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Electronic Interface Properties of Low Temperature Ultrathin Oxides on Si(111) Surfaces Studied by Contactless Capacitance-Voltage and Photoluminescence Methods

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By using the contactless C-V, PLS^3 and XPS techniques, electronic properties of ultrathin-oxide formed Si(111) surface were characterized with particular attention to the affect of using nitrogen related plasmas. Hydrogen termination was used as the initial surface treatment prior to oxidation. Both of chemical oxidation and low-temperature (300-400°C) thermal oxidation processes produced SiO_2/Si interfaces with high-density of interface states that caused limited C-V variation and low PL efficiency. Treatment of low-temperature thermal oxides in N_2-plasma had no effect. On the other hand, good C-V behavior was obtained at the surface after N_2O plasma treatment at 400°C.

1. Introduction

An atomic scale understanding and control of ultrathin oxide/Si interfaces will become more and more important in future for the continued scale-down of Si CMOS ULSIs as well as for successful development of the Si-based single electron transistor technology. However, in spite of recent great advances in surface science techniques for characterization of surface nano-structures, there has been no well established method for characterizing electronic properties of ultrathin oxide/Si interfaces. In an attempt to overcome this difficulty, we have recently applied contactless C-V method[1] and the photoluminescence surface state spectroscopy(PLS^3)[2]method to the hydrogen terminated and ultra-thin low-temperature oxide covered (111) surfaces of Si.[3] It was shown that combined use of these two methods is extremely useful in characterizing electronic properties of ultra-thin insulator covered surfaces. It was also shown that it is difficult to realize ideal ultra-thin insulator covered surfaces free of Fermi-level pinning with various known low-temperature oxidation processes.

The purpose of this paper is to further characterize the electronic properties of various low-temperature ultrathin oxide/Si (111) interfaces to realize pinning-free high quality ultrathin insulator-Si interfaces, using the contactless C-V and PLS^3 methods. XPS measurements were also made. Ultrathin oxide films were formed by various low-temperature processes with a particular attention to use of nitrogen related plasmas[4-5]. Hydrogen (H-) termination was used as the initial surface treatment prior to oxidation in order to taking full advantage of its well-defined atomic structure, flatness and high reproducibility.

2.Contactless C-V and PLS^3 techniques

The principle of the contactless C-V method used in this study is shown in Fig. 1. C-V measurements can be performed from the field electrode that is placed above the sample, being separated from the sample surface by a thin "air-gap" (300-400nm) using a commercial measurement system (CV8000, Dainippon screen Mfg. co, Ltd.). In this system, the "air-gap" is maintained by a piezo-mechanism with capacitance feedback from the three surrounding "parallelism electrodes". The area of the electrode for C-V measurement was 7.5×10^{-3} cm^2 and Cr was used as the field plate metal.[1),6)]

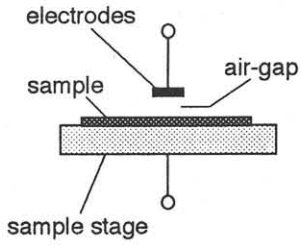

Fig.1. Basic principle of the contactless C-V method.

The PLS^3 method measures the excitation power dependence of the PL efficiency which is very sensitive to surface properties. The interface state density distribution can be determined by fitting the measured data with the results of rigorous computer simulation taking account of all possible recombination processes.[2)]

3. Sample Preparations

Wafers used in the present study were n-type Si (111) with the carrier concentration of $1\text{-}2 \times 10^{15}$ cm^{-3}. H-terminated surface was formed by the method of Higashi et al[7]. First, thick thermal oxide films with the thickness of about 150nm were formed in dry O_2 at 1000°C. Then, after removing the thick oxide films in a buffered hydrofluoric acid, native oxide films were formed by immersion of the surface in an HCl-H_2O_2 solution at 80°C for 10min. Finally, the surface was immersed in a 40% NH_4F solution. After each process, the sample was rinsed in deionized water. Then the atomically flat

H-terminated surface was given.

Thin oxides were formed on these atomically flat H-terminated surfaces at low-temperature environment. Chemical oxides were formed in a hot HNO_3 solution (60 °C) for 5min. Thermal oxidation was made on the H-terminated surface at 300-400°C for 30min in dry O_2 with a pressure of 1 Torr in an UHV chamber (base pressure is less than 10^{-9} Torr). Thermal oxides were farther treated in an electron- cyclotron- resonance (ECR) enhancec N_2 plasma. Furthermore, by exposing the H-terminated surface to the N_2O plasma at 400°C for 30min in an UHV chamber, oxynitridation of the surface was attempted. The thicknesses of various thin oxide films were deduced by analyzing the Si2p photoelectron spectra.[8)]

4. Results and Discussion

4.1 Behavior and Stability of H-terminated Initial Surface

Fig. 2 shows an example of the contactless C-V curve taken on a H-terminated surface. The curve is very different from one which was obtained for the surface covered with a thick high-temperature thermally oxide. Flattening of capacitance under positive bias and a very large hysteresis under negative bias are the characteristic feature for the H-terminated surface, showing presence of strong Fermi-level pinning[6)]. Figure 3 shows the XPS spectrum of Si2p core level from the H-terminated surface. Valence band spectrum is also shown in the inset. No oxide phase was seen in the spectrum. Presence of Fermi-level pinning was also confirmed from the XPS valence band spectrum and from the XPS peak position of Si2p level consistently, and the pinning position was estimated to be Ev+0.6-0.7 eV.

