

Influence of Microscopic Chemical Reaction on the Preparation of Oxide Free Silicon Surface in Fluorine-Based Solution

Yoshihiro Sugita and Satoru Watanabe

Fujitsu Laboratories Ltd., 10-1 Morinosato-Wakamiya Atsugi 243-0197, Japan
Phone: +81-462-50-8241, Fax: +81-462-48-3473, E-mail: sugita@flab.fujitsu.co.jp

Introduction

Protective oxide on Si surface should be removed with fluorine based solution to form low resistance metal contact. It is known that the removing oxide from damaged Si surface, highly boron doped (P⁺⁺) Si surface or poly-Si surface requires longer etching time than that expected from the oxide thickness [1-4]. The residual oxide will degrade the electric performance of high speed devices. Furthermore, the residual oxide as hydrophilic site on the surface will cause unfavorable additional oxide growth under subsequent water rinse and transportation in moist atmosphere and enhance the fluctuation of process conditions. However, long time dipping in fluorine based solution degrade the reliability of isolation insulator.

From a view point of wet chemistry, complete removal of the oxide from Si surface means the formation of hydrogen terminated hydrophobic surface. It can be said that problems on oxide removing is not caused by the "strong oxide film" against wet etching but some kinds of chemical reaction which interrupt the hydrogen termination of surface Si bond.

We found an interruption reaction of surface hydrogenation in HF solution [5, 6], that is, mono-hydride silicon (Si-H) was selectively replaced with hydroxyl group (Si-OH) while di-hydride silicon (Si-H₂) was stable against such reaction. Because Si-H is formed on such surface defect as (111) or (110) facets on the (100) substrate, the reaction on micro-facet-defects must be clear. In this paper, the re-oxidation mechanism during oxide removing in fluorine based solution is discussed and the improving of oxide removal for ion implanted surface is shown.

Results and Discussion

We compared the contact angle of water on Si(100), (110) and (111) surfaces with a dropped water method after immersion in fluorine based solution, because the contact angle is quite sensitive to the residual oxide and hydroxyl (OH) on Si surface [2, 3]. The observation gave us important information to understand the reaction on "processed Si(100) surfaces" with (110) and/or (111) oriented micro facets. We also observed the surface silicon-hydride and hydroxyl structure with Fourier transform infrared spectroscopy (FT-IR) sensitized with attenuated total reflection (ATR) technique.

Figure 1 shows the contact angle of water on thermally oxidized Si surfaces as a function of the immersion time in 0.6% HF solution (etch rate: 3nm/min). The hydrogenation rate of Si surfaces are different in the substrate crystal orientations, that is, it takes a very long time to hydrogenate the (111) or (110) surfaces while the (100) surface is immediately hydrogenated at when the oxide film is removed. It is known that the surface hydride structure on (111) and (110) are mostly mono-hydride and

mono-hydride chain, and the (100) surface is mainly terminated with di-hydride [7-9]. We have already revealed that the byproduct of oxide dissolution selectively re-oxidize the mono-hydride silicon [6]. In Fig. 2, it is shown that the evidence of selective oxidation in byproduct (H₂SiF₆) solution, that is, mono-hydride on both (111) and (110) surfaces are replaced with OH in H₂SiF₆ solution while the (100) surface does not oxidized in that solution. When the substrate surface was roughened by reactive ion etching or ion implantation, OH will be formed on the (110) or (111) related facets on the (100) substrate during oxide dissolution in HF solution, as illustrated in Fig. 3.

It was suggested that SiF₆²⁻ ion was thermodynamically unstable and turn to be oxide state silicon in low pH fluorine based solution (< pH 2) and the oxidation formation from such byproduct could be suppressed in higher pH solution [10]. We examined the oxide removal property changing the pH of solutions buffered with NH₄F (pH 2~7, etch rate: 3nm/min) and found that hydrogen termination degree was drastically improved with increasing the pH, as shown in Fig. 4. Homogeneous mono-hydride termination both on Si (110) and (111) surfaces were quickly formed in the neutral (pH 7) solution. It is supposed that the morphological influence on the hydrogenation of Si surface could be negligible in such solution.

