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Chemical Bonding Configurations at the Interface of SiO_2/Si(111)

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The interface and near interface regions of SiO_2/Si and related films have received attentions for several decades. Silicon dioxide has been used as a realistic gate dielectric material in complementary metal-oxide-semiconductor (CMOS) components because the interface between silicon dioxide and silicon substrate is amorphous. In the present work, ultra thin silicon dioxide (below one nm) films have been grown on Si(111) at 700 ºC and the chemical bonding configurations of interface states between silicon dioxide and silicon substrate have been investigated with synchrotron radiation induced photoelectron spectroscopy.

Key Words: Thin film, Nano transistor, Synchrotron radiation technique, Surface and Interface states.

INTRODUCTION

Silicon perhaps is the most important element today. The majority of all electronics such as computer processors and memory chips are made using silicon as the base material. This is due to several reasons. First of all silicon is an abundant material and therefore relatively cheap. It has some useful physical properties and by sophisticated manufacturing methods it can be utilized for a large number of different applications. This has led to an enormous development in the electronics and nano-electronic industry[1-9]. Although some issues such as increasing leakage current, tunneling through ultrathin silicon oxide and also boron penetration through the gate impose a practical limit on oxide thickness[6-11], no other interface approaches the amorphous case and the other properties quoted above for SiO_2/Si interface at low temperatures.

In a recent study[9], the developments of the chemical bonding configuration of the surface, bulk and interface of the oxide film formed onto Si were observed. Similarly, a series of studies of a Si(111) and its reaction with oxygen at 700 ºC were performed, with synchrotron radiation induced photoelectron spectroscopy. Furthermore, the thickness of the oxide/silicon interface was measured with conventional X-ray photoemission spectroscopy (XPS) and the film thickness is estimated below 1 nm[5].

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In this study, the chemical bonding configurations at the surface, at the interface of SiO_2 and the Si surfaces, the composition and structure in the bulk of the oxide layer were estimated.

EXPERIMENTAL

The photoemission experiments were carried out at the electron storage ring at Aarhus University, Denmark, with the light from a bending magnet using a spherical grating monochromator. One beamline is fitted with a standarnted VG (Vacuum Generators Ltd.) ultrahigh vacuum (UHV) system connected to a Zeiss SX700 monochromator. The system is equipped with a VG CLAM electron analyzer and is pumped by ion-, turbo- and Ti-pumps. The other system consists of a VG double chamber with separate preparation and measurement compartments on a beamline with an SGM monochoromator and a SCIENTA SES-200 analyzer. It only allows one sample to be mounted at a time, but uses the same heating principle. This equipment has a significantly better performance in terms of resolution and transmission than the other system.

The silicon samples (n-type, 5 Ω cm, 3 cm × 1 cm) were cut out of wafers and introduced in the UHV chamber after a rinse with ethanol in an ultrasonic bath. The chamber was then baked before the experiments. After baking the background pressure was 2×10^{-10} Torr. All further cleaning was done inside the UHV chamber by heating with a direct current through the sample, initially up to 1200 ºC and later at higher temperatures to restore a clean Si surface. Earlier measurements with a residual gas mass spectrometer in the line of the beam has shown that a very high proportion (about 50 per cent) of oxygen is produced with this setup. Typical total pressures in the chamber during exposure were around 2×10^{-7} Torr. The incident angle of the light on the sample is 40 degrees from the normal. The Si(111) substrate is kept at a temperature of 700 ºC. Temperature is measured by an optical pyrometer.

The signs of the beginning oxidation are evident from the spectra shown in Fig. 1. This figure shows the results of adsorbing oxygen on a moderately heated Si(111) surface, on the Si 2p high resolution core level photoemission spectra excited with 131 eV synchrotron radiation. It is already known that the clean silicon surface region has a bulk Si $2p_{3/2}$ level at 31 eV kinetic energy corresponding to a binding energy of 99 eV. The foot at ~ 31.8 eV is the Si $2p_{3/2}$ core level position assigned to the rest atoms and the peak at ~ 30.7 eV is a composite of the Si $2p_{1/2}$ bulk peak and a Si $2p_{3/2}$ core level due to the ad-atoms in the notation of the dimer-ad-atom-stacking fault (DAS) model for the 7 × 7 surface reconstruction[12]. The kinetic energies in these spectra are determined with a very high precision, while the calibration of the monochromator is only accurate to within 1 eV on an absolute scale. Therefore, kinetic energies were normally used.

