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Stability of hydrogen-terminated vicinal Si(1 1 1) surface under ambient atmosphere

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ABSTRACT

In this paper a comparative study of different wet-chemical etching procedures of vicinal Si(1 1 1) surface passivation is presented. The stability against oxidation under ambient atmosphere was studied by X-ray photoelectron spectroscopy and atomic force microscopy. The best results were achieved by the buffered HF etching and the final smoothing of the surface by hot (72 °C) NH_4F. The procedures consisting of a large number of etching steps were unsatisfactory, since the probability of contamination during each step was increasing. The passivated surface was stable against oxidation for at least 3 h under ambient atmosphere.

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1. Introduction

The passivation of silicon surface has been attracting attention of physicists and technologists since Yablonovitch et al. [1] showed that a simple HF treatment results in an inert hydrogen-terminated surface, which is stable against native oxidation for a long time. Since then, a significant effort was put to the understanding of the nature of passivation and optimization of the etching process, so that a surface as close as possible to an ideal hydrogen-terminated one would be created. Such a hypothetical surface consists of atomically flat terraces divided by monoatomic steps, contains no defects and is stable against oxidation for an infinite time. Higashi et al. [2] have shown that NH_4F is a better etchant than HF, since the resulting surface is very smooth and shows no microscopic roughness as observed on HF etched samples [3,4]. The microscopic roughness is controlled by the pH value of the etchant [5] the best results were achieved with pH 3–8. The use of an etchant with pH < 3 consequently resulted in rough terraces. However, if the 40% NH_4F solution is used (pH 7.8) the surface may exhibit so-called etch-pits [6]. These have a triangular shape on Si(1 1 1) and can be several nanometers deep, thus increasing surface roughness. The dissolved oxygen contained in an etchant solution was identified to be responsible for the etch-pit initiation and growth [6–8]. It has been shown by several groups, that if etchant with a significantly low concentration of dissolved oxygen is used, an atomically smooth surface is obtained. The preparation procedures of such a superior surface differ from group to group [8–11]. Generally, the first step is degreasing (usually in acetone), followed by different cleaning procedures, with a so-called Radio Corporation of America (RCA) process being the most widely used. Afterwards, the sample may undergo a final etching, or a sequence of oxidizing/etching steps. As a final etchant NH_4F is usually used.

In semiconductor industry, many steps in nanostructure fabrication are (and will be) inevitably interrupted with queue times, which increases the probability of silicon wafer oxidation, particle contamination and an increase of microroughness, finally resulting in a degradation of device characteristics or eventually malfunction. As many passivation procedures have been published, comparative studies of their efficiency are useful. The oxidation of a passivated surface under ambient conditions was previously studied [12–17], however, in these studies only a small

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variety of preparation procedures was tested. The main purpose of this paper is to compare a wider ensemble of several different procedures for the passivation of silicon samples with respect to their stability against oxidation in time.

The surface studied is vicinal Si(1 1 1) due to its importance as a natural template for ordered growth of quantum dots and nanowires [18]. A high density of steps makes this surface more susceptible to oxidation in comparison with low miscut angle samples, since the oxidation starts at surface steps and kinks. We show that the sample treated by an optimum etching procedure remains free from the oxide even for a few hours after its exposure to ambient atmosphere.

2. Experimental details

We used an n-type Si(1 1 1) wafer (P-doped, 0.03 Ω cm) cut at 4° off the (1 1 1) plane to the $\langle 1\ 1\ \bar{2} \rangle$ direction. Samples cut to the $\langle \bar{1}\ \bar{1}\ 2 \rangle$ direction were not tested; note that the optimum procedure for this miscut direction may differ due to a different nature of hydrogen termination at step edges [19]. The wafer was cut into 12 mm × 14 mm samples; these were blown over with nitrogen gas and treated in a hot (120 °C) piranha solution (1:4 solution of concentrated H_2SO_4 and 30% H_2O_2) for 10 min to remove organic contaminants. Afterwards they were thoroughly rinsed in ultrapure water (>10 MΩ cm) and treated according to different preparation procedures as listed in Table 1. These can be systematically divided into two groups – the first one with procedures carried out by etching in 40% NH_4F and buffered HF (further denoted as BHF, 1:5 solution of 38% HF and 40% NH_4F) for various times (4–30 min) or by the BHF pre-etch and the final preparation of the surface using room temperature or the hot (70 °C) NH_4F solution. The second group includes procedures containing oxidation steps (using 80 °C H_2O, 120 °C piranha solution or a 1:1:4 solution of 35% HCl, 30% H_2O_2 and H_2O). Between each step (pre-etching, oxidation, final etching step) the sample was rinsed in water. In order to remove dissolved oxygen, the final etchant (NH_4F or BHF, except hot NH_4F) was sparkled by N_2 gas for at least 30 min. The samples were etched in a carefully cleaned teflon labware, preferably in the vertical position, since NH_4F etching is accompanied by the formation of hydrogen bubbles at the edges of the sample, which may cause an inhomogenous etching.