The complete removal of oxide from P⁺⁺ Si surface is quite difficult and the oxide residence increase with the increasing of hole (h⁺) concentration in the substrate [2, 3]. In Fig. 5, hydrophobicity measured with the contact angle of water are shown for BF₂⁺ (25kV, annealing: 950°C- 5min) implanted 5nm-SiO₂/Si(100) samples. Using a neutral fluorine based solution (pH 7), hydrophobicity on P⁺⁺ surface was also improved. This is attractive for metallization process, because the reaming surface OH population can be reduced with the same or less etching thickness of isolation insulator. The saturated hydrophobicity depends on boron concentration or boron dose in both pH 7 and pH 2.6 solutions, as seen in Fig. 5. We suppose that the effect of h⁺ and surface-defects on OH formation reaction could be separated using a neutral solution. This will be helpful to resolve the complex phenomena on the P⁺⁺ surface in solution.

Summary

It was found that selective oxidation reaction limited the hydrogen termination of Si surface during the oxide removing from Si surface in HF solution. Formation of OH group on mono-hydride on Si surface was suppressed in neutral fluorine based solution. The oxide removing property from highly boron implanted surface was also improved by using the solution. This is attractive for the metallization of electronic devices.

References

- [1] N. Aoto, M. Nakamori, H. Hada, T. Kunio and E. Ikawa: Ext. Abst. 1993 Int. Conf. Solid State Devices and Materials, Makuhari (1993) 101.
- [2] Y. Sato and M. Maeda: Jpn. J. Appl. Phys. **33** (1994) 6508.
- [3] T. Kosugi, H. Ishii and Y. Arita: J. Vac. Sci. Technol. **A15** (1997) 127.
- [4] A. Philipossian, M. Moinpour, R. Wilkinson and V. H. C. Watt: Mat. Rec. Soc. Sympo. Proc. **386** (1995) 75.
- [5] S. Watanabe: Surf. Sci. **341** (1995) 304.
- [6] Y. Sugita and S. Watanabe: Ext. Abst. 1997 Int. Conf. Solid State Devices and Materials, Hamamatsu (1997) 446. Jpn. J. Appl. Phys. **37** (1998) 1193.
- [7] E. Yablonovitch, D. L. Allara, C. C. Chang, T. Gmitter and T. B. Bright: Phys. Rev. Lett. **57** (1986) 249.
- [8] Y. J. Chabal, G. S. Higashi, K. Raghavachari and V. A. Burrows: J. Vac. Sci. Technol. **A7** (1989) 2104.
- [9] S. Watanabe: Surf. Sci. **341** (1995) 304.
- [10] K. Osseo-Asare, D. Wei and K. K. Mishra: J. Electrochem. Soc. **143** (1996) 749.

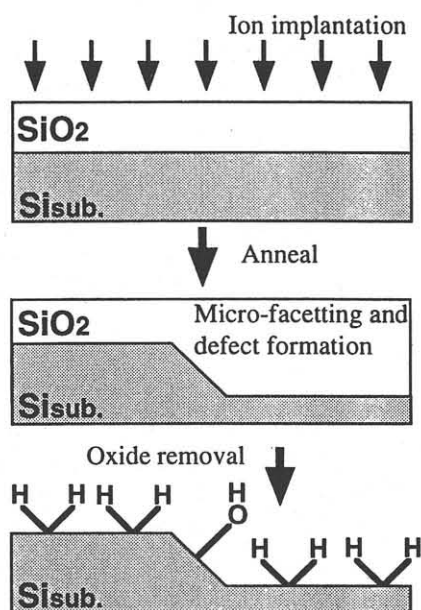


Fig. 3 A model of hydroxyl formation on ion implanted Si(100) surface in HF solution.

