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Influences of Impurities on Oxidation Processes of Si(100) Substrates

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1. Introduction

With reduction of device dimensions in ultra large-scale integrated circuits (ULSIs), understanding and precise control of oxidation on Si surfaces becomes strikingly important since the electrical characteristics of metal-oxide-semiconductor field-effect transistors (MOSFETs) are seriously ruled by the roughness at the SiO_2/Si interfaces and SiO_2 bonding structures. Especially, the impurity diffusion from the gate poly-Si to the gate oxide film has been pointed as an important factor governing the ultra-thin gate-oxide reliability [1]. Therefore, it is essential to clarify the influences of impurity atoms on SiO_2 network structures. It has been also reported that the oxidation rate of Si substrates is strongly governed by the impurity concentration in the Si substrate [2]. It can be expected that impurities are made use of cotrolling the oxidation reaction of Si surfaces and the atomistic structures of the SiO_2 films and the SiO_2/Si interfaces.

We have studied the effect of H atoms on the oxidation processes and SiO_2 bonding structures on Si(100) surfaces by high-resolution electron energy loss spectroscopy (HREELS) [3-5]. In the present study, we have investigated the influence of the impurity atoms on the oxidation processes of D-terminated Si(100) surfaces and on the relaxation of SiO_2 structures.

2. Experimental

Experiments in the present study were carried out in an ultrahigh-vacuum (UHV) chamber, equipped with apparatuses of HREELS, low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The base pressure of the UHV chamber was less than 3×10^{-10} Torr. Atomic D and O were produced using a W filament heated at 1500°C.

The B concentrations of p- and p^+-Si(100) substrates used were 4×10^{15} and 1×10^{19} cm^{-3}, respectively, and the P concentration of n-Si(100) substrates was 1×10^{15} cm^{-3}. The D-saturated Si surfaces were prepared by atomic D exposure after thermally cleaning Si substrates at 1200°C. The oxidation was performed by exposing the Si surfaces to atomic O at room temperature. Oxide film thickness is defined as the ratio of the number of O atoms to that of surface Si atoms, determined by AES measurements. HREELS measurements were performed at room temperature under a specular reflection condition.

3. Results and discussion

Figure 1 shows HREELS spectra of D-terminated n-type Si(100) surfaces before and after exposure to atomic O at room temperature. Energy loss peaks for Si-2D species are observed in the spectrum of as-terminated Si(100) surfaces at about 60, 82 and 190 meV, which correspond to wagging (ν_{D1}), scissors (ν_{D2}) and stretching (ν_{D3}) modes, respectively [6]. The LEED observation confirms that this surface has a 1x1 structure. Therefore, it can be concluded that a dideutride structure is formed on the D-terminated Si(100) surface. Moreover, the atomic O exposure leads to the appearance of two loss peaks at about 50 and 130 meV, corresponding to a symmetric bending (ν_{O1}) and an asymmetric stretching (ν_{O2}) mode, respectively [7]. It is found from Fig. 1 that the peak of the asymmetric stretching mode (ν_{O2}) shifts to higher energy losses with the progress of oxidation. This behavior is the same as the case of H-terminated p-type Si(100) surfaces [4].

The energy-loss changes of (a) the symmetric bending (ν_{O1}) and (b) the asymmetric stretching (ν_{O2}) modes for n-, p- and p^+-Si(100) substrates are shown in Fig. 2, as a function of SiO_2 film thickness. From Fig. 2(a), the energy loss of the ν_{O1} peak hardly depends on the SiO_2 thickness above 1 ML and there are few differences among the types of Si substrates. On the other hand, in the case of ν_{O2}, the energy loss keeps constant up to about 0.8 ML and then increases with an increase in SiO_2 thickness for the whole substrate types. This behavior in the ν_{O2} energy loss for the oxide thickness indicates that there is a two-step process in the initial oxidation [4]: O atoms preferentially adsorb on one of the two back-bond sites of a surface Si atom until the oxide thickness is 0.8 ML and in the sequential oxidation process, other back-bond sites become occupied by O atoms [4]. In the second oxidation step, the O adsorption on Si back bonds is accompanied with the structural relaxation of Si-O-Si bonds. Estimating the force constants of Si-O bonds and the Si-O-Si bond angles from the energy losses of ν_{O1} and ν_{O2} in Fig. 2 using a central-force network model [8], the Si-O-Si structural relaxation in the second step was found to originate mainly from the change in the force constant.

