PERGAMON

Vacuum 67 (2002) 525–529

VACUUM

SURFACE ENGINEERING, SURFACE INSTRUMENTATION
& VACUUM TECHNOLOGY

www.elsevier.com/locate/vacuum

Physical properties of plasma deposited SiO_x thin films

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Abstract

The composition ($x = [\text{O}]/[\text{Si}]$), hydrogen content, bonding configuration and paramagnetic defects of SiO_x films were studied. Films were deposited by the electron cyclotron resonance plasma method at room temperature using SiH_4 and O_2 as precursor gases, and depending on gases flux ratio, films from $x \approx 2$ to 0.9 were obtained. Infrared spectroscopy analysis showed the presence of different vibration modes: Si–O stretching, used to estimate film composition, bending and rocking with positions nearly independent on film composition, and various Si–H peaks: stretching and wagging-bending. Films with non-stoichiometric composition show a wider peak than the ones deposited at higher gas ratios. Ellipsometry measurements showed a refractive index at $\lambda = 632.8$ nm comprised between 1.45 and 2.04. Electron spin resonance measurements shows that the stoichiometric films ($x \approx 2$) present the well known E' centre ($\bullet\text{Si}\equiv\text{O}_3$) with concentrations in the 10^{16} cm^{-3} range, while for Si-rich films ($x \ll 2$) the Si dangling bond centre (D centre, $\bullet\text{Si}\equiv\text{Si}_3$) is dominant, with concentrations in the 10^{18} – 10^{19} cm^{-3} range. For near-stoichiometric ($x \approx 1.9$) films also both E' and D centres are present, but in this case the E' centre is dominant. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Si-rich $\text{SiO}_x\text{:H}$ films (in the following, SROX) have a wide and increasing interest in the field of Si-based device technology due to several reasons:

- (i) SROX films are always present on the Si/ SiO_2 interface [1] and on many high-K dielectric/Si interfaces [2], depending on surface preparation, annealing temperatures, etc. The presence of these suboxides introduces defect states and may limit effective dielectric thickness, which limits device performance [1].

- (ii) SROX films have recently found application in non-volatile memory devices, where the use of a stack of dielectrics SROX/ SiO_2 allows to obtain a reduction in both erase time and threshold voltage [3,4].

The physical characteristics of SROX films that mainly influence device behaviour are, among others, the high hydrogen content, bonded in different vibrational modes [5,6] and the presence of paramagnetically active defects (dangling bonds) [7]. These defects have a determinant role on device performance. Depending on film composition, the dominant defect is different, changing from the well known E' centre ($\bullet\text{Si}\equiv\text{O}_3$) on SiO_2

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films to the Si-dangling bond one ($\bullet\text{Si}\equiv\text{Si}_3$) (in the following, *D*) on SROX films far from the stoichiometric SiO_2 composition [8]. The study of defects on SROX films is scarce and only few papers dealing with this problem can be found in the literature [7,9,10].

The aim of this paper is to analyse the presence of hydrogen and to study the structure and concentration of paramagnetically active defects present on SROX films. The analysed films were deposited by the electron cyclotron resonance plasma method (in the following, ECR). Deposition conditions were adjusted to scan a wide range of compositions, from SiO_2 to $\text{SiO}_x\text{:H}$ with oxygen content as low as the system was capable.

2. Experimental

SROX samples were deposited at room temperature from mixtures of SiH_4 and O_2 with different gas ratios in our ECR system which has been described elsewhere [11]. Two series of samples were deposited with different values of gases flow ratio, R_b , defined as $[\text{SiH}_4]/([\text{SiH}_4] + [\text{O}_2])$. This value ranged from 0.2 to 0.9, producing films with compositions comprised between stoichiometric ($x \approx 2$) and low-oxygen content suboxide ($x \approx 0.9$). Both series were deposited onto high resistivity $\text{Si } 1 \times 1 \text{ cm}^2$ substrates. Each series had the same deposition parameters (100 W microwave incident power, room temperature and gas ratios) except for deposition time, which was adjusted for every process in order to achieve the desired thickness.

The first series (from now on SI) was projected to a film thickness of 250 nm, and it was characterised with Fourier transform infrared spectroscopy (FTIR) and electron spin resonance (ESR). In order to get a higher effective thickness for ESR characterisation after FTIR measurement each sample was cleaved into five $1 \times 0.2 \text{ cm}^2$ pieces which were stacked together.

FTIR spectroscopy was performed in a Nicolet Magna-IR 750 series II spectrometer. Following the method proposed by Lucovsky and co-workers [1,5] the peak position of the main Si–O–Si

stretching band was used to determine the oxygen to silicon ratio of films.

ESR measurements were performed in a Bruker ESP 300E spectrometer operating in the X-band working at 0.5 mW power to ensure that the signal is not saturated. The density of Si dangling bonds was quantified by comparison with the signal of a weak pitch calibration standard. The measurements were performed at room temperature.