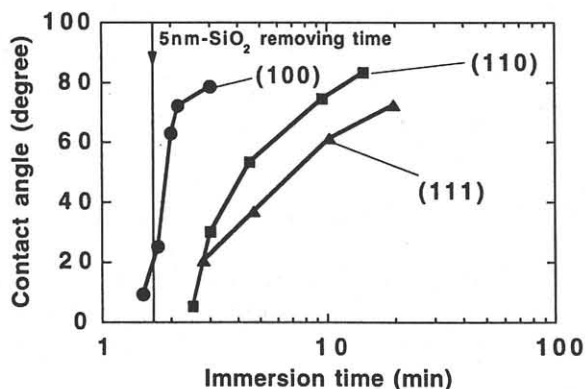


Fig. 1 Contact angle of water on Si surfaces as a function of immersion time in 0.6% HF solution (3 nm/min). The substrates were initially covered with 5nm-thick thermally grown oxide.

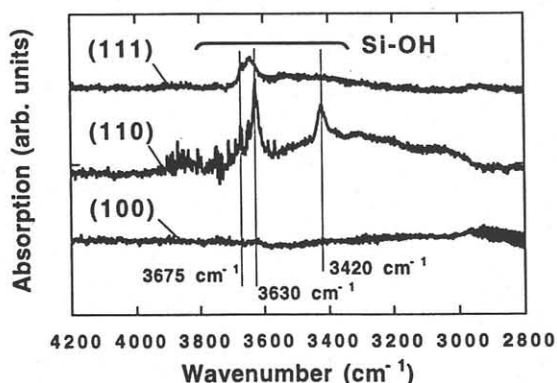


Fig. 2 FT-IR ATR spectra of O-H stretching on Si(111), (110) and (100) surfaces. The substrates were initially terminated with hydrogen using 5% HF solution, and then immersed in 3% H_2SiF_6 solution for 120 min.

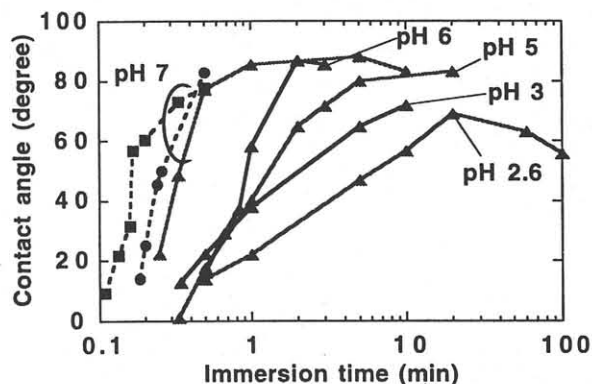


Fig. 4 Contact angle of water on Si(100), (110) and (111) surfaces as a function of immersion time in some fluorine based solutions. The substrates were initially covered with chemically grown oxide. The triangles mean the (111), the circles mean the (110) and the squares mean the (100).

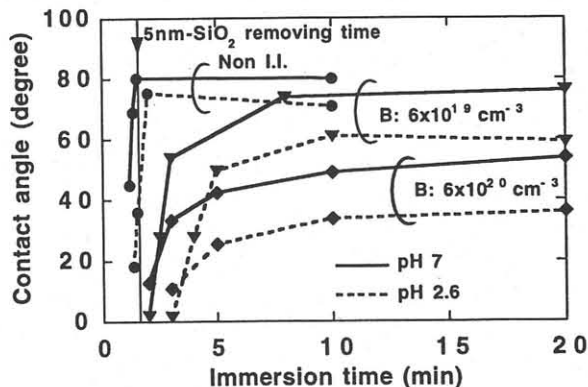


Fig. 5 Contact angle of water on BF_2^+ implanted Si(100) surfaces as a function of immersion time both in a pH 7 solution and a conventional HF solution (pH 2.6). The substrates were initially covered with thermally grown oxide. The solid lines means a pH 7 solution and the dotted lines means a HF solution.