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SiO_xN_y Films deposited with $SiCl_4$ by remote plasma enhanced CVD

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Silicon oxynitride films have been deposited with $SiCl_4$ by remote-plasma enhanced chemical vapor deposition (PECVD) at a substrate temperature of 250 °C. Different mixtures of O_2 and NH_3 were used to obtain different oxynitride compositions ranging from SiO_2 to an stoichiometry close to that of silicon nitride. Rutherford backscattering spectrometry was used to determine the chemical composition of the SiO_xN_y films. The behavior of the IR absorption spectra as well as the refractive index measured by ellipsometry were used to estimate the effect of the different deposition parameters. It was found that the IR spectra show a shift of the characteristic peak associated with the stretching vibration mode of the Si-O-Si bonds towards lower wavenumbers as the relative concentration of ammonia was increased with respect oxygen. No double peaks associated with silicon oxide and silicon nitride were observed, indicating the formation of an homogeneous alloy. The IR spectra did not show any presence of water or hydrogen related impurities in the film. Also the effect of a hydrogen flow added during the deposition process on the structural characteristics of the deposited films was studied using dielectric spectroscopy and atomic force microscopy measurements showing that the hydrogen flow added during deposition results in a reduction of the film roughness and a planarization effect, which is very interesting for the application of these films in microelectronics devices. © *1999 Kluwer Academic Publishers*

1. Introduction

Insulating films of SiO_xN_y with values ranging from 0 to 2 for x and 0 to 4/3 for y have been widely used in silicon based microelectronics applications. Silicon oxynitrides films have received an increasing amount of interest due to the possibility that, by choosing the proper composition, the excellent electronic characteristics of the SiO_2 and the moisture and alkali ion diffusion barrier properties of the Si_3N_4 may be preserved. On the other hand, low temperature deposition of high quality insulators is strongly required for surface passivation and interlevel dielectrics of future ULSI. In conventional plasma assisted chemical vapor deposition (PACVD), silane SiH_4 is the silicon source and it induces much hydrogen incorporation into the deposited films which causes thermal instability in physical and electrical properties during subsequent processes [1].

The use of silicon halides as a source of Si instead of SiH_4 [2, 3] has been successful in obtaining good electronic quality silicon dioxide films at 200 °C in the case $SiCl_4$ and 250 °C with SiF_4, without any further thermal treatment needed. Also good quality silicon nitride films have been obtained using SiF_4 as a source of silicon [4].

In this work we have used in the deposition of silicon oxynitrides $SiCl_4$ gas as silicon precursor, instead of the convencional SiH_4 in order to obtain low hydrogen concentration in the deposited films. The structural and optical characteristics of these silicon oxynitride films deposited at 250 °C by remote-PECVD are reported. Oxygen and NH_3 on different relative flow ratios were used to obtain oxynitrides with different composition. The IR absorption characteristics show a single peak associated with the stretching vibration mode, indicating the formation of an homogeneous oxynitride alloy rather than a two phase composition. Rutherford Backscattering Spectrometry (RBS) was used to determine the composition of the deposited films. The effect of adding hydrogen to the reactant gases during the deposition process on the structural characteristics of the

deposited films was determined by Atomic Force Microscopy. It was found that the average roughness of the films decreased as the amount of hydrogen added was increased, therefore the planarity of the films is improved. Also, the dielectric parameters calculated from the C-F curves measured under an external sinusoidal electric field [5] indicates that the addition of hydrogen causes positive influence in the electric response of the deposited films.

