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Rapid thermal annealing effects on plasma deposited SiO_x:H films

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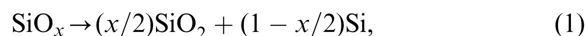
Abstract

The bonding configuration, hydrogen evolution and defect content of rapid thermally annealed (RTA) SiO_x:H films of different initial compositions were studied. Infrared absorption measurements showed that all the hydrogen present in the films was lost at temperatures lower than 700°C without any change in the oxygen to silicon ratio of films. RTA temperatures higher than 700°C promote a change in the Si–O–Si stretching position from the initial unannealed value to the 1070–1080 cm^{-1} range independent of the initial film composition. Electron Spin Resonance (ESR) measurements show that all the films contained two types of paramagnetic defects: E′ ($\bullet Si\equiv O_3$) and D ($\bullet Si\equiv Si_3$). Annealing up to 700°C promotes the disappearance of the E′ centre. For films where the D defect is present (all except the film with $x\approx 2$), the concentration of these defects initially decreases for annealing temperatures of 400°C, then continuously increases for temperatures up to 700°C, getting a saturation value in the 10^{18}–10^{19} cm^{-3} range for higher temperatures. ESR characterisation suggests that annealing at higher temperatures promotes the formation of a high-quality SiO_2 matrix in which Si nanocrystals are formed, the D defects being located within these nanocrystals. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

It is well known that the Si/SiO_2 interface is composed of stoichiometric SiO_2 within 4–6 Å of the interface, where Si-rich sub-oxides, SiO_x:H layers ($x<2$) are present [1]. The presence of these sub-oxide layers strongly limits the electrical characteristics of devices where the Si/SiO_2 interface plays a main role, like field effect transistors. Si-rich sub-oxides are also present in high-k/Si interfaces, as the Ta_2O_5/Si system [2]. The sub-oxides also put severe limitations on the device performance.

It is also known that during thermal anneals, SiO_x:H films experience the following network reaction [1]:



$$SiO_x \rightarrow (x/2)SiO_2 + (1 - x/2)Si, \quad (1)$$

i.e., the annealing promotes the formation of both stoichiometric SiO_2 and Si clusters of nanometer size (in the following, nc-Si) [3]. This network reaction takes place both at the transition region of SiO_2/Si interface and in bulk thin films [2].

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The above reaction does not contain information about other processes also taking place during thermal treatments: hydrogen release, that occurs at moderate temperatures [4], and defect evolution. In fact, thermal annealing can modify both the types of defect present in the film and also their concentration. The influence of rapid thermal annealing (in the following, RTA) on the evolution of defects has been recently analysed by our group on stoichiometric, almost hydrogen-free, SiO_2 films [5].

The aim of this paper is to analyse the thermal behaviour of bulk SiO_x:H films deposited by the Electron Cyclotron Resonance (in the following, ECR) plasma method in a wide range of film composition. The main emphasis will be made on the changes that the type and concentration of defects undergo during thermal anneals.

2. Experimental

Films 2000–3000 Å thick were deposited onto RCA cleaned semi-insulating Si substrates. Deposition process was conducted in a home-made chamber attached with an ECR Astex 4500 reactor [6]. The precursor gases used were high-purity SiH_4 and O_2 and films of different compositions were obtained depending on gases flow ratio, which we define in this article in the same way of that of Bulkin [7], i.e., $\mathbf{R}_b = [SiH_4]/([SiH_4] + [O_2])$. Low values of $\mathbf{R}_b$ (0.2–0.4) give stoichiometric, hydrogen-free SiO_2 films, while higher values (in the 0.6–0.9 range) produce off-stoichiometric films with high hydrogen content, that we will refer to as SiO_x:H (x being the oxygen to silicon ratio of films, $x < 2$). After the deposition, films deposited at any particular value of $\mathbf{R}_b$ were cleaved into squared pieces (1×1 cm) and subjected to RTA treatments from 400°C to 1000°C for 30 s in Ar atmosphere.

Films were characterised by means of the Fourier transform infrared spectroscopy (FTIR) in the 400–4000 cm^{-1} range with a Nicolet Magna-IR 750 series II spectrometer. The spectra were recorded with a resolution of 16 cm^{-1}, resolution which led to accurate spectra. Trying to use better resolutions produced interferences that made the measurements less accurate. The peak position of the main Si–O–Si stretching band was used as a measure of the oxygen to silicon ratio of the films (x) with an error of about 20% [1,8]. The peak in the range 2100–2200 cm^{-1} was used to measure the hydrogen content of the film.