After the first, short exposure included here, (total oxygen exposure for 20 min), the bulk Si $2p_{3/2}$ and Si $2p_{1/2}$ peaks are reduced in intensity but the Si $2p_{3/2}$ rest atom peak has disappeared, indicating a change of the surface reconstruction. This structure is due to the formation of oxide.

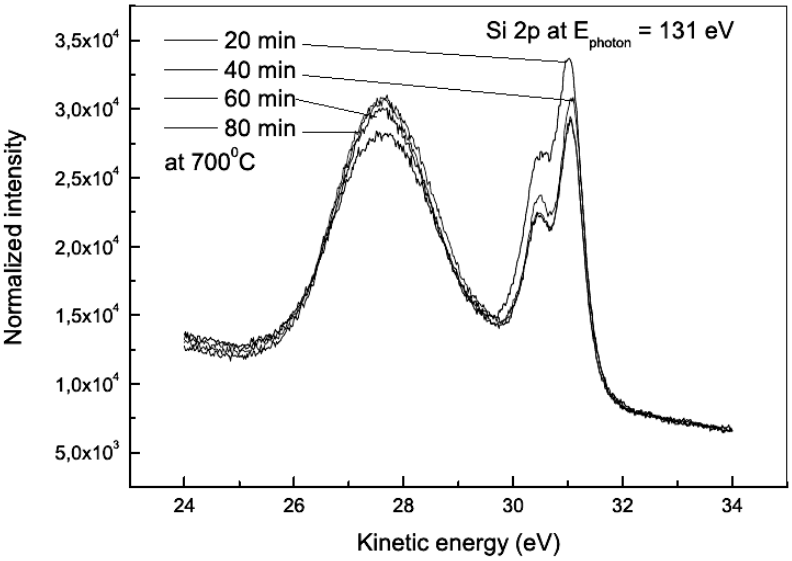

Fig. 1. Si 2p spectra of Si(111) after exposure to 20 -80 min oxygen at 700 ºC

The following, larger exposures change the structure of the entire spectrum (40, 60 and 80 min). The chemically shifted structures towards higher binding energies compared to the bulk peaks (lower kinetic energies) become more dominating.

RESULTS AND DISCUSSION

All Si 2p core-level spectra were systematically analyzed with standard curve-fitting procedures. Using the well known program FitXPS[12] to decompose the Si 2p spectra at all steps, in folded, spin-orbit split-, Gaussian-Lorentzian peaks, the spectra were seen to consist of the bulk (Si-Si) and up to four components ascribed to various Si-O nearest neighbour configurations. In the other words, the intensities could be extracted from the areas of the Si 2p spectra fitted with components of combined Gaussian-Lorentzian line shapes, (*i.e.*, both GFWHM (Gaussian full width half maximum) and LFWHM (Lorenzian full width half maximum) using the "FitXPS" program. It contains five pairs of spin orbit components (Fig. 2). These distinguished attributed to Si atoms in different chemical bonding configurations and assigned them formally to Si^{+}, Si^{2+}, Si^{3+} and Si^{4+}. Hence, the near interface consists of a few atomic layers containing Si atoms in intermediate oxygen states, *i.e.*, Si^{+}, Si^{2+} and Si^{3+}. The unaffected Si atoms are assigned Si^{0}. Si^{4+} is above the interface and Si^{3+} is also top layer. The Si^{3+} coordinated atoms are all counted as oxide surface atoms, although this could be debated, if some of the Si atoms at the interface are also coordinated with three neighboring oxygen atoms. Thus, there is a degree of uncertainty involved in assigning all the Si^{3+} intensity to the surface, as some Si atoms bound to 3 oxygen atoms may also be part of the interface.