2. Experimental

The remote-PECVD system used in this work consisted of a cylindrical cavity capacitively coupled to an rf power generator (13.56 MHz) and positioned to create a plasma region away from the sample [6]. A flow of O_2, NH_3 and N_2 was passed through this cavity generating a plasma that was directed to the substrate surface. The nitrogen flow was kept constant at 20 sccm but the oxygen to ammonia ratio was varied between 0 to 2, maintaining a total constant flow for both gases at 54 sccm. The $SiCl_4$ and H_2 were fed through a dispersor ring placed near the substrate surface. The silicon tetrachloride was obtained from a liquid source and a 4 sccm flow was maintained constant in the deposition of the oxynitride films used in this work. The hydrogen flow was varied in the range of 0 to 30 sccm to check on the effect of the hydrogen presence during the deposition process, in the rest of the samples a 30 sccm flow of H_2 was used unless otherwise noted. The deposition chamber pressure was kept at 300 mTorr during the deposition of the films. The substrate was a p-type 200 $\Omega \cdot$ cm silicon wafer with a (100) crystalline orientation. The substrate temperature during deposition was held constant to 250 °C and no further thermal annealing was given to the samples. The thickness and refractive index of the films were determined by ellipsometry measurements using the 630 nm line of a He-Ne laser. The deposition rate was estimated from the final thickness of the film assuming a constant deposition rate throughout the whole process. The IR% transmission spectra were obtained with a Fourier-Transform spectrophotometer in the range of 400–4000 cm^{-1}.

Rutherford Backscattering Spectrometry (RBS) was used to analyze the amounts of the cations (silicon atoms) in the films. Nuclear microanalysis by direct observation of nuclear reactions and backscattered particles was utilized to complete the analysis of the samples. The oxygen (^{16}O) and nitrogen (^{14}N) contents of the films were measured by the use of $^{16}O(d, p)O^*$ and $^{14}N(d, \alpha)^{12}C$ nuclear reactions respectively, by comparison with reference targets. The precise depth distribution of the various elements in the films were determined by using RUMP simulation program [7]. The surface morphology and roughness of the films were determined with an Atomic Force microscope operated in air. For the dielectric measurements parallel plate capacitors were prepared depositing gold contacts in both sides of the samples by rf sputtering. The contact deposited on the oxynitride side was circular with 3 mm diameter. The I-V characteristics of these sandwiches showed good ohmic behaviour at applied voltages below 0.15 V. The values of the capacity (C) and conductance (G) of the samples were measured in the frequency range between 0.1 to 10^3 kHz, with a HP84A bridge. The samples were placed in a tubular furnace to perform isothermal measurements at different temperatures (300–423 K). The amplitude of the external electric signal was 100 mV and data were recorded automatically. The interpretation of the dielectric results was made on the basis of the cooperative dipoles and charge carriers interacting model, due to Joncher, *et al.* [8–11]. In order to obtain the best understanding of the materials response in terms of the complex capacity a computer program was elaborated based on the methodology reported by Jonscher [11], for dielectric data processing.

3. Results

The characteristic behavior of the IR% transmitance spectra in the range of 400–4000 cm^{-1} is shown in Fig. 1 for oxynitrides deposited with different flows of oxygen (the sum of the O_2 and the NH_3 flows was kept constant), the rest of the deposition parameters were maintained fixed. Those spectra show a dominant peak that shifts its location towards lower wave numbers as the relative amount of oxygen is reduced. This peak is associated with the stretching vibration mode of the Si-O-Si bonds and it is located at 1075 cm^{-1} in the case of stoichiometric SiO_2. Silicon nitride also shows a dominant peak but it is located at about 835 cm^{-1} and it is associated with the stretching vibration mode of the Si-N bond [12]. It is important to notice that the spectra in Fig. 1 shows a gradual shift of the stretching peak as the amount of oxygen is changed, in contrast with the possible presence of two peaks located at 1075

