

SiO_x structural modifications by ion bombardment and their influence on electrical properties

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The effect of an Ar/O₂ plasma treatment with additional ion bombardment delivered towards silicon suboxides layers has been investigated in terms of induced surface modifications, i.e., morphology, chemistry and electrical properties. Atomic Force Microscopy witnesses the smoothening of the silicon suboxide surface, dependent on the developed bias voltage at the substrate and the treatment time. Spectroscopic ellipsometry points out the optical properties of the modified surface: a thin silicon dioxide layer (5-17 nm) develops as a consequence of the surface process densification, also found to be dependent on the bias voltage and treatment time. Electrical properties (in terms of electric conductivity and layer capacity) are also reported on both the as deposited and ion bombarded samples.

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1. Introduction

The silicon oxide alloys, SiO_x (with 0 < x < 2), are among the most studied materials in the last decade, especially because of their interesting optical and dielectric properties. Having a good cohabitation with crystalline silicon, the SiO_x thin films have found important technological applications as gate insulator in the MIS devices, passivation layers in microelectronics, optical transparent parts in optoelectronic devices [1-3]. Several of these applications require low deposition temperatures, but good and stable structural material properties.

The deposition techniques - and within the same technique, the deposition conditions - determine the physical properties of the SiO_x layer. In this framework, films grown by physical vapor deposition at low temperatures (i.e. temperatures less than ~0.3 T_m, with T_m being the melting point of the deposited material) are typically composed of open columnar structures with extended voids along the column boundaries. Monte Carlo simulations have shown that the open columnar structure is caused by low-species mobility combined with self-shadowing by previously deposited atoms. Increasing surface diffusion at higher growth temperatures gives rise to denser, though still columnar structures, while at much higher temperatures (T > 0.5 T_m) grain growth occurs [4].

Some applications require a smooth SiO_x surface and/or a dense structure. Thin films deposited at low temperature values need special post-deposition treatment in order to achieve such properties. Ion bombardment delivered during an Ar/O₂ plasma treatment is the technique that we have investigated on SiO_x layers deposited by rf reactive magnetron sputtering. In this paper we report on the tuning of the surface modification of the SiO_x (smoothening) keeping an eye on electrical properties of the film.

2. Experimental

2.1 Deposition of SiO_x layer

Layers of a-SiO_x have been deposited in a reactive 13.56 MHz r.f. magnetron sputtering system. Using argon plasma, silicon atoms are sputtered from a polycrystalline silicon target situated at 7cm from the sample-holder. Keeping constant the rf power (2.2 kW) and the argon pressure (0.3 Pa) various SiO_x compositions are obtained by adding O₂ to the sputtering gas. Details about the geometry of the r.f. magnetron sputtering system have been given in ref. [5].

During depositions the plasma emission has been monitored by optical emission spectroscopy. No notable intensity variations of the emitted light assigned to silicon and oxygen atoms have been measured during the deposition. This suggests a homogeneous layer composition. Samples with a thickness of 600 nm have been deposited onto c-Si substrates for IR measurements and Cr/glass substrates for electrical measurements. The substrate was not heated externally, but immediately after deposition the film surface temperature was found lower than 100 °C.

The layer composition has been determined by energy dispersive x-ray (EDX) technique calibrated by a standard SiO₂ thermally grown sample and it was found as x=1.4.

2.2 Post-deposition plasma treatments

Argon/oxygen plasma treatments were carried out in the expanding thermal plasma (ETP) set-up [6-8] shown in Fig. 1. This is an example of remote plasma [9-11] since plasma production, active species transport, and treatment/deposition are geometrically separated. Briefly describing, Ar plasma is generated in a dc cascaded arc operating in a pressure range 1-4 × 10⁴ Pa, and then

expands supersonically through the nozzle in the deposition chamber kept at the pressure of 10-30 Pa. During processing, the system is evacuated through roots pumps, while overnight it is pumped by a turbo pump. Oxygen is injected in the plasma through the nozzle. The substrate is placed at a distance of 60 cm from the nozzle; the substrate temperature can be controlled in the range from $-50\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$, through ohmic heaters and liquid N_2 . For the present study all treatments were carried out at $25\text{ }^{\circ}\text{C}$. The ion bombardment is generated by applying 13.56 MHz rf power to the substrate holder. The negative dc bias voltage is measured with an oscilloscope.

