

In situ Raman spectroscopy study on silicon surface in $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ and $\text{HCl}/\text{H}_2\text{O}_2$ aqueous solutions

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Abstract

The chemical nature of Si(100) surfaces during immersion in $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (SC-1) and $\text{HCl}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (SC-2) has been investigated in situ using confocal Raman spectroscopy. In SC-1 solution, there are two kinds of oxides at the silicon surfaces. One oxide is originated from the effect of NH_4OH , the other is associated with hydrogen and forms due to the coaction of NH_4OH and H_2O_2 . In SC-2 solution, the silicon surface is covered mainly with oxides caused by H_2O_2 . It has been found that a few Si–H bonds exist at the silicon surfaces in both solutions. The chemical model of the silicon surface in the solutions has been discussed in the paper. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicon wafer; Raman spectroscopy; Surface; Chemical bonds; Chemical cleaning

1. Introduction

In the fabrication of ultra-large-scale integration circuits (ULSI), RCA wet chemical cleaning process is one of the widely used cleaning techniques for obtaining extremely clean silicon surface. In RCA process, $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (SC-1) mixture is used for the removing of particle on the wafer surface, and $\text{HCl}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (SC-2) mixture is applied to clean the surface metal contaminant [1]. However, the etching mechanism of silicon surfaces in these solutions has not been understood very well. It is necessary to elucidate and examine how the chemical state of silicon surface changes in these solutions. In the past, Fourier transform infrared spectroscopy in the attenuated total internal reflection geometry (ATR-FTIR) was generally used to investigate the surface chemical states [2,3]. There were only few reports of Raman study on silicon surface bonds [4,5]. Surface Raman spectroscopy has some advantages over other vibrational spectroscopy in monitoring the surface bonding in situ during the etching process [5]. Our approach is to in situ measure the Raman spectra of Si(100) surface during immersion in SC-1 and SC-2 mixture. From these spectra, the chemical model of the silicon surface in these solutions may be developed.

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2. Experimental

Experiments were performed on 200 mm diameter, $\rho \sim 15\text{--}25 \text{ } \Omega\text{cm}$, p-type Si(100) polished wafers. Before Raman measurement, the wafer surface was roughed to obtain a better ratio of signal to noise because the Raman signal from mirror-polished surface was very weak. An electrochemical roughing was applied in this experiment. After RCA cleaning, the Si wafer was anodized with a current of about 5 mA cm^{-2} for 2 min in $\text{HNO}_3\text{:HF:H}_2\text{O}$ (3:5:1). It was then rinsed with and preserved in deionized (DI) water prior to Raman measurement. A scanning electron microscopic result of Si surface after enduring the above roughing process showed that the surface was rough but not porous, there were fine structures in each bump of average diameter of about $2\text{--}5 \text{ } \mu\text{m}$. Raman measurements were performed on a confocal Raman system (Renishaw 1000) with microscope. Each measurement was repeatedly taken at least twice. The excitation line was 514.5 nm from an Ar^+ laser. Acquisition time was 200 s. To observe the etching process, the solutions used in the experiment were very dilute. $\text{NH}_4\text{OH:H}_2\text{O}_2\text{:H}_2\text{O}$ in SC-1 and $\text{HCl:H}_2\text{O}_2\text{:H}_2\text{O}$ in SC-2 were 1:1:100. To study the respective effect of NH_4OH and H_2O_2 , the Raman spectra of Si wafers during immersion in $\text{NH}_4\text{OH/H}_2\text{O}$ ($\text{NH}_4\text{OH:H}_2\text{O} = 1:100$) and $\text{H}_2\text{O}_2\text{/H}_2\text{O}$ ($\text{H}_2\text{O}_2\text{:H}_2\text{O} = 1:100$) were also measured in situ.

