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# In-situ UPS observation of epitaxial growth, etching and oxidation reactions on Si surfaces at high temperatures under a reactive gas atmosphere

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Chemical reactions with reactive gases are predominantly employed in various semiconductor processes for the fabrication of Si VLSI and ULSI devices. With lowering temperature to reduce the devise size, the surface migration of Si adatom becomes less active, leading to the generation of growth defect and the degradation of surface morphology, and the surface coverage of foreign atoms resulted from the dissociative adsorption of source gases increases to prevent further chemical reactions. Thus it is of practical importance in the low-temperature semiconductor process to clarify the chemical reactions on the surface and develop a technology to excite them by non-thermal methods with photon, electron and ion. In this study, surface chemical reactions during epitaxial growth, etching and oxidation on Si surfaces have been observed by ultraviolet photoelectron spectroscopy (UPS) with high surface sensitivity. In our apparatus, UPS measurements can be performed *in situ* under a reactive gas atmosphere up to $5x10^{-5}$ Torr for Si surfaces annealed at high temperatures. We have investigated each surface reaction kinetics in the light of (a) Si adatom and (b) Si dangling bond appearing on the surface during the chemical reaction.

It is well known that surface chemical reactions are strongly influenced by the surface crystal structure. For example, the hydrogen desorption kinetics is first-order on Si(100)-2x1 but second-order on Si(111)-7x7 with respect to the surface hydrogen coverage [1]. Most of surface reaction models for the hydrogen desorption kinetics are constructed based on the ideal surface structure accomplished at room temperature (Fig.1). At high temperatures where semiconductor processes are really carried out, however it should be noted that a lot of Si adatoms are released and sinked at step edges and migrate on terraces (Fig.1). Namely surface chemical reactions take place on the surface with migrating Si adatoms. Therefore the surface chemical reactions seem to be affected by the Si adatom, but its role in the surface reaction model is hardly taken into account. From the present *in-situ* UPS observations, we clarified that the Si adatom plays an important role in many surface chemical reactions: (1) the hydrogen desorption during gas-source molecular beam epitaxy (GSMBE) with $Si_2H_6$ on Si(100) is disturbed by Si adatoms [2], (2) the formation of desorption species SiCl during etching is accompanied with them, and (3) the thermal decomposition of $SiO_2$ films with void formation is caused by the supply of Si adatoms from the clean void area and Si adatoms are incorporated into oxide islands during the initial two-dimensional oxidation [4].

On the other hand, the dissociative adsorption of source gases takes place at Si

dangling bond sites on the surface, so that the surface chemical reaction rate depends strongly on the amount of Si dangling bond. Such Si dangling bonds can be apparently observed by the present *in-situ* UPS as demonstrated in Fig.2, which shows UPS spectra of the surface state (SS) due to dimer dangling bonds on Si(100)-2x1 during GSMBE with $Si_2H_6$ at $1x10^{-5}$ Torr, compared with those on the clean surface. The SS intensity during the growth decreases with temperature, indicating the increase of the surface hydrogen coverage. We found that the SS intensity shows a periodic oscillation during GSMBE, which corresponds to the Si layer-by-layer growth and enables us to measure the growth rate [5]. We call this "UPS intensity oscillation". Furthermore, by the use of the SS intensity the appearance of voids during oxide decomposition is clearly discerned [4] and the surface roughness produced by etching is examined [3].

Consequently the *in-situ* UPS observation is very useful and powerful to investigate the surface chemical reactions during semiconductor processes. Then it is important that such observations are conducted on the surfaces annealed at high temperatures under a reactive gas atmosphere.

[1] M.L.Wise *et al.*, Surf. Sci. **258**(1991)166. [2] Y.Takakuwa *et al.*, J. Cryst. Growth **136**(1994)328. [3] H.Sakamoto *et al.*, Appl. Surf. Sci. **75**(1994)27. [4] T.Horie *et al.*, Jpn. J. Appl. Phys. **33**(1994)4684. [5] Y.Takakuwa *et al.*, Appl. Phys. lett. **64**(1994)2013. Y.Enta *et al.*, Surf. Sci. **313**(1994)L797.

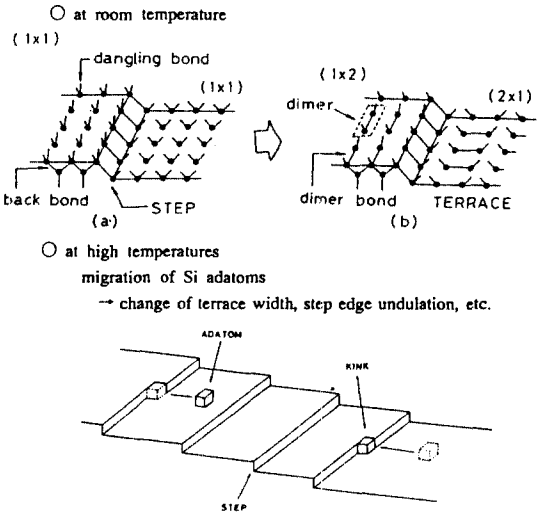


Fig.1. Schematic model of the surface morphology at room and high temperatures.

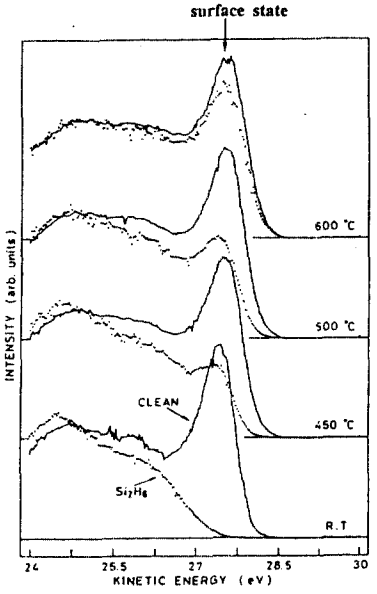


Fig.2. UPS spectra of the surfaces during GSMBE with $Si_2H_6$ at $1x10^{-5}$ Torr.