

Oxygen to silicon ratio determination of SiO_xH_y thin films

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Abstract

The oxygen to silicon ratio of several SiO_xH_y thin films deposited by the electron cyclotron resonance plasma method was studied by several methods (heavy ion elastic recoil detection analysis, energy dispersive X-ray spectroscopy, Auger spectroscopy and infrared spectroscopy). Among these methods, other groups found that x scales linearly with the wavenumber of the Si–O–Si stretching vibration (ν_{st}) by the relation $x = 0.020\nu_{\text{st}} - 19.3$. This equation has been used by many different groups to determine x of SiO_x thin films, but we have found that in our ECR deposited films the above mentioned formula gives accurate results for x values higher than 1.5, but for Si richer films the formula overestimates the x value, with values well outside the 20% accuracy range. A possible explanation of this discrepancy may be the bonded hydrogen of the films: in the plasma deposited samples used in this study the hydrogen content was high, above 20 at.% for silicon-rich samples. As a consequence, the Si–O–Si groups were immersed in a more electronegative matrix than in the usual case (SiO_x with a low hydrogen concentration) and thus the variation of the position of the stretching peak was less pronounced.

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1. Introduction

Silicon suboxide (SiO_x) is a very interesting material in the microelectronics field for two main reasons: its high dielectric permittivity and its luminescence properties. SiO_x thin films exhibit a relative dielectric permittivity, ϵ_r , comprised between 3.8 (SiO_2) and 11.9 (Si). Therefore, the commonly used SiO_2 gate could be substituted by a thicker SiO_x gate with the same capacitance per unit area ($\epsilon_0\epsilon_r/t_{\text{diel}}$, where ϵ_0 is the vacuum dielectric permittivity and t_{diel} the gate dielectric thickness). With this substitution in mind, the problem with SiO_x is that its band gap decreases as the Si content increases, so the advantage in permittivity may be lost by gate leakages. Also, the interface SiO_x/Si is

more defective than the SiO_2/Si one, so a common approach is to use a stacked gate dielectric, i.e., $\text{SiO}_x/\text{SiO}_2/\text{Si}$ [1]. With this approach, the interface quality and the bulk dielectric constant can be controlled independently. On the other hand, the electroluminescence and photoluminescence properties of SiO_x thin films are very interesting issues due to its possible use in optoelectronic devices. Nowadays much work is being devoted into investigating the promising luminescence properties of annealed SiO_x films [2–5]. When annealing SiO_x films above 700 °C a phase separation occurs and network reactions lead to the formation of nano-crystalline Si clusters inside a high quality SiO_2 matrix [6]. The size and the concentration of the Si nano-clusters are determined by the as-grown composition of the SiO_x film and by the annealing conditions. The clusters are believed to be the source of the strong luminescence detected, therefore, for SiO_x applications involving luminescence there is an imperative

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necessity of determining accurately the oxygen to silicon ratio (x) of as-grown suboxide films.

A wide variety of methods can be used to deposit SiO_x thin films. Plasma processes are widely used due to the possibility of depositing thin films at very low temperatures from high purity gases. The results of the plasma processes are high quality films with a small increase on the thermal budget of the process (this is a very important issue, having in mind the integration of these processes into fabrication routes). Among the high variety of different excitation methods, the electron cyclotron resonance method (ECR) has several advantages, such as the very high degree of excitation of species, or the fact that it is a remote plasma method, so there is reduced damage to the surface of the sample by accelerated ions or electron bombardment.

A widely used method to estimate x in silicon suboxide films lies on the measurement of the wavenumber of the Si–O–Si stretching peak (ν_{st}) by infrared spectroscopy (IR), that is in a linear relation with x according to the following relationship:

$$x = 0.020\nu_{\text{st}} - 19.3. \quad (1)$$

Eq. (1) was obtained by Tsu et al. [7,8] from X-ray Photoelectron Spectroscopy and Auger Spectroscopy as an estimation of x with a 20% of error. The main source of uncertainty is the determination of the endpoints of the formula, that may be affected by many reasons, among them the hydrogen content of the films. Even with that uncertainty, the relation (1) has been used by many different groups to determine x [5,9–13]. The advantages of this method of measuring x are that it is non-destructive, that it is a straightforward method and that infrared spectroscopy is a commercial, easily available technique. In this article we will compare the results obtained by Eq. (1) with direct composition measurements of ECR deposited suboxides. We found discrepancies between Eq. (1) and the direct composition measurements used in this study when x is below 1.6. We propose that the most feasible reason of this discrepancy may be the high hydrogen content of our films.

