Protective Properties of Silicon Nitride, Deposited by Bias Reactive Sputtering

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ABSTRACT

Silicon nitride coatings, deposited by RF reactive magnetron sputtering, have been studied. Parameters of the deposition process are presented. It is shown that application of radio frequency improves optical, mechanical and protective properties of the coating dramatically.

EXPERIMENT

The silicon nitride coatings are characterized both by high adhesion to many metals and dielectrics and by chemical inertness, wear resistance, heat resistance. Therefore they present interest as anticorrosive and sufficiently wear resistant layers. Analysis of known methods of DC and RF reactive magnetron sputtering of a silicon target [1,2] for silicon nitride deposition shows the RF method effectiveness for both research and practical purposes. In our work the sputtering was carried out at the machine, equipped with the magnetron of 13.56 MHz frequency and 950 W power. Etching of the samples prior to coating and bias during coating were provided with another power supply of 27.12 MHz frequency. The experiment outline is presented in Figure 1.

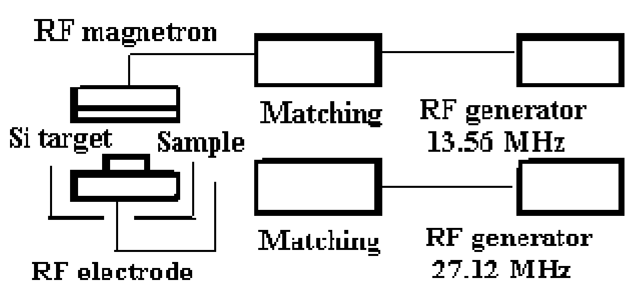

Figure 1. Diagram of the experiment

Depending on the samples type bias during etching was set at values up to 400 V. Bias during deposition was 150 V (or coating without bias) for all samples.

The pumping system on the basis of oil diffusion pump enabled to have preliminary vacuum 2·10**-5 torr. During deposition general pressure of argon-nitrogen mixture was 5·10**-3 torr, while relation of nitrogen partial pressure to general pressure was changing at range a = 0 - 0. 6.

Equally with plasma electric parameters intensity of emission of excited silicon atoms I in plasma at wavelength 252 nm was monitored. As nitrogen partial pressure grows up to *a* = 0. 2 intensity of silicon emission decreases (Figure 2) because of the target poisoning, but due to RF sputtering the process is stable even with the poisoned target.

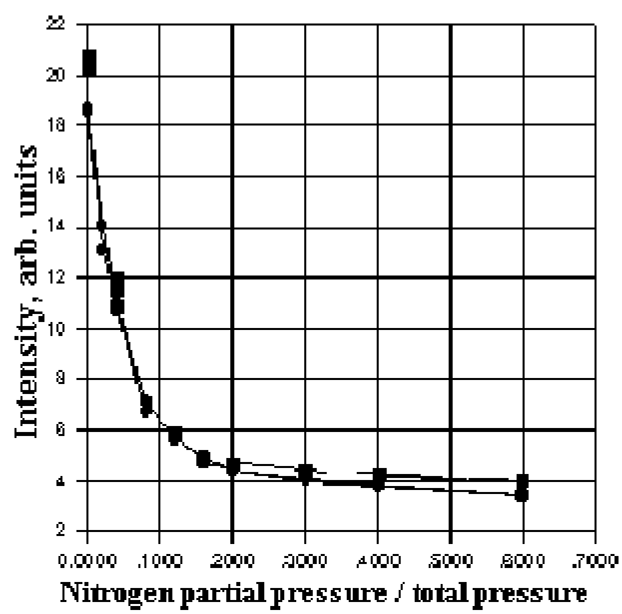

Figure 2. Intensity of the silicone emission line at different nitrogen pressures. The top curve is at no bias on the substrate and the bottom curve is at bias 150 V.

At a > 0.3 intensity I decreases because of noticeable drop of argon partial pressure in the mixture under conditions of the poisoned target, which defines the sputtering rate.

The bias increases the intensity of emission. Evidently it is connected with re-evaporation and additional excitation of silicon atoms.

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Already at $a > 0.1$ the rate of silicon nitride deposition is of little dependence on a and is equal 0.24 nm/s (U_{cm} = 0 V) and 0.18 nm/s (U_{cm} = 150 V). The rate of silicon deposition is 0.43 nm/s and 0.33 nm/s correspondingly. As sputtering power grows the curve I is displaced rightward upwards (Figure 2) and the deposition rate grows. Variation of the deposition rate of silicon nitride depending on a is shown in Figure 3. As it is obvious from Figure 3 the deposition rate practically does not vary at $a > 0.2$. It is connected with RF sputtering of the poisoned targets.

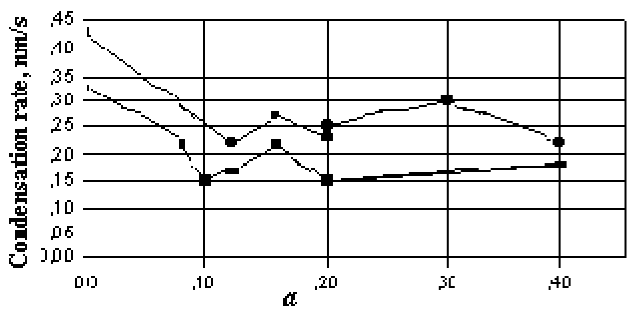

Figure 3. Condensation rate variation at different *a*. The top curve is at no bias on the substrate and the bottom one is at bias 150 V.

