JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 8, No. 2, April 2006, p. 769 - 775

SiO_x thin films deposited by r.f. magnetron reactive sputtering: structural properties designed by deposition conditions

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The main subjects studied on this paper are the influence of the rf power, deposition pressure and oxygen partial pressure on the sputtering rate of silicon and on the oxidation process during the a-SiO_x deposition by magnetron reactive sputtering. It was found that the r.f. power influences drastically both: the sputtering and the oxidation processes, while the deposition pressure determines the sputtering rate but, for the investigated range, does not influence the oxidation process. No influence on the sputtering rate has been seen for the oxygen partial pressure within metallic mode of plasma, but it determines the composition of the deposited SiO_x layer. The sputtering deposition conditions determine both the layer composition and the internal SiO_x structure. Infrared spectroscopy performed on samples with the same composition but deposited under different input parameters revealed different shape of the spectra. Spinodal decomposition of the deposited SiO_x material induced by the particles' bombardment (ions, fast neutrals and UV photons) on the surface deposition seems to happen during the deposition process.

(Received January 8, 2006; accepted March 23, 2006)

Keywords: Silicon suboxide, Reactive sputtering, IR spectroscopy, Structural properties, Spinodal decomposition

1. Introduction

Silicon suboxide (a-SiO_x) films have been the subject of intensive research in the past decade. These films, because of their properties and a very good cohabitation with crystalline silicon, have found important technological applications as gate insulator in the MIS devices, passivation layers in microelectronics, optical transparent parts in optoelectronic devices [1-3]. Many such applications require low deposition temperatures and high deposition rates. Much attention is therefore being devoted to plasma assisted thin film deposition, whereby the properties of the films can be controlled through the plasma input parameters. Radio-frequent (rf) magnetron sputtering is a very common and versatile technique for low temperature amorphous materials deposition. Working with a silicon target, in a well-controlled oxygen environment, the argon plasma can be successfully used in a-SiO_x deposition. The oxygen incorporation in the silicon matrix has a great influence on the physical properties of the obtained material.

The amorphous silicon deposition via sputtering using argon plasmas has been studied and theoretically modelled [4,5]. When the oxygen is added in the deposition chamber, the plasma related processes: sputtering, particles transport, deposition and oxidation become very complicated since the plasma chemistry and the dynamics of the processes are changed. This is why, nowadays the scientific community makes several efforts to completely understand the mechanisms that governs the deposition process using the reactive sputtering technique. In this paper, experimental and theoretical results on a-SiO_x deposition are reported. Special attention is paid to phenomena such as target and surface substrate oxidation. The silicon deposition rate is estimated from experimental data and compared with data theoretically calculated within a simple model. The influence of the deposition input parameters on the plasma properties and on deposition rate is underlined.

Special attention is paid to a-SiO_x structural properties. Many physical properties of a certain material are determined by its structure. The structural properties of SiO_x thin films deposited by various techniques have been studied during last decade and two models have been developed:

- the random bonding model (RBM) where the Si-Si and Si-O bonds are considered as being randomly spread in the volume of the material, defining its amorphous structure [6];
- the random mixing model (RMM), where clusters of silicon rich and oxygen rich silicon suboxide are considered [7,8].

We note that in literature both these structural models are used and choosing one or another is not depended on the deposition technique. It seems that the oxygen content from the film plays a very important role in designing the SiO_x structure. It has been previously shown [9] that for samples deposited by reactive magnetron sputtering, the RBM describes well the atomic arrangements for $x<1.2$, while the RMM is more reliable for samples with $x>1.2$.

This x value is a kink point in optical and electrical properties as a function of oxygen content [10].

More recently it was shown that the SiO_x structure is the result of spinodal decomposition, process enhanced by bombardment with neutrals and ions during deposition [11]. From this point of view, the present paper offers some interesting experimental evidences.

