Deposition of silicon oxynitride films by low energy ion beam assisted nitridation at room temperature

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Abstract. The possibility is studied of growing thin silicon oxynitride films by e-gun evaporation of SiO and SiO$_2$ together with concurrent bombardment with low energy N$_2^+$ ions from a cyclotron resonance (ECR) source at room temperature of substrates. The degree of nitridation and oxidation of the films is investigated by means of X-ray spectroscopy. The optical characteristics of the films, their environmental stability and adhesion to different substrates are examined. The results obtained show that the films deposited are transparent. It is found that in the case of SiO evaporation with concurrent N$_2^+$ ion bombardment, reactive implantation of nitrogen within the films takes place at room temperature of the substrate with the formation of a new silicon oxynitride compound even at low ion energy (150-200 eV).

1. Introduction

Silicon oxynitride (SiO$_x$N$_y$) is a representative of a new type of material without analogue in the nature. SiO$_x$N$_y$ films have widespread applications in microelectronics and optoelectronics as insulating and antireflection layers, optical filters, etc. due to their extraordinary properties [1].

Chemical vapor deposition has been widely used for fabricating silicon oxynitride films. However, some problems have been encountered when attempting to obtain high-performance characteristics, such as films transparency in the visible and near infrared ranges and to prepare the films at low temperatures near room temperature (RT) and so on [2]. The ion beam assisted deposition technique (IBAD) has been widely used as a powerful tool for depositing homogeneous, high-quality thin layers with good adhesion to the substrates without increasing the substrate temperature. This fact is of particular importance for the deposition of coatings on polymer substrates such as polymethylmetacrilate (PMMA) and polycarbonate (PC). Although IBAD is considered to be very promising in preparing silicon oxynitride films, only few works have so far been reported concerning mainly the evaporation of Si [3, 4].

In the present work we studied the possibility for growing thin silicon oxynitride films by e-gun evaporation of SiO and SiO$_2$ together with concurrent bombardment with low energy N$_2^+$ ions from a cyclotron resonance (ECR) source at room temperatures of substrates. To evaluate the properties of the films deposited, their composition, optical properties, environmental stability and adhesion to different substrates were examined.
2. Experimental

High vacuum coating equipment (Varian 3119) with a cryopump was used for conventional electron beam evaporation of SiO$_2$ and SiO. The source materials were synthetic quartz pellets and silicon monoxide powder. The rate of deposition and the thickness of the films were controlled by an Inficon IC 6000 crystal monitoring system and were adjusted to be about 0.15 nm s$^{-1}$ and 100 nm, respectively.

The total residual gas pressure in the system was $1 \times 10^{-5}$ mbar, rising to $4 \times 10^{-4}$ mbar during ion beam operation. Additional ECR plasma deposition apparatus was attached to the vacuum chamber to provide a N$_2^+$ ion beam incident on the substrate surface at angles within the range 40-50° [5]. A microwave power of 350 W with a frequency of 2.45 GHz was introduced into the plasma chamber through a rectangular waveguide and a window made of synthetic quartz plate. The ion flux characteristics (energy $E_{\text{ion}}$ and current density $I$) depend on the total voltage applied between the grids used to extract the ions. For singly charged ions, the ion energy in eV is regarded to be equal to that of the applied voltage in V [6]. We used one graphite grid with applied voltage of 150-200 V in order to obtain high ion current density (up to 150 $\mu$A cm$^{-2}$) at low ion energy of 150-200 eV. The ion beam current density was measured at the position of the substrates using a Faraday cup.

The analysis of the composition of the films deposited on Si wafers was performed using an ESCALAB MkII electron spectrometer. The spectra were excited with MgK$\alpha$ source. The photoelectron lines of C 1s, Si 2p, O 1s and N 1s were recorded from film surfaces without preliminary ion cleaning. All spectra were calibrated using the C 1s line at 284.8 eV as a reference. The sensitivity factors were determined by taking synthetic quartz as standard for SiO$_2$.

The optical constants (refractive index $n$ and extinction coefficient $k$) of the films were determined by an algebraic inversion method based on three spectrophotometer measurements- transmittance and reflectance of a film deposited on a BK7 glass substrate and an opaque Si wafer [7]. The measurements were carried out with a Cary 5E spectrophotometer at normal light incidence in the spectral range $\lambda = 400$-1000 nm.

An accelerated corrosion test was applied to evaluate the environmental resistance of the films. Adhesion of films on substrates was evaluated with adhesive tape (3M Scotch Magic Type 810) according to ASTM D3359-97. Both tests are described in detail in [5].

