Chemical Stability of HF-Treated Si(111) Surfaces

T. Yasaka, K. Kanda, K. Sawara*, S. Miyazaki and M. Hirose

Department of Electrical Engineering, Hiroshima University *Research Center for Integrated Systems, Hiroshima University Kagamiyama 4-1, Higashi-Hiroshima 724, Japan

Growth kinetics of native oxide on Si(111) surfaces treated in pH modified BHF solutions has systematically been studied by angle-resolved x-ray photoelectron spectroscopy. A BHF treated (pH=5.3) Si(111) surface has no Si-F bonds and it is not oxidized for 300 min in clean room air. FT-IR-Attenuated Total Reflection (ATR) measurements of Si-H bonds on the BHF treated Si(111) surface have revealed that the surface is nearly step free and atomically flat. This explains the chemical stability of the Si(111) surface.

1. Introduction

A silicon surface cleaned in aqueous HF solutions is terminated mostly by Si-H bonds and a little by Si-F bonds, becoming chemically stable against the oxidation¹⁻³. It is also shown that Si-F bonds being a minority species on the surface selectively passivate chemically reactive sites such as the atomic steps³. Recently, Higashi et al.⁴ reported that atomically flat and ideally H-terminated Si(111) surfaces can be obtained by using pH modified HF solutions (pH≥5).

In this paper, the native oxide growth on Si(111) surfaces treated in aqueous HF (5% in H_2O) or pH modified HF solutions has been comparatively studied by x-ray photoelectron spectroscopy in order to get further insight on the surface chemical stabilization associated with fluorine termination and to examine the influence of the surface roughness on the native oxide growth. Based on the result of FT-IR-ATR, the origin of the chemical stability is discussed.

2. Experimental

N-type cz Si(111) wafers ($N_D \sim 10^{15} \text{ cm}^{-3}$) were used as substrates. They were cleaned in an organic solution, boiled in H₂O:H₂O₂:HCl = 86:11:3 for 10 min and dipped in H₂O:H₂O₂:NH₄OH =

4:1:1 for 2min (no boiled). The wafer was finally dipped in a 5 % HF solution or buffered HF (BHF) solutions (40% NH₄F : 50% HF=4:1 or 7:1). Si-H bonds on the chemically treated wafer was examined by FT-IR-ATR in which the incident light was P-polarized and the ATR crystal was Ge. The silicon wafer was stored in clean room air. At each step of storage time, the chemical bonding features of the Si surface was measured by x-ray photoelectron spectra (XPS) of Si_{2p} and F_{1S} core levels. The angle between the photoelectron detector axis and the direction normal to the Si surface was normally kept at 75° for the surface sensitive measurements.

3. Results and Discussion

The pH value of buffered HF solutions was varied by adding NH₄OH as shown in Fig. 1 for preparing a wide variety of surfaces. The influence of surface fluorine bonds and the surface roughness on the native oxide growth is examined. The 5% HF treated or BHF (pH=3.5, 4.5 and 5.3) treated n-Si(111) surfaces without pure water rinse were mainly characterized because the fluorine coverage is very different for these three cases as shown in Figs. 2 and 3. The Si-F bond concentration on an Si(111) surface processed in a BHF solution is reduced down to



Fig. 1 pH value for buffered HF solutions as a function of NH_4OH content X.



Fig. 2 F_{1S} core level spectra of HF-treated or BHF (pH=3.5,4.5)-treated Si surfaces.

less than one third of the HF cleaning case. NH_4OH addition to the BHF solution causes the gradual decrease of the surface fluorine bonds whose minimum quantity appears at pH=5.3 for NH_4F :HF = 7:1. Further increase of the NH_4OH concentration results in the increase of fluorine bonds originating from the surface products such as $(NH_4)_2SiF_6$. At NH_4OH fractions above X=2.5, such microcrystalline silicates precipitate on the surface and the N_{1s} XPS signal is observable at a binding energy of 398 eV and the F_{1s} signal exhibits a chemical sift from 686 eV to 688 eV.

In clean room air with 1.2% H_2O concentration at 25°C, the native oxide growth on HF or BHF treated Si surfaces is examined by analyzing the Si_{2p} spectra. The average oxide thickness is



Fig. 3 Integrated intensity ratio of F_{1s} to Si_{2p} for n-Si(111) surfaces prepared by BHF solutions as a function of NH₄OH content X.



