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Sputtered Silicon Nitride Coatings for Wear Protection

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SPUTTERED SILICON NITRIDE COATINGS FOR WEAR PROTECTION

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ABSTRACT

Silicon nitride films were deposited by rf sputtering on 304 stainless steel substrates in a planar rf sputtering apparatus. The sputtering was performed from a Si_3N_4 target in a sputtering atmosphere of argon and nitrogen. The rate of deposition, the composition of the coatings, the surface mic. ohardness and the adhesion of the coatings to the substrates have been investigated as a function of the process parameters, such as: substrate-target distance, fraction nitrogen in the sputtering atmosphere and sputtering pressure. Silicon rich coating have been obtained for fraction nitrogen below 0.2. The rate of deposition decreases continuously with increasing fraction nitrogen and decreasing sputtering pressure. It was found that the adherence of the coatings improves with decreasing sputtering pressure, almost independently of their composition.

1. 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,[1-4] but it is also used for formaton of glass to metal seals,[5] for electrode insulation in high temperature chemistry and

has been proposed as an antireflection coating for solar thermal collectors.[6] Its mechanical properties, especially its high hardness[7] (>2000 Kg·mm^{-2}) 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,[8,9] CVD,[10] by sputtering from silicon nitride targets[6,11] or by reactive sputtering from silicon target.[12] Due to the difficulties of controlling impurity levels and stoichiometry,[6] sputtering methods are not generally used for microelectronic applications of this material since the relevant electrical properties are very sensitive to these parameters. RF sputtering does, however, offer the advantage of low substrate temperature. This feature can be of consequence in the application of wear resistant coatings since the mechanical properties of the substrates may be affected by high temperatures.

The aim of the present research is to investigate the wear properties of silicon nitride coatings deposited by rf sputtering from a silicon nitride target and to relate these properties to the parameters of the deposition process.

2. EXPERIMENTAL

The silicon nitride coatings were deposited in a diode type rf sputtering system from a 15 cm diameter commercial high purity silicon nitride target prepared by powder technology. The substrates were of 304 stainless steel polished with 1 µm diamond. The sputter chamber was initially pumped to less than $5·10^{-4}$ Pa with a LN$_2$ trapped oil diffusion pump. The deposition was performed at a rf power density of 2.7 W·cm^{-2} in flowing gas mixtures of Ar and N$_2$. Since the pumping speed was different for Ar

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and N_2 in the working pressure range, the fraction nitrogen has been calibrated with a mass spectrometer for different gas mixtures and total pressures. The total pressure was kept constant during deposition by a Veeco APC 1000 pressure controller.

The rate of deposition was determined by measuring the height of a step, formed by masking a part of the substrate during deposition, with a profilometer. The microhardness of the coated surface was measured with a Knoop diamond indenter at a load of $1.02x10^{-3}$ N (10 g).

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[13,14] and absolute composition cannot be obtained in this way, the relative dependence of the composition on deposition conditions should be exposed. Due to the high resistivity of the films it was necessary to work with films less than 0.1 µm thick to avoid charging problems. AES measurements were made in a baked ultra high vacuum system which was ion pumped to $<2\cdot7x10^{-8}$ Pa then backfilled with ultra high purity argon to $5\cdot10^{-3}$ Pa. A commercial single pass cylindrical mirror analyser with an integral electron gun was used. The gun was operated at a voltage of 2 kV and a current of 2 µA. The detection system was operated in the dN/dE mode with a modulator amplitude of ±1 volt.

The adhesion of the different films to the substrates was compared by a scratch test. The scratch was produced on the coated surface by sliding a spherical diamond indenter of radius 86 µm over the surface under a load of 0.0102 N. The formed tracks were examined by scanning electron microscopy.

The influence of the following parameters on the deposition process and properties of the coating were investigated:

(1) Target-substrate distance (3.3 and 4.5 cm)

(2) Fraction nitrogen in the Ar + N_2 sputtering gas (0 to 0.7)

(3) Total pressure in the sputtering chamber (1.1 and 2.9 Pa)

3. RESULTS AND DISCUSSION

The thickness measurements indicated that for all considered conditions, the deposition rate was about 30 percent lower at a target-substrate distance of 4.5 cm than at 3.3 cm. The AES measurements showed that there is no composition difference between the coatings deposited at the two target-substrate distances. Since 1.2 cm thick disks have to be coated for the available wear test apparatus, the following characterization was performed only for coatings deposited at a target substrate distance of 3.3 cm.

Rate of Deposition

Figure 1 presents the rate of deposition as a function of fraction nitrogen, F_{N_2}, in the sputtering atmosphere, at two sputtering pressures. These rates were determined for coatings deposited for 1 hr. A gradually decreasing rate of deposition, with increasing f_{N_2} is observed at both pressures. An increase of f_{N_2} over 0.25 does not result in a severely reduced rate of deposition as reported by Kominiak.[6] The rate of deposition is about 70 percent higher at 2.9 Pa than at 1.1 Pa at all gas compositions.