After the final step, the sample was dried again with nitrogen and inserted into an UHV chamber for X-ray photoelectron spectroscopy (XPS). In order to increase surface sensitivity a photoelectron emission angle of 80° (according to the surface normal) was used. After XPS analysis the sample was transferred back into ambient conditions (clean-room grade 100,000, T = 24 °C, humidity 45%) and periodically (1 h periods) inserted again into the UHV chamber to monitor the oxidation process by XPS. The XPS measurement usually took 35 min from the insertion of the sample into the vacuum to its re-exposure to ambient atmosphere.

Table 1
Cleaning sequences used in this study.

Procedure	Pre-etch	Oxidation step	Final etch
1	×	×	BHF
2	BHF	×	NH_4F, RT, 6 min
3	BHF	×	NH_4F, 70 °C, 30 s
4	×	×	NH_4F, 4–30 min
5	BHF	H_2O, 80 °C, 10 min	NH_4F, RT, 6 min
6	BHF	Piranha, 120 °C, 10 min	NH_4F, RT, 6 min
7	BHF	$HCl/H_2O_2/H_2O$, 10 min	NH_4F, RT, 6 min

The optimum value for stripping out the native oxide using BHF (pre-etch) was 6 min.

The surface roughness was measured on a separate set of samples (prepared in the same way) by atomic force microscopy (AFM AutoProbe CP-R, Veeco) in contact mode using the same tip with a nominal diameter <10 nm. Since the tip dimensions are larger than the expected terrace width (4.5 nm at 4° miscut), we cannot resolve individual steps laterally from each other. Nevertheless, single etch-pits and step bunches were clearly observed in our images as the vertical resolution was well below 1 nm.

3. Results of etching experiments

A typical Si 2p peak obtained using XPS after the initial cleaning in piranha solution is shown in Fig. 1a; the same part of the spectra taken after etching in NH_4F for 15 min is shown in Fig. 1b. No peak component related to an oxide is present in the spectrum taken from the etched sample. The Si 2p peak was fitted using the Voigt functions. The parameters of the peak components used for the decomposition of the Si 2p peak are given in Table 2. The Si^{2+} component related to the SiO suboxide is not shown in the table due to a very low intensity in each fit as expected, for the SiO suboxide is extrinsic for the (1 1 1) surface orientation [20].

The oxide thickness was determined according to the procedure described by Seah and Spencer [22]. Note that for an emission angle of 80° this procedure underestimates the oxide thickness by ∼10% in the thickness range studied in this paper (due to a strong effect of elastic electron scattering). In the calculation the oxide layer is considered to grow in the layer-by-layer growth mode.

The time evolution of oxide thicknesses as determined from XPS measurements is shown in Fig. 2. The results from the samples treated by the procedures 1–4 are shown in the upper graph. The lower graph shows the data taken from the samples treated by the procedures 5–7, which all include an oxidation step between the

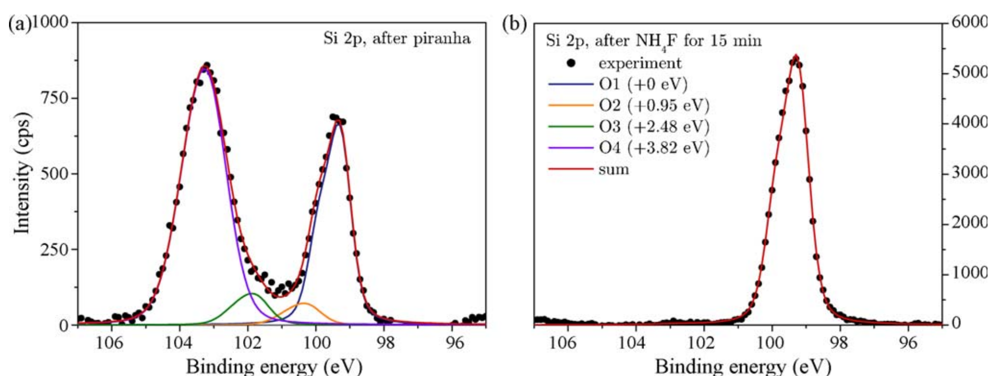

Fig. 1. The detail of the Si 2p peak taken after the initial cleaning in the piranha solution (a) and after the etching in NH_4F for 15 min (b). The decomposition into peak components is shown in different colours; the peak component parameters are given in Table 2.

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