Surface Science 605 (2011) 1027–1033

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/ locate/susc

X-ray diffraction analysis of the silicon (111) surface during alkaline etching

I.A. Shah, Q.D. Nguyen, H.G.G. Philipsen, B.M.A. van der Wolf, R.G. Algra, P. Tinnemans, A.J. Koekkoek, N. Panina, F.J.M. van den Bruele, W.J.P. van Enckevort *, E. Vlieg

Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

ARTICLE INFO

Article history:
Received 15 November 2010
Received in revised form 15 February 2011
Accepted 28 February 2011
Available online 9 March 2011

Keywords:
Surface X-ray diffraction
Silicon
Alkaline etching
Surface termination
Interface structure

ABSTRACT

We present a surface X-ray diffraction determination of the silicon (111)-liquid interface structure during alkaline etching. Preparation of an atomically smooth surface was realized by an *in-situ* procedure using an aqueous NH_4F solution devoid of oxygen. Using diluted aqueous potassium hydroxide (KOH) and ammonium fluoride (NH_4F) etchant, we have observed that the crystal surface is hydrogen terminated and is not reconstructed at open circuit potential. In addition, a partial liquid ordering of two water layers on top of the crystal surface was found, indicating a weak interaction with the hydrophobic, hydrogen terminated surface. We have followed *in-situ* the development of the oxide layer by a birth and spread mechanism during anodic passivation of the silicon surface.

1. Introduction

Aqueous Potassium Hydroxide (KOH) and Ammonium Fluoride (NH_4F) solutions are commonly used as etching solutions in wet chemical anisotropic etching of silicon, a widely used bulk technique in the manufacturing of Micro Electro Mechanical Systems (MEMS) [1,2]. In terms of chemical and electrochemical reaction mechanisms, the etching process appears to be well understood [3–6]. The simplicity of the overall reaction, however, masks the complicated etching mechanism and the solid–liquid interactions at the surface involved. Understanding the fundamental way in which the silicon {111} surfaces etch is of high importance in understanding and influencing the aspect ratio of etching different crystallographic planes of silicon, the basis of MEMS manufacturing.

Several studies have discussed the surface termination during alkaline wet chemical etching of silicon [7–10] and all conclude a H-terminated silicon surface. A variety of studies has been conducted to investigate the dynamic changes during etching [9,11,12] and the role of surface preparation. As a result, several reaction mechanisms are proposed. More recently, experiments were performed to further investigate the surfaces under electrochemical etching conditions [5,6]. These researches were conducted to study the dynamic changes during etching, e.g. by using voltammogrammy, spectroscopy or optical methods. Although these methods have been used extensively, the resulting information on the interface structure is only derived indirectly. Therefore, the most suitable *in-situ* techniques are scanning probe microscopy and surface X-ray diffraction. Observing the surface with Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) provides interesting and detailed information on small areas [7,13]. On the contrary, the surface X-ray diffraction technique gives direct information on large sample areas.

The aim of this study is to determine the surface structure of silicon (111) and its interaction with the etchant liquid under etching conditions. Surface X-ray Diffraction (SXRD) is a very suitable technique for studying the solid–liquid interface of the silicon in the alkaline etchant. Therefore, we present an *in-situ* SXRD investigation of the silicon-etchant interface under electrochemically controlled conditions. This research focuses on the solid–liquid interface of silicon (111) in anisotropic wet chemical solutions with KOH and NH_4F. Knowledge of the interface interactions during etching obtained in this way may provide a better understanding on the overall reaction mechanism and the underlying atomic processes.

2. Experimental procedure

In order to perform *in-situ* SXRD on this system, the surface has to be clean and smooth at an atomic level and etching needs to proceed slowly to avoid kinetic roughening during the measurements. In addition, the electrochemical potential of the sample needs to be controlled in order to avoid rapid roughening by etching through the electrochemical pathway. Subtle changes in sample preparation can have detrimental effects on the obtained surface quality and therefore an extensive investigation was undertaken to obtain the best recipe for obtaining atomically smooth surfaces.

* Corresponding author. Tel.: +31 24 3653433; fax: +31 24 3653067.
E-mail address: W.vanEnckevort@science.ru.nl (W.J.P. van Enckevort).

0039-6028/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2011.02.025

2.1. Sample cell and specimens

The purpose of the sample cell is to observe the surface structure by X-rays during etching in a transmission geometry (Fig. 1). In designing the *in-situ* cell, the sample surface was chosen to be above all other cell parts, as in this way the incoming X-rays arriving at low angles are not blocked. The materials chosen to construct the cell had to be inert to the chemicals used during the experiments. The cap was made of poly(methylmethacrylate) (PMMA) with a thickness of 1 mm, as this has the lowest absorbance of X-rays in the energy range used of the suitable materials. The other parts of the cell were made from standard laboratory glassware. The design of the cell allows for easy filling and replacing of the different solutions before and during the experiments.

The sample holder on which the silicon sample was mounted was made out of Kel-F (Fig. 1b). To create a back contact with the working electrode, the silicon sample was scratched from the backside, and cleaned with Piranha Acid (98% H_2SO_4:35% H_2O_2 3:1) for 10 min to remove any organic contaminants and consecutively rinsed 10 times with ultrapure water and blown dry in a stream of argon. Ga–In eutectic was applied to part of the silicon backside and the sample was glued to the copper back contact on the remaining part using a two component epoxy resin. As direct contact between glue and etching solution leads to additional roughness, a viton O-ring is mounted on the silicon sample to seal the sample. This assembly is then placed in a Kel-F sample holder and tightened with a nut from the back side to assure a leak-proof connection. The connection was tested for conductivity in a saturated KCl solution, after which the sample was rinsed 10 times with ultrapure water. All connections in the cell were sealed with silicone and viton O-rings (see Fig. 1).

