In situ ESR observation of interface dangling bond formation processes during amorphous SiO_2 growth on Si

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Abstract

We report on the first observation of the processes of formation of interface dangling bond (P_b centers) during amorphous SiO_2 thin-film growth on a clean Si(1 1 1) substrate. After initial termination of the surface dangling bonds on the clean surface, rapid formation of P_b centers was observed. Even for a few monolayers of a-SiO_2 film (<0.4 nm), the number of P_b centers reached the same order of magnitude as that in thick a-SiO_2 films. These results suggest that the interface defect density between Si and a-SiO_2 originates statistically from the short-range chemical bonding configurations and not from the long-range accumulation of the structural misfits between the two materials. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Oxidation of silicon wafer is one of the most basic processes of semiconductor engineering. Recent device technology requires the thickness of the gate insulating oxide to be reduced to 1 nm, but under such conditions, small concentrations of dangling bond defects have a fatal influence on device performance. In order to control the properties of such a thin oxide layer and its interfaces,

a fundamental understanding of the process of formation of the oxide layer is necessary. Under the usual conditions, silicon substrate has three-fold co-ordination silicon atoms with a neutral dangling bond, namely P_b center, at the Si/a-SiO_2 interface. This P_b center is detrimental to electrically active interface defects [1]. There have been some reports on studies which successfully reduced the interface defect density (for example, [2]). Also, there have been several works using scanning tunneling microscopy (STM) which revealed the change of the electronic states on the top surface during oxidation (for example, [3]). However, the basic understanding of defect formation for very thin layers remains inadequate. A method of

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detecting defects with atomic-scale resolution needs to be developed.

Electron spin resonance (ESR) is one of the most powerful tools available for investigating paramagnetic centers including neutral dangling bonds. There have been many reports of P_b centers using ESR, although they basically investigate the interface between Si and thick a-SiO$_2$ [2,4]. Umeda et al. [5] developed a combination of an ESR system and an ultra-high vacuum (UHV) chamber to study the clean silicon surface and its chemical reaction with oxygen molecules, and successfully traced the change of the dangling bond states during the first-layer oxidation process of a clean silicon surface with oxygen molecules at room temperature; however, the subsequent oxidation of a few monolayers was not sufficiently investigated. In this study, we focus on the change in the interface dangling bond defects at the subsequent stage of the oxidation process on a clean silicon surface.

2. Experiment

Fig. 1 shows a schematic diagram of the UHV ESR system used in this study. An X-band ESR spectrometer is attached to a UHV chamber with a sample cell made of a silica tube (10 mm diameter). The UHV chamber is arranged so that the sample cell is located within the microwave cavity of the ESR system. Base pressure of the UHV chamber is approximately 10^{-10} Torr. Si(1 1 1) wafers ($7 \times 0.3 \times 0.03$ cm^3) were used as a sample

in our study. The resistivity of the crystalline silicon is higher than 1000 Ω cm. The samples were supported with sample holders at the end of a vacuum transfer rod after conventional wet treatment by so-called RCA cleaning, and pre-heated at 600 °C in the UHV chamber [5]. The transfer rod rotates so that the ESR spectrum can be measured as a function of the angle, θ, between the [1 1 1] direction and the magnetic field **B** (namely, when $\theta = 0°$ and 90°, i.e. when the magnetic field is parallel to the [1 1 1] and [$\bar{1}\,\bar{1}\,2$] axes, respectively).

The Si(1 1 1)-7 × 7 surface was prepared in the UHV chamber by direct current heating above 1500 K. The surface structure was confirmed by reflection high-energy electron diffraction (RHEED).

For oxidation experiments, the sample was heated to 780 °C ($\approx$ 1050 K) by direct current heating. Oxygen molecules were introduced into the chamber through a variable leak valve. Oxygen doses, to which the clean silicon surface was exposed, were controlled by the pressure and the exposure time. Typical oxygen partial pressure was 1×10^{-6}–1×10^{-4} Torr. All measurements (ESR, RHEED) were carried out at room temperature. The total thickness of a-SiO$_2$ layer was estimated using Auger electron spectroscopy (AES) in a different vacuum system after the sample was exposed to the air.

