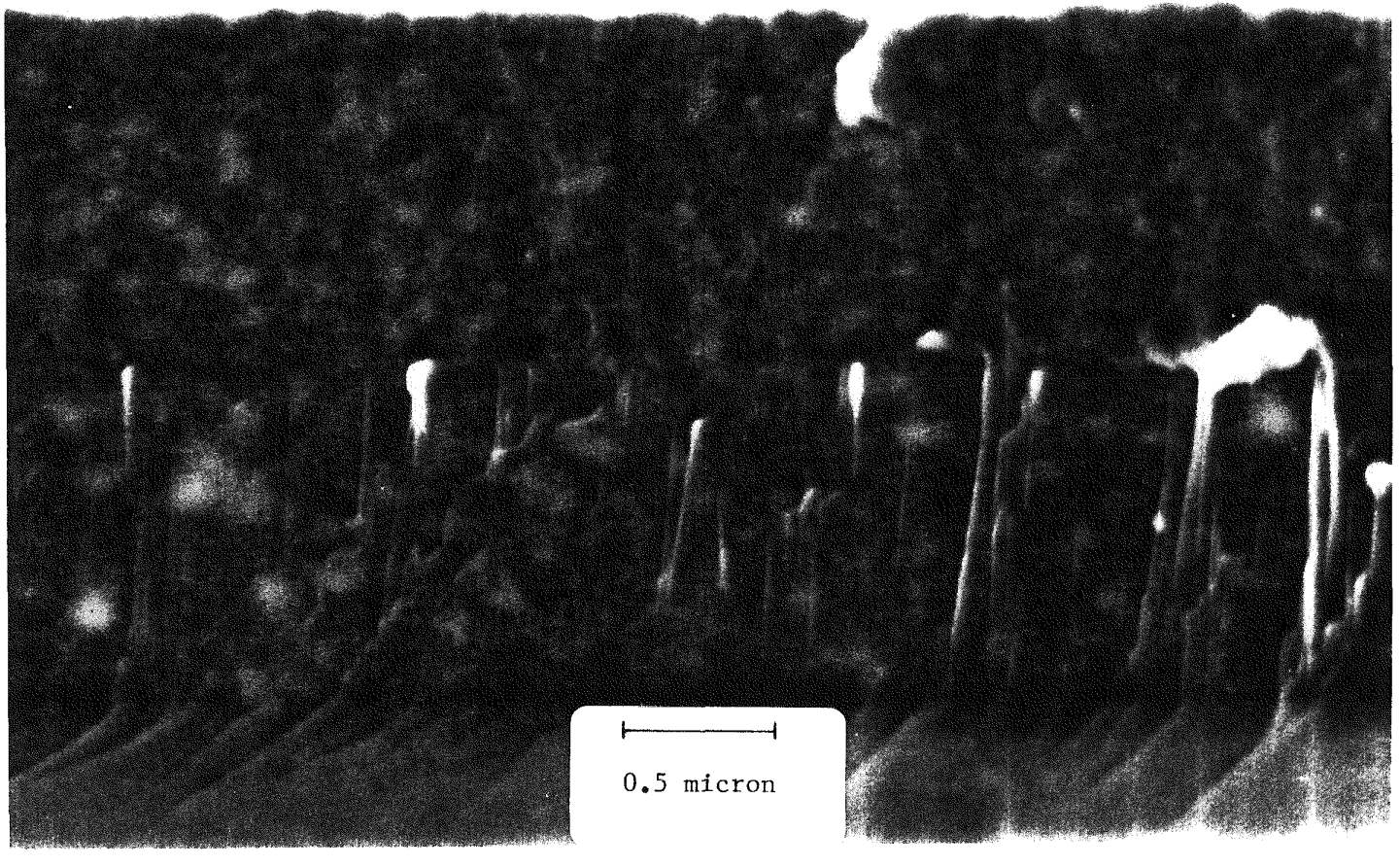

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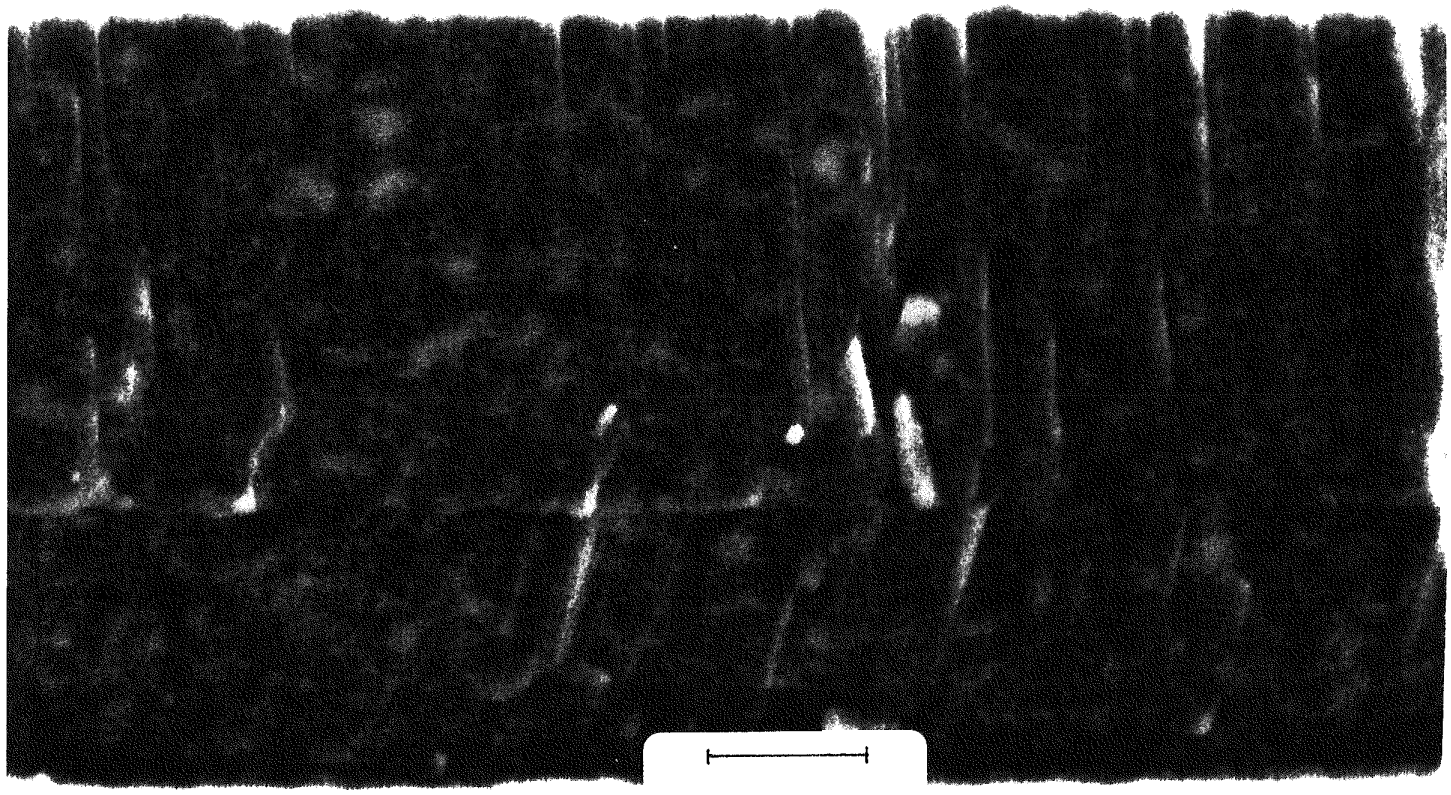