2. Experimental

Layers of amorphous silicon suboxide SiO_x ($0<x<2$) were deposited in a sputtering system equipped with a 13.56 MHz rf magnetron source. Argon plasma was developed in the space between cathode (target) and anode (sample holder), which amounts to 6 cm, under various rf power values. In this way, silicon atoms were sputtered from a circular polycrystalline silicon target with 10 cm radius. In order to obtain SiO_x, O_2 was added to the sputtering gas. The cathode is characterised by an unbalanced magnetic configuration with a magnetic field at the target surface of about 500 Gauss. The deposition chamber has a volume of 10^5 cm^3 and was pumped down to a base pressure of less than 5×10^{-5} Pa before the plasma gas (Ar) was introduced. To avoid the contamination of the plasma by spurious oxygen, the polycrystalline Si target was "clean-sputtered" prior to each new deposition. This cleaning involved exposure to an oxygen-free Ar plasma for at least 2 min before the substrate was moved, from a load lock chamber, to its deposition location. Before entering the deposition chamber, the c-Si substrates samples were HF dipped in order to remove the native oxide layer.

Firstly, the deposition conditions have been determined in order to deposit SiO_x with x ranged between 0 and 2. The input parameters in the plasma formation (rf power, pressure, gases flows and their nature) have been modified and the target voltage (U_{tar}) has been monitored. It is well known that U_{tar} determines the energy value of the ions that arrive at the target surface and, consequently it plays a crucial role in the sputtering process. Secondly, SiO_x thin films have been deposited and their compositional, structural and optical properties were investigated. During depositions, the temperature of the substrate was not controlled, but previous temperature measurements in our setup have shown that the substrate temperature remains below 80 ^oC.

During deposition, the gas pressure was 0.56 Pa, not significantly influenced by the maximal 1 sccm O_2 flow.

3. Results

The target voltage measured for different argon plasmas as a function of rf power is shown in Fig. 1. The rf power was varied between 25 W and 250 W for different values of the argon flow. During depositions, the pressure was varied between 0.4 and 8 μbar. From Fig. 1 it is clear that the higher the rf power, the larger the target bias value. Except for the first two pressure values, the target voltage does not depend significantly on pressure. Contrarily, the very low-pressure (0.4 μbar) provides a target voltage larger with 30-50 V than the higher-pressure values correspondent. All the plasmas, except the one produced with 250 W rf power, have been stable.

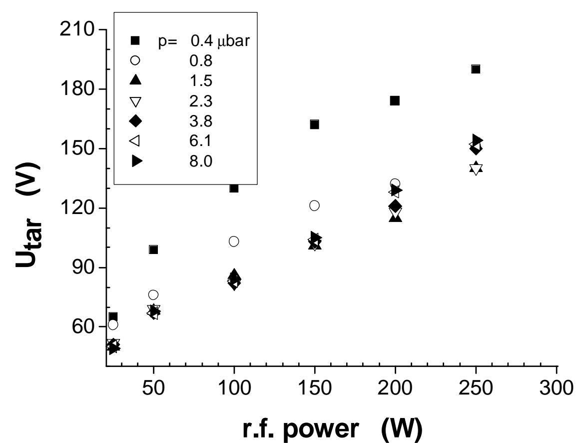

Fig. 1. Target voltage versus rf power for argon plasmas produced under various pressure values.

Adding oxygen to the plasma gas, the target voltage is changed. Fig. 2 shows the target voltage versus the oxygen partial pressure (OPP) for various plasmas powered with 140 W. Independently on the total pressure value, an OPP of 0.08 μbar means a steep decrease of the target voltage. This value is specific to 140 W rf power and represents the amount of oxygen that makes the plasma acting in so-called *oxidic mode*. In this sputtering regime, the silicon from the target surface is completely oxidised and both, the silicon and oxygen atoms are sputtered. In these conditions, the amount of oxygen that will participate in the deposited silicon atoms oxidation process has the two components: one directly from the oxygen supplier and the second one from sputtering process. The efficiency of silicon atoms sputtering diminishes in the oxidic mode. The OPP value that defines the plasma transition to an oxidic mode can be changed by rf power: increasing the applied power, the argon ions' bombardment on the target surface increases. In this way for a certain amount of oxygen in the vessel, the target oxidation process could be stopped. These are speculations, supposing that the sputtered entities are particles and not molecules. Under this assumption, Fig. 3 supports the model.