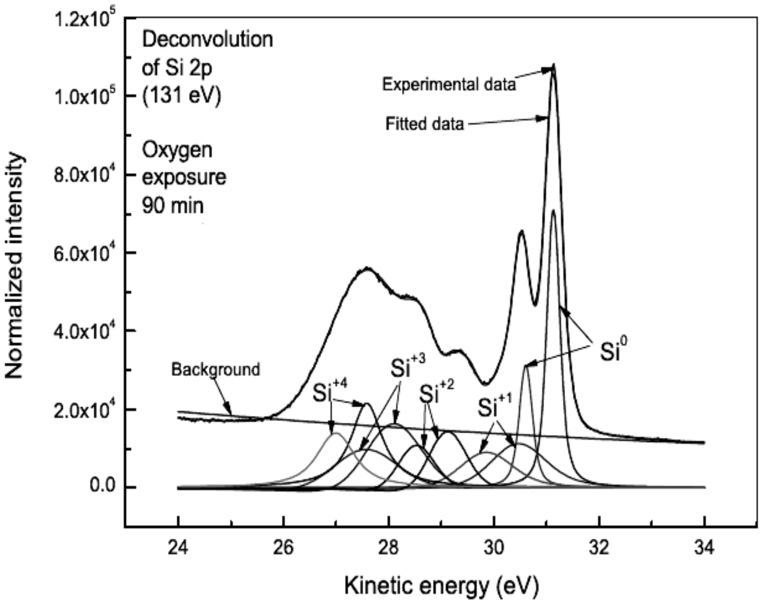

Fig. 2. Fit of Si 2p spectrum of Si(111)- 7 x 7 exposed to 90 min O_2 at 700 ºC

After the first, short exposure, the bulk Si $2p_{3/2}$ and Si $2p_{1/2}$ peaks are barely reduced in intensity but the surface peaks of the clean surface disappeared, indicating a change of the surface reconstruction. The following larger exposures change the structure of the entire spectrum. The chemically shifted structures towards higher binding energies compared to the bulk peaks become more dominating due to the oxidation. The reason for self-limiting growth is not yet clear, but one reason could be due to a stress-free oxide at this temperature and above. The second reason as mentioned above may be due to less supply of oxygen than the desorption probability of SiO. The third and more significant reason is due to local barrier which causes the oxide network not to be able to rearrange fast enough by viscous flow, therefore the resulting film maintains substantial stress and strain as local barrier.

Roughness may enhance the tunneling current and increase the amount of traps and charge at the interface and create extra energy states. Although Si is crystalline and the oxide is amorphous, the interface has an extremely low density of dangling bonds or other electrically active defects[3-7]. When the silicon surface is oxidized, the interface between the two materials can no longer be perfect. The average distance of atoms in crystalline silicon differ from that in amorphous oxide. On the other hand, the volume per silicon atom in a silicon dioxide is about twice that in silicon crystal, which means that silicon atoms are inevitably emitted from the interface to release stress during oxidation[1,5]. Depending on the oxidation procedure interface roughness between silicon and silicon dioxide layer has been reported[3] to be up to 1 nm and can be changed by surface orientation and film thickness.

Nevertheless, the origin of interface states has been based on the assumptions of unsaturated dangling bonds at the interface. In addition to the free dangling bonds, silicon and oxygen bonds in the oxide are distorted at the interface to match the silicon lattice. In the Chemist's language: near the interface, Si is Si^{4+} as in SiO_2, at the interface Si is also found in its Si^{+}, Si^{2+} and Si^{3+} states.

However, the interface region width depends not only on the substrate and oxide layer fabrication procedure, but also on the measurement techniques used[7,8]. Therefore, some workers[3] suggested in the near-interface region there is a zone with excess Si in the SiO_2 region. From the technical point of view, for instance, from ellipsometery measurements, the interface region is understood as a layer with optical properties different from both bulk oxide and crystalline silicon, although it is not very clear. The interpretation of the Si 2p photoemission consider this region as a layer of Si^{n+} suboxide states (such as Si^{2+} from SiO)[3] with local electronic configurations different from pure Si and bulk SiO_2. The present authors face two problems: (a) the refractive index of thin films (ellipsometery and other optical techniques) and (b) the photoelectron mean free path (photoemission) which are not universally agreed upon. Both change as the composition of this region changes.The case of forming Si^{+}, is thought as the insertion of an oxygen atom between two Si atoms consisting of a Si-Si bond oriented along the Si directions, while in the case of forming Si^{3+}, the insertion of an oxygen atom is between two Si atoms consisting of a Si-Si bond at the interface expanding the oxide network mostly along the direction perpendicular to substrate direction. Therefore, the formation of Si^{+} at the interface results in an increase in surface roughness caused by the formation of protrusions on the oxide surface. Thus, the saturated level of intermediate oxidations states is slightly larger. Furthermore, the relative number of intermediate oxidation states does not change significantly upon increasing the oxidation temperature[1].

