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Valence Band Spectra of Photochemically Etched Silicon Surfaces

Tsuyoshi OGURA, Tsukasa HAYASHI, Seiichi MIYAZAKI and Masataka HIROSE Department of Electrical Engineering, Hiroshima University Higashihiroshima 724, Japan

Silicon (100) surfaces were photochemically etched in NF₃ under ArF excimer laser irradiation. The valence band spectra of fluorosilyl layer formed on the etched surface have been systematically measured for the first time by using x-ray photoelectron spectroscopy (XPS). It is found that the valence band spectra clearly indicate the existence of SiF₃ and SiF₄ molecular units on the reacting surface. Also, the top of the silicon valence band underneath the fluorosilyl layer is found to shift with the progress of etching. This is explained in terms of the band bending caused by the photogenerated majority carriers trapped in the semiinsulating fluorosilyl layer.

1. Introduction

Laser induced etching process involves no high energy particles, and hence it is appropriate to produce nearly damage-free surface. In order to utilize this technique for future VLSI fabrication process. extensive work has been carried out so far.^{1,2)} In the photochemical etching of silicon with fluorine or ion induced etching, SiF_{X} (X=1,2,3,4) molecular units are created on the reacting Si surface as demonstrated from the analysis of Si2p core level photoelectron spectra measured with XPS or SOR.^{3,4)} Recently Winters⁵⁾ has proposed a fluorine etching model, in which he assumed that adsorbed fluorine atoms on the insulating fluorosilyl layer is negatively charged by capturing free electrons from the Si conduction band and consequently upward surface band bending is caused irrespective of impurity concentrations and dopants.

In this paper the valence band spectrum of reacting Si surface during the laser induced etching in NF_3 has been measured with in

situ XPS in order to investigate the chemical bonding features and electronic states of the fluorosilyl layer and near surface Si layer.

2. Experimental

The surface native oxide of a Si(100) substrate was removed by BHF solution and the specimen was mounted in a reaction chamber equipped with an XPS system. An ArF excimer laser light (193 nm in wavelength) with a pulse energy of $25 \sim 30 \text{ mJ} \cdot \text{cm}^{-2}/\text{shot}$ was incident at 45° on the silicon surface at a repetition rate of 80 Hz. NF₃ gas pressure was kept at 760 Torr. At each step of the photochemical etching the specimen was transferred into the XPS chamber with an MgKa (1253.6 eV) excitation source. The signal to noise ratio of the measured spectrum was significantly improved by the use of a microcomputer.

3. Results and Discussion

It is already established that the fluorosilyl layer is existing on the silicon

surface exposed to reactive fluorine.^{3,4)} Further study on electronic states of this fluorosilyl layer leads us to more deep understanding of the etching surface. The valence band spectra for p- and n-type Si at each stage of laser etching are shown in Fig. 1, where the binding energy was calibrated by the Si_{2p} core level signal (99.5 eV) from bulk Si. Progressive reaction on the surface results in remarkable increase of the density of states (DOS) at binding energies deeper than 10 eV. The DOS increase in the energy range 12 to 15 eV at the beginning of etching (30 sec) could be

associated with SiF and SiF_2 molecular units formed at the surface as indicated by the deconvolution study of the Si_{2p} core level spectra.³⁾ The progress of etching produces SiF_3 and SiF_4 molecular units as predominant surface products. This result coincides with the calculated density of states for SiF_3 configuration⁶⁾ and the measured valence band spectrum for SiF_4 molecule. The DOS shoulder observed at about 12.8 eV is assigned as SiF_3 and the one at 16 eV as SiF_3 and SiF_4 .^{6,7)} The DOS peak near 10.8 eV is not yet identified, but it is perhaps attributable to O_2-Si-F_2



Fig. 1 Valence band spectra for p-type Si(100) $(0.4 \sim 0.6 \Omega \text{cm})(a)$ and n-type $(3.0 \sim 4.0 \Omega \text{cm})$ (b)at each step of etching.