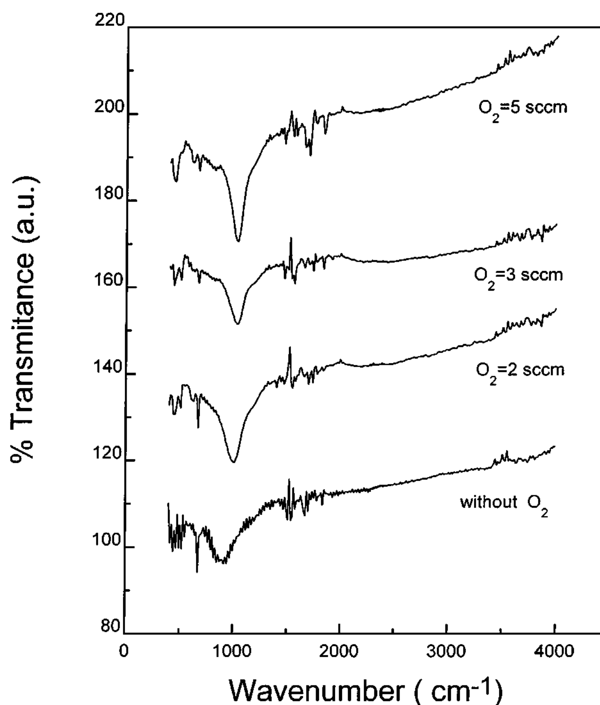

Figure 1 Infra-red spectra for oxynitride films obtained with different relative concentrations of O_2 and NH_3. These films were deposited adding 30 sccm of H_2 and 20 sccm of N_2 to the reactant gases. The deposition pressure was 300 mTorr and the power and substrate temperature were 175 W and 250 °C respectively.

TABLE I Characteristics of SiO_xN_y samples deposited with different relative amounts of oxygen and ammonia: x and y parameters, refractive index (n) and IR peak position

Sample	Oxygen (sccm)	Refractive index	x	y
ON44	0	1.74	0.5	0.9
ON47	2	1.59	1.3	0.37
ON48	3	1.57	1.8	0.2
ON49	5	1.53	1.6	0.16

and 835 cm^{-1} each, which is characteristic of a two phase formation. None of the spectra measured show any absorption peaks due to the presence of hydrogen or water related bonds (in the 2000–3500 cm^{-1} range) even though the films in Fig. 1 were deposited with 30 sccm of hydrogen mixed with the reactant species. Table I lists the x and y values for the SiO_xN_y stoichiometry calculated from the RBS measurements and the corresponding refractive index at 630 nm. RBS measurements also indicate the presence of chlorine in the deposited films. The index of refraction values are between the reported values for silicon dioxide and silicon nitride depending on the relative amount of oxygen used for the deposition. It is noticeable that if there is no oxygen in the gas mixture, the refractive index corresponding to the deposited sample is slightly lower than the reported values corresponding to the silicon nitride obtained by PACVD (1.8). This low value can be explained by the presence of low oxygen concentrations in these films according to the RBS results. Also, RBS measurements indicate the presence of chlorine atoms in the films. The chlorine concentration in the films is higher in the films obtained from gas mixtures without oxygen, decreasing exponentially as long as oxygen present in the gas mixture increases. This behaviour can be observed in Fig. 2.

The effect of hydrogen addition to the reactant gases on the refractive index and the deposition rate is illustrated in Fig. 3 for samples deposited with no O_2 (sim-

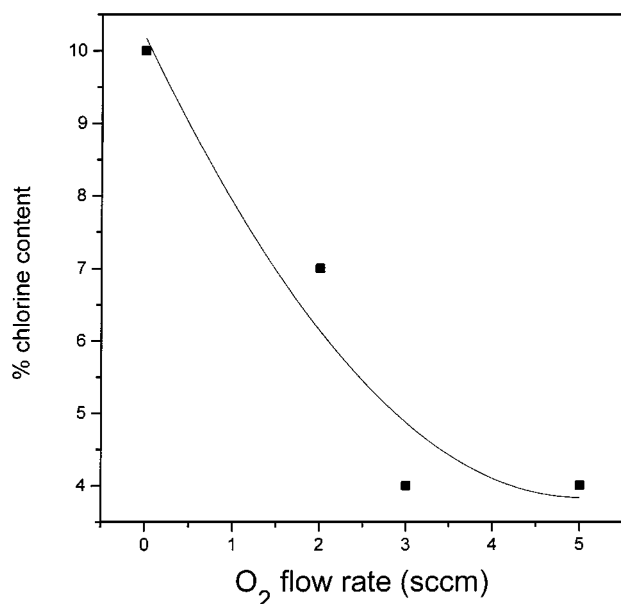

Figure 2 Variation of the chlorine content with the oxygen flow used in the deposition of the oxynitride films.