3. Results and discussion

In situ Raman spectra of Si surface from SC-1 are shown in Fig. 1. Since the band around 2110 cm^{-1} is attributed to surface Si–H bond vibration based on the IR results [6,7], the left-hand scale of Fig. 1 demonstrates that there are a few Si–H bonds at the silicon surface during immersion in SC-1. The right-hand scale of Fig. 1 indicates the change of silicon surface oxides during the etching

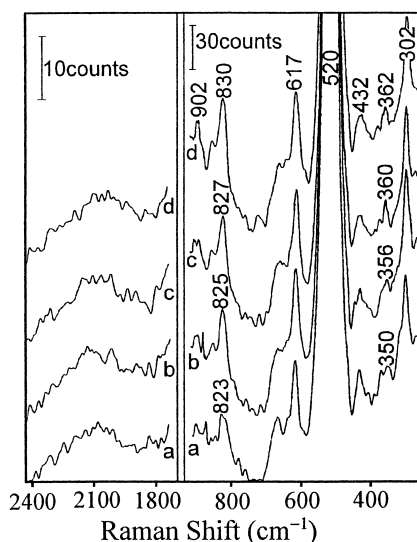


Fig. 1. In situ Raman spectra of Si surface during immersion in SC-1 of different etching time: (a) 0 min, (b) 10 min, (c) 20 min, and (d) 30 min.

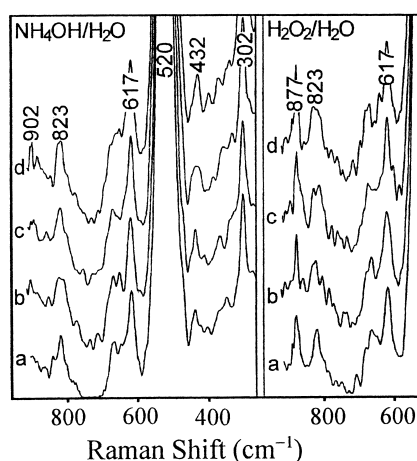
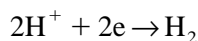


Fig. 2. In situ Raman spectra of Si surface during immersion in $\text{NH}_4\text{OH}/\text{H}_2\text{O}$ (left-hand scale) and $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (right-hand scale) of different etching time: (a) 0 min, (b) 10 min (c) 20 min, and (d) 30 min.

process. The bands at 520 cm^{-1} , 302 cm^{-1} , 617 cm^{-1} and 432 cm^{-1} in this scale are assigned to silicon [8].

Fig. 2 shows the in situ Raman spectra of Si surface during immersion in $\text{NH}_4\text{OH}/\text{H}_2\text{O}$ and $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixtures. In this figure, the left-hand scale demonstrates the process of NH_4OH etching, whereas the right-hand scale shows the effect of H_2O_2 at silicon surface. Since the intensities of two bands at 902 cm^{-1} and 877 cm^{-1} in the figure increase gradually during the etching process, the two bands should be assigned to oxides caused by NH_4OH and H_2O_2 , respectively.

According to the Raman result in $\text{NH}_4\text{OH}/\text{H}_2\text{O}$ mixture (see Fig. 2), it can be concluded that the band at 902 cm^{-1} in Fig. 1 is originated from NH_4OH of SC-1 solution. Because the intensity of this band increases gradually, more and more oxides are generated at the silicon surfaces during the SC-1 etching process. In basic solutions, silicon is etched through the following reactions:



Silicon is oxidized in the reactions, and then the resultant is dissolved by the solution. During the period of reaction, there would be an oxide transition layer whose Raman frequency is 902 cm^{-1} . Hydrogen might be associated with the oxide since the oxide layer forms due to the effect of OH^- ions.