Electron spin resonance (ESR) characterisation was performed with a Bruker ESP 300E spectrometer operating in the X band at a microwave power of 0.5 mW. After annealing, each film for ESR measurements was cut into five pieces of 0.2×1 cm which were stacked to enhance the microwave level signal. The density of paramagnetically active centres was quantified by comparison with the signal of a calibrated weak pitch standard [9].

3. Results

3.1. Structural characteristics

In Fig. 1 we present the dependence of the peak position of the main Si–O–Si stretching band as a function of the RTA temperature for five samples of different initial composition: one SiO_2 hydrogen-free film, one SiO_x:H ($x \approx 1.9$) low hydrogen content film, that we will define in this paper as near-stoichiometric sample and three SiO_x:H films with high hydrogen content and x values of 1.4,

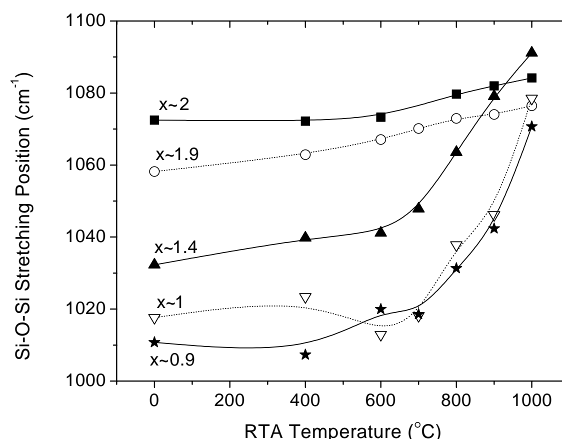


Fig. 1. Peak position of the Si–O–Si stretching band as a function of RTA temperature for five samples of different initial oxygen to silicon ratio. Lines are drawn as a guide to the eye.

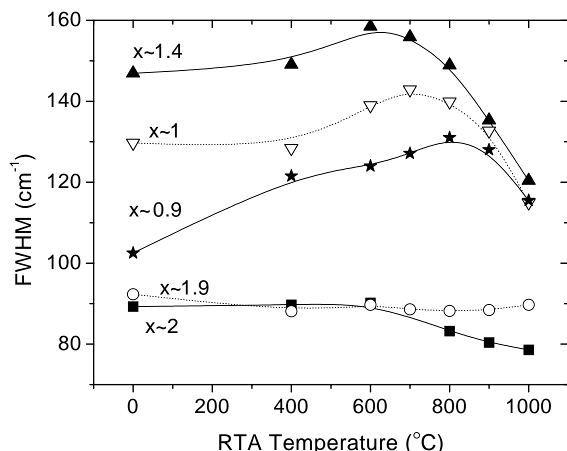


Fig. 2. Full width at a half maximum (FWHM) of the Si–O–Si stretching band as a function of RTA temperature for the same samples quoted in Fig. 1. Lines are drawn as a guide to the eye.

1 and 0.9, that we will define as off-stoichiometric samples. In Fig. 2 we show the full width at a half maximum (FWHM) of the main stretching Si–O–Si peak as a function of the RTA temperature for the same films as in Fig. 1. From the results of both figures, we can deduce the following characteristics of the annealed films:

In the stoichiometric SiO_2 film, the peak position of the stretching band experiences a minor change with the RTA (from 1072 to 1080 cm^{-1}), while the FWHM decreases from 89 to 80 cm^{-1}. The behaviour of the near-stoichiometric SiO_x:H film is very similar to the SiO_2 sample, as Figs. 1 and 2 are the evidence. The main difference is that this film presents a small amount of hydrogen in the form of Si–H bonds, being this hydrogen partially released for RTA temperatures above 400°C, as indicates the monotonous decrease in the intensity of the Si–H stretching vibration located at 2260 cm^{-1}. This wavenumber is related to the O_3-Si–H bonding, and this position did not experience any change with the annealing temperature, revealing that during annealing the hydrogen effusion takes place without changes in the bonding configuration of the film.