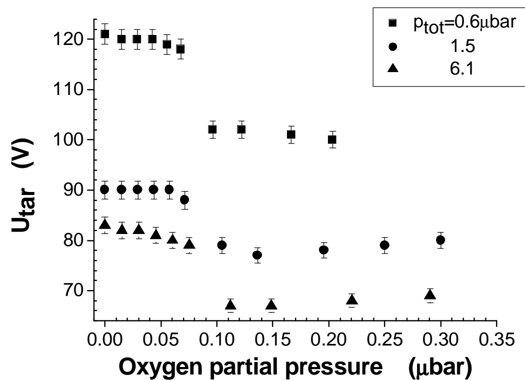

Fig. 2. Target voltage versus the oxygen partial pressure when plasmas have been produced under a rf power of 140 W. The steep diminishing shows the plasma transition to the oxidic mode.

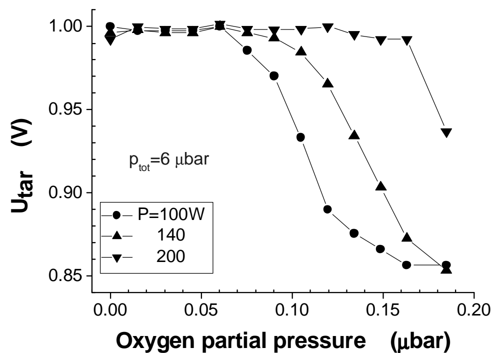

Fig. 3. The oxidic mode of the plasmas can be shifted to higher values of the OPP by increasing the rf power.

More important in SiO_x deposition is the sputtering with smaller OPP values (under the steeply decrease in Fig. 2) that defines the so-called *metallic mode*. The results of such depositions, varying OPP, are thin films of silicon suboxides (SiO_x, with $0<x<2$). The effect of the plasma conditions on the compositional properties of the SiO_x thin films is presented in Fig. 4. For comparison series of samples deposited with the same rf power (140 W) and two different values of the total pressure: 0.61 µbar and 6.1 µbar are shown.

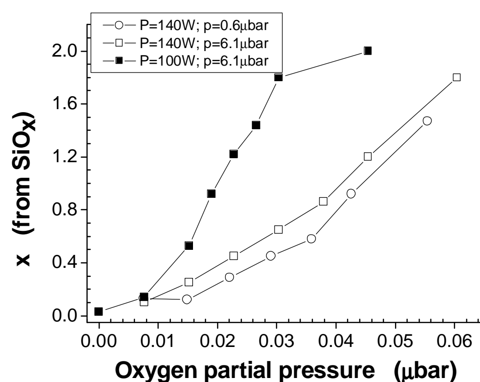

Fig. 4. Compositional properties of SiO_x thin layers deposited under various plasmas conditions.

The figure also presents results of two series deposited using plasmas obtained under 6.1 µbar and different r.f. power: 100 W and 140 W.

The same x value can be obtained with a small amount of oxygen in the vessel if low rf power is used or depositions at higher pressure values are performed.

As long as the plasma is maintained in the metallic mode, the sputtering efficiency of silicon atoms is defined by the values of the input parameters as rf power and pressure. Keeping constant these parameters, the influence of the OPP is practically negligible. This explains the cvasi-linear dependency of the x value with the OPP (see Fig. 4). Another proof is shown in Fig. 5 where the deposition rate versus the x values is given. Less silicon is sputtered with plasma developed at low rf power. This is a direct consequence of the argon ion energy involved in the sputtering process. But, the amount of sputtered silicon is a function of Ar ions' density that bombard the target surface. Thus, a higher deposition rate is obtained for higher pressure in the vessel, when the rf power is constant.