Measurement of optical transmission in the visible spectrum (Figure 4) showed that bias supply during deposition enhances the transmission. It is ascribed to more perfect structure of the coating (at $a > 0.2$). The transmission decrease at $a < 0.2$ is connected with decrease of nitrogen content in the plasma at the set sputtering power. The coating visually looks achromatic in the layers up to 1 micron thick. The refraction coefficient of silicon nitride layers, deposited in optimal conditions, is equal to 2. That corresponds to stoichiometric silicon nitride.

All coated samples for testing were manufactured 0.10-0.15 micron thick and by dimensions 80 × 80 mm at $a = 0.3$.

As protective coating silicon nitride is interesting for anticorrosive protection of metals (aluminum, brass) and for increase of wear resistance of plastics. Relative to this possible application adhesion, corrosion resistance, vapor permeability and wear resistance of the coating, which determine the protective layer quality in the first place, were investigated.

Adhesion on various materials was measured by the method of normal breakaway. The following values were received for various materials: brass - 4 MPa, glass - more than 8 MPa.

Adhesion of silicon nitride to silver is low. Metal samples with protective layer of silicon nitride were subject to standard testing of protective properties. They were tested in the environmental chamber at temperature 40°C and humidity 100%. Silicon nitride on glass did not change visually after 15 days of testing. The transmittance did not change either. The layers of aluminum 0.12-micron thick, deposited on glass, with silicon nitride protective coating were not changed visually after 10 days testing, reflectance in the visible spectrum was not changed either. Layers of aluminum on unprotected samples were oxidized and became transparent already after 15 hours of testing.

The brass samples coated with silicon nitride were tested on porosity and corrosion resistance. Porosity was tested by overlay of the filter paper, soaked with the solution of potassium ferricyanide and potassium chloride. No pores were found visually. Corrosion testing was carried out in the desiccator in ammonia vapors. After twenty four hours of testing no signs of corrosion attack were found.

Results of vapor permeability testing testify about protective properties of silicon nitride coatings. Thus, the silicon nitride coating 0.1 - 0.12 micron thick on PET film 25 micron thick decreases vapor permeability in up to 50 times. The coefficient of vapor permeability of silicon nitride is only two times higher than the coefficient of vapor permeability of the aluminum coating, which is the best barrier layer for polymeric films. Valuable properties of the silicon nitride coating were also revealed by wear resistance testing.

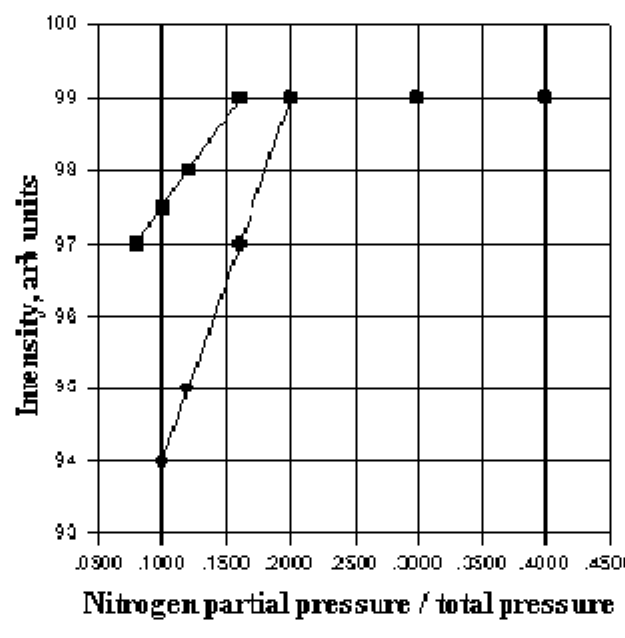

Figure 4. Optical transmission in visible spectrum area at various partial nitrogen pressures. The top curve is at no bias on the substrate and the bottom one is at bias 150 V.

Thus, uncoated polyamide was covered by a dense grid of scratches up to 0.5 micron deep already after 2700 cycles of galling with coarse calico under the load of 0.25.

While the polyamide samples coated with silicon nitride 0.15 micron thick had no visible scratches even after 15000 cycles of galling.

Effect of bias during deposition of silicon nitride on protective properties was not found visibly. Evidently, RF plasma etching of the samples provides efficient cleaning of the surface and it is a crucial impact on the formation of the protective properties. More delicate effects, connected with structural changes of the growing film under ion bombardments, leading to densification of the coating and decrease of microporosity, have little influence on the protective properties and are not detected by coarse methods of testing. At the same time bias influences on optical properties, which are connected first of all with the material structure. The transmission curve path at $a < 0.2$ (Figure 4) shows that RF bias activates nitrogen in the plasma and less nitrogen is necessary to provide the same transmission

CONCLUSION

Thus, employment of RF sputtering enables to operate over a wide range of values a without essential variation of the target sputtering rate. Application of RF sputtering in combination with the substrate bias allows depositing reliable wear and corrosion resistant coatings with high transparency for various purposes.

REFERENCES

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