It is found from Fig. 2(b) that the Si-O-Si structural relaxation on the p^+-Si surface is hard to occur compaired with that on the p- and n-Si surfaces. The surface coverage of B atoms on the p^+-Si substrate was evaluated to be 0.08 ML (4×10^{20} cm^{-3}) by AES measurements, which results from the surface segregation of B atoms by annealing. The coverage of 0.08 ML means that about 8% of the adsorbed O atoms are bonding with B atoms. Taking account of the fact that the atomic radius of B atoms is smaller than that of Si atoms, compressive stress induced by the formation of Si-O-Si bonds may be diminished by the existence of B atoms. This explanation is consistent with the report that impurity

atoms from the gate poly-Si film relax the compressive stress near the SiO_2/Si interface [9].

Figure 3 shows the relationship between the oxide thickness and the amount of O_2 exposure, where the dissociative ratio of O_2 by the W filament heated at 1500°C was estimated to be 0.12%. The oxidation rate on D-terminated Si surfaces by O atoms is hardly influenced by the impurity. This finding is thought to be consistent with the reports that the dissociation of O_2 occurs through the electron transfer from the substrate to O_2 molecules [2] and the dissociation sites of O_2 such as dangling bonds vanish by the termination with H [3].

4. Conclusions

We have investigated the influences of substrate impurities on the initial oxidation processes and the relaxation of Si-O-Si strucrures on D-terminated Si(100) surfaces in the oxidation using O atoms at room temperature by HREELS. It is found that the impurities hardly influence the oxidation rate and the preferential adsorption of O atoms on one of two back bonds of a surface Si atom at oxide thicknesses below 0.8 ML. Moreover, B atoms influence the relaxation of Si-O-Si structures during oxidation, which may be related to the compressive stress in Si-O-Si structures.

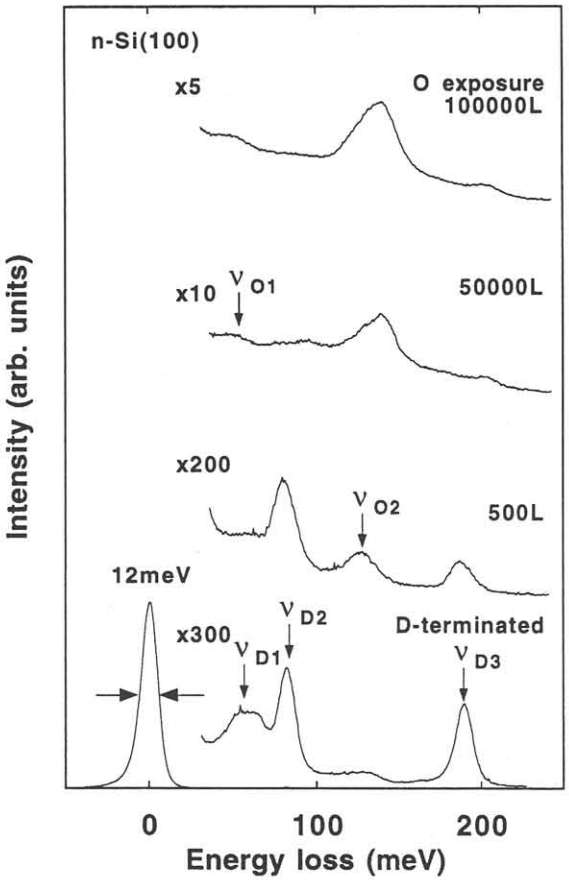

Fig. 1 HREELS spectra of D-terminated n-type Si(100) surfaces before and after O exposure at room temperature.