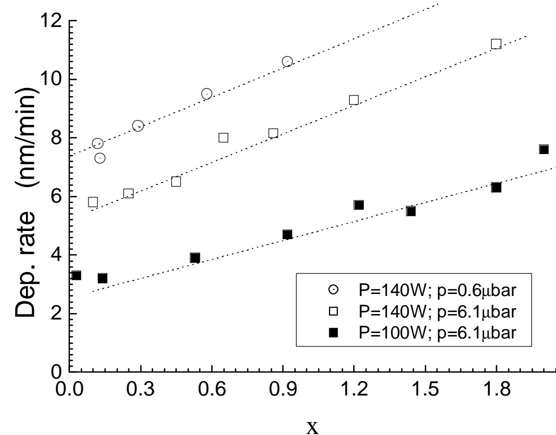

Fig. 5. The plasma parameters influence the deposition rate values of various SiO_x layers.

The structural properties of the layers are determined by the composition of the layer and the conditions during the deposition. The peak position of the Si-O-Si stretching vibration mode in the IR spectra is related to the structure of the material. In Fig. 6 is shown the IR peak position versus the x values for SiO_x samples deposited under various plasma conditions. This picture shows clearly that samples with the same composition (x value) are characterised by different peak position values in the IR spectrum. The structural changes influence the density of states distribution and implicitly the optical and electrical characteristics of the layer.

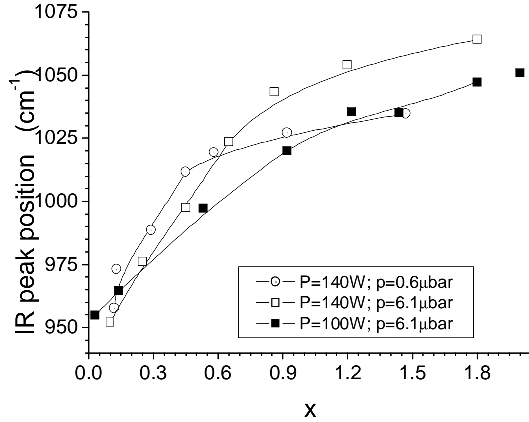

Fig. 6. IR peak position as a function of x parameter shows the SiO_x structural properties depending on the layer composition. It has to be underlined that for the same composition, the structural properties varies with the deposition conditions.

4. Discussions

4.1 The sputtering mechanism

By applying rf power to the deposition system electrodes, a large dc electrode voltage develops in addition to the applied voltage. This effect is known in the literature as self-biasing and in this paper it is referred to as target voltage, the silicon target being part of the powered electrode. It is caused by the difference in the mobility between electrons and ions. The electrons are able to follow the electrical field that is oscillating at rf frequency and thereby oscillate in energy. Ions are to heavy to respond to the electrical field oscillations. This difference in velocity of the charged particles causes an excess of negative charge on the electrode surface determining a negative dc offset voltage. The positive ions are accelerated towards the electrode (target) by this negative self-bias, while electrons are repelled. In this way the plasma sheath is generated. It is generally considered that the sheath thickness is constant in time and no ions' collisions are present into this region: the ion mean free path is larger that the sheath thickness.

The target voltage determines the ions' energy in the plasma sheath region. For rf plasmas, Kuypers and Hopman [12] have calculated the ion energy at the cathode surface:

$$E \approx eU_{eff}\left[1-\frac{\lambda\, n}{\omega\, d}\cdot\sqrt{\frac{2eU_{eff}}{M}}\cdot(\sin\omega\, t_1-\sin\omega\, t_0)\right] \qquad (1)$$

where e is the electron charge, $U_{eff} = |U_{tar}| + V_p$ is the bias over the cathode plasma sheath. The parameter λ describes the relative magnitude of the rf and dc components of the electric field and it was estimated as λ=-1 for reactor where the grounded electrode has larger capacitance (the largest area). According to Ref. [12] the constant n determines the dependence of sheath potential on the distance to the electrode surface, ω is the angular frequency of the rf field, while t_0 and t_1 are the times the ions enter the sheath and reach the target surface, respectively.