Composition

The AES data with respect to composition is summarized in Fig. 2. In Fig. 2(A) the ratio of the nitrogen to silicon peak height (dN/dE) is plotted as a function of fraction nitrogen. These ratios are uncorrected

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for sensitivity factors or preferential sputtering effects. The data does demonstrate that for $f_{N_2} > 0.2$ the silicon to nitrogen ratio is independent of f_{N_2} in agreement with the work of Kominiak.[6] Besides nitrogen and silicon a sometimes prominent feature of the AES spectrum was the KLL oxygen peak at 508 kV. Figure 2(B) exhibits the range of the ratios between the oxygen and silicon peak amplitudes observed in this work. No consistent dependence on total sputtering pressure was observed. It does appear however that the oxygen impurity level tends to increase with f_{N_2} in roughly the same manner as the deposition rate decreases (Fig. 1). The only other significant AES peak seen was due to carbon at 272 eV, typically of an amplitude that would suggest a contamination level of at most a few percent. It has been shown,[15] however, that the carbon seen under these conditions may be an artifact of the methane background in the AES vacuum system.

Microhardness

Figure 3 presents the microhardness of the coated surfaces as a function of fraction nitrogen in the sputtering atmosphere. This microhardness was measured on coatings about 1 μm thick, thus the presented results do not represent the hardness of the coating but a combination of hardness of coating and substrate. It can be seen that the hardness of the coated surface is about 650 Kg mm^{-2} as compared to the substrate hardness of 300 Kg mm^{-2}. About the same hardness was obtained for coatings deposited at both 1.1 Pa and 2.9 Pa for f_{N_2} below 0.15. It was not possible to measure the microhardness of samples coated at 2.9 Pa and f_{N_2} above 0.20 since the coating developed cracks around the indentation. These cracks suggest low adhesion between the corresponding coatings and substrates.

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Adhesion

The scratch test was performed on films about 1 μm thick. The scratch tests on samples deposited at 2.9 Pa resulted in breaking up the coating over a wide area around the sliding track and a scratch track in the substrate. This behavior is independent of the f_{N_2} and composition. A typical scratch track is shown in Fig. 4(A). Scratches produced on coatings deposited at 1.1 Pa resulted in only a partial cracking of the coating as seen in Fig. 4(B). The diamond indenter did not scratch the substrate. Again, the behavior was the same for all f_{N_2} investigated.

The difference between the behavior of the coatings deposited at the two different pressures indicates that the coatings deposited at the lower pressure have better adherence than these deposited at the higher pressure. This is consistent with the microhardness measurements. However the different behavior of the coatings deposited at the two different pressures may also be a result of different internal stresses in these coatings. In order to check the effect of the thickness of the coating on the adhesion of the coating, a 0.5 μm thick coating was deposited at 2.9 Pa and $f_{N_2} = 0.25$. This coating, too, developed cracks around the indentation produced by the microhardness tester and showed the same scratch track as the thicker coating. This result indicates that of all investigated parameters the total pressure of the sputtering atmosphere is the most important parameter affecting adhesion of the coatings to the substrates. The coatings deposited at the lower pressure may be able to protect the metallic substrate against wear better than the coatings deposited at the higher pressure.

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4. CONCLUSION

Silicon nitride coatings of different compositions have been deposited by rf sputtering in gas mixtures of Ar + N_2. It was found that:

1. The composition of the coating is not dependent on the substrate-target distance.

2. The microhardness of the coated surface and the adhesion of the coating to the substrate is almost independent of the concentration of nitrogen in the sputtering atmosphere and on the composition of the coating.

3. The adhesion of the coating to the substrate increases with decreasing sputtering pressure.

4. The adhesion of the coating to the substrate is not dependent on sputtering rate and on the composition of the sputtering atmosphere.

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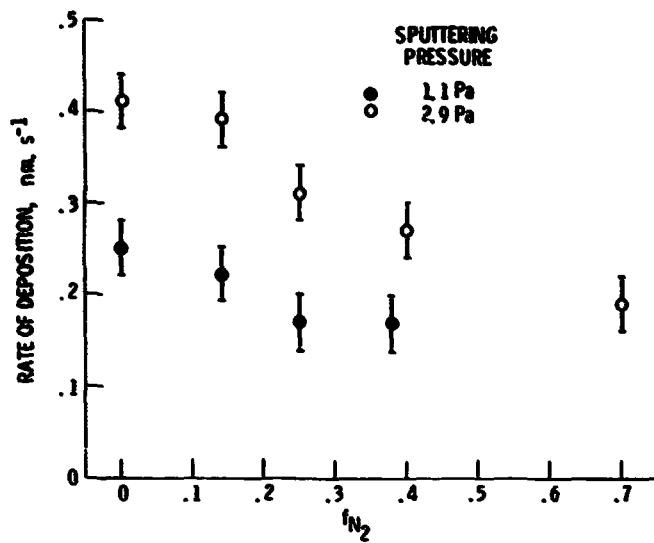   National Symposium, Anaheim, California, Nov. 2-6, 1981.