References

[1] D. Wristers, H. H. Wang, L. K. Han, C. Lin, T. S. Chen, D. L. Kwong and J. Fulford, in The Physics and Chemistry of SiO_2 and the SiO_2-Si interface-3 eds. by H. Z. Massoud, E. Poindexer and C. R. Helms (Electrochem. Soc. 1996) p. 733.

[2] M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami and M. Ohwada: J. Appl. Phys. **68** (1990) 1272.

[3] H. Ikeda, K. Hotta, T. Yamada, S. Zaima, H. Iwano and Y. Yasuda: J. Appl. Phys. **77** (1995) 5125.

[4] H. Ikeda, K. Hotta, S. Furuta, S. Zaima and Y. Yasuda: J pn. J. Appl. Phys. **35** (1996) 1069.

[5] Y. Nakagawa, H. Ikeda, S. Zaima and Y. Yasuda: Appl. Surf. Sci., in press.

[6] H. Froitzheim, U. Köhler and H. Lammering: Surf. Sci. **149** (1985) 537.

[7] J. A. Schaefer and W. Göpel: Surf. Sci. **155** (1985) 535.

[8] P. N. Sen and M. F. Thorpe: Phys. Rev. **B15** (1977) 4030.

[9] K. Morino, S. Miyazaki and M. Hirose: Ext. Abst. of the 1997 Int. Conf. on Solid State Devices and Materials, Hamamatsu, 1997, p. 18.

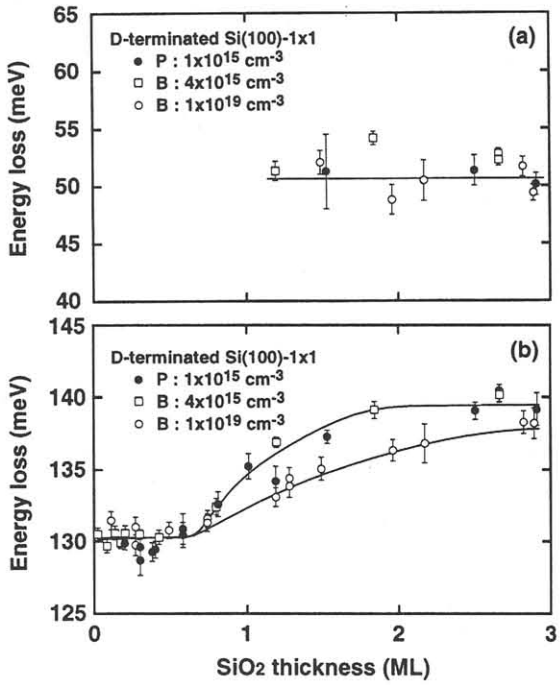

Fig. 2 Energy losses of (a) the symmetric bending and (b) the asymmetric stretching modes for n-, p- and p^+-Si(100) substrates as a function of oxide thickness.

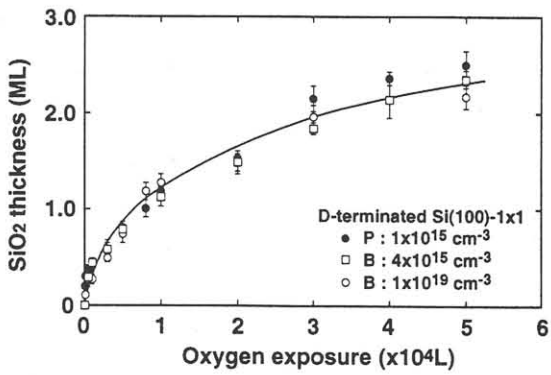

Fig. 3 Relationship between the oxide thickness and the amount of O_2 exposure.