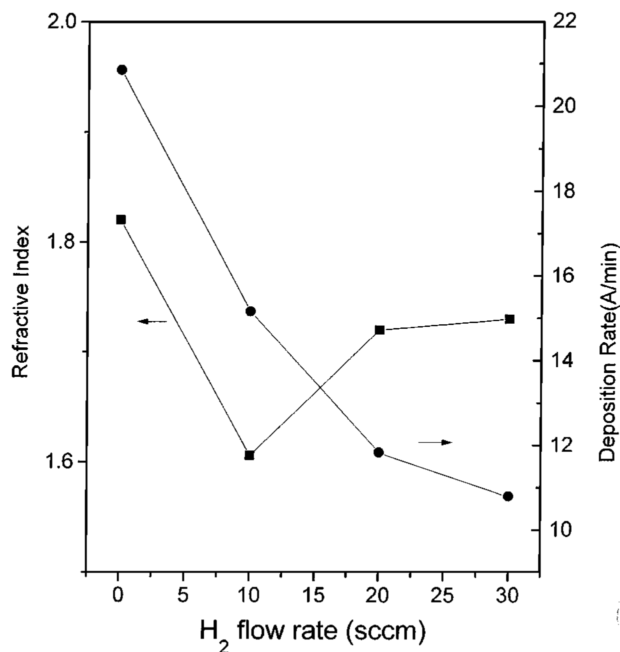

Figure 3 Refractive index and deposition rate as a function of the hydrogen flow used in the gas mixture.

ilar results were obtained films deposited using only oxygen and no ammonia). There is a general trend of a slight reduction of the refractive index and a sharp decrease in the deposition rate with hydrogen flow that is accentuated for low flows. The Atomic Force Microscopy (AFM) images shown in Fig. 4, illustrate the effect of the added hydrogen on the surface topography of the deposited films. In this figure a composition of the three-dimensional images for samples deposited with 0, 10 and 30 sccm of hydrogen flow are shown. Image a, corresponding to the sample deposited with no H_2 flow, has a 0–1000 Å vertical scale, while image c, corresponding to 30 sccm of H_2, has a 0–10 Å scale. It is clear that a 30 sccm flow of H_2 added to the reactant gases results in about *two or more* order of magnitude reduction on the average roughness of the deposited film. We have performed C-F electric measurements in samples obtained with and without hydrogen in the frequency range 0.02–10^3 kHz and varying the temperature from -70 to 160 °C. In Fig. 5 the normalized spectra of the imaginary capacitance for samples deposited without H_2 (a) and with 30 sccm of H_2 are shown. From the figure it is clear that there are dipolar relaxation processes in the measured samples. According to the results obtained using the other analytical techniques, we think that these polarization processes are produced by dipolar centers associated to the silicon atoms bonded to oxygen and/or chlorine atoms. In Table II also the most important dielectric parameters

TABLE II Dielectric parameters calculated from the C-F measurements according to the Dissado and Hill Theory for the dipolar relaxation in solid

Hydrogen flow (sccm)	n_1	m_2	n_2	$G(0) \times 10^{-9}$ (S)	E_r (eV)	E_c (eV)	$\varepsilon(0)$
0	0.42	0.95	0.28	17	0.55	0.37–0.41	5.8
30	0.70	0.55	0.35	7.5	0.55	0.41–0.49	7.5