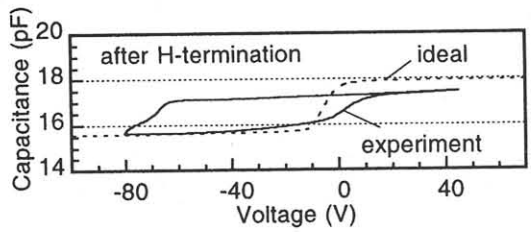

Fig.2. Contactless C-V curves taken on a H-terminated surface.

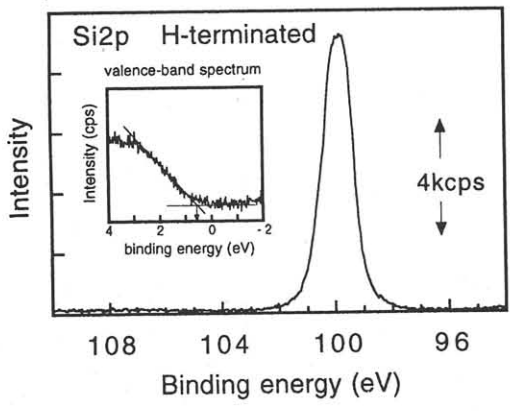

Fig.3. XPS spectrum of Si2p core level from the H-terminated surface. Inset shows the valence-band spectrum.

Stability of the H-terminated surface was investigated by changes of the C-V curve with time when the H-terminated surface was exposed to air in clean room. The result is shown in Fig. 4. The C-V curve remained more or less the same with that at the initial H-terminated surface for 5 hours. Then the H-terminated surface was gradually oxidized in air and the C-V curve after 1-day air-exposure became one obtained from the as-received bare Si surfaces. Separate C-V studies revealed that the H-terminated surfaces were found to be stable even after 350°C annealing in an UHV chamber (<10^{-9}Torr) for 30min and after immersing in deionized water for 120 min.

4.2 Properties of Ultrathin Oxide-Si Interface and Effect of Nitrogen Plasmas.

Figure 5 shows the contactless C-V curves of HNO_3 treated surface and as-grown and N_2-plasma treated surfaces having low-temperature thermal oxide. In all cases, very limited range of C-V variation at lower capacitance level was obtained, indicating the presence of high density of interface states. N_2 plasma treatment at 400°C for 30min had no effect on C-V curves. XPS analysis showed that surfaces have large amounts of suboxides which may be related the Fermi level pinning. From the capacitance analysis and peak positions of the $Si2p_{3/2}$ spectra, it was found that the Fermi level was pinned at around Ev+0.3-0.4 eV, i.e., being downward shifted from the H-terminated surface. The result can be

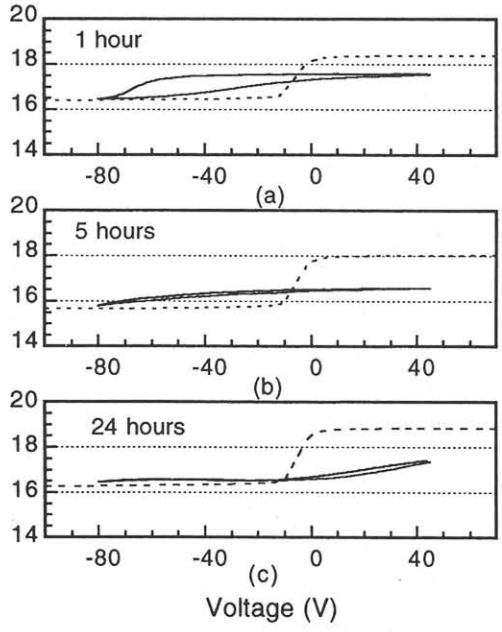

Fig.4 Time-dependent changes of the C-V curve for the H-terminated surface exposed to air in clean room.

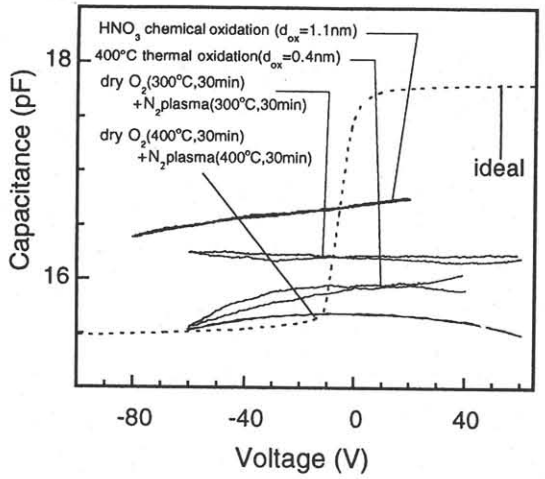

Fig.5. The contactless C-V curves of HNO_3 treated surface, low-temperature thermally oxidized surface and N_2 plasma exposed surfaces.

explained in terms of the DIGS model, as discussed previously[3].

