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DEPOSITION OF REACTIVELY ION BEAM SPUTTERED
SILICON NITRIDE COATINGS

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SUMMARY

E-1310

An ion beam source was used to deposit silicon nitride films by reactive sputtering a silicon target with an Ar + N₂ beam. The fraction nitrogen in the sputtering gas was 0.05 to 0.80 at a total pressure of 6 to 20 x 10⁻⁵ torr. The ion beam current was 50 mA at 500 V. The composition of the deposited films was investigated by Auger Electron Spectroscopy and the rate of deposition of about 2 nm·min⁻¹ (0.12 μm·h⁻¹) was found. AES spectra indicated that Si₃N₄ was obtained for a fraction of nitrogen higher than 0.50. However, the AES spectra also indicated that the sputtered silicon nitride films were contaminated with oxygen and carbon and contained significant amounts of iron, nickel, and chromium, most probably sputtered from the holder of the substrate and target.

INTRODUCTION

Silicon nitride is characterized by high chemical stability and good dielectric and mechanical properties. As a coating it is mainly used in the microelectronic industry (refs. 1 to 4), but it is also used for formation of glass to metal seals (ref. 5), for electrode insulation in high temperature chemistry and has been proposed as an antireflection coating for photothermal solar energy conversion (ref. 6). Its mechanical properties, especially its high hardness (>2000 g·mm⁻²) (ref. 7) and its chemical stability, make the silicon nitride a candidate for use as a wear resisting coating for metals.

Silicon nitride coatings have been produced by glow discharge methods (refs. 8 to 9), CVD (ref 10), by sputtering from silicon nitride targets (refs. 6, 11 to 12) or by reactive sputtering from silicon nitride targets (ref. 13). Sputtering offers the advantage of low substrate temperature, which can be important in the application of wear resistant coatings, since the mechanical properties of the substance may be affected by high temperatures.

The ion beam deposition technique, used initially by Aisenberg and Chabot (ref. 14) to deposit diamond-like carbon films, was further developed for surface treatments and deposition of different coatings (refs. 15 to 16). Weissmantel et al (ref. 16) investigated different configurations of ion beams for coating processes and used a dual beam method to deposit silicon nitride films. The ion beam system can be used to sputter at total pressures from 5x10⁻⁵ to 5x10⁻⁴ torr., which is about two orders of magnitude smaller than that used in a conventional sputtering unit (ref. 12). If a higher rate

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of deposition could be achieved in the ion beam apparatus, in combination with the low gas pressure, films with low oxygen contamination may result.

The aim of the present work was:

(1) To investigate the feasibility of depositing silicon nitride films by reactive sputtering a silicon target with beams of Ar + N₂ mixtures, in the existing ion beam apparatus.

(2) To characterize the deposited films.

EXPERIMENTAL PROCEDURE

Film Deposition

The sputtering was performed using a 2.5 cm diameter ion beam source contained together with the substrate and target holders in an 18 inch diameter pyrex bell jar. A schematic of the system is shown in figure 1. A close-up photograph of the substrate and target holder is shown in figure 2. The apparatus allows adjustment of the angles of both the target and the substrate relative to the direction of the ion beam which coincides with the axis of the bell jar.

The voltage of the ion beam could be adjusted up to 1500 eV and its current up to about 70 mA. A heated tungsten filament was used to neutralize the ion beam by adjusting the neutralizer current until the emission current equaled the ion beam current. The bell jar was initially pumped to about 3×10^{-6} torr with a LN₂ trapped oil diffusion pump. Ultra high purity argon and nitrogen were then introduced in the bell jar until the desired total pressure and gas mixture was obtained. The composition of the gas mixture was determined by the partial pressure of the argon and nitrogen gases.

The pressures were measured with an ion gauge which initially was inside the sputtering chamber, partially covered with a half-cylindrical stainless steel foil. As such, it was not possible to measure the pressure after the ion beam was initiated. In order to measure the pressure during sputtering, thus being able to control the pressure, the ion gauge was moved into an extension outside the bell jar and the opening of that extension was covered with a grounded stainless steel mesh.

The target was a boron doped single crystal silicon wafer 0.5 mm thick of (100) orientation which completely covered the target area facing the beam. The deposition was performed on substrates of glass and of 304 stainless steel. Microscope slides were used as glass substrates while stainless steel substrates were cut from a sheet and polished with 3 μ m diamond paste. Both substrate materials were ultrasonically cleaned in acetone and washed with Freon before inserting into the deposition chamber.