From Fig. 1, we can find that the position of bands at 823 cm^{-1} and 350 cm^{-1} shifts gradually during the etching process. One band shifts from 823 cm^{-1} at the beginning of etching, to 825 cm^{-1} (etching time is 10 min), 827 cm^{-1} (20 min) and 832 cm^{-1} (30 min). The other band shifts from 350 cm^{-1} to 356 cm^{-1} , 360 cm^{-1} , and 362 cm^{-1} . The intensities of both bands increase continuously in the etching process. Only Si–H, Si–O or hydrogen-associated SiO_x could be generated at the silicon surface in SC-1 mixture. Based on the theory of Raman excitation [9], the vibrational frequency of hydrogen-associated oxide should vary with the content of hydrogen. With the increasing of hydrogen content, the frequency should increase. Accordingly, the two bands should be attributed to hydrogen-

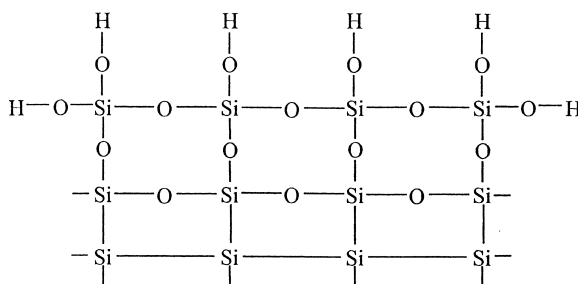


Fig. 3. Chemical model of silicon surface in SC-1 solution.

associated oxide, in which the hydrogen content increases along with the etching process. This oxide forms owing to the coaction of NH_4OH and H_2O_2 , and is different from that caused by NH_4OH . As a result, there are two kinds of oxides at the silicon surface in SC-1 mixture.

Based on the Raman results, a possible chemical model of the silicon surface in SC-1 solution may be developed. At the beginning the etching, the surface should be covered by Si–O, Si–F, or Si–H bonds because of the electrochemical roughening in $\text{HNO}_3/\text{HF}/\text{H}_2\text{O}$ solution. As the etching processes, the surface bonds are gradually substituted by Si–O–H bonds, as shown in Fig. 3. Accordingly, the hydrogen content at the silicon surface increases gradually along with the etching process. Both Si–O–H and Si–O–Si bonds at the surface are attacked by OH^- ions in the solution and break up. As a result, Si=O bonds are generated and make up of $(\text{SiO}_3)^{2-}$ ions, which can be dissolved by the solution. This will require further investigations since the silicon surface chemical reaction in SC-1 mixture is a very complex process.

In situ Raman spectra of Si surface during immersion in SC-2 mixture are shown in Fig. 4. The left-hand scale of the figure demonstrates that there are a few Si–H bonds at the silicon surface. From the right-hand scale, we can identify clearly the 877 cm^{-1} band caused by H_2O_2 according to the

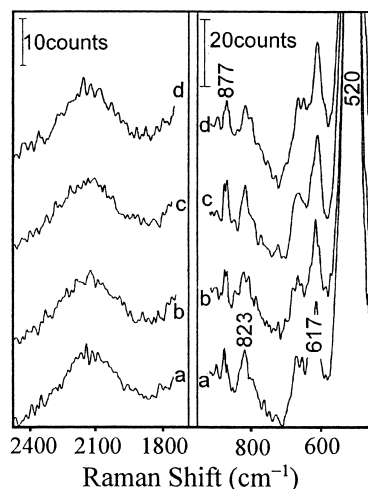


Fig. 4. In situ Raman spectra of Si surface during immersion in SC-2 of different etching time: (a) 0 min, (b) 10 min, (c) 20 min, and (d) 30 min.

above analysis. Therefore, the silicon surfaces are oxidized by H_2O_2 and terminated mainly with Si–O bonds. The hydrochloric acid in SC-2 solution does not etch the silicon surface.

4. Conclusions

A method of confocal Raman spectroscopy has been applied to study the chemical state of Si surfaces during immersion in SC-1 and SC-2 solutions. It has been observed that two kinds of oxides exist at the Si surface in SC-1 mixture. One is caused by NH_4OH , the other forms owing to the coaction of NH_4OH and H_2O_2 and is associated to hydrogen, in which hydrogen content increases gradually during the etching process. In SC-2 solution, the oxidation of silicon by H_2O_2 is the main reaction at the Si surfaces. There are a few Si–H bonds at the Si surfaces in both solutions.

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