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Two-Dimensional Growth and Decomposition of Initial Thermal SiO₂ Layer on Si(100)

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The growth and decomposition kinetics of initial thermal oxide layers on Si(100) was investigated by measuring *in situ* the amount of oxidized and clean area with ultraviolet photoelectron spectroscopy. It was found that the initial thermal oxidation as well as the decomposition proceeds two-dimensionally with the formation of oxide islands having a height of as thick as about 3.4 monolayers until the surface is fully covered with oxide, and then the oxide film extends deeply with a very slow rate. This indicates that adsorbed oxygen atoms migrate smoothly on the surface to be captured by oxide islands and otherwise they desorbs as SiO molecules.

1.INTRODUCTION

Oxide films on Si play a very important role in the field of semiconductor devices. In particular, owing to continuous scaling down of device size to VLSI/ULSI, ultrathin oxide films are urgently required. Since the physical and chemical nature of the ultrathin oxide affects strongly the electrical performance of submicron and quatermicron metal-oxide-semiconductor silicon devices, the reaction kinetics of thermal growth and decomposition of oxide layers have been extensively investigated.

Recent thermal desorption spectroscopy (TDS)¹⁾ and scanning tunneling microscopy (STM)²⁾ studies demonstrated that the thermal proceeds decomposition of SiO₂ films inhomogeneously with circular voids. Then voids with a clean surface are developed laterally with keeping the thickness of SiO₂ films between them unchanged. In contrast, X-ray photoelectron spectroscopy study³⁾ suggested that the thermal oxide growth on Si(100) proceeds under a layer-by-layer growth mode at an initial oxidation stage. However no obvious information about the oxidation kinetics was obtained for the first atomic layer formation in such a mode.

We observed *in situ* the growth and decomposition reaction of initial oxide layers on Si(100) by measuring the oxidized and clean

* Present address : Research Institute for Scientific Measurements, 2–1–1 Katahira, Aobaku, Sendai 980, Japan. area with ultraviolet photoelectron spectroscopy (UPS). Owing to the direct observation of the unoxidized area during oxidation, we found that the thermal oxidization is promoted two-dimensionally with the oxide island formation as the thermal decomposition with the void formation. It was clarified that a height of such islands is as thick as about 3.4 monolayers. This means that when the clean surface is fully oxidized, the oxide layer is not of one atomic layer but is rather thick.

2. EXPERIMENTAL

All of our measurements were performed in an ultrahigh vacuum reaction chamber which has facilities for UPS and reflection high energy electron diffraction (RHEED). The base pressure was 1×10^{-10} Torr. Photoelectron spectra were obtained by He–I (21.2eV) resonance line. UPS spectra were taken at a temperature ranged from 680° C to 820° C and at a O₂ pressure ranged from 5×10^{-8} Torr to 5×10^{-6} Torr.

The sample used were B-doped p-type $Si(100)-4^{\circ}$ off wafer. Thermal oxidation was carried out with dry O_2 gas (purity 99.9%). O_2 gas was introduced through a variable leak valve and was quickly stopped within a few seconds for thermal decomposition.

3. RESULTS AND DISCUSSION

An UPS spectrum of a clean surface shows a sharp peak of the surface state (SS) due to dimer dangling bond (DB). During thermal oxidation, two



Fig.1 Transition conditions from etching to oxide formation.

peaks due to O-2p state grow pronouncedly as the SS intensity is reduced. We noticed that the clean and oxidized area can be obtained independently during oxidation by measuring the SS and O-2p intensity, respectively, and therefore the oxidation kinetics at an initial stage, in which a clean area coexists with an oxidized layer, can be clarified and a void formation in decomposition is detected with high sensitivity.

First we examined a transition from etching to oxidation on Si(100).⁴⁾ In the etching, no O-2p intensity is seen because adsorbed oxygen desorbs immediately as SiO. When an oxidation condition is changed from the etching to the oxidation, a rapid drop of the SS intensity and an increase of the O-2p intensity is displayed. Figure 1 summarizes the transition conditions of temperature and pressure compared with recent results.⁵⁾ Because of a good agreement in activation energy of our results with previous ones, it is concluded that the present UPS



Fig.2 Time dependence of the surface state and O-2p state intensity during oxidation and decomposition at 760 $^{\circ}$ C and 2.0x10⁻⁶ Torr.

method is very useful for investigation of thermal oxide growth and decomposition at an initial stage. The difference in the absolute value seems to be ascribed to the surface sensitivity, because very high sensitivity is necessary to determine exactly the transition condition.