The temperatures of the substrate and target were measured by thermocouples welded to their holders. Due to the fact that the thin substrates and target were in close contact with the holders, it can be assumed that the measured temperatures were close to the bulk temperatures of substrates and target.

After deposition the bell jar was pumped out. Only after both substrates, and target, cooled to room temperature, the bell jar was filled up with nitrogen and opened to atmosphere to remove the coated samples. Typical fixed and variable deposition parameters are given in table I.

Characterization of Films

The thickness of the deposited films was determined by measuring the height of the step formed on the glass substrate with an interferometric microscope.

The film composition was determined with Auger Electron Spectroscopy (AES) while simultaneously sputtering with 3 kV Ar⁺ ions, to remove contaminated surface layers until a constant spectrum was obtained. Although preferential sputtering is expected (refs. 17 and 18) and absolute composition cannot be obtained in this way, the relative dependence of the composition on deposition conditions should be exposed. AES measurements were made in a baked ultra high vacuum system which was ion pumped to $<2 \times 10^{-10}$ torr then backfilled with ultra high purity argon to 3.8×10^{-5} torr. A commercial single pass cylindrical mirror analyzer with an integral electron gun was used. The gun was operated at a voltage of 2 kV and a current to 2 μ A. The detection system was operated in the dN/dE mode with a modulation of 1 volt.

RESULTS AND DISCUSSION

Effect of Ion Beam Voltage

Initial trials were performed to deposit films at ion beam voltages up to 1000 V. However, films deposited at 750 or 1000 V crumpled and peeled off the substrate almost immediately after removal from the deposition chamber. The appearance of a film deposited at a beam voltage of 750 V after exposure to atmosphere is shown in the optical micrograph in figure 3.

If, however, the coated substrate was left under vacuum the coating kept its smooth appearance. Moreover, if a film which started to crumple was reinserted into vacuum, the crumpling did not advance and the rest of it remained smooth while under vacuum. The films deposited at an ion beam voltage of 500 V remained adherent to the substrate, had a smooth appearance and had a yellow green color on the glass substrate. Since neither the thickness of the films nor the substrate temperatures were significantly different for the films deposited at beam voltages of 750 V or higher, the different behavior suggests that the films deposited at higher voltages have a different interface composition. After removing from vacuum, the films react with the ambient atmosphere, the strength of the interface is reduced and internal stresses cause the film to peel off the substrate and crumple. Since adherent films are required for characterization or practical applications, the study was continued for films deposited at an ion beam voltage of 500 V as shown in table I.

Rate of Deposition

The deposited films varied in thickness between 80 and 250 nm. The corresponding rate of deposition varied between 1.6 and 2.3 nm \cdot min⁻¹ (0.027 to 0.038 nm \cdot s⁻¹). These rates of deposition are about one order of magnitude lower than those obtained by RF sputtering from a silicon nitride target (ref. 12). These low rates of depositions may be impractical for wear protective coatings, where thicknesses of several micrometers are required. No systematic dependence of the rate of deposition on the nitrogen fraction or total pressure was observed.

Composition of Films

Figure 4 presents two typical AES spectra of the deposited films. The two spectra correspond to films deposited at different nitrogen fractions in the sputtering atmosphere. Besides silicon and nitrogen, the AES spectra revealed the existence of carbon, oxygen, iron, and chromium in the deposited films. Although the carbon peak may be an artifact of the methane background in the AES system (ref. 19), the heights of the peaks indicated the existence of carbon as a contaminant in the film.

Figure 5 presents the ratio of peak heights of nitrogen to silicon as a function of the nitrogen fraction in the sputtering atmosphere. The ratio corresponding to Si_3N_4 (ref. 20) is indicated by the broken line. The results indicate that for nitrogen fractions smaller than 0.50 silicon rich films are formed. For nitrogen fractions higher or equal to 0.50, the nitrogen to silicon ratio is independent of the nitrogen fraction and, taking into consideration the errors of measurements, corresponds to silicon nitride.

Although figure 4 indicates a difference between the intensities of the oxygen peaks, none of the peak intensities of elements other than Si or N showed a systematic dependence on the nitrogen fraction in the sputtering atmosphere. The source of the carbon contamination is probably the ion source, which contains graphite accelerator grids. It is possible that the ion beam erodes these grids, providing carbon particles in the sputtering atmosphere.