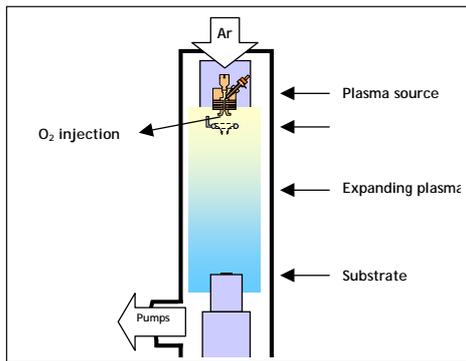


Fig. 1. Schematic of the expanding thermal plasma set-up used for the treatment of the SiO_x .

Plasma treatments were carried out at a fixed Ar flow rate of 100 sccs and arc current of 75 A. The pressure in the vessel during the treatments was 33 Pa. The Ar ion and electron flow expanding from the arc are fully controlled by the arc plasma parameters, i.e. Ar flow and arc current, and can be measured by means of Langmuir Probe in the downstream region [12,13]. Moreover, in previous studies it has been proved that Ar ions are consumed by the oxygen injected in the plasma, thus the flux of the Ar ions is determined by the oxygen flow rate used, being all the other arc parameters kept constant [13]. The negative dc bias voltage was varied by changing the rf power applied to the substrate holder and the O_2 flow rate. In conclusion, by tuning the rf power and the oxygen flow rate, the dc bias voltage, V_{dc} , and the flux of ions impinging the surface can be controlled.

Based on the assumption that all the energy delivered to the system is used to accelerate ions without generating an extra plasma, and that the plasma potential is zero, the maximum mean kinetic energy of the ions arriving at the substrate can be calculated from equation:

$$E_i = e|V_{dc}| \quad (1)$$

Correspondingly, the flux of ions is given by equation

$$\Phi_{ions} = \frac{P_{rf}}{eA|V_{dc}|} \quad (2)$$

where, P_{rf} is the rf power applied to the electrode and A is the area of the sample holder

Table 1 summarizes the explored process conditions for the plasma treatments.

Table 1. Experimental parameters for the plasma treatment of the SiO_x films.

O_2 (sccs)	P_{rf} (W)	V_{dc} (V)	Treatment time (min)
5	15	-25	7; 15; 30
5	30	-50	7; 15; 30
10	30	-121	7; 15; 30

Film chemical composition and structure were investigated by Fourier transform infrared (FTIR) spectroscopy. Spectra were acquired in transmission mode using a Bruker Vector 22 spectrometer, over an average of 50 scans and with a resolution of 4 cm^{-1} . For direct comparison, spectra of the as-deposited and of the plasma treated SiO_x were normalized.

Optical analysis of the films was carried out by means of *in situ* spectroscopic ellipsometry (SE, Woollam M2000) before and after the plasma treatment at an angle of 68° with respect to the surface normal of the sample, over an average of 100 scans. The modeling of the recorded data provided the film refractive index and extinction coefficient prior to the modification, as well as optical properties of the modified surface and the change in surface roughness.

Atomic force microscopy (AFM, NT-MDT Solver Pro Scanning Probe) was used to determine surface roughness and the overall appearance of the surface. AFM was used in non-contact mode with a silicon tip. Images of $2 \times 2\text{ }\mu\text{m}^2$ were acquired on different spots on each sample.