2. Experimental details

The SiO_xH_y films were deposited on Si (111) substrates by an ECR plasma [14] using high purity SiH_4 and O_2 as precursor gases. Films of several compositions were obtained depending on the gases flow ratio, that we define in the same way as Bulkin et al. [15] as:

$$R_b = [\text{SiH}_4] / ([\text{SiH}_4] + [\text{O}_2]) \quad (2)$$

R_b values between 0.2 and 1 were used in this study. The total gas flow, chamber pressure, and microwave power were kept constant in all deposition processes at 10.5 sccm, 9.3×10^{-2} Pa, and 100 W, respectively. Substrates were not intentionally heated and the deposition temperature was in the 50–60 °C range. The thickness of the deposited films

was about 250 nm, as measured with a Dektak profilometer. The film composition was measured by one of the techniques used to obtain Eq. (1), Auger electron spectroscopy (AES), by heavy ion elastic recoil detection analysis (HI-ERDA) and by energy dispersive X-ray spectroscopy (EDS). AES characterization was done in a Jeol system, model JAMP-10S. The atoms were excited with a 5 keV electron beam, and the error was less than 10%. HI-ERDA measurements were carried out with a mass and energy dispersive time-of-flight setup [16], and the ions used as projectiles were 230 MeV ^{129}Xe ions. These measurements provided the absolute atomic concentrations of every species of the samples, including hydrogen, i.e., the x and y values in the SiO_xH_y formula, without the need of calibration samples. The error of these measurements is less than 5%. EDS measurements were performed with a Hitachi S-4100 scanning microscope attached to a Si-Q-Detector Pioneer of NORAN. The acceleration voltage was 5 keV and the take off angle was 30°. The correction was calculated by the Proza method [17], and the estimated uncertainty is 0.3%. A certified SiO_2 stoichiometric layer deposited by Low Pressure Chemical Vapor Deposition was used as a calibration standard. Since with an acceleration voltage of 5 keV the interaction depth is about 200 nm, and the suboxide films were 250 nm thick, there was no influence from the Si substrate. EDS and AES are techniques that are not able to detect hydrogen, so these measurements only yielded information on the x value. These methods provided three independent direct measurements of the x value of each suboxide film. Additionally IR measurements were performed on the same samples in the range 350–4000 cm^{-1} with a Nicolet Magna-IR 750 series II spectrometer working in the transmission mode at normal incidence. To obtain the spectra of the thin film a bare-Si spectrum was subtracted from the total measured spectra (film+substrate) after conversion to absorbance units.

3. Results and discussion

Fig. 1 shows the IR spectra of selected samples in the 350–1400 cm^{-1} region. In this range of wavenumbers several Si–O related peaks were found. The most intense feature in the spectra appeared around 1068–1000 cm^{-1} with a shoulder at 1120 cm^{-1} . This is the well known Si–O–Si stretching vibration. In Fig. 1, to highlight the tendency with the silane ratio R_b of the Si–O–Si stretching peak, the position of its maximum is marked by straight lines.

The estimated x values obtained from Eq. (1) as a function of silane ratio R_b are depicted in Fig. 2 as * symbol. In this figure are also shown the x values obtained by HI-ERDA as \square , AES as \triangle , and EDS as \diamond . From this figure it is clear that these last three methods, which make a direct measurement of x , provided very comparable values in all the range of R_b studied. On the other hand, it is

