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Analysis of Nitrogen-Pulsed Sputtered Beryllium

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1. Introduction

Mirror-quality beryllium films deposited by DC magnetron sputtering[1] usually form columnar grain structures that are highly detrimental to the properties of the films. These columnar structures can be modified by imposing periodic pulses of nitrogen gas during sputtering.[2] This paper describes ion microanalyses of beryllium films produced by this technique.

2. Experimental Procedure

The DC magnetron sputtering system and the technique used to deposit beryllium films are described elsewhere.[1] Nitrogen pulses could be introduced into the vacuum chamber at specified pulsing frequencies by an electronically controlled valve. To facilitate comparisons of pulsed and nonpulsed films, composite films were prepared by first depositing about a 1.0-µm thick layer on a glass substrate using only unbiased sputtering and then depositing a second layer using nitrogen pulsing.

The beryllium films were brittle and tended to fracture along the columnar grain boundaries. Therefore, grain structure in the films was analyzed by fracturing films intact on the glass substrate and examining the fractured films in an Hitachi S-800 scanning electron microscope equipped with a field-emission gun (FESEM).[3] To reduce charging, the specimens were carbon coated on both sides before fracturing, and the FESEM yielded reasonable resolution from the uncoated fracture surfaces at 2.5 kV.

Secondary ion mass spectroscopy (SIMS) was performed with a CAMECA IMS-3f ion microanalyzer using a $^{133}Cs^{+}$ primary ion beam. The

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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). Previous analyzes for nitrogen in silicon using the SiN^- signal yielded analyses in the appb (atomic parts per billion) range.[4]

Quantitative analyses were conducted for nitrogen and oxygen using standards prepared by ion implantation; standards were not available for carbon. Oxygen standards prepared in previous work used 150-keV O^+ implants in polycrystalline beryllium;[5] nitrogen standards prepared for this study used 200-keV N^+ implants in similar material. The lower limits of detectability in the implanted specimens were 11 ± 2 appm oxygen and 210 ± 70 appb nitrogen. The primary contribution to the oxygen limit appeared to be residual gaseous contamination in the specimen chamber. Roughly half of the nitrogen limit was matrix nitrogen in the beryllium; the remainder was residual gaseous contamination. The accuracy of the quantitative analyses is estimated to be about ± 25 per cent.

3. Results

Microstructures in composite nitrogen-pulsed/unbiased films are shown in Figs. 1a, 1b, and 1c for pulse intervals of 2.5, 5.0, and 10.0 minutes, respectively. The 2.5- and 5.0-minute intervals, Figs. 1a and 1b, 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. 1c) only slightly modified the columnar structure.

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. 2a, 2b, and 2c, respectively. The low sputtering rate of 1 nm/s resolved the individual nitrogen pulses and also revealed sympathetic oscillations of the carbon and oxygen profiles. The oscillations coincide with the numbers of pulses that were used for each film (26 pulses for the 5.0-minute interval in Fig. 2b and 14 pulses for the 10.0-minute interval in Fig. 2c), but individual pulses become difficult to resolve in Fig. 2a as the profile approaches the interface between the nitrogen-pulsed film and the unbiased film. The increases in the carbon and oxygen contamination were large and somewhat unexpected.

Quantitative analyses were performed for nitrogen and oxygen at the faster sputtering rate of 6 nm/s through both the nitrogen-pulsed and the unbiased layers. Individual pulses were only partially resolved. The profiles revealed noticeable contamination 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. 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 between 5000-9000 appm, but nitrogen remained reasonably constant. Nitrogen varied from about 280 to 2400 appm in the 10-minute pulsed film, 1300 to 3500 appm in the 5.0-minute pulsed film, and fluctuated about 3200 appm in the 2.5-minute pulsed film -- because of depth-resolution problems, no attempt was made to determine minimum and maximum values of individual pulses.

4. Discussion and Summary

The SIMS signal is plotted on a linear scale in Figs. 2a to 2c 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. 2a to Fig. 2c as the pulse interval decreases; the amplitude also decays with depth into the specimen. Both effects are considered to be associated with depth resolution, and care must be exercised in annalyzing 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 significant.

The increase in carbon and oxygen contamination at the inception of nitrogen pulsing diminishes as pulsing continues, but the carbon and oxygen contents remain higher than the prepulsing concentrations. Carbon also increases slightly more than oxygen during nitrogen pulsing. In addition, 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. These results also demonstrate 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 or lowest frequency that reliably produces the desired 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 should be 5.0 minutes or less. However, contamination levels can be dangerously high, and the minimum pulsing frequency and duration should be selected that provides grain refinement with a minimum amount of contamination.

Acknowledgments

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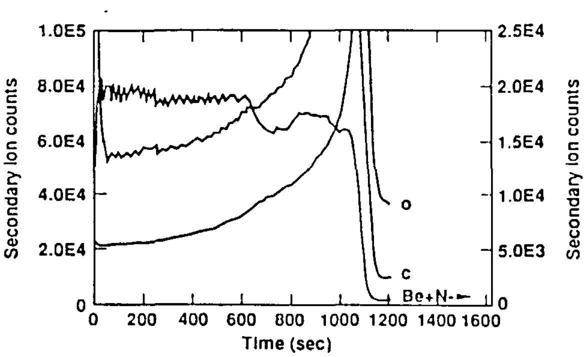
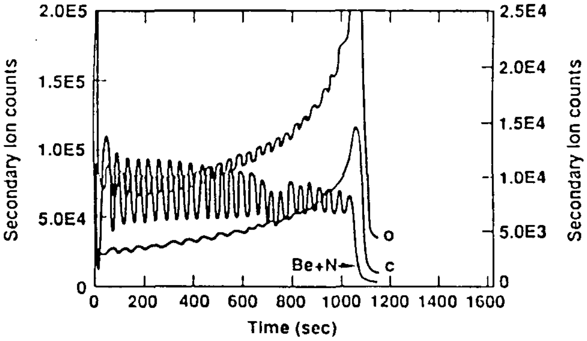
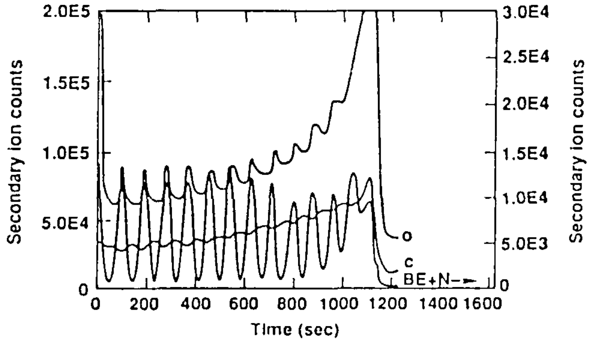


a. 2.5 minute pulses.



b. 5.0-minute pulses.



c. 10.0-minute pulses.

Fig. 1. LVSEM of films pulsed at different pulse intervals (left) over unbiased films; bar = 0.5 μm.

Fig. 2. SIMS depth profiles from the nitrogen-pulsed films; scale for O and C at left, scale for Be + N at right.