Current- voltage characteristics have been measured at room temperature using a Keithley 238 Current Source Unit. The sample was introduced within a Faraday cage and all measurements were computer controlled. The voltage has been varied between 0.01V and 100V and a delay of 1.4 s was kept constant for each experimental point between the moment of the voltage application and the current measurement.

3. Results and discussion

3.1 Morphological analysis

Fig 2 shows 2D AFM surface image of the as-deposited 600 nm-thick SiO_x film. The film exhibits a rough surface with nanometer-scale mounds, probably due to the presence of columnar microstructures underneath.

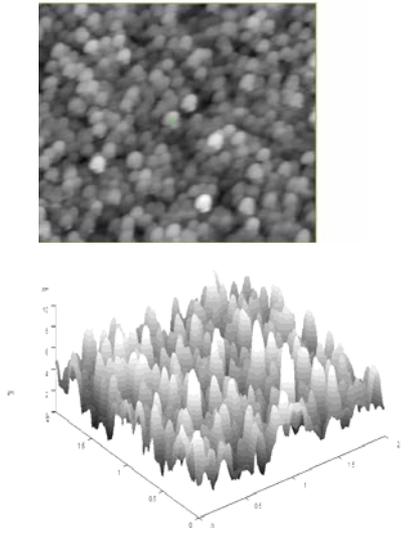
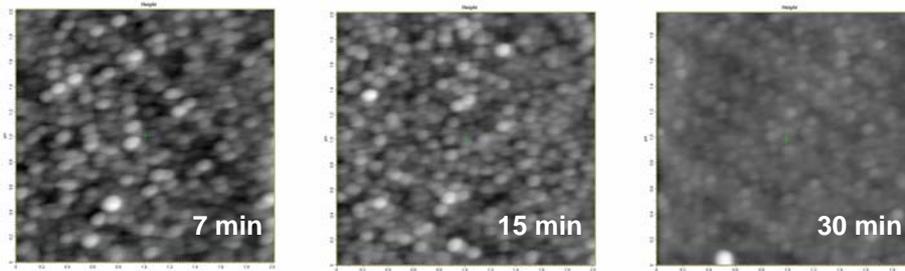


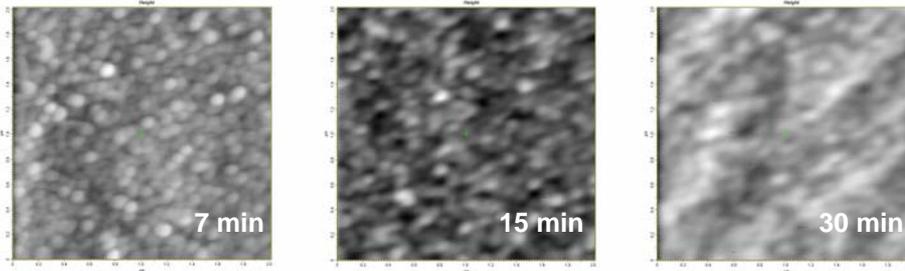
Fig. 2. Two-dimensional (left) and three-dimensional (right) AFM images of as-deposited SiO_x films.

Fig. 3 shows how the surface topography changes upon ion bombardment in Ar/O₂ plasmas under different experimental conditions. From a qualitative point of view it can be noted that the height of the mounds progressively decreases with time plasma treatment and the edges' boundaries become less distinguishable, thus pointing out surface smoothing and densification. This effect seems to be more pronounced for dc bias values higher than -25 V.

V_{dc} = - 25 V



V_{dc} = - 50 V



V_{dc} = - 121 V

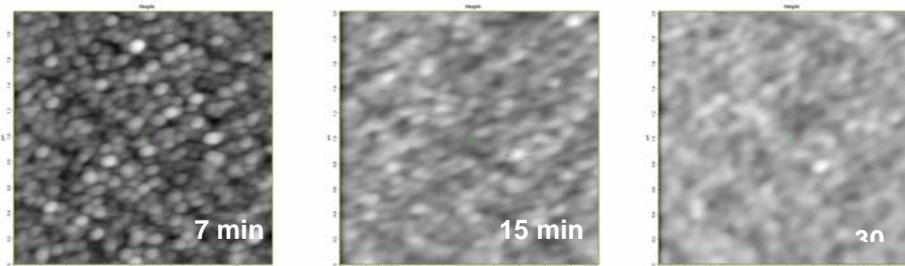


Fig. 3. Evolution of surface morphology of SiO_x film with treatment time and dc bias voltage.