The second series of samples (from now on SII) were projected to a thickness of 80 nm, and it was characterised with ellipsometry to obtain the refractive index of the samples. Ellipsometry measurements were performed on a Gaertner L116B ellipsometer to determine the refractive index of films at $\lambda = 632.8 \text{ nm}$.

3. Results and discussion

3.1. Compositional study

FTIR analysis shows that the peak position of the Si–O stretching mode range from 1070 cm^{-1} for the films deposited with $R_b = 0.23$ to 1013 cm^{-1} for Si-rich films ($R_b = 0.9$). The oxygen to silicon ratio (x) varies from 2 to 0.9. The Si–O stretching peak of the stoichiometric films ($x = 2$) present a full-width at half-maximum (FWHM) of about 90 cm^{-1} , which increases with silicon content to get values of about 140 cm^{-1} . The evolution of this parameter indicates a greater disorder of films as silicon content increases. In Fig. 1a we present the FTIR spectrum of a film with $x = 1.9$. The Si–O stretching peak position in this case is 1059 cm^{-1} . Also the Si–O rocking (808 cm^{-1}) and bending (446 cm^{-1}) are present. The presence of smaller peaks located at 2266 and 881 cm^{-1} can be also observed. These vibration modes are related to the hydrogen content of films. This is a common characteristic of all the silicon rich samples and will be discussed in detail in the next paragraphs.

Now we will analyse the main characteristics of films attending to the film composition:

(i) Stoichiometric samples ($x \approx 2$, $R_b < 0.5$): These films present only Si–O related vibrational modes (stretching, bending and rocking) with no hydrogen related peaks.

Fig. 1. (a) FTIR spectrum of a $x = 1.9$ film. The figure shows the Si–O and Si–H vibration modes. Letters in brackets mark the vibration modes: stretching (s), bending (b), rocking (r), (b) ESR spectrum of the same film with g values for the E' defect (2.0009) and the D defect (2.004). It is also marked the position of the 74 G doublet.

(ii) Near Stoichiometric samples ($x \approx 1.9$): For these films, deposited with gas ratios between 0.5 and 0.7, in addition to Si–O peaks some Si–H related modes appear. At these compositions three main features are observed: Si–H stretching mode in which the silicon atom is bonded to three oxygen atoms taking place at 2260 cm^{-1} [6], the bending mode of the H–Si–O₃ vibration at 880 cm^{-1} , and a peak at 640 cm^{-1} related to the Si–H wagging mode. The presence and peak position of these modes of vibration are in agreement with the film composition. When the silicon content increases the areas of these modes increase strongly maintaining their vibrational positions.

(iii) Silicon-rich samples: Raising R_b above 0.7 ($x \leq 1.75$) produces the 880 cm^{-1} H–Si–O₃ bending mode to be gradually substituted by the 830 – 890 cm^{-1} doublet, related to the wagging–bending vibration of the Si–H₂ bond [6]. Also the Si–O bending peak located at 810 cm^{-1} disappears being substituted by a mode at 795 cm^{-1} due to vibrations of the Si–H bond coupled with Si–O–Si bonds. A mode at 2100 cm^{-1} smoothly replaces the 2260 cm^{-1} peak. This mode is related to the H–Si–Si₂O bond. The justification of all these changes

is the substitution of many Si–O bonds by Si–Si or Si–H bonds.

All these hydrogen-bonding related configurations are coherent with a model for the deposition process in which during growth time there is not enough oxygen concentration in the plasma to saturate all the four silicon bonds. Therefore, many silicon atoms have to saturate some of their bonds to another silicon atoms, or remain unbonded. Since silicon electronegativity (1.8 eV) [7] is lower than hydrogen electronegativity (2.2 eV) [7], Si is not able to displace all hydrogen atoms of the SiH₄ molecule. So, several hydrogen atoms of the SiH₄ precursor molecule remain bonded to silicon and are incorporated to the SROX film. This process produces Si-rich films with a high hydrogen content. To calculate the total hydrogen content of the films, the method developed by Lanford et al. in Ref. [12] has been used employing the normalised areas of 2260 – 2100 cm^{-1} peaks. The proportionality constant used was $2.2 \times 10^{20}\text{ cm}^{-2}$ [13] and results are presented in Fig. 2. For oxygen to silicon ratios under 1.6, the hydrogen is present in the SROX films in atomic concentration ($2.4 \times 10^{22}\text{ cm}^{-3}$) and similar to the reported values of Bulkin et al. for ECR plasma deposited samples [13].

Ellipsometric measurements were performed on the SII series films. Refractive index (n) as a function of oxygen to silicon ratio are shown in Fig. 3. It is noted that samples deposited at the

Fig. 2. Hydrogen content as a function of Oxygen to Silicon ratio (x) for SROX films. Line is drawn as a guide to the eye.