The contamination of the deposited films with iron and chromium was not dependent on the substrate used and was probably provided by the support of the target and substrate, made of stainless steel. As seen in figure 2 a part of the walls of the support cage was sputtered during the deposition of the coatings. This indicates that the ion beam is widely spread, part of it sputtering the substrate and holder and only part of it sputtering the target. This assumption is supported by the fact that the temperature of the target reaches only 110°C , while when the substrate is inserted in front of the ion beam, at a much shorter distance, its temperature reaches a value of about 400°C . As most of the heat is lost by radiation in the present conditions, the heat losses at 110°C are much smaller than at 400°C indicating that the heat input from the ion beam decreases strongly with the distance between target and ion beam, due to a divergence of the ion beam. It is also possible that secondary sputtering from the area indicated in figure 2 occurs. Particles sputtered or reflected from the target may cause sputtering of materials from the side walls of the supporting cage. The sputtering of the support may also contribute to the oxygen contamination of the films.

CONCLUSIONS AND RECOMMENDATIONS

Silicon nitride films of different composition have been reactively sputtered from a silicon target with beams of Ar + N_2 mixtures. It was found that:

- (1) Ion beam voltages below 500 V have to be used to obtain films adherent to glass or 304 stainless steel.
- (2) For nitrogen fractions higher than 0.50 the AES spectra were consistent with a Si/N ratio corresponding to Si_3N_4 .
- (3) The rate of deposition was about $2\text{ nm}\cdot\text{min}^{-1}$.
- (4) Although it was assumed initially that films with low oxygen content may be obtained by the ion beam sputtering method, in the present

configuration of the ion beam system, the sputtered films are contaminated with carbon, oxygen, and stainless steel.

An increase in the sputtering rate and reduction of the contamination of the films may be achieved by changing the configuration of the system as following:

(1) Reducing the distance between ion source and target from its current value of 7.5 in., or focusing the ion beam such as the whole beam will be concentrated on the target. Thus the sputtering rate of the target will be increased and the sputtering of the support reduced.

(2) Modifying the support of target and substrate such that no foreign material is exposed between the ion beam source, target and substrate.

REFERENCES

1. Seki, H.; et al.: Passivation of gallium arsenide with silicon nitride. *Electr. Commun. Lab. Rev.*, vol. 20, no. 9-10, Sept. - Oct. 1972, pp. 810-816.
2. Swaroop, B.: Effect of Various Ambients on Dielectric Films Silicon Dioxide-Silicon Nitride ($\text{SiO}_2 - \text{Si}_3\text{N}_4$) Deposited on Silicon - II. Ionic Charge. *Electrical Insulation and Dielectric Phenomena*, IEEE, 1972, pp. 75-83.
3. Chaudhari, P. K.; Bhattacharyya, A.; and Beyar, D. C.: Surface - State Generation During Stress Aging of HCl Thermal Si-SiO_2 Interfaces. *J. Electrochem. Soc.*, vol. 121, no. 3, March 1974, p. 89c.
4. Sekimoto, M., et al.: Silicon Nitride Single-Layer X-ray mask. *J Appl. Phys. Jpn*, vol. 20, no. 9, Sept. 1981, pp. L669-L677.
5. Stoller, A. I.; Schilp, W.; and Benbenek, J.: Novel Technique for Forming Glass-to-Metal Seals Using a Silicon Nitride Interface Layer. *RCA Rev.*, vol. 31, no. 2, June 1970, pp. 443-449.
6. Komoriak, G. J.: Silicon Nitride Films by Direct RF Sputter Deposition. *J. Electrochem. Soc.*, vol. 122, no. 9, Sept. 1975, pp. 1271-1273.
7. Engineering Property Data on Selected Ceramics - Vol. I Nitrides. MCIC-HR-07-VOL-1, Battelle Columbus Labs, 1976. (AD-A023773).
8. Pliskin, W. A.: Comparison of Properties of Dielectric Films Deposited by Various Methods. *J. Vac. Sci. Technol.*, vol. 14, no. 5, Sept. - Oct. 1977, pp. 1064-1081.
9. Reinberg, A.: RF Plasma Deposition of Inorganic Films for Semiconductor Application. *J. Electrochem. Soc.*, vol. 121, no. 3, Mar. 1976, p. 85c.
10. Parekh, P. C.; Molea, J. R.: The Uniformity of Vapor Deposited Si_3N_4 Film. *Solid-State Electron.*, vol. 16, 1973, pp. 954-955.
11. Reisse, G., Gunther, W.; and Henry, F.: Preparation and Properties of High-Frequency Sputtered Silicon Nitride Films. *Wiss. Z. Techn. Hochsch.*, Karl-Marx-Stadt, vol. 20, no. 7, 1978, pp. 835-844.
12. Grill, A.; and Aron, P. R.: Sputtered Silicon Nitride Coatings for Wear Protection. NASA TM-82819, 1982.
13. Mogab, C. J.; and Lugujo, E.: Backscattering Analysis of the Composition of Silicon-Nitride Films Deposited by RF Reactive Sputtering. *J. Appl. Phys.*, vol. 47, no. 4, Apr. 1976, pp. 1302-1309.
14. Aisenberg, S.; and Chabot, R.: Ion-beam Deposition of Thin Films of Diamondlike Carbon. *J. Appl. Phys.*, vol. 42, no. 7, June 1971, pp. 2953-2958.