For a more quantitative comparison, in Fig. 4 the values of mean peak-to-valley distance (R_{p-v}) and of the RMS roughness are reported as a function of the treatment time at different dc bias values. From these data it can be concluded that: a) smoothing appears to saturate with plasma exposure time since an asymptotic behavior for both R_{p-v} and root mean square (RMS) roughness can be observed; b) the RMS roughness data suggest that the surface modification occurs more rapidly at higher bias (-121 V) for treatment times shorter than ten minutes, then, it starts slowing down, eventually becoming as effective as the treatment at lower bias. This outcome is in agreement with what was found by other researchers in a similar study [14]. The best result is achieved after a 30 min treatment at -50 V of voltage, which leads to a reduction in the RMS roughness of about ~ 70%, compared to that before the treatment. When comparing results obtained at different bias values, it appears that the treatment seems more effective at -50 V, though considering the standard deviation, variations are not so pronounced.

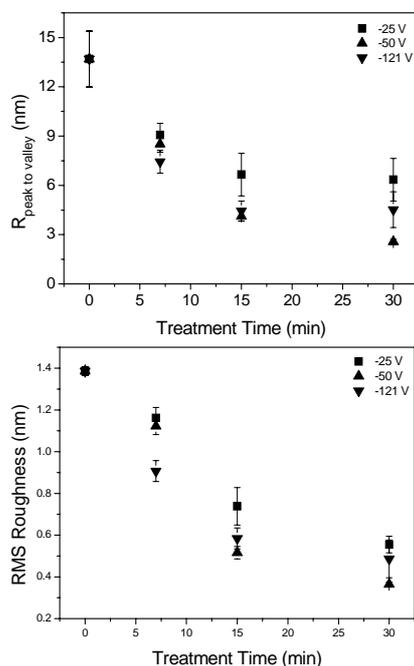


Fig. 4. Plot of the mean peak to valley distance (top) and of the RMS roughness (bottom) as a function of the treatment time for different dc bias voltages.

Film modification during ion bombardment is governed by the ion flux and energy, tuned by means of plasma chemistry (progressive addition of O_2 to the Ar-fed ETP) and the rf power applied to the substrate

holder. Recently, Granier *et al.* [15] have shown that the ion energy has a key role in the oxidation of organosilicon films by O_2 plasma treatment. In particular, the mechanism involved in the oxidation was elucidated and it was found that when the ion energy is higher than a threshold value, the film is only partially oxidized, while when the energy is low enough, the oxidation occurs at a greater extent and thus a thicker oxidized layer forms. This behavior has to be ascribed to the fact that very energetic ions ($E_i > 10$ eV) can induce the formation of a dense surface SiO_2 layer, which prevents the further diffusion of O atoms in the film. In order to understand whether a similar mechanism occurs during the oxidation of SiO_x film by Ar/ O_2 plasma treatment, *in situ* SE was used.

3.2 Optical analysis

Silicon suboxides were analyzed before and after the treatment with spectroscopic ellipsometry. The optical model used for the fitting basically consists of *c*-Si substrate, native oxide, the silicon suboxide layer and the roughness top layer. The latter was described using the BEMA model [16]. Using the Cauchy function [3,16], which includes also the Urbach expression [16] to describe the absorption tail of photons with energy below the material band-gap, a good agreement is obtained between experimental and modeled data, as it can be observed in Fig. 5.

From the optical analysis the refractive index, the extinction coefficient and the thickness of the SiO_x as-deposited film were determined before the treatment, and results are reported in Table 1.