The sputtering yield is a function of ions energy that reaches the target surface. According to Sigmund's model [13] the sputtering yield can be described by:

$$Y = \left(\frac{3\gamma}{4\pi}\right)\cdot\frac{M_t M_i}{(M_t+M_i)^2}\cdot\frac{E}{E_t}\ , \qquad (2)$$

where the coefficient γ depends linearly on the (M_i/M_t) ratio, M_i is the incident ion mass, while M_t and E_t are the target atoms' mass and bonding energy respectively.

Combining (1) and (2) it results that a larger target voltage increases the sputtering efficiency. The extreme values of the time-dependent factor from Rel. (1) are: -2 and 2. Mathematically, this means that the ions energy will vary between a minimum value of $E_{min} \approx eU_{eff}\left(1+2\cdot\frac{\lambda\, n}{\omega\, d}\sqrt{\frac{2eU_{eff}}{M}}\right)$ and a maximum of $E_{max} \approx eU_{eff}\left(1-2\cdot\frac{\lambda\, n}{\omega\, d}\sqrt{\frac{2eU_{eff}}{M}}\right)$. The sputtered silicon atoms can be easily expressed in terms of argon ions' bombardment and sputtering yield:

$$N_{Si} = Y\cdot N_i \propto Y\cdot J_i\ , \qquad (3)$$

where the number of argon ions, N_i, is determining the ionic current at the cathode, J_i.

Using a simple model to describe the current-voltage characteristics in the plasma sheath, (no ions' collisions in the sheath region), the ionic current is expressed by the Child-Langmuir law [14]:

$$J_i \propto \frac{U_{eff}^{3/2}}{d^2} \qquad (4)$$

The plasma sheath thickness, d, has been found large in comparison with the Larmor radius and quasi-constant for plasmas produced under the input parameters (pressure, rf power, gas flows) here used [5]. The plasma voltage, V_p, is 30÷38 V.

From (2), (3) and (4), considering the extremes for the energy values of the argon ions, the deposition rate of silicon, which is proportional to its sputtering rate, can be expressed as:

$$[Si]_{dep} \propto U_{eff}^{5/2}\left(1+\xi\cdot U_{eff}^{1/2}\right) \qquad (5a)$$

with

$$\xi = \begin{cases} -\dfrac{\lambda n}{\omega \cdot d} \cdot \left(\dfrac{4 \cdot e}{M}\right)^{1/2}, & \text{for high energy} \\ \dfrac{\lambda n}{\omega \cdot d} \cdot \left(\dfrac{4 \cdot e}{M}\right)^{1/2}, & \text{for low energy} \end{cases} \qquad (5b)$$

This result must be verified by the experimental data from Fig. 5. The SiO$_x$ deposition rate, δ, varies linearly with the x values according to the equations given in Table 1. The linear fit reproduces the experimental data with a correlation factor of 0.998.

For x=0, the silicon deposition rate can be estimated for each case. The target voltage, U_{tar}, has been measured and the plasma potential has been estimated according to the data published in ref. [15, Figs. 2 and 3]. In this way the U_{eff} values can be calculated (see Table 1). Considering the Rel. (5a) for silicon depositions under the same pressure value (p=6.1 μbar) and under the same rf power value (rf P=140 W), respectively, the power index, α, that characterises the sputtered silicon versus the target voltage can be calculated from:

$$\frac{\delta^{(i)}}{\delta^{(j)}} = \left(\frac{U_{eff}^{(i)}}{U_{eff}^{(j)}}\right)^{\alpha} \qquad (6)$$

where i and j describe the plasma conditions given in Table 1. The values for the α index calculated with (6) are 2.45 and 2.47, very close to 2.5 from Rel. (5a).