Looking back at the core-level photoelectron spectra (Fig. 2), the presence of specially suboxide in these figures means that silicon oxide is amorphous. Three other peaks, the bulk peak Si^{0}, the bulk oxide Si^{4+}, the Si^{+} and Si^{3+} peaks are also changing (Fig. 3). The intensity of the bulk peak Si^{0} peaks decreases exponentially, the Si^{+} and Si^{2+} peaks are changed. Both Si^{3+} and Si^{4+} peaks increase linearly and sigmoid-like, respectively. The saturation of the bulk oxide peak, Si^{4+} is clearly shown. They move towards lower kinetic energy with temperature. The faster rate of Si^{3+} could be due to an enhanced oxygen uptake as seen in Fig. 3 or could be due to a fundamentally different form of oxide structure. The intensity distribution of intermediate-oxidation states, $Si^{+}+ Si^{2+} + Si^{3+}$, varies with the oxide overlayer thickness as shown in Fig. 4. The interface intensity in Si(111) decreases exponentially.

It implies that after the interface layer becomes continuous, the thickness of silicon dioxide only increases with further oxidation up to saturation. The increase in the area of Si^{2+} with the progress of oxidation implies that the microroughness at the interface increases as oxidation proceeds.

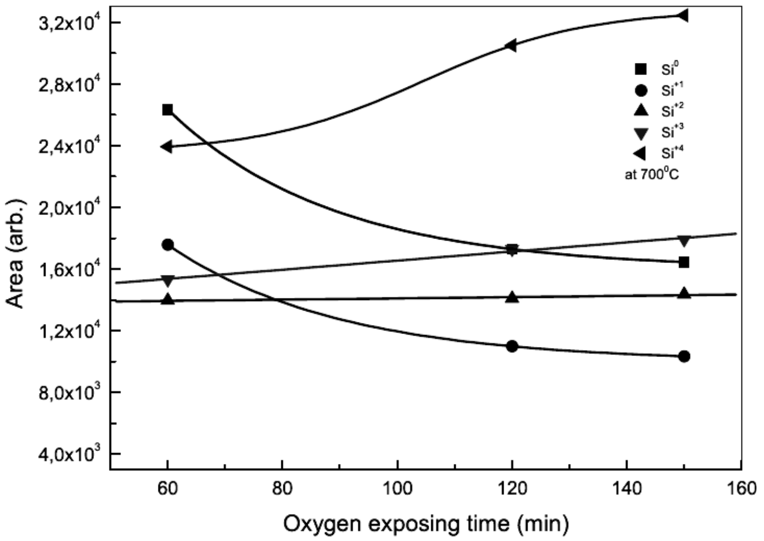

Fig. 3. Variation in intensities of deconvoluted peaks at 700 ºC on Si(111)-7 x 7

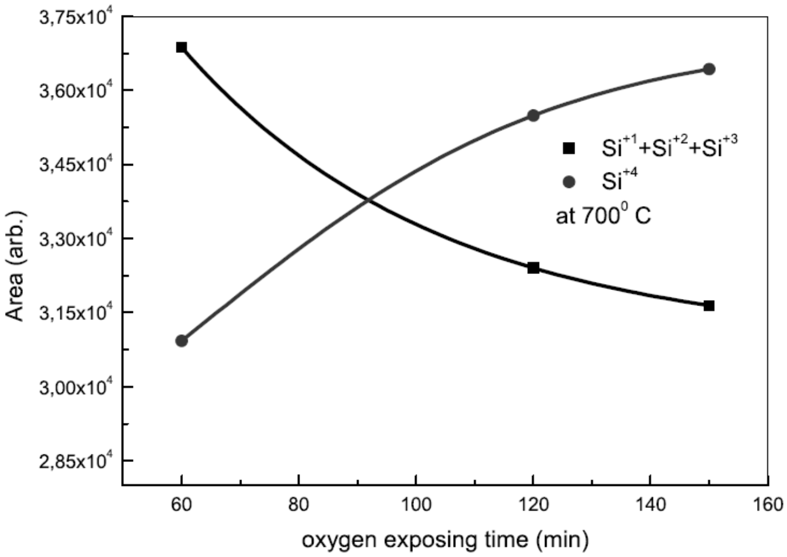

Fig. 4. Variation in intensities of deconvoluted peaks at 700 ºC on Si(111)-7 x 7

Conclusion

Thin films of SiO_2 on Si(111) have been grown and studied with synchrotron radiation induced core level photoemission spectroscopy. The Si 2p spectra provide the necessary details for monitoring the structure of the oxide and the resulting interface- and surface structures. By looking at the relative intensities of the shifted Si 2p peaks and interface states due to the different Si-O configurations, it is possible to study the variation of interface states in the ultrathin oxide film, as well. The results indicate that the growth of oxide is self limiting. We suggest a new ultra thin oxide growth model for ultrathin oxide film[10-19].

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