Table 1. Results of the optical analysis on the untreated SiO_x .

Refractive index @ 633 nm, n	2.081
Extinction coefficient @ 633 nm, k	0.018
Thickness (nm)	515

The proposed model for the O_2 plasma-modified SiO_x layers consisted of the substrate, the native oxide layer, the unmodified SiO_x layer, a top layer of SiO_2 ($n=1.46$) and the surface roughness. In order to avoid correlation between fitting parameters, only the thickness values of the SiO_x , the SiO_2 and the roughness layers were fitted.

The Mean Squared Error (MSE) value was used as indicator of the goodness of the fit. Large values of the final MSE are usually indicative of a poor fit to the experimental data. An example of a measured and a

modeled spectrum of plasma treated SiO_x is given in Fig. 6, together with the model used for the fit.

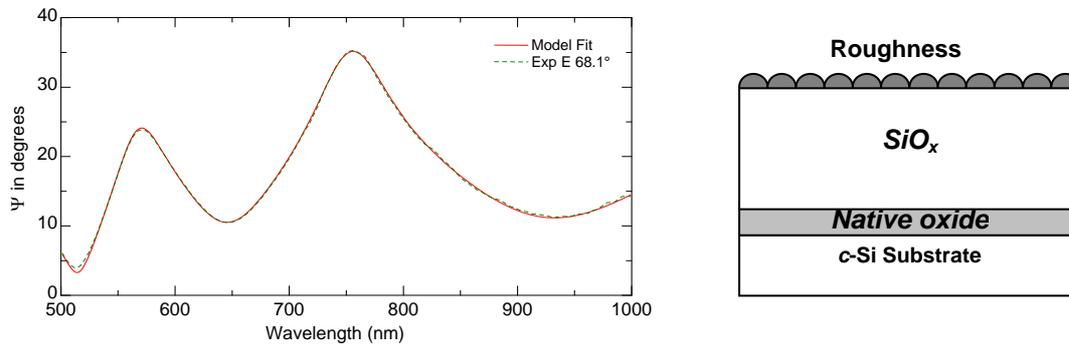


Fig. 5. The measured and modeled ellipsometric spectra (left) and the model (right) consisting of substrate, native oxide layer, the SiO_x film and the roughness top layer.

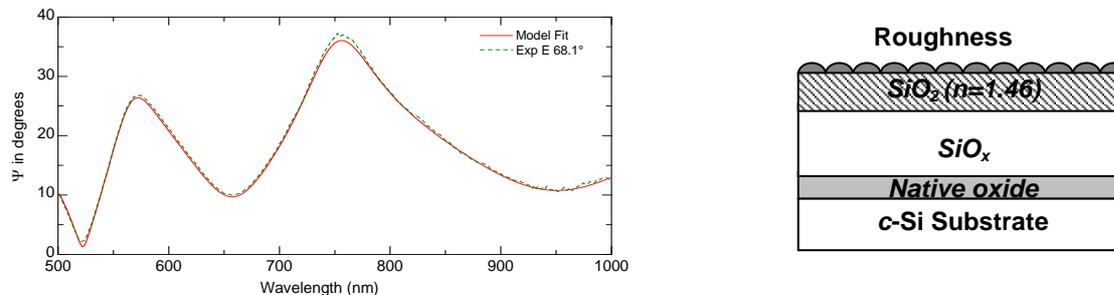


Fig. 6. The measured and modeled ellipsometric spectra (left) and the model (right) consisting of substrate, native oxide layer, the SiO_x film, SiO₂ layer and the roughness top layer.

The oxidized thickness values as a function of the treatment time for different bias voltages are reported in Fig. 7. For all bias values, the oxidation appears to reach a plateau with time. Moreover, by increasing the bias from -25 V to -50 V the oxidized thickness clearly increases, thus, indicating that the modification occurs at larger extent and the oxygenated species can penetrate deeper under this condition. However, an inversion occurs when going to even higher bias values (i.e. -121 V), the oxidized thickness decreases. It is interesting to comment these results considering the ion flux and the product of ion energy by ion flux (Table 2), calculated from relations (1) and (2), respectively.