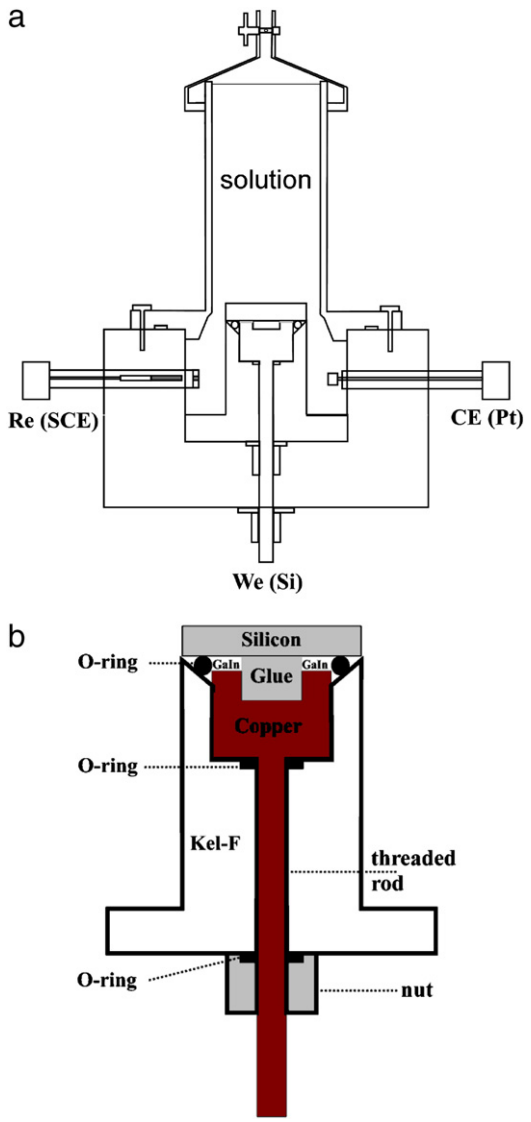

Fig. 1. Schematic drawing of the sample cell used for the X-ray diffraction experiments: (a) overview; (b) detail, showing the Kel-F sample holder with the silicon crystal mounted on top. The sides of the silicon crystal are unprotected and serve as a sacrificial area promoting oxide removal and formation of stepped terraces. The total height of the cell is approximately 15 cm.

To obtain a well-defined initial surface for surface diffraction, the silicon sample was immersed in an NH_4F solution as elaborated in Section 2.3. This extremely anisotropic etchant is known to give ultra-flat silicon(111) surfaces, provided that the solution is oxygen-free and the sample is 'cathodically protected' by a sacrificial anodic area [7,12,14–18]. To create such a sacrificial area, the silicon samples were connected to a Cu mount in such a way that the sample sides remain in free contact with the solution as can be seen in Fig. 1 and thus provide the cathodic protection [5].

Experimentally, X-ray photons can excite electrons into the conduction band and introduce a photocurrent through the electrochemical pathway [4,5]. This leads to significant etching and creates surface roughness that prohibits the diffraction measurement. Specifically on n-type material this effect is observed and preliminary experiments confirmed these observations. To avoid this, full electrochemical control is necessary and p-type material has to be used. A cathodic potential (-1.3 V) is applied. To avoid influence of photocurrents induced by normal light, all experiments were performed in the dark by fully covering the cell with thin aluminium foil, to minimize blockage of the X-rays. The Cu working electrode is joined with a Pt counter electrode and a Saturated Calomel Electrode (SCE) reference electrode in an electrochemical setup in which a potentiostat is used for control. The Pt and SCE electrodes are placed in the designated positions of the *in-situ* cell (Fig. 1). The electrodes are connected with the potentiostat, first the reference, then the counter and finally the working electrode. The potentiostat (PalmSens) is set on a cathodic potential applied to the silicon sample before filling the cell with an etchant solution, to avoid surface roughening due to the initial etching of the surface. The experiments were performed at room temperature and during etching the current was measured using the potentiostat.

Hexagonal shaped p-type silicon (111) samples, with 6.8 mm diameter and cut from p-type silicon (111) wafers (Okmetic, Boron doped, diameter 100 ± 0.5 mm, thickness 525 ± 25 μm, resistivity 5–10 Ω·cm, miscut $< 0.5°$) were used. The hexagonal shape of the silicon fits best with the shape of the used o-rings and thus a leak tight sealing of the sample back contact is achieved. The silicon used was as-grown and underwent several cleaning steps as described above to reduce the impact of any organic or metal impurities.

2.2. Surface X-ray diffraction

The surface X-ray diffraction technique (SXRD) is very useful for the structure determination of the interface between a crystal surface and solution [19]. In SXRD, diffracted X-ray intensities along the so-called crystal truncation rods are measured [20]. These rods are tails of diffuse intensity connecting the bulk Bragg peaks in the direction perpendicular to the surface. Their exact shape is determined by the atomic structure of the solid–liquid interface.

In the setup used (see Fig. 1), the silicon crystals can be completely surrounded by bulk etchant solution, but ambient air conditions are also possible. The experiments were performed at the DUBBLE, ID03 and ID32 beam lines of the European Synchrotron Radiation Facility (ESRF) in Grenoble, using an X-ray energy of 20 keV, as lower X-ray energies do not sufficiently penetrate the liquid layer surrounding the