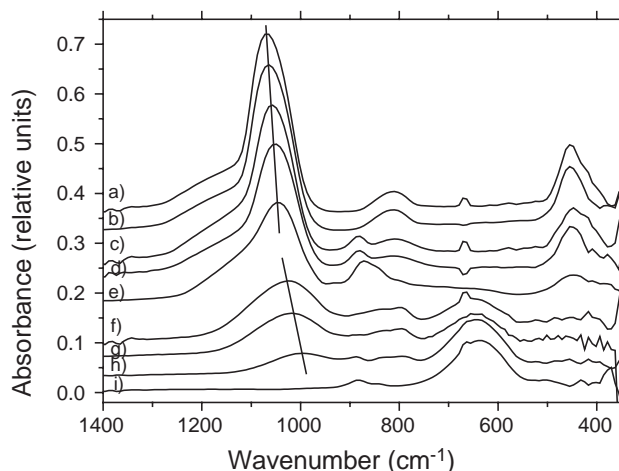


Fig. 1. IR absorbance spectra of several SiO_xH_y samples in the $350\text{--}1400\text{ cm}^{-1}$ range: silane ratio R_b values: a) 0.23, b) 0.33, c) 0.59, e) 0.67, f) 0.74, g) 0.8, h) 0.91, i) 1.0. Straight lines are drawn to mark the Si–O–Si stretching peak wavenumber.

observed that equation [1] leads to x values similar to those of the other methods for compositions above 1.6 ($R_b \leq 0.6$), but overestimates the x value for silicon rich suboxides ($R_b > 0.6$), even taking into account the 20% of uncertainty of expression (1).

A possible reason for this discrepancy may be found on the higher hydrogen content of our samples when compared to the ones studied by other groups. Those films presented hydrogen concentrations below 10 at.%, while the silicon-rich samples which were studied in this work had concentrations above 20 at.%. In Fig. 3 it is depicted the IR spectra of the SiO_xH_y films in the $1900\text{--}2500\text{ cm}^{-1}$ region, where the Si–H stretching peak is present. In that figure it can be observed how as the Si content increases, the absorbance of the Si–H stretching peak increases significantly. Fig. 4 depicts the total hydrogen concentration as a function of the

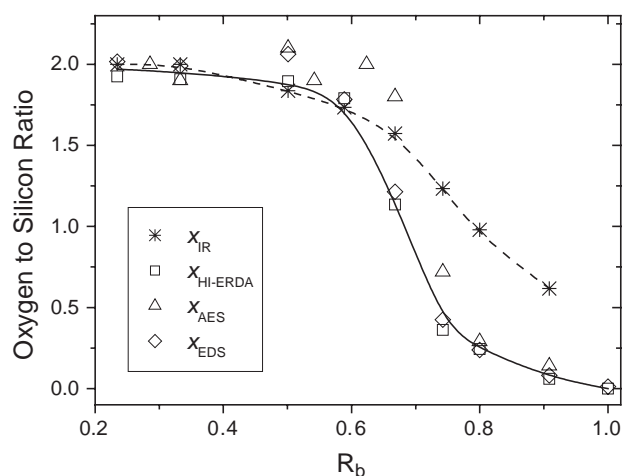


Fig. 2. Oxygen to Silicon ratio of the films (x) as a function of silane ratio R_b : estimation from IR (*), and HI-ERDA (\square), AES (\triangle) and EDS (\diamond) measurements. The lines are drawn as a guide to the eye: actual film oxygen to silicon ratio (solid line) and IR estimation (dashed line).

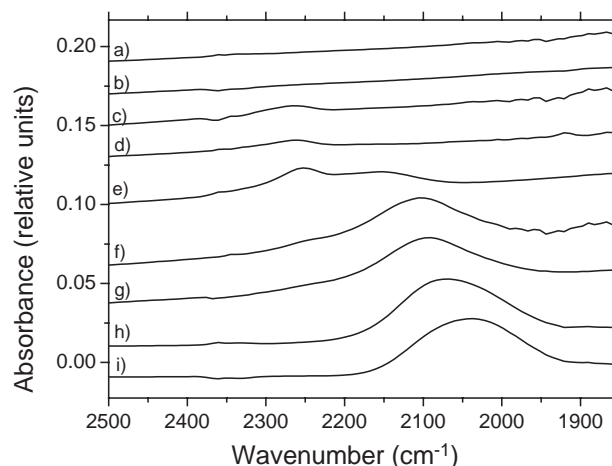


Fig. 3. IR absorbance spectra of the same samples as Fig. 1 in the $1900\text{--}2500\text{ cm}^{-1}$ range showing the Si–H stretching mode.

x value obtained from HI-ERDA measurements. Also, these measurements provided the total atomic density of each sample, so the 10 at.% value can be calculated for each composition, and it is also depicted in Fig. 4 with a dashed line.