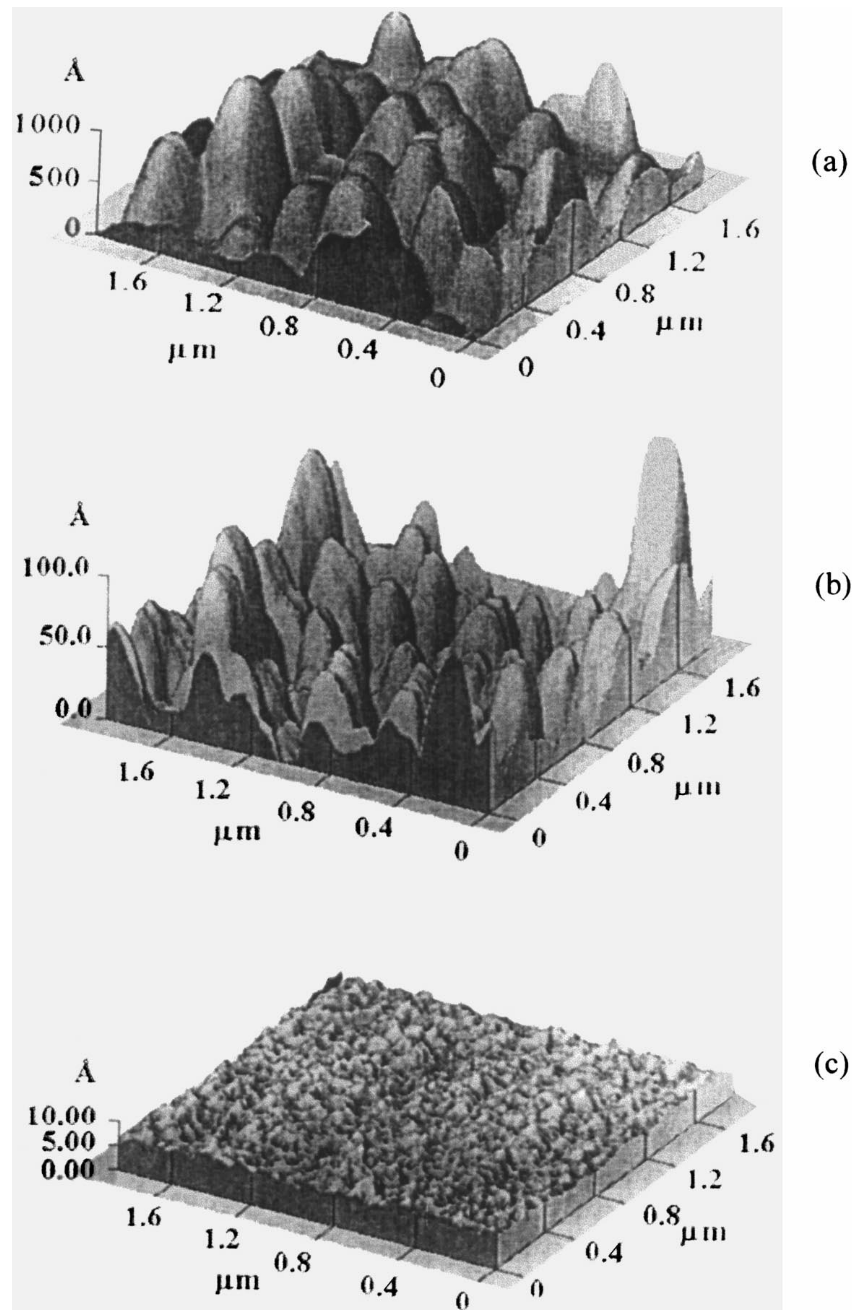

Figure 4 Atomic Force Microscope images of samples deposited with different amounts of H_2 keeping the rest of the deposition parameters fixed. (a) 0 sccm H_2, (b) 10 sccm H_2 and (c) 30 sccm H_2.

are reported. These values, as we mentioned before, have been obtained according to Dissado and Hill relaxation theory in solids [5, 8–11]. The n_1 and n_2 parameters are determined from the slopes at high frequency in the curves for each dipolar process detected in the samples and the m_2 parameter is related to the slope in the curves at low frequency. $G(0)$ is the conductance at zero frequency, so the dc conductance, and E_r and E_c are the activation energies corresponding to the dipolar orientation and the free charge conduction, respectively. Also in Table II the relative permitivity at zero frequency $\varepsilon(0)$ is shown. The calculated permitivities correspond only to the oxynitride film because, in the frequency and temperature ranges studied, there is no influence of the substrate in the electrical response.