The three off-stoichiometric films analysed undergo a completely different behaviour with the RTA. The Si–O–Si peak position did not change up to RTA temperatures of 600–700°C. For $T > 700$°C, the Si–O–Si stretching band shifts progressively to the SiO_2 value. At the RTA temperature of 1000°C, all the analysed samples exhibited the peak position in the 1070–1085 cm^{-1} range. This margin has been reported to be the range of the stretching band values for SiO_2 films [8,10]. The dependence of the FWHM with the RTA is also completely different to the exhibited for both the SiO_2 film and the near-stoichiometric one. Up to 700°C, the FWHM increases with RTA temperature and for higher values the FWHM decreases, but for all the range of annealing temperatures, the FWHM is always above 110 cm^{-1}. Concerning the behaviour under annealing of the hydrogen present in these off-stoichiometric films, the hydrogen was completely released in the 400–700°C range, as indicated by the disappearance of the peak located at 2100 cm^{-1}, related to Si_3–Si–H bonds. As in the near-stoichiometric film previously described, the RTA process did not produce a change in the Si–H stretching position, which remained stable during the hydrogen effusion for any of the analysed films.

3.2. Defect type and concentration

ESR measurements showed that two types of paramagnetic defects were present in the films, the well-known E′ centre ($\bullet Si{\equiv}O_3$) [11] and the Si dangling bond centre ($\bullet Si{\equiv}Si_3$), which some authors define as D centre [12]. The concentration of each defect was strongly dependent on film composition.

On SiO_2 films, only the E′ defect was present, with a concentration previous to the RTA treatment in the $(2\text{–}3) \times 10^{16}$ cm^{-3} range. The influence of the RTA process on the E′ concentration is shown in Fig. 3 for this film. As can be seen, a slight dependence with the annealing can be observed in the low temperature range, but the E′ concentration remains in the range of $(3\text{–}4) \times 10^{16}$ cm^{-3} for all temperatures.

In all other types of films (i.e., the near-stoichiometric sample and the three off-stoichiometric ones), both E′ and D centres were present, the unannealed concentration being dependent on

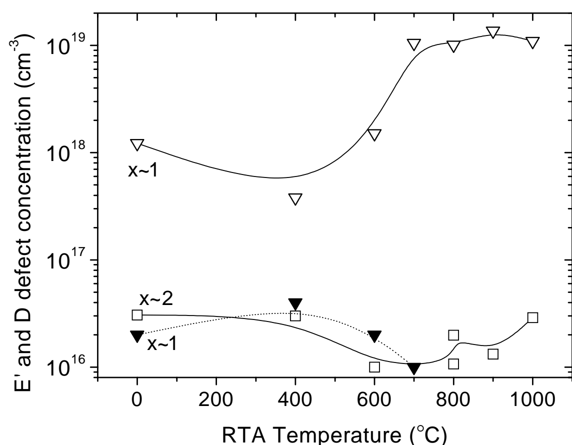


Fig. 3. Concentration of E′ and D defects as a function of RTA temperature for two films with different oxygen to silicon ratio (x): $x\approx 2$: (□)E′ concentration; $x\approx 1$: (▼)E′ concentration; (▽)D concentration. Lines are drawn as a guide to the eye.

the initial film composition [12]. The dependence of these concentrations with the RTA temperature was similar for all these samples. For the sake of clarity, we present also in Fig. 3 the dependence of the E′ and D concentrations with the RTA for only one of the off-stoichiometric samples ($x\approx 1$). The other samples exhibited almost quantitative agreement with data of Fig. 3. The following two main facts can be observed.

The concentration of the E′ defect decreases with the annealing and vanishes at RTA temperatures above 700°C. The concentration of D defects first decreases for low annealing temperature and then sharply increases for temperatures 700–800°C. At higher temperatures the D concentration saturates in the $10^{19}\,cm^{-3}$ range. It should be remarked that in the near-stoichiometric sample ($x\approx 1.9$), the behaviour with the annealing of the D defect was similar to that showed in Fig. 3, but the saturation value was one order of magnitude lower than that exhibited for the $x\approx 1$ sample.

4. Discussion

We will now explain all the results previously shown in Figs. 1–3 attending to the initial composition of the different samples analysed.

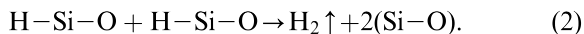
(i) SiO_2 film. The behaviour of this film with the annealing can be explained as reported elsewhere [5]. It is due to a trend to structural order induced by the RTA. Since the main objective of this article is focused on non-stoichiometric SiO_x:H films, we do not bring further explanations here (see Ref. [5]).

(ii) Near-stoichiometric film. From the structural point of view there are no significant differences between the SiO_2 film and this film, as Figs. 1 and 2 show. However, the defect behaviour with the annealing is similar to the off-stoichiometric films, as it was quoted in the previous paragraph. The results obtained for this sample will be explained together with the off-stoichiometric films in the next paragraph.