It is known that the wavenumber of the Si–O–Si stretching peak is influenced by the electronegativity of the matrix surrounding the group (this is the reason for the shift of ν_{st} with x). In the case of pure silicon suboxide, as x decreases, oxygen atoms (electronegativity equal to 3.44) are substituted by silicon atoms (1.9), so there is a big change of the average electronegativity of the surrounding matrix: from 2.93 in SiO_2 to 1.9 in pure Si. The samples studied to obtain relation (1) are close to this ideal case, since they have hydrogen concentrations well below 10 at.%. In our silicon rich samples the hydrogen content was above 20%. Hydrogen has an electronegativity value of 2.2 – higher than Si, 1.9 – so in our samples the Si–O–Si bonds were surrounded by a more electronegative matrix than in the case with lower hydrogen content. This higher effective

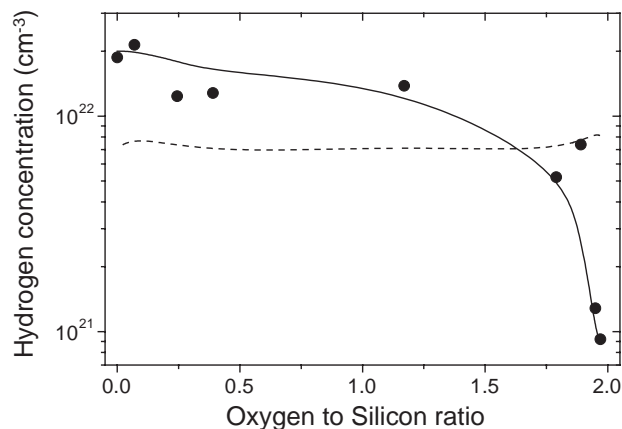


Fig. 4. HI-ERDA measurements of hydrogen concentration as a function of the oxygen to silicon ratio (x). The continuous line is drawn as a guide to the eye. The 10 at.% value is depicted by the dashed line.

electronegativity of the surrounding matrix forced the shift of the Si–O–Si stretching wavenumber to be less pronounced. Therefore, the “attenuated” shift of the Si–O–Si stretching mode made the Eq. (1) to produce inaccurate results in the Si-rich samples studied, with the result of an overestimated x -value.

Another possible explanation of this discrepancy may be a possible heterogeneity of the films (the presence of nanocrystalline Si inside a SiO_x matrix). These SiO_xH_y samples were deposited at room temperature, and the phase separation of the SiO_x films usually happens at temperatures higher than 700 °C [6]. This phase segregation occurs by the separation of the unstable SiO_x film on two different thermodynamically stable phases, SiO_2 and Si. Also we have not found any evidence of heterogeneity in any characterization that has been performed to the as-deposited SiO_xH_y films. These reasons make us think that heterogeneity does not play a significant role in the x results obtained, and that the main reason of the discrepancies found is the hydrogen content of the samples, but the hypothesis of the heterogeneity cannot be completely rejected.

In any case, caution should be taken about the procedure used to determine the suboxide composition because, as we have shown, the linear relation (1) is not generally valid and can produce inaccurate results depending on the deposition method used to obtain the SiO_xH_y films.

4. Conclusion

Summarizing, in this paper it has been shown that the linear Eq. (1) that relates the Si–O–Si stretching wavenumber with the oxygen to silicon ratio of silicon suboxide films gives results that are in agreement with the composition measurements when x is higher than 1.6. However, for $x < 1.6$, we have found that in the case of high Si content ECR deposited suboxides the relation (1) overestimates the x value. It has been proposed that this behaviour is due to the high hydrogen content (well above 10 at.%) that makes the electronegativity of the surrounding matrix of the Si–O–Si bond to be significantly higher than in the low hydrogen content case. Thus, the Si–O–Si stretching peak does not shift as much as in samples with

low hydrogen content and, therefore, the Eq. (1) overestimates the x value.

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