Fig. 4 Native oxide growth on n-Si(111) after 5%HF or BHF (pH=4.5 and 5.3) cleaning in clean room air with 1.2 %H₂O at 25°C.

calculated from the integrated photoelectron intensity of the chemically shifted Si_{2p} spectrum and that of the metallic Si signal by taking into account the escape depths of the Si_{2p} photoelectrons from SiO₂ (25 A) and Si (23 A)⁵ as well as the spectrometer function³. The oxidation rate of Si(111) after BHF (pH=4.5, NH₄F:HF=4:1) cleaning is significantly faster than the case of 5% HF treatment (Fig. 4) because of the depletion of the surface fluorine bonds which passivate reactive sites on the surface3. However, note that the (111) surface obtained by the BHF cleaning with pH=5.3 for NH₄F:HF=7:1 is extremely stable despite the negligible amount of the surface fluorine bonds and no oxidation proceeds for 300 min. This apparent contradiction for the chemical



Fig. 5 Integrated intensity ratio of C_{1s} to Si_{2p} observed from n-Si(111) surfaces prepared by 5% HF or BHF (pH=5.3) solution as a function of air exposure time in a clean room.

stability of the surfaces treated with pH=4.5 and 5.3 is explained as follows: The surfaces of the HF or BHF (pH=4.5) treated wafers are atomically rough and hence the surface fluorine bonds are necessary for passivating the reactive sites such as In contrast to this the BHF (pH=5.3) steps. treated surface is atomically flat without any significant reactive sites⁴. Very low level physisorbed carbon on such a chemically inert BHF (pH=5.3) treated Si(111) surface also suggests the existence of the fairly flat (111) surface (Fig. 5). In order to verify the above model explaining the extent of the chemical stability of the surfaces, 5 % HF treated or BHF (pH=4.5, 5.3) treated Si(111) surfaces are analyzed by FT-IR-ATR. The surface roughness of the hydrogen passivated Si surfaces are evaluated from the ATR spectra as shown in The spectrum of the Si(111) surface Fig. 6. prepared in BHF with pH=5.3 is dominated by a very sharp vibrational line at 2083.7 cm⁻¹ which refers to the stretching mode of monohydride (Si-H) bond perpendicular to the surface. A shoulder at 2087 cm-1 arises also from the uncoupled vibration of monohydride bonds. The absorption intensity at 2083.7 cm⁻¹ is close to a value observed for Si-H bonds on an atomically flat surface². A small peaks at 2098 and 2107 cm⁻¹ are assigned to be Si-H₂ bonds. Main peak (2083.7 cm⁻¹) intensity of BHF (pH=4.5)-treated Si (111) is smaller than the case of pH=5.3, showing a deteriorated flatness of the surface. For a 5% HFtreated Si(111) surface the absorption intensity of



Fig. 6 Internal reflection spectra of HF-treated or BHF (pH=4.5, 5.3)-treated Si(111) surface.

Si-H is small and its linewidth is very broad. Also, the dihydride mode appears at 2098 and 2107 cm⁻¹. This indicates that the HF treated surface is significantly rough. Nevertheless, the native oxidation rate of 5% HF treated Si(111) is slower than that of BHF (pH=4.5) treated surface because the surface reactive site such as steps is passivated with Si-F bonds³.

In conclusion, an atomically flat surface is found to be chemically stable as demonstrated for the case of a BHF (pH=5.3) treated Si(111) surface. HF-treated Si(111) surface is rather rough, but it is fairly stable because reactive sites such as atomic steps or microfacets are protected by fluorine. A rough surface with very low fluorine coverage is easily oxidized.

References

- T. Takahagi, A. Ishitani, H. Kuroda, Y. Nagasawa, H. Ito and S. Wakao: J. Appl. Phys. 68 (1990) 1.
- Y. J. Chabal, G. S. Higashi and K. Raghavachari: J. Vac. Sci. & Technol. A 7 (1989) 2104.
- T. Sunada, T. Yasaka, M. Takakura, T. Sugiyama, S. Miyazaki and M. Hirose: Jpn. J. Appl. Phys. 29 (1990) L2408.
- G. S. Higashi, Y. J. Chabal, G. W. Trucks and K. Raghavachari: Appl. Phys. Lett. 56 (1990) 656.
- S. I. Raider and R. Flitsch, IBM J. Res. Develop. 22 (1978) 294.