FIGURE CAPTIONS

Figure 1. – Rate of deposition vs. fraction nitrogen in Ar + N_2 sputtering atmosphere.

Figure 2. – The ratios of the intensities of the AES peaks of nitrogen to silicon and oxygen to silicon vs. fraction nitrogen in the Ar + N_2 sputtering atmosphere.

Figure 3. – Surface microhardness vs. fraction nitrogen in sputtering atmosphere.

Figure 4. – SEM micrographs of scratch tracks on silicon nitride coated 304 SS samples.

    A. coating deposited at 2.9 Pa

    B. coating deposited at 1.1 Pa.

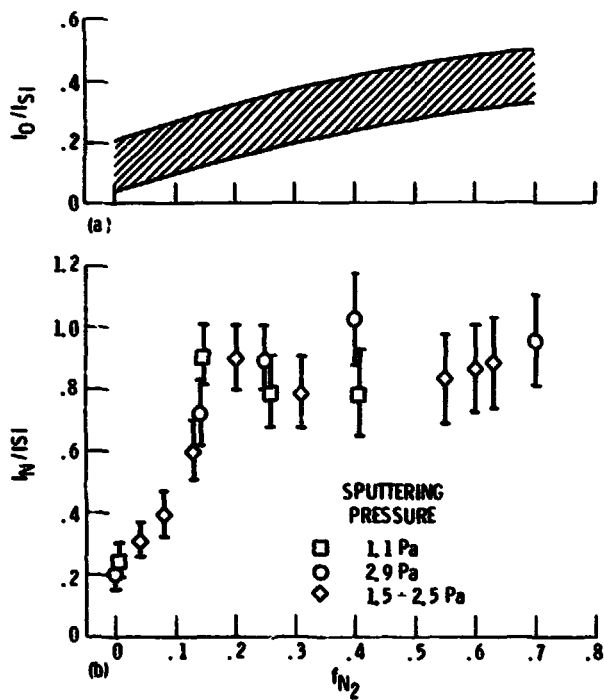Figure 1. - Rate of deposition vs. fraction nitrogen in Ar + N$_2$ sputtering atmosphere.

Figure 2. - The ratios of the intensities of the AES peaks of nitrogen to silicon and oxygen to silicon vs. fraction nitrogen in the Ar + N$_2$ sputtering atmosphere.
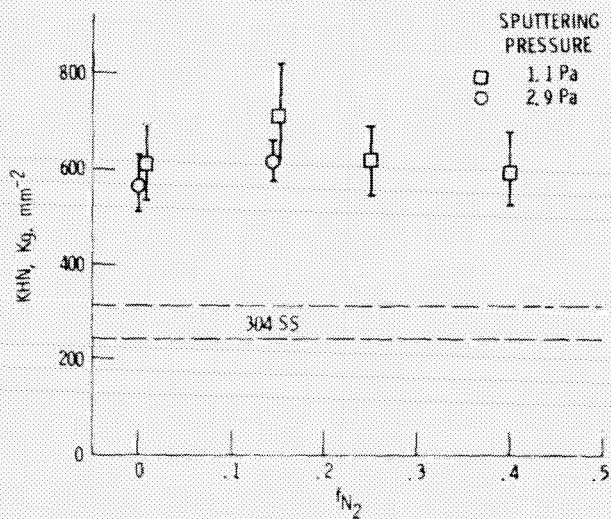
Figure 3. - Surface microhardness vs. fraction nitrogen in
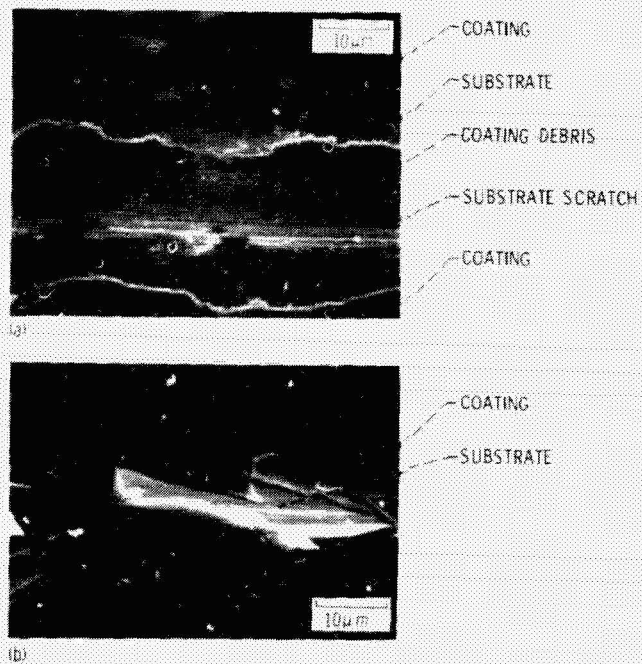sputtering atmosphere.

Figure 4. - SEM micrographs of scratch tracks on silicon nitride coated 304
SS samples. (a) Coating deposited at 2.9 Pa; (b) Coating deposited at 1.1
Pa.