(iii) Off-stoichiometric films. From the structural point of view, the results of Figs. 1 and 2 can be explained as follows.

At annealing temperatures below 700°C, films release the hydrogen without compositional changes, as it is deduced from the independence of the Si–O–Si peak position with the temperature shown in Fig. 1. The results of Fig. 2 for the FWHM (increasing values of this parameter in the 400–700°C annealing range) suggest that, following Ref. [13], there is a formation of Si–O bonds after the hydrogen release and that this process occurs with the induction of structural disorder on the films. Exception to this rule is for the near-stoichiometric film ($x\approx 1.9$), where the small amount of hydrogen present seems to be released without significant structural changes.

We explain these results according to the following network reaction:

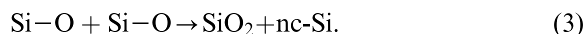


$$H-Si-O + H-Si-O \rightarrow H_2\uparrow + 2(Si-O). \quad (2)$$

The above reaction accounts for the hydrogen release of both near and off-stoichiometric films, that occurs without changes in the oxygen to silicon ratio, in agreement with Fig. 1.

On the other hand, at annealing temperatures higher than 700°C, the results of Fig. 1 suggest the formation of SiO_2, as the peak position of the Si–O–Si stretching band shifts to the stoichiometric value [1]. This is also in agreement with results of

Fig. 2, where a reduction in the FWHM at this temperature range can be seen. It may also indicate that bonds with low mode frequencies are decreasing, suggesting that Si–O changes to Si and SiO_2 [13]. The results of Fig. 3 confirm this hypothesis, since the concentration of the main defect present in SiO_2 films, the E′ defect, disappears at this temperature range, suggesting again the formation of high-quality, almost defect free SiO_2 film. The very high values of the FWHM (Fig. 2) and the presence of a high concentration of the D defect in all the non-stoichiometric films (Fig. 3), clearly indicate that these films undergo a transformation in which the formation of SiO_2 is accompanied with the formation of highly defective clusters, where the D centres agglomerate. This is a known fact and has been explained by the formation of nanocrystaline Silicon (nc-Si) [1–3]. The results of Fig. 3 suggest that these nanocrystals act as getters for the D defects. The presence of such high concentration of D centres in the nc–Si is due to the hydrogen release process described by equation [1]. A network reaction similar to equation [1] can explain this process:



$$\mathrm{Si{-}O + Si{-}O \rightarrow SiO_2 + nc\text{-}Si}. \quad (3)$$

In this way, our results of ESR measurements seem to indicate that the thermal treatment carried out on SiO_x:H films promotes the formation of a high quality, almost defect free SiO_2 matrix, in which highly defective nc-Si are embedded. In the near-stoichiometric film, the amount of these nc-Si clusters would be small and, as a consequence, the structural characteristics of this film after the annealing are almost identical to those of SiO_2 films. Also, after the annealing the concentration of D defects is lower than in off-stoichiometric samples.

On the other hand, on films with initial off-stoichiometric compositions ($x \approx 1.4$, 1 and 0.9), the annealing promotes the formation of a great number of highly defective nc-Si, as the results shown in Fig. 3 for the D defect concentration evidence. Then, the structural characteristics of these films after the annealing are very different from both the SiO_2 and the near-stoichiometric one. The main influence of these differences is accounted for by the high values of the FWHM that these films present after the annealing.

5. Conclusions

We have deposited by the ECR plasma method SiO_x:H films of different compositions (from $x \approx 0.9$ to 2) and subjected them to RTA treatments. After these, films experience two different processes, depending on annealing temperature. Up to 700°C, films release the hydrogen, without modification in the oxygen to silicon ratio of films. The concentration of defects present in the films (both E′ and D) does not experience significant changes in this temperature range.

Annealing at temperatures in the 700–1000°C range induces the formation of a high-quality SiO_2 matrix, almost defect free, in which nc-Si is embedded. The ESR characterisation shows that the nc-Si is highly defective (the concentration of D centres is in the $10^{19}\,cm^{-3}$ range). Depending on the initial composition of SiO_x:H films, the number of these nanocrystals is different, being higher in the films with lower values of x. In this type of films, the nc-Si influence the structural characteristics of films (high values of the FWHM of the Si–O–Si stretching band). On the other hand, on films with $x \approx 1.9$, the nc-Si concentration should be low and then the FWHM of the stretching band is not influenced by the nanocrystals.

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