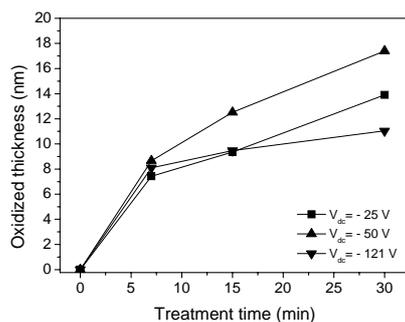


Fig. 7. Thickness of the oxidized layer as a function of the treatment time at different dc bias.

Table 2. Ion flux and products of the ion flux by energy of the ions at different bias values.

V _{dc} (V)	$\Phi_{\text{ions}} (\text{m}^{-2}\text{s}^{-1})$	$\Phi_{\text{ions}} * E_{\text{ions}} (\text{eV}/\text{s} * \text{m}^2)$
-25	$3.10 * 10^{20}$	$7.75 * 10^{21}$
-50	$3.10 * 10^{20}$	$1.55 * 10^{22}$
-121	$1.28 * 10^{20}$	$1.55 * 10^{22}$

For dc bias voltages ranging between -25 V and -50 V, the ion flux impinging the surface is the same while the energy is different and it is essential in controlling the oxidation extent, since more energetic ions can penetrate more deeply. At dc bias of -121 V, instead, both the ion flux and the ion energy are different with respect to -50 V, but their product is the same. In this case it seems that both parameters play a key role in determining the surface modification extent. At -121 V there are less ions impinging the surface, but more energetic. It seems reasonable, like Granier *et al.* found [15] that a thin and dense SiO₂ layer develops, under this condition, thus, preventing ions and other oxygenated species from further penetration.

Fig. 8 reports the evolution of the roughness layer with treatment time for different bias, according to SE.

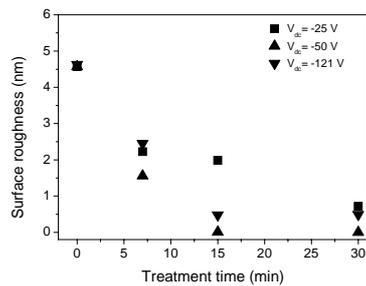


Fig. 8. Evolution of the roughness with treatment time for different bias, according to SE.

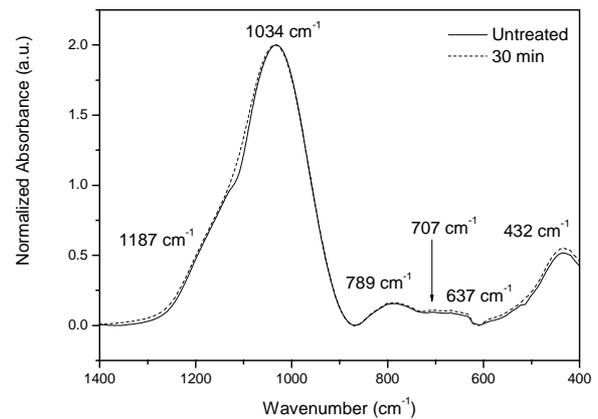


Fig. 10. Infrared spectra of SiO_x film before and after the Ar/O_2 plasma treatment at -50 V of dc bias voltage for 30 min.