3. Results

Fig. 2 shows ESR spectra of various steps of the oxidation. As shown in the figure, a dynamic change of the spectra is successfully traced during oxidation. Especially, atomic layer scale detection of the defect signal is achieved because the total a-SiO$_2$ thickness grown in this study is approximately 0.4 nm. At first stage of the process, conventional wet treated (RCA cleaning) Si wafer before flashing shows an ESR signal of approximately 4 G linewidth which originates from P_b centers. This initial interface dangling bond disappears in the Si(1 1 1)-7 × 7 clean surface although this surface should have a large density of dangling bonds. This was thought to be due to the broadening effect caused by the metallic nature of
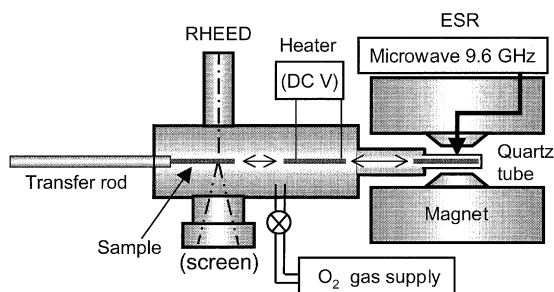

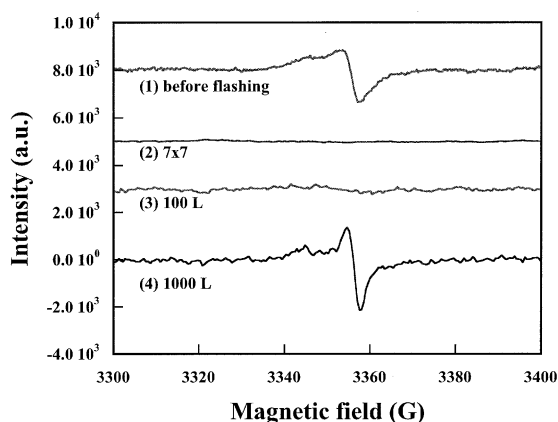Fig. 1. A schematic diagram of the UHV ESR system.

Fig. 2. ESR spectra of various steps of the oxidation; (1) before flashing, (2) 7 × 7 surface, (3) 100 L oxygen exposure, (4) 1000 L oxygen exposure.

the 7 × 7 surface structure [5,6]. A detailed interpretation is given elsewhere [7].

Introduction of oxygen molecules of approximately 100 Langmuir (1 L: 1×10^{-6} Torr s) at 780 °C resulted in a very small change of the spectrum as shown. The previous study demonstrated that even at room temperature, 50 L of molecular oxygen is enough to make most of the surface dangling bond signal disappear [5]. Therefore it is reasonable to regard that the top surface oxidation is completed at this dose. Subsequent introduction
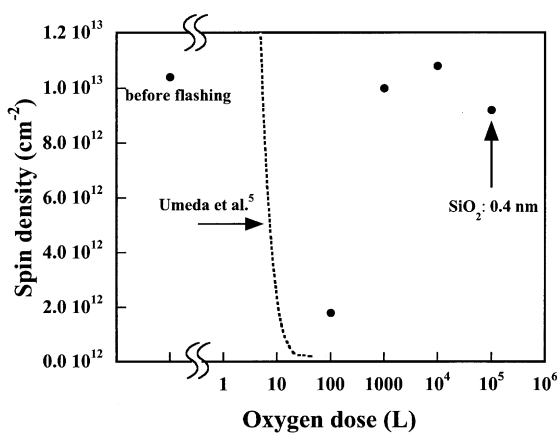

Fig. 3. Spin density estimated from double integration plotted as a function of oxygen dose. Spin density measured before flashing is indicated for comparison. The dotted line indicates the result of monolayer oxidation reported by Umeda et al. [5].

of oxygen molecules ($\approx$ 1000 L) resulted in the appearance of the ESR signal. Angular dependence of the g-value of the signal demonstrated that this signal mainly originated from a spin center whose axis was parallel to the [1 1 1] direction. These results indicate that this second step of the oxidation process produces the dangling bond defect, namely P_b center. The linewidth of approximately 3 G was slightly small compared to that observed in the wet treated sample (top). This might originate from the small structural fluctuation of the smoother interface structure.