4. Discussion

An important characteristic of the spectra shown in Fig. 1 is the smooth shift of the single dominant absorption peak from the location associated with the stretching vibration mode of the Si-O-Si bond in silicon dioxide to the stretching vibration mode of Si-N in silicon nitride, as the relative amount of oxygen is decreased. This type of behavior is indicative of an homogeneous oxynitride alloy [12] as opposite to a two phase mixture of SiO_2 and Si_3N_4 in which a two different peaks spectrum is characteristic [13]. Similar type of behavior has been reported by Tsu *et al.* [12], on samples deposited by remote-PECVD using SiH_4 as silicon source, but at higher deposition temperatures (400 °C). Lower deposition temperatures generally require of a

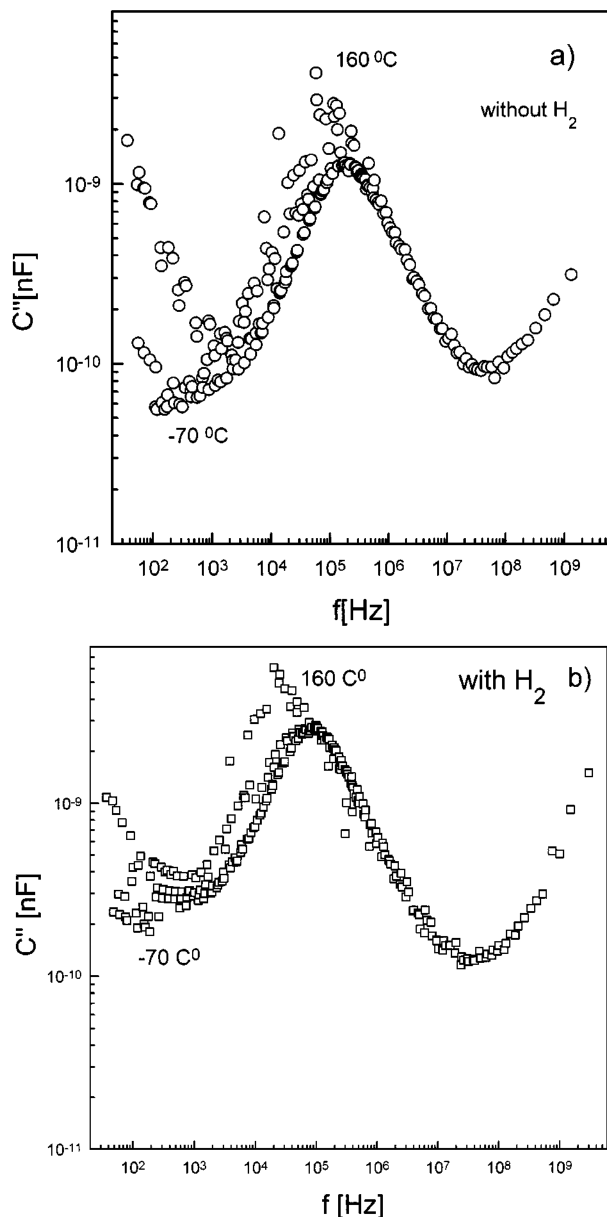

Figure 5 Normalized spectra of the imaginary part of capacitance for samples obtained without H_2 (a) and with 30 sccm of H_2 in the reactive gas mixture varying the temperature from −70 °C (upper curve) to 160 °C (lower curve).

postdeposition thermal treatment to reduce the amount of hydrogen related impurities [14]. Regarding the content of hydrogen, the IR spectra for samples deposited with $SiCl_4$ at 250 °C (Fig. 1) do not present evidence of O-H or Si-H absorption peaks even though no further thermal treatment was given. The use of silicon halides as a source of silicon on the deposition of SiO_2 by PECVD and remote-PECVD has been suggested previously as a way to lower the deposition temperature of this material without incorporating hydrogen related impurities [2, 3]. In particular, the hydrogen gettering action of the residual chlorine from the reaction of the $SiCl_4$ with the oxidant gas has been reported for the deposition of SiO_2 at low temperatures (<200 °C) [6]. A similar mechanism seems to be occurring in this case, in which the large chemical affinity between chlorine and hydrogen most likely propitiates the formation of HCl gas or related species that are removed from the deposition chamber.