15. Pranevicius, L.: Structure and Properties of Deposits Grown by Ion-Beam-Activated Vacuum Deposition Techniques. *Thin Solid Films*, vol. 63, 1979, pp. 77-85.
16. Weissmantel, C.; et al.: Preparation of Hard Coatings by Ion Beam Methods. *Thin Solid Films*, vol. 63, 1979, pp. 315-325.
17. Thomas, S.; and Mattox, R. J.: An Attempt at the AES Evaluation of the Composition of Off-Stoichiometric Silicon Nitride. *J. Electrochem. Soc.*, vol. 124, no. 12, Dec. 1977, pp. 1942-1945.
18. Delord, J. F.; Schrott, A. G.; and Fain, S. C., Jr.: Nitridation of Silicon (100) - Auger and LEED Results. *J. Vac. Sci. Technol.*, vol 17, no. 1, Jan. - Feb. 1980, pp. 517-520.
19. Ingreys, S.; Johnson, M.; and Streater, R. W.: Artifacts Observed During Auger Profiling of TA, Ti, and W Metals, Nitrides and Oxynitrides. Presented at the 28th. American Vacuum Society National Symposium, (Anaheim, CA.), Nov. 2-6, 1981.
20. McGuire, G. E.: Auger Electron Spectroscopy Reference Manual. Plenum Press, 1979.

TABLE I. TYPICAL PARAMETERS FOR REACTIVE ION
BEAM SPUTTERING OF SILICON NITRIDE

Fixed parameters:

Beam-target angle, deg	29
Beam-substrate angle, deg	225
Beam voltage, V	500
Beam current, mA	50

Variable parameters:

Sputtering pressure, torr	6 to 20×10^{-5}
Fraction nitrogen in sputtering gas	0.05 to .78
Sputtering times, min	30 to 90

Independent parameters:

Target temperature, °C	78 to 110
Substrate temperature, °C	50 to 70
Film thickness, nm	80 to 250

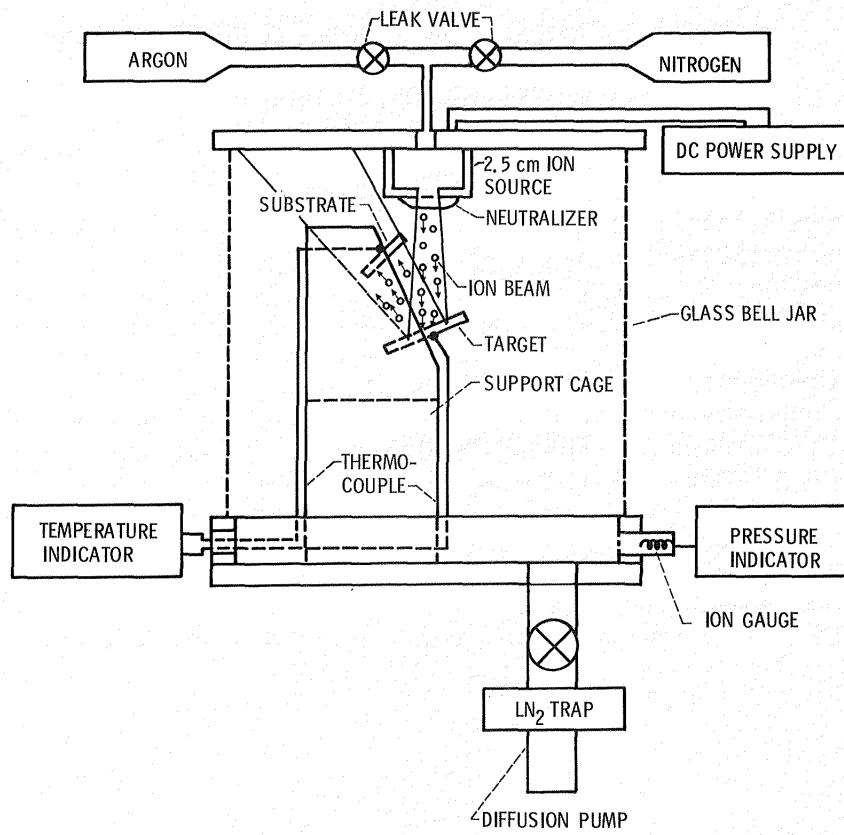


Figure 1. - Schematic of the ion beam sputtering system.