Table 1. The linear fit of the deposition rate as a function of x value, the voltage across the plasma sheath and the α parameter for various plasmas' conditions.

Plasma conditions	δ =f(x)	Ueff (V)	α
rf P=100W; p=6.1 μbar	3.01+1.94·x	110	2.45
rf P=140W; p=6.1 μbar	5.17+3.41·x	137	
rf P=140W; p=0.61 μbar	7.24+3.55·x	157	2.47

Therefore, the silicon sputtering rate, and as a consequence, the silicon deposition rate is a power function of the potential across the plasma sheath that accelerates the argon ions and determine their energy for the sputtering process. It has to be noted that this relationship is specific to the deposition systems where the plasma sheath is large in comparison with the Larmor radius of the secondary electrons. Also, all depositions are in the metallic mode of the plasma.

4.2 The oxidation process reflected in SiO$_x$ deposition rate

The most used technique to determine the deposition rate of a thin film is to measure the layer thickness and to normalize it to the deposition time. This was the procedure for data from Fig. 5. The previous section has shown that the silicon sputtering depends on the plasma conditions. On the other hand, the gas mixture is part of the input parameters in the sputtering process. For the metallic mode of plasma, the oxygen content in the vessel does not affect the target voltage. Also, in a previous paper we have shown that the silicon deposition rate does not depend on the x values, especially for x<1.4 [9]. For such kind of layers, the deposition rate is proportional to the amount of oxygen that interacts with the sputtered silicon. If N_{tot} is the total number of the deposited atoms, than the deposition rate is:

$$\delta = \frac{dN_{tot}}{dt} = (1+x)\frac{dN_{Si}}{dt} \qquad (7)$$

where dN_{Si}/dt is the silicon deposition rate. As long as dN_{Si}/dt does not depend on the amount of oxygen from the vessel (under conditions of a plasma in metallic mode), Fig. 5 reflects Rel. (7).

Taking into accounts the linear part from Fig. 4 where x is given as a function of oxygen partial pressure (OPP), the x values can be determined. For OPP= 0.03, the values are given in Table 2. Considering the definition for the x parameter - the ratio between the deposited oxygen and the deposited silicon atoms, $x = [O]_{dep}/[Si]_{dep}$, the influence of the oxygen atoms can be estimated. The deposited silicon contribution to the total deposition rate it is known from Table 1. Considering the Table 2, it results:

a) for depositions under the same rf power but various pressure values, the x value is defined by the deposited silicon. A very small influence (about 5%) on the x value has been found because of the oxygen amount in the vessel and the pressure variations. The oxidation process does not depend on pressure values.
b) for depositions under the same pressure values, but different rf power, the late will influence drastically the silicon deposition and the oxidation processes. The oxidation process depends on the rf power.

Table 2. The influence of the deposited silicon on the value of the x parameter. The calculations are performed for the same oxygen partial pressure in the vessel.

	$x^{(i)}/x^{(k)}$	$[Si]_{dep}^{(k)}/[Si]_{dep}^{(i)}$
rf P =140 W; pressure varies	0.75	0.72
P=6.1 μbar; rf power varies	0.39	0.58

The oxidation process is a complex one. There is no control on the dissociation process of the molecular oxygen when the pressure and/or the rf power are varied. More than this, the surface oxidation can be done either by atomic or molecular oxygen if the local sticking coefficient, s, allows. Generally, the sticking coefficient for oxygen is considered s=1 for a silicon atom bonded to

other three silicon atoms and s=0 if the nearest neighbors of the considered silicon atom are only oxygen atoms. What is the s value for intermediary situations and how the deposition parameters influence it, is a subject for debate.