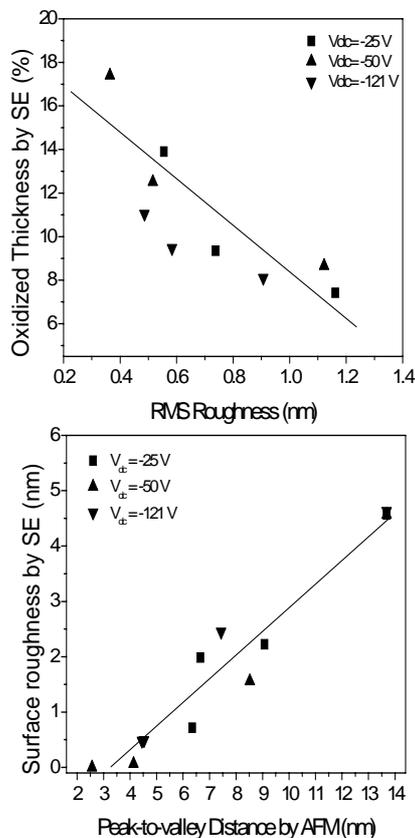


Fig. 9. Oxidized thickness and surface roughness as a function of the RMS roughness determined by AFM.

It is worthy to note that the trends are the same observed from AFM and that the best results in terms of surface smoothing are achieved at -50 V.

To further support the results found by SE, the trends of the oxidized thickness and of the surface roughness, as determined by SE, are reported in Figure 9 as a function of the RMS roughness and the peak-to-valley distance determined by AFM, respectively. In both cases a linear correlation is observed between results obtained from the two techniques.

3.3 Infrared analysis

The infrared spectra of silicon suboxides before and after the plasma treatments are reported in Fig 10. The spectra show the SiO bands at 1034 , 810 and 432 cm^{-1} which are associated to the stretching, bending and the rocking oscillating modes, respectively [17]. However it can be observed that the band at 810 cm^{-1} overlaps with another band at 790 cm^{-1} which is due to the SiH bending vibration. The band at 635 cm^{-1} is also characteristic of the bending modes. Some authors showed that bending vibrations at 790 and 635 cm^{-1} occur when the SiH group has one O-atom nearest neighbor, i.e. for the HSi-OSi_2 configuration. Moreover, they observed that by increasing the oxygen concentration in the film, both bands disappear and are replaced by the 876 - cm^{-1} band [18]. Finally it should be mentioned that no band related to the SiH stretching vibration was observed in the spectra around 2000 cm^{-1} as this absorption is characterized by a lower absorption coefficient [19].

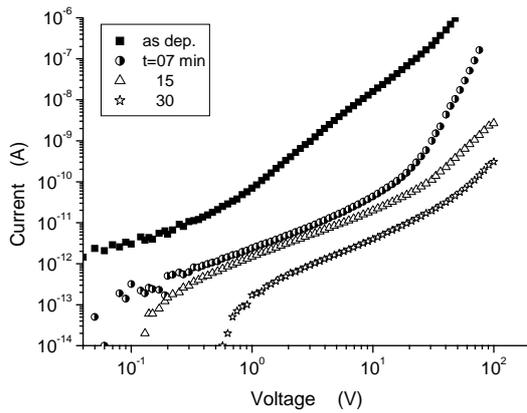


Fig. 11. Current-voltage characteristics of as deposited SiO_{1.4} film and ion bombarded samples.

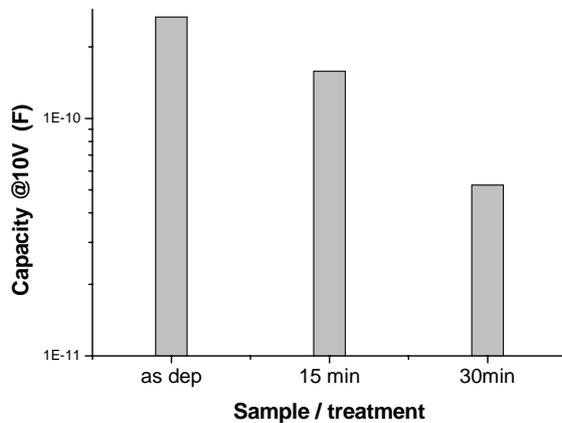


Fig. 12. The modifications of the layer capacity by the ion bombardment

As far as the changes induced by the treatment on the silicon suboxides' chemical composition are concerned, almost no difference can be observed from the normalized IR spectra. This can be explained by considering that the modified thicknesses, as determined by the SE analysis, are in the range of 7-17 nm thus FTIR, which is a bulk technique, has not enough sensitivity to monitor this surface modification. This is an extra proof that the plasma treatment is modifying only the surface of the SiO_x films.