In Fig. 3, the effective spin density estimated from double integration of the ESR signal is plotted as a function of the oxygen dose. The initial P_b center density before flashing is also indicated as 'before flashing' for comparison. The dotted line shows the result of Umeda et al. [5] which traced the effective surface dangling bond density at a very early stage of the oxygen exposure. In that case, spin density decreased due to the oxidation. Although the oxidation temperature is different in this study, the small spin density observed at 100 L exposure can be understood in terms of monolayer oxidation observed by Umeda. As clearly shown in the figure, introduction of oxygen of 1×10^3 L resulted in the appearance of the signal again. The spin density reached as large a number as that of P_b centers seen before flashing. Even after an exposure of 10^5 L oxygen molecules, the spin density was not drastically changed. The thickness of the surface amorphous SiO_2 estimated by AES was approximately 0.4 nm at this dose.

4. Discussion

Many efforts have been made to understand the initial oxidation, and several good microscopic models have already been proposed for oxygen molecular adsorption [3,8,9]. However, in contrast to these efforts, understanding of the process of formation of the initial oxide layer on an atomic scale remains insufficient. Especially from an engineering point of view, investigation of interface defects such as P_b centers is crucial. As shown in Fig. 3, even at an early stage of oxidation (1000 L oxygen exposure), the number of P_b centers

reached the same order of magnitude as that observed in the thick a-SiO$_2$ films although the thickness of the a-SiO$_2$ layer is less than 0.4 nm in this case. As mentioned above, angular dependence showed that the signal axis was parallel to the [1 1 1] direction. These results indicate that the observed P$_b$ center is located at the bond between the second and third atoms from the rest layers, because it is the only layer whose bonding direction is parallel to the [1 1 1] direction within 0.4 nm from the top surface. The bonding density of this layer is approximately 1×10^{15} cm^{-2}, and the observed number, 1×10^{13} cm^{-2}, corresponds to 1% of the total silicon bonds.

This defect density number is difficult to attribute to any specific regular structure. Therefore, it is more realistic to consider the thermodynamic statistics. Stesmans [2] reported the relationship between P$_b$ generation and stress, through a temperature dependence study of oxide formation. According to the study, the stress at the interface, which arises from lattice mismatch, is one of the most dominant factors determining the P$_b$ density, and relaxation of this stress reduces the P$_b$ defect density. They also reported that the ESR linewidth of P$_b$ centers could be well explained by the two-dimensional distribution of P$_b$ centers [4]. The present results are consistent with this two-dimensional distribution. Moreover, the present results surprisingly demonstrate that a thick layer of a-SiO$_2$ is not necessary to produce the usual number of P$_b$ centers, indicating that the very thin interface structure rather than the bulk lattice mismatch determines the number of such defects. In other words, the long-range accumulation of structural misfits between Si and a-SiO$_2$ does not play an important role in determining the defect density. Further experiments should be carried out for more precise discussions.

5. Conclusion

The first observation of the processes of formation of the interface dangling bond (P$_b$ centers) during amorphous-SiO$_2$ thin-film growth on a clean Si(1 1 1) substrate was reported. After monolayer coverage of the clean surface with oxygen, rapid formation of P$_b$ centers within 0.4 nm of the oxide layer was observed. Even for a few monolayers of a-SiO$_2$ film (< 0.4 nm), the number of P$_b$ centers reached the same order of magnitude as that in thick a-SiO$_2$ films. These results indicate that the interface defects between Si and a-SiO$_2$ originate statistically mainly from the short-range chemical bonding configurations, not from the long-range accumulation of structural misfits between the two materials.

Acknowledgements

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