molecular unit produced by oxygen contamination on the surface. As shown in Fig. 1 (a) and (b) the top of the valence band shifts downward for p-type silicon and upward for n-type silicon (see Fig. 2). This is due to the band bending of near surface Si layer underneath the fluorosilyl layer. The surface fluorosilyl layer contains bonded fluorine exceeding 40 at.% and must be amorphous with an optical band gap of about 2 eV.⁸⁾ This amorphous layer is a semiinsulating semiconductor with high density of gap states. Therefore, a possible model for explaining the Si band bending is as follows: Hole-electron pair generation by a laser pulse flattens the silicon surface band as schematically illustrated in Fig. 3 (a) and (b). Photogenerated minority carriers might quickly decay through recombination, while the majority carriers are trapped into the surface fluorosilyl layer. The majority carriers trapped by the deep states can remain in the surface layer for a fairly long time, causing the band bending as shown in Fig. 3 (c) and (d).

In the case of heavily doped Si etching, n^+ -type (2×10¹⁷ \sim 1×10¹⁸ cm⁻³) and p⁺-type (3×10¹⁸ \sim 8×10¹⁸ cm⁻³) samples exhibit DOS



Fig. 2 Relative shift of the valence band edge for n- and p-type Si.

curves similar to Fig. 1. Regarding the band bending, the present model predicts that shift of the valence band edge is less significant for the heavily doped material. In fact the measured spectra definitely show no significant shift of the band edge (see Fig. 2). The result of Fig. 2 and the surface band bending model as illustrated in Fig. 3 basically agree with our previous reaction model in fluorine etching³⁾: Fluorine atom has the largest electronegativity in all elements of the periodic table, and hence fluorine atom adsorbed either on Si surface or on native oxide surface cleaves Si-Si bond or Si-O bond as a consequence of valence electron transfer from silicon site to fluorine.^{3,9)} Also the tetrahedral radius of fluorine atom





Fig. 3 Energy band diagram of Si etching surface under laser irradiation [(a) and (b)] and after the irradiation [(c) and (d)]. The thickness of the fluorosilyl layer is estimated by the Si_{2p} core level signal intensity. (0.672 A) is considerably small compared to that of Si (1.173 A), so that adsorbed fluorine can easily attack the backbonds of surface Si atom to promote the etching reaction. For explaining the high reactivity of fluorine it seems unnecessary to assume the free electron transfer from Si to adsorbed F as in the case of Winters' model.⁵⁾ Indeed, the silicon etch rate is very insensitive to the carrier concentration and dopants.³⁾ Also, the observed direction of the surface band bending of the etched surface (Fig. 2) is inconsistent with Winters' model, in which only upward band bending is assumed irrespective of carrier concentrations and dopants.

In order to have an insight on the structure of the fluorosilyl layer, we have measured the plasmon loss spectrum of the reacting surface for the first time. The spectrum is slightly broad as compared to that of crystalline Si. The loss peak appears at 17.5 eV less than the Si_{2p} core level binding energy, being identical to that of crystalline Si. The loss peak energy $\hbar\omega_{\rm p}$ is given by¹⁰⁾:

$$\hbar\omega_{\rm p} = \hbar[(\epsilon_{\rm s}/(\epsilon_{\rm s}-1))(4\pi n e^2/m)]^{1/2}.$$
 (1)

Here, n is the valence electron density, e the electronic charge, ε_s the dielectric constant and m the electron mass. Since ω_p is determined with the valence electron density, it is likely that the atomic density of the fluorosilyl layer containing a lot of fluorine is not significantly different from that of bulk Si layer.

In conclusion, SiF_3 and SiF_4 molecular units are existing in the fluorosilyl layer as revealed by the valence band spectrum. Also the valence band edge of lightly doped silicon underneath the fluorinated layer moves with the progress of etching reaction and the direction of the band bending is opposite for p-type and n-type silicon.

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