3.4 Electrical characteristics

The I-V curves of the as-deposited and plasma-treated samples are shown in Figure 11. The electrical conduction mechanism in SiO_x thin films was found to be the variable range hopping (VRH) of carriers (electrons) [5]. This means that the structural properties of the layer (especially, the dangling bond defects' density) play an important role on electrical conductivity. Elsewhere, it was shown that the electrical conductivity of amorphous SiO_x is strongly dependent on the oxygen content (x value): it decreases over one order of magnitude when x

value increases. The drop in conductivity was seen to accelerate if the oxygen content is raised above x=1.2 [20]. In the frame of VRH model, the Pollak and Reiss formula described the I-V characteristics for medium- and high-field regions.

The as-deposited SiO_{1.4} sample is characterised by an electrical resistance of $1.43 \cdot 10^{10} \Omega$ for U= 1V and $2.82 \cdot 10^6 \Omega$ for U= 100V: the non-Ohmic character is obvious. These data are compared in Figure 11 with those of a plasma- treated sample under a 50V dc voltage for various treatment times. The electrical conductivity decreases when prolonged ion bombardment was used. According to the structural and compositional changes induced in SiO_x layers and described in previous sections of this paper, the change in electrical resistance could be attributed to more defects created by bombardment and a thin film of SiO_y, with x<y→2. A simple calculation shows that an electrical resistance of the as- deposited layer of $3 \times 10^9 \Omega$ (U= 10V) becomes $1.7 \times 10^{11} \Omega$ after 30 min ion bombardment.

The as-deposited sample has in the non-ohmic region (U> 5V) a "hump" that was observed more clearly at samples richer in oxygen. This anomalous behavior in the I-V curve is assigned to the layer's property to retain charge by trapping electrons. When electrical charge (electrons) passes through a SiO_x sample, part of it will be trapped on dangling bonds defects placed deep into the band gap. The releasing time of the electrons from these energy states depends on the phonon frequency, temperature and the associated energy level. The capacity of the layer can be calculated if the voltage and the amount of trapped charge are known. The latter is obtained from the time variation of the discharging current curves. More details concerning this technique has been published in ref. [21].

The results of the capacity calculation are shown in Fig. 12. It is clear that the plasma treatment (30 min with V_{dc}=-50V) has reduced the layer capacity at about 20% from the initial value (as- deposited sample). This is the result of a SiO₂-like thin film created on the SiO_x surface by ion bombardment, which will electrically act as a new electrical capacitor in series with the most part of the SiO_x capacitor. It can be argued that the amount of deep traps (placed deep into the bandgap) decreases by ion bombardment.

4. Conclusions

Post- deposition Ar/O₂ plasma treatments were used to improve surface density of SiO_x films deposited by RF magnetron sputtering.

Densification and surface smoothing were found to be dependent on the treatment time and on the dc bias voltage applied during the plasma treatment. Generally, longer treatment times resulted in smoother films with a best-case RMS roughness reduction of about 70%. As far as dc bias voltage is considered, an optimum value (around -50 V) appears to exist in order to get the most effective surface smoothing. A model for film densification was

proposed, based on the development of a SiO₂ top layer with a thickness strictly dependent on the treatment time and on the dc bias voltage. In particular, at too high dc bias voltages, a thin and dense SiO₂ layer develops, thus, preventing ions and other oxygenated species to penetrate further into the SiO_x bulk layer. These last findings were corroborated by the electrical analyses.

Acknowledgements

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