Figure 2 represents typical time-dependent intensities for the isothermal oxide growth and decomposition at 760°C and 2.0x10⁻⁶ Torr. By O, supply (ON), the SS intensity begins to drop slowly. The reduction of the SS intensity gradually accelerates and has a maximum rate at a normalized intensity of about 0.5, and eventually disappears. The O-2p intensity increases and saturates at the disappearance of SS intensity, indicating that the oxidation rate is considerably reduced when a oxide film covers a whole surface area. When O₂ supply was quickly stopped (OFF), the SS and O-2p intensity was very gradually changed. For a while, they reach their initial values, proclaiming the surface clean. The time-dependent feature shows a quite similar trend over a wide range of temperature and pressure. This means that the reaction kinetics of oxide growth and decomposition is hardly dependent on the reaction condition.

A correlation of the normalized SS intensity versus the normalized O–2p intensity is shown in Fig.3. The solid (open) circles indicate the results of the oxide growth (the decomposition). All data points are distributed closely along a dot–broken line, which is given under an assumption that the oxidized area is complementary to the clean area and an oxidized film extends two–dimensionally. A good linear correlation in Fig.3 means that the oxidation as well as the decomposition proceeds two–dimensionally. In the case of decomposition, it



Fig.3 The surface state intensity versus the O-2p intensity.

was reported that voids are developed through a thick oxide film and are expanded extensively with keeping the film thickness unchanged²⁾. Therefore it is of very important interest whether an oxidized film thickness during the two-dimensional oxidation is an atomic layer or several monolayers.

To measure the oxide island thickness, we obtained UPS spectra of a H2O-adsorbed surface at R.T. and a fully thermal oxidized surface. By use of the amount of oxygen for H2O-adsorbed surface, 0.5ML of Si-O bond,6) as criterion, the amount of oxide for fully thermal-oxidized surface was evaluated to be about 3.4ML. This estimation indicates that the oxidized film is not an atomic oxide laver but is an oxide island having a rather large height of about 3.4ML. This suggests that the initial thermal oxidation does not proceeds by a layer-by-layer mode proposed by XPS,³⁾ in which first oxygen atoms adsorbed dangling bond sites on the surface, next back bonds of surface Si atoms are attacked to form Si-O-Si bonds, and deeper Si atoms are oxidized in further oxide growth.

In Fig.4, we illustrate the present results of thermal oxidation and decomposition using a schematic reaction model. By O_2 gas supply, SiO₂ islands were made on the surface. After then, they spread over with an almost constant height of about 3.4ML, until the oxide covers a whole surface area. This inhomogeneous oxidation is similar to the oxide decomposition with void formation.

In conclusion, the thermal oxidation kinetics at an initial stage clarified by present observation is summarized as follows.

(1) The vertical oxidation rate due to oxygen diffusion through an oxide layer is very slow in comparison to the lateral one.

(2) Adsorbed oxygen atoms migrate actively on the surface and desorb if they are not incorporated into oxide islands. In the etching condition, it is considered that adsorbed oxygen desorbs because oxide islands playing a role of nucleation are not formed.

(3) The meaning that an oxide island layer is as thick as about 3.4ML is that an island consisting of suboxide components is so unstable that they are easily decomposed, and a considerably-oxidized state, that is, SiO₂ should be included in oxide islands for resistance to decomposition.

(4) The enlargement of an oxide island is balanced between the incorporation of migrating oxygen and the decomposition. Such a decomposition reaction is caused locally at a peripheral region of island as in thermal decomposition under no O_2 .

(5) Near a transition condition, two reactions of

oxidation and etching due to SiO desorption take place simultaneously and compete with each other. When a surface is fully covered with oxide, etching is considerably reduced. This is supported by the observation of the decomposition reaction, in which an oxide layer removal is considerably accelerated once voids are formed.



Fig.4 Schematic reaction model of thermal oxide growth and decomposition on Si(100).

4. REFERENCES

1) Y.-K.Sun, D.J.Bonser and T.Engel, J. Vac. Sci. Technol. A10(1992)2314.

2) K.E.Jahnsun and T.Engel, Phys. Rev. Lett. <u>69</u> (1992)339.

3) V.D.Borman, E.P.Gusev, Yu.Yu.Lebedinskii and V.I.Troyan, Phys. Rev. Lett. 67(1991)2387.

4) R.E.Walkup and S.I.Raider, Appl. Phys. Lett. 53(1988)888.

5) F.W.Smith and G.Ghidini, J. Electrochem. Soc. 129(1982)1300.

6) C.U.S Larsson, A.S.Flodström, R.Nyhdm, L.Incoccia and F.Senf, J. Vac. Sci. Technol. A5(1987)3321.