3. Results and discussion

The parameters which determine to a great extent the film modification during IBAD are the ion energy $E_{\text{ion}}$ and the ion-to-atom arrival rate ratio $c_{\text{ion}}$ [6]. The latter is the ratio of the ion flux density (for an ion with given $E_{\text{ion}}$) to the condensing material atom flux density. The quantity $c_{\text{ion}}$ is a criterion for the degree of ion bombardment.

Figure 1 shows an example of XPS analysis of chemical bonding states of Si 2p, O 1s and N 1s of the film grown by SiO evaporation at pressure $4 \times 10^{-4}$ mbar without and with concurrent N$_2^+$ ion beam bombardment at ion-to-atom arrival rate ratio $c_{\text{ion}}$ of 2.1.

The O 1s peak, located at 532.8 eV is typical for the oxides and oxynitrides. The N 1s peak recorded only for the film bombarded with N$_2^+$ ion is complicated and can be fitted with three components, as can be seen in figure 2a. The shape and position of the main contribution to the N 1s peak at 398.5 eV is typical of a N-Si-O bond structure formed in silicon oxynitrides [8]. For the case of Si-O bonding, four Si 2p components are well known (Si 1+, Si2+, Si3+ and Si4+), which correspond to Si atoms with one, two, three and four oxygen nearest neighbors, respectively. It is well established that each Si-O bond induces a Si 2p shift of about 0.9 eV relatively to elemental Si (99.6 eV), which increases in a linear way upon increase of the oxidation states [9]. On the other hand, the corresponding Si 2p shift of the different nitridation states is not well established.

The Si 2p peaks recorded for our films can be fitted with three component as it is seen in figure 2 b and c. The film grown without N$_2^+$ ion bombardment is mainly formed of Si$^{4+}$ (103.5 eV) and Si$^{3+}$ (102.1 eV) species (figure 2b). The N$_2^+$ ion bombardment (figure 2c) leads to a shift of the Si$^{3+}$ peak to
the higher energies (102.8 eV), which is in good agreements with the position of peaks reported for silicon oxynitrides in the literature [8, 10].

![O 1s, N 1s and Si 2p spectra](image)

**Figure 1.** O 1s, N 1s and Si 2p spectra of films grown by evaporation of SiO at pressure $4 \times 10^{-4}$ mbar without and with N$_2$ ion bombardment at $c_{\text{ion}} = 2.1$.

The stoichiometry of the samples was determined by measuring the intensity of the corresponding photoelectron peaks (i.e. O 1s, Si 2p, N 1s peak area integration with Shirley’s corrections accounting for the inelastically scattered electrons). According to this data the composition of the film grown by SiO evaporation without N$_2$ ion bombardment is SiO$_{1.3}$ which is in accordance with the literature data [11]. The concurrent bombardment with low energy N$_2^+$ ions leads to both an oxygen decrease and to incorporation of nitrogen. These results and the well defined shape of the photoelectron spectra in figure 1 and 2 suggest that a new silicon oxynitride compound is formed with approximate stoichiometry of SiO$_{1.25}$N$_{0.03}$ and SiO$_{1.17}$N$_{0.1}$ during N$_2^+$ ion bombardment at $c_{\text{ion}}$ of 1.3 and 2.1.

It should be noted that the XPS characterization of films obtained by SiO$_2$ evaporation indicates that similar N$_2^+$ ion bombardment at low energy does not lead to nitrogen incorporation in the films.

The results obtained show that the films deposited on all type of substrates are transparent. Figure 3 shows the spectral dispersion of the refractive index $n$ of the films obtained by evaporation of SiO and SiO$_2$ without and with N$_2^+$ ion bombardment. In accordance with the XPS results, the increase in $c_{\text{ion}}$ leads to a more pronounced increase in the refractive index of the films grown by SiO evaporation, while no change in $n$ is observed for the films grown by SiO$_2$ evaporation.
The results obtained show that films formed by $N_2^+$ ion bombardment have good environmental stability and adhesion to polycarbonate substrates.

![Figure 3](image-url)

**Figure 3.** Spectral dispersion of the refractive index of 100 nm thick films obtained at the indicated deposition parameters. Vertical lines indicate errors.

4. **Conclusion**

The results obtained show that in the case of SiO evaporation with concurrent $N_2^+$ ion bombardment, reactive implantation of nitrogen within the films takes place with the formation of a new silicon oxynitride compound even at low ion energies (150-200 eV). The films deposited are transparent, with refractive index within the range 1.6-1.65 (at 633 nm). Similar $N_2^+$ ion bombardment of films obtained by SiO$_2$ evaporation does not lead to nitrogen incorporation in the films.

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