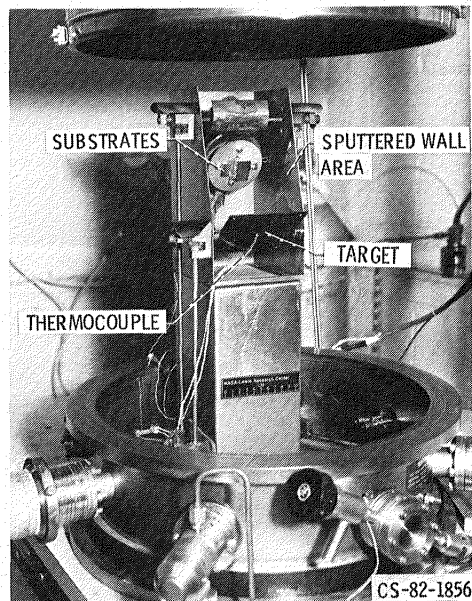


Figure 2. - Close-up view of the support of the target and substrate.

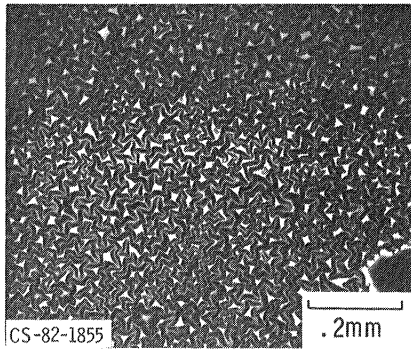
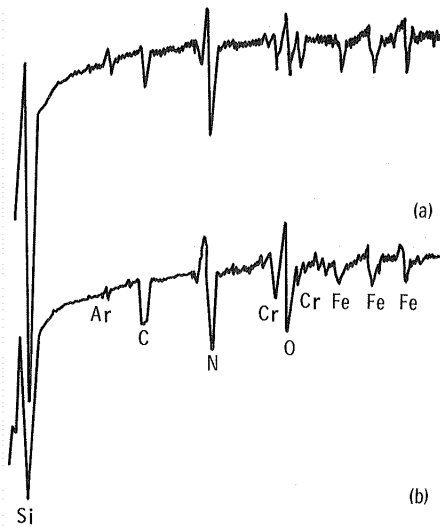


Figure 3. - Optical micrograph of silicon nitride film deposited on glass at an ion beam voltage of 750 V. Fraction nitrogen - 0.27; total pressure - 9×10^{-5} torr; deposition time - 1 hr.



(a) Fraction nitrogen = 0.11.

(b) Fraction nitrogen = 0.22.

Figure 4. - Auger electron spectra of ion beam reactively sputtered silicon nitride films. Ion beam voltage 500 V; total pressure = 9.10×10^{-5} torr.

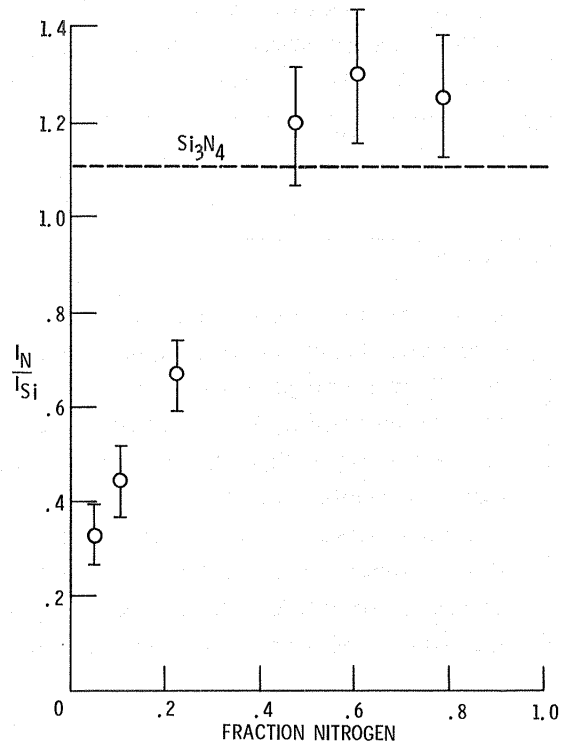


Figure 5. - The ratios of the intensities of the AES peaks of nitrogen to silicon vs fraction nitrogen in the ion beam sputtering atmosphere.

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