Fig. 2c
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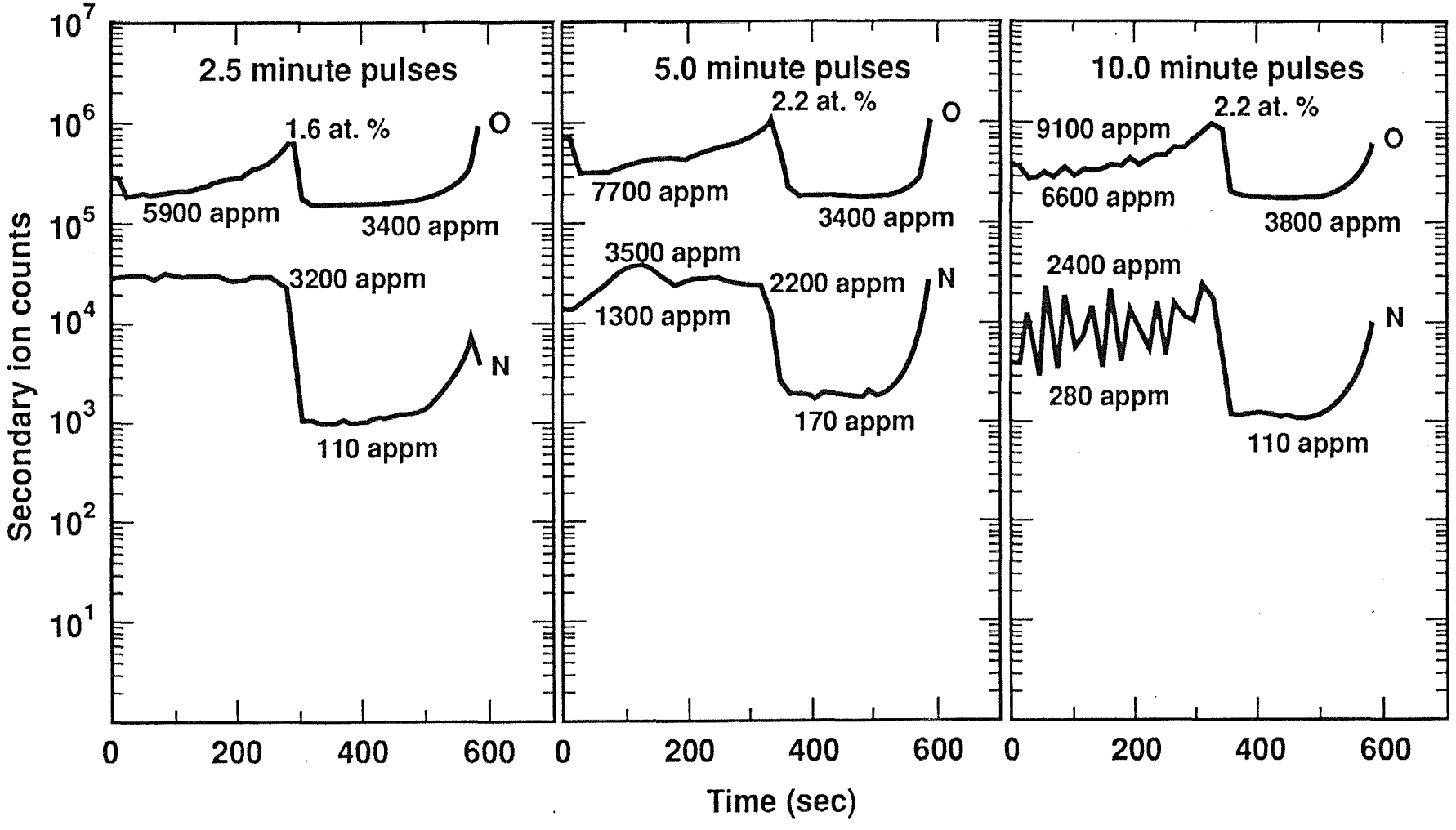

Fig. 3a
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Fig. 3b
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Fig. 3c
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