In fact, the addition of hydrogen to the reactant gases has a planarization effect on the film (Fig. 4) which seems to be related to an etching effect due to the formation of the HCl. This effect could explain the decrease in the deposition rate detected by ellipsometry (Fig. 4) and IR measurements.

On the other hand, the positive influence of the hydrogen addition is also confirmed by the C-F dielectric results. The physical information of the n and m parameters concerns to the atomic order inside the amorphous atomic network [11]. In these films, which have a stoichoimetry close to silicon nitride, the oxygen and chlorine atoms play the role of impurities participating in the observed dipolar relaxation. The values of the m and n parameters corresponding to the samples deposited with and without hydrogen suggest that the utilization of hydrogen in the oxynitride deposition results in films with a more ordered atomic network, although both films have the same stoichiometry, according to the RBS results. In other words, the two samples have similar composition and similar oxygen and chlorine concentrations but the sample deposited without hydrogen contains silicon bonded structures (to oxygen and/or chlorine) more varied in shape and size than the films obtained with hydrogen.

The effect of the temperature on the variation of the relaxation peaks also confirms that the oxynitride films grown without hydrogen have more inhomogeneous atomic distribution in the network. The activation energies E_r and E_c, calculated from Arrhenius plots and also the permitivity values, $\varepsilon(0)$, are in the range of the values reported by other authors using different analytical techniques [15]. The values calculated for E_r are only for the temperature range from 58 to 65 °C. For higher temperatures, the values for these energies strongly decrease and the corresponding error in its determination increases, indicating that a simple Arrhenius law is not adequate in this range. E_r has the same value for the two samples studied which suggests that both samples contain similar dipolar centers, as we mentioned before. The conductance at zero frequency ($G(0)$) has been calculated according the method described in previous works [16] and in the temperature range where the Arrhenius law is not accomplished. This conductance is likely due to that oxygen and chlorine atoms which are weakly bonded in the network, acting as quasi-free charges under the effect of the electric field. From this point of view, notice that the sample deposited without H_2 has a conductance one order of magnitude higher than the sample grown with 30 sccm of H_2, indicating a lower dielectric quality. Therefore, this result shows again the beneficial role of the hydrogen addition in the deposition of oxynitride films when $SiCl_4$ is used.

5. Conclusions

Oxynitride films with low content of hydrogen related impurities have been deposited at 250 °C by remote-PECVD, using $SiCl_4$ as a source of silicon. The IR spectra of these films show a single dominant peak associated with the stretching vibration mode of the silicon bonds with either oxygen or nitrogen, indicating

the formation of an homogeneous alloy. RBS measurements have been used to estimate the stoichiometry of the films, ranging from SiO_2 to a stoichiometry *near* to that of silicon nitride. Atomic force microscopy measurements indicate that the addition of hydrogen to the reactant gases has a planarization effect in the surface of the films, reducing the average roughness of the deposited films as the amount of hydrogen is increased. The presence of hydrogen also results in a drop of the deposition rate which could be related to a competitive etching effect produced by the byproducts of the reactant gases (possible formation of HCl). The capacitance versus frequency measurements in these films indicates the presence dipolar centers which we have associated to the presence of silicon atoms bonded to oxygen and/or chlorine atoms. These dipolar structures are distributed inside the atomic network in a more homogenous way when hydrogen is used in the deposition process although the global composition of the deposited films is independent of the hydrogen presence in the reactant gas mixture.

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