4.3 The influence of the deposition conditions on SiO_x structural properties

The deposition techniques and, in the frame of the same technique, the input parameters used for deposition are “designers” for the SiO_x structure. It is well known that the shape of the IR absorption spectrum is a signature of the structural properties. From Fig. 4 it is clear that samples with the same composition (x value) provide various peak positions of the Si-O-Si stretching vibration mode. Table 3 shows the IR wave-number values where the samples with x=0.5 and x=1.4 will maximum absorb. At the same time, Table 3 reveals that, for the same composition, the peak position is a function of the deposition parameters:

- for the same deposition pressure value, a higher power means a positive shift in the IR peak position;
- for the same rf power as input parameter, the IR peak position is positively shifted when the pressure decreases.

In order to discuss these behaviors, we have to point out that, in the frame of the RBM model, the IR peak position is shifted towards high wave-number values (positive shift) when the oxygen concentration increases. More oxygen atoms around the Si-O-Si bridge mean a larger wave-number value (i.e. 940 cm^{-1} when only silicon atoms are the nearest neighbors and 1054 cm^{-1} when only oxygen atoms are bound). But, in Table 3 we deal with the same x value: the average number of silicon and oxygen atoms is the same in all samples.

Table 3. The IR absorption peak position of SiO_x depends on the deposition conditions.

	Wave-number (cm^{-1})	
Plasma conditions	x=0.5	x=1.4
rf P=100W; p=6.1 μbar	992	1038
rf P=140W; p=6.1 μbar	1005	1057
rf P=140W; p=0.61 μbar	1014	1033

The differences in the peak positions are explained by various structures induced by the energy deposited into the layer during the deposition process. The deposited surface is subjected to ions (and neutral atoms) bombardment and plasma photons irradiations. In [11,B] it was shown that as-deposited SiO_x samples, with various x values, have been subject of phase separation when, deliberately, they have been ion bombarded [11] with energetic ions or irradiated with UV photons [B]. In [A] it was shown that the spinodal decomposition of SiO_x structure is a multi-steps process where the reduction of one Si atom must necessarily lead to the oxidation of another one (and so, the composition is “conserved”). This can explain different structural properties (reveled by various IR peak positions) for the same composition.

Indeed, increasing the rf power the target voltage increases and the ions’ energy is higher. So, more energy is deposited into the layer during deposition. If the rf power is the same, but the pressure decreases, the target voltage increases: according to the Fig. 2, U_{tar} =120 V for p=0.61 μbar and U_{tar} =82 V for p=6.1 μbar. Also, the mean free path increases when the pressure is lower, so the ions’ probability of loosing energy by collisions decreases.

For high x values, more oxygen is need into the vessel. Increasing the rf power both, the production of sputtered silicon and the dissociation probability of the molecular oxygen increase. At low-pressure values, the molecular oxygen dissociation is diminished by small probability of collision with argon and electrons. This means less atomic oxygen ready for direct surface oxidation and it could be an explanation for an IR peak position at smaller wavenumber values (see Table 3).

5. Conclusions

The influence of the rf power, deposition pressure and oxygen partial pressure on the silicon sputtering process using argon plasmas has been studied. The parameter used in describing these influences is the target voltage. Working in the plasma metallic mode, the oxidation process of the sputtered silicon has been also investigated. The main results are:

a) the target voltage determines the amount of sputtered silicon;

b) the r.f. power influences drastically both: the sputtering and the oxidation processes (more r.f. power, more silicon is sputtered);

c) the deposition pressure determines the sputtering rate and no influences in the oxidation process have been found;

d) the oxygen partial pressure smaller than the value corresponding to oxidic mode of the plasma has no influence on the sputtering rate, but determines the composition of the deposited SiO_x layer.

The internal structure of the SiO_x thin film is a function of the layer composition and deposition conditions. For the first time are presented and discussed experimental data where samples with the same composition show different structure reflected in IR spectra. Spinodal decomposition of the deposited SiO_x material seems to happen during deposition induced by the particles’ bombardment (ions, fast neutrals and UV photons) on the surface deposition.

Acknowledgements

Prof. F.H.P.M. Habraken and dr. A. Palmero from Utrecht University are gratefully acknowledged for very useful and stimulating discussions. Océ Technologies B.V. is acknowledged for the support given to this work.

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