Figure 6 shows the contactless C-V result for the surface treated by N_2O plasma in a UHV chamber at 400°C for 30min after H-termination. Large variation of C-V range was achieved in this case. This curve was found to be comparable that from Si(100) surface after the 850°C thermal oxidation as far as the amount of capacitance variation is concerned. XPS spectra of Si2p and N1s core levels are shown in Fig. 7. The thickness of the oxidized surface was estimated to be 4nm. The peak position of N1s is close to those of Si_3N_4 and SiON phases[4]. In addition, angle-resolved study revealed that the nitrogen atoms distributed very near the SiO_2/Si interface, indicating the presence of thin nitridized and/or oxynitridized phase at the interface. Lu et al[4] recently reported that such phase is effective to reduce the interface strain due to a mismatch in the Si atomic density. Thus, a possible reason for the improvement of the C-V behavior at the N_2O plasma treated surface is that the nitridation or oxynitridation of the Si surface takes place at the initial stage of plasma treatment.

4.3 PLS³ Study

The PL efficiency values measured in detail vs the excitation intensity. The H-terminated surface gave very low PL efficiencies where the slope of the PL efficiency vs excitation intensity was unity. This shows that high density of discrete surface states exist on the H-terminated surface.

On the other hand, various ultrathin oxidized surfaces, good correlation between PL intensity and C-V results. At the same time, the slopes of the curves became less than unity, indicating that the interface states have continuous U-shaped distributions.

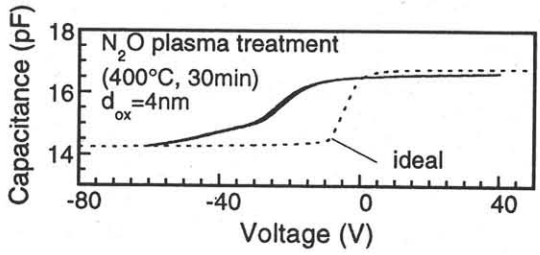

Fig.6. Contactless C-V curves for the surface treated by N_2O plasma in a UHV chamber at 400°C for 30 min after H-termination.

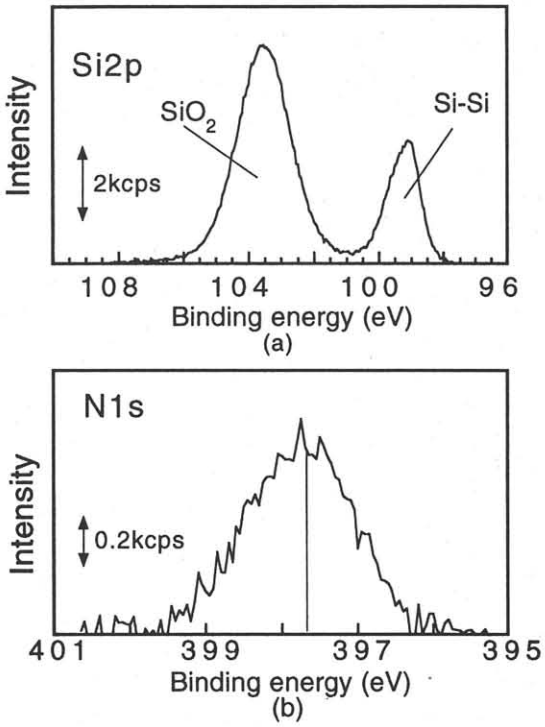

Fig.7. XPS spectra of Si2p and N1s core levels for the surface treated by N_2O plasma in UHV chamber.

References

1) T. Sakai, M. Kohno, S. Hirae, I. Nakatani and T. Kusuda, Jap. J. Appl. Phys. **32** (1993) 4005.

2) T. Saitoh, H. Iwadate and H. Hasegawa, Jap. J. Appl. Phys. **30** (1991) 3750.

3) T. Hashizume, S. Koyanagi and H. Hasegawa, accepted for publication in J. Vac. Sci. Technol. vol.14, no.4 (July/August issue), 1996.

4) Z. H. Lu, S. P. Tayand, R. Cao and P. Pianetta, Appl. Phys. Lett, **67**(19) (1995) 2836.

5) D. R. Lee and G. Lucovsky, J. Vac. Sci. Technol. **A13**(1995) 607.

6) S. Koyanagi, T. Hashizume and H. Hasegawa, Jpn. J. Appl. Phys. **35** (1996) 630.

7) G.S. Higashi, Y.J. Chabal, G.W. Trucks and K. Raghavachari, Appl. Phys. Lett. **56** (1990) 656.

8) H. Ogawa and T. Hattori, Appl. Phys. Lett. **61** (1992) 577.