Fig. 3. Refractive index (n) at $\lambda = 632.8$ nm, as a function of Oxygen to Silicon ratio (x) for SROX films. Line is drawn as a guide to the eye.

lowest gas ratios ($R_b < 0.7$) which yields stoichiometric films ($x = 2$), present a value of n comparable to the thermally grown oxide (1.45) [14], while at $x = 1.4$ the refractive index presents a sharp increase to reach a saturation value of 2.04. These results are consistent with the work of Lin et al. who showed in Ref. [8] that the increase of refractive index for silicon suboxide films is a direct consequence of increased silicon content in the film, a proposal that is consistent with our results.

3.2. Defect content

Five samples with compositions of 2.0, 1.9, 1.4, 1.0 and 0.9 were selected to be characterised by ESR. These selected films presented two kinds of paramagnetic defects: the dangling bond of the silicon atom bonded to three oxygen atoms ($\bullet\text{Si}\equiv\text{O}_3$) commonly known as E' centre [10], and the dangling bond of the silicon atom bonded to other three silicon atoms ($\bullet\text{Si}\equiv\text{Si}_3$), known as the D centre [10]. In Fig. 1b we present the ESR spectra of the film with $x = 1.9$. From this spectrum, it is obvious that the presence of both type of defects in this film can be deduced from the g value of the two main defects: $g = 2.0009(E')$ and $g = 2.004(D)$. There is also present a doublet, separated by 74 G, related to the interaction

between hydrogen and the E' defect [8]. Further details will be published elsewhere.

The total amount of defects versus oxygen to silicon ratio is depicted in Fig. 4. The kind and concentration of these defects are strongly dependent on film composition, as will be detailed. The stoichiometric film ($x = 2$, $R_b = 0.23$) presents only E' defects in the low 10^{16}cm^{-3} range. This result is coincident with previously reported values [15]. Otherwise, non-stoichiometric films present both kinds of defects in a much higher amount. The near-stoichiometric film ($x = 1.9$, $R_b = 0.5$) presents more E' ($1.32 \times 10^{19}\text{cm}^{-3}$) than D ($1.18 \times 10^{18}\text{cm}^{-3}$) centres, in a total amount of $1.44 \times 10^{19}\text{cm}^{-3}$. On the other hand, films far from stoichiometric present a much higher D than E' concentration but in a total amount that monotonically decreases with x (as an example, the $x \approx 1$ sample presented $1.22 \times 10^{18}\text{cm}^{-3}$ D centres and $2.0 \times 10^{19}\text{cm}^{-3}$ E' centres). The described behaviour can be seen in Fig. 4. This is consistent with the fact that in stoichiometric samples there are no Si–Si bonds, so there cannot be any $\bullet\text{Si}\equiv\text{Si}_3$ centres. Whereas, for x slightly below 2, bonding between silicon atoms appear, so the D centre begins to be detected at the expense of the E' centre. As x is far below 2, the concentration of D centres is higher than the E' concentration, as was reported previously by Inokuma et al.

Fig. 4. Total concentration of paramagnetic defects as a function of the oxygen to silicon ratio (x) for SROX films. Line is drawn as a guide to the eye. The dominant defect type is also indicated in the figure.

[10]. It should be remarked that the higher concentration of defects is found in near-stoichiometric films ($x \approx 1.9$). A possible explanation for this behaviour can be found in the role of hydrogen whose tendency to passivate dangling bonds is well known. The high defect content of the near-stoichiometric film is justified by its low hydrogen content: although there are fewer silicon atoms not totally bonded to oxygen than in the rest of the samples, most silicon dangling bonds are not saturated with hydrogen, so that unpaired electrons contribute to the ESR signal. For samples far from stoichiometry, although presenting a much higher probability that a silicon electron is not paired with an oxygen electron, the high hydrogen content bonds this otherwise unpaired electron. From these considerations about the passivation role of hydrogen, the decreasing tendency of the total defect concentration the increase in silicon content, is justified.

4. Conclusions

The structural properties of some ECR deposited silicon suboxide films was studied. The composition and structural arrangement of the samples was determined via FTIR. Using the Si–O peak position to calculate the oxygen to silicon ratio the films varied from stoichiometry (SiO_2) to Si-rich samples ($\text{SiO}_{0.9}$). FTIR analysis of the samples also revealed a high amount of bonded hydrogen ($2.4 \times 10^{22} \text{ cm}^{-3}$) in $\text{SiO}_{0.9}$ films. Ellipsometry measurements showed a variation of the refraction index (at $\lambda = 632.8 \text{ nm}$) from 1.42 to 2.04 with a sharp increase for a gas ratio of 0.7. The big influence of the bonded hydrogen on the structure of defects of the films were confirmed by ESR measurements, which demonstrated the role of the hydrogen in passivating defects. ESR also showed a change of the dominant type of defects from E' to D as the oxygen to silicon ratio of the samples varied from SiO_2 to Si-rich suboxide,

which is totally coherent with the compositional calculations.

Acknowledgements

The authors acknowledge C.A.I. de Implantación Iónica (U.C.M.) for technical support and C.A.I. de espectroscopía (U.C.M.) for availability of the FTIR spectrometer. The work has been partially financed by the CICYT (Spain) under Grant TIC 2001-1253.

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