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Chemical treatment effects of silicon surfaces in aqueous KF solution

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Abstract

The physical and chemical properties of Si(1 1 1), (1 1 0) and (1 0 0) surfaces treated in aqueous KF solution have been studied by means of spectroscopic ellipsometry (SE), ex situ atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and wettability measurements. The SE data indicate that the solution causes the removal of the silicon native oxide upon immersing the sample in the solution. The KF-treated Si(1 1 0) and (1 1 1) surfaces are nearly flat even after long-time etching. By contrast, the Si(1 0 0) surface is found to be considerably etched and roughened even if the etching time is shorter than the native oxide is completely etch-removed ($t < 30$ min). The SE-estimated surface roughness is in reasonable agreement with the AFM rms value. The XPS data suggest that the KF-treated surface is cleaner than that etched in an HF solution. The as-degreased silicon surface is hydrophilic ($\theta \sim 35^\circ$), while the KF-treated surface is hydrophobic ($\theta \sim 80^\circ$). The properties of the KF-treated surface have also been discussed as compared to those obtained in aqueous NaF and HF solutions.
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1. Introduction

A clean silicon (Si) surface is one of the most important requirements in the fabrication of various silicon devices. Aqueous HF solution is popularly used for this purpose. It has now been well established [1–5] that the cleaning of silicon surfaces in HF, buffered-HF or NH_4F solution can produce stable, hydrogen-terminated surfaces. Such a hydrogen-terminated surface is hydrophobic and passivated against oxidation in air.

Recently, Levenets et al. [6] reported that treatment with aqueous HBF_4 solution results in the removal of the silicon native oxide and may leave behind the

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silicon surface terminated by atomic hydrogen and fluorine. Aqueous solutions of another fluorine-based chemicals, such as NH_4BF_4 and H_2SiF_6, have also been shown to attack the silicon native oxide and leave behind a shiny flat surface [7–9].

More recently, it has been shown that an aqueous solution of NaF causes the removal of the native oxide on Si(1 1 1) upon immersing the sample into the solution [10]. Note that NaF is a salt and is popularly used in dental clinics as protecting a decayed tooth. The etching rate of the 1 M NaF solution for the silicon native oxide was determined to be ∼0.2 Å/min. It is interesting to point out that an aqueous salt solution can etch-remove the silicon native oxide. We speculated in Ref. [10] that etching of the silicon native oxide is due to HF species produced by an alkaline reaction caused by partial hydrolysis:

$$NaF + H_2O \leftrightarrow Na^+ + OH^- + HF \quad (1)$$

If it is fact, we can also expect an etching of the silicon native oxide in aqueous KF solution. This is because there is no significant chemical difference between these two solutions. The only difference may be the pH value, i.e. the pH of a freshly prepared saturated (∼1 M) NaF solution is 7.4, while that of a saturated (∼16 M) KF solution is larger than this value.

The main objective of this study is to examine whether aqueous KF solution can etch-remove the silicon native oxide. The use of alkaline solutions, such as aqueous KOH, NaOH and NH_4OH, as anisotropic etchants for crystalline silicon was popularized about 30 years ago [11]. The large etching anisotropy in such alkaline solutions makes it possible to prepare structures such as V-shaped, vertical and inclined grooves in Si(1 0 0), (1 1 0) and (1 1 1) wafers [12–17]. Because of the alkaline solution of aqueous KF (see Eq. (1)), we can also expect an anisotropic etching of silicon using this solution. In order to confirm this, we study the chemical treatment effects on Si(1 1 1), (1 1 0) and (1 0 0) in aqueous KF solution. Spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and contact-angle measurements are performed for these purposes. The surface properties of silicon treated in 5 M KF solution are discussed as compared to those obtained in 1 M NaF and 0.75 M (1.5%) HF solutions. It should be noted that KF is less toxic and easier to handle than HF. Of course, preparing clean semiconductor surface is of both technological and scientific interests.

2. Experimental

The samples used in this study were single crystals of (1 1 1), (1 1 0) and (1 0 0) orientations. They were first degreased using organic solutions in an ultrasonic bath and then rinsed in deionized (DI) water. No further cleaning of sample surfaces was performed. The sample surfaces to be studied were, therefore, covered with native oxide of 1–2 nm thickness.

The KF chemical used was of 99.0% purity supplied by Wako Pure Chemicals Industries, Japan. The 5 M KF solution (pH ∼ 7.6) was prepared by dissolving KF in DI water. For comparison, 0.75 M (1.5%) HF solution was prepared by diluting high-purity (50%) HF with DI water. A large quantity of both the solutions was prepared to prevent a variation of the etching solution composition during the experiment. Chemical treatments were performed at room light and at 20 °C. The chemically treated samples were rinsed in DI water.

The automatic ellipsometer used was of the polarizer–sample–rotating–analyzer type (DVA-36VW-A, Mizojiri Optical). A 150 W xenon lamp was used as a light source. SE data were measured over the photon-energy range of 2.5–5.0 eV at room temperature. The angle of the incidence and the polarizer azimuth were set at 70° and 30°, respectively. The SE measurements were performed immediately after the sample was rinsed in DI water.

The surface microstructures were investigated by ex situ AFM, using a Digital Instruments Nanoscope III. The AFM images were acquired in the tapping mode and in the repulsive force regime with a force constant of the order of 1 nN between the AFM tip and sample surface. The silicon wafers were cut in sizes of about 8 mm × 8 mm squares, and the central area of each sample was examined using AFM.

The XPS measurements were performed using an ULVAC-PHI Model 5600 spectrometer equipped with a Mg Kα (1253.6 eV) line as an X-ray source. The taking-off angle of photoelectrons was 45°. Si 2p and C 1s core levels were mainly examined.

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