Analyses of HF/NH₄F buffer-treated Si(111) surfaces using XPS, REM and SIMS

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Abstract. The effect of different cleaning procedures on Si(111) wafers has been studied. A three-step cleaning process was used. The first two steps (thermal oxidation followed by RCA cleaning) were common to all samples. The final step involved rinsing in one of a set of HF/NH₄F buffer solutions with a wide range of pH values. Three different surface techniques were used for characterizing the chemical condition and morphology of the treated surfaces: XPS (X-ray Photoemission Spectroscopy), REM (Reflection Electron Microscopy) and SIMS (Secondary-Ion Mass Spectroscopy). It has been found that the pH value of an HF solution does significantly affect the etching rate and morphology of the Si(111) surface: For the same type of solution, the smaller the pH value, the higher the etching rate. Basic solutions with pH values larger than eight have a much weaker etching effect on the surface, which is contradictory to some previous reports. The most effective solutions for the etching of the Si(111) surface are the solutions of HF buffered by NH₄F, with the pH in the range of 2-6. REM images indicate that the surface morphology after etching in the HF solution is strongly affected by the length of the etching time: Over-etching will roughen the surface. The SIMS data show that water rinsing in air during the cleaning process does speed up oxidation, but it is necessary to use water to clean off the residuals from the HF solutions.

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The dimensions of electronic devices are progressively decreasing. In electronic circuits with structure of dimensions well below a micron and film thickness in the range of nanometers, even a small number of atoms of the wrong kind or at the wrong sites may devastate the performance of the device [1, 2]. This makes silicon-wafer-surface preparation increasingly important in semiconductor manufacturing and it is clear now that the key to high yield is to pay particular attention to wafer cleaning. On the other hand, preparing a silicon surface, with the chemical status and morphology well characterized and controlled at the atomic level, also merits fundamental interest in surface science. The understanding of the detailed mechanisms of the oxidation, reduction and etching processes involved in wafer cleaning is both essential for high device yield and challenging to surface science. But current knowledge of the cleaning mechanism is very limited.

The traditional RCA cleaning [3-5] used by electronics industries for many years is currently challenged by processes such as H-termination of the silicon-wafer surface, in which the wafer surfaces are first oxidized thermally or by UV/ozone photooxidation and then cleaned by HF-dipping [6-21]. The chemical condition and morphology of HF-treated silicon surfaces have been studied by various techniques: X-ray Photoemission Spectroscopy (XPS) [7-9, 11, 13], Infrared Spectroscopy (IRS) [6, 10, 14, 15, 17, 20, 22, 24], Auger Electron Spectroscopy (AES) [12, 14], Electron Energy-Loss (reflection) Spectroscopy (EELS) [13], Scanning Tunneling Microscopy (STM) [16, 19], Atomic Force Microscopy (AFM) [18, 23], and Secondary-Ion Mass Spectroscopy (SIMS) [21]. The HF-treated surface is passivated against reoxidation and becomes hydrophobic because of the hydrogen termination of the surface [7]. In this paper, we report the results of wet cleaning of the Si(111) wafer surface by using HF/NH₄F buffer solutions with different pH values. Some results contrary to previous reports are discussed. Three different techniques are used for characterizing the chemical states and morphology of the surface: XPS, Reflection Electron Microscopy (REM) and SIMS.

1 Experimental

An As-doped n-type Si(111) wafer (~ 2 Ω·cm) misoriented by less than 3° was used in this study. Surface cleaning was carried out in three major steps: 1) Conventional thermal oxidation (1000°C for 2h) to move the interface away from any residual polishing damage, followed by dipping in an [HF-buffered] solution (NH₄HF:HF = 7:1) for 10 min to remove the silicon oxide layer; 2) a complete cycle of RCA cleaning [3-5] to remove both organic and
inorganic particles from the surface; 3) the thin silicon oxide layer formed after the RCA cleaning was then stripped off by dipping in HF-buffered solutions with different pH values for different lengths of time. All HF-buffered solutions were at room temperature. The wafer surface was rinsed with purified Deionized (DI) water (ρ > 18.2 MΩ) between each two sequential cleaning steps. After the final steps of dipping and rinsing, the wafer surface was blown dry with N₂ from the gas outlet in the laboratory.

The sample was then mounted onto the sample holders in air and installed in the chambers of the XPS (Perkin Elmer 5400) and SIMS (Cameca IMS 5F) spectrometers and the electron microscope (Philips EM420) within ~5 min. The load-locks were prepumped [to a pressure < 10⁻⁶ torr] within ~5 min. Both the XPS and SIMS spectrometers operated under UHV conditions with a base pressure of ~10⁻⁹ torr, while the electron microscope had a conventional vacuum, pressure ~10⁻⁷ torr. The technique of surface imaging by REM has been well documented [25, 26]. For XPS, the take-off angle was set at 30° and an MgKα (1253.6 eV) X-ray source was used. Throughout the preparation, Teflon vessels and tweezers were used. They have been cleaned with a strong oxidation solution [H₂SO₄ + K₂Cr₂O₇, 9000: 5 (wt)] and repeatedly rinsed by purified DI water. The chemicals used throughout the experiments were purchased from Aldrich Chemical Co.: HF (liquid, 48.5 wt.%, 99.99 + %), NH₄F (37.04 wt.%, 99.99 + %), H₂O₂ (31.4 wt.%, 99.999%), NH₂OH (35.05 wt.%, 99.99 + %) and HCl (36.46 wt.%, 99.999%).

The first column of Table 1 lists seven different HF solutions. C₁ is HF at high concentration with pH < 1, while in C₂ the HF solution is diluted by purified DI water. The HF-buffered solution (C₃) was made by dissolving solid NH₄F in the HF solution with the mole ratio of NH₄F: HF = 7:1. C₃ was made from C₄ by adding HCl acid of high concentration and adjusting the pH value lower to ~2. C₅ and C₆ are two NH₄F solutions with different weight percentages, 28.6 wt.% and 40 wt.%, respectively. The pH value of an NH₄F solution with a normal concentration ( < 30 wt.%) is 6.2, while the solution with extremely high concentration ( > 40 wt.%) becomes a base, pH = ~8. The pH value of C₆ was measured with a pH meter with two-digits accuracy. C₇ and C₈ were made by adding NH₂OH to C₄ and C₆ to give pH values 9.0 and 9.5, respectively. Thus we have eight solutions with both H⁺ cations and F⁻ anions, while their pH values are in the range from strong acid to strong base. The presence of F⁻ anions is necessary for the etching and H-terminated passivation of Si but the concentration of the ions does not seem to be important.

### Results and discussions

The first sign of obtaining a clean and passivated Si-wafer surface was the hydrophobic nature of the treated wafer: small pieces of wafer floating on the surface of the aqueous solutions. After RCA cleaning without further HF-dipping (Co), all wafers showed a clear hydrophilic property: the aqueous solution wets the wafers very well. In other words, the surfaces were covered by oxide layers as previously reported [3–5]. However, the nature of the oxide layer formed during the RCA cleaning procedure is not within the scope of the present paper. All samples just before being dipped in the HF-buffered solution were considered to be in the same condition since they were collectively processed in the RCA solutions. The wafers further treated by C₇ and C₈ solutions were also hydrophilic. All wafers further treated by C₁–₆ presented hydrophobic properties. The wafers treated by C₈ appear less hydrophobic: The floating pieces are easy to sink. This hydrophobic vs hydrophilic nature of processed wafers is well correlated with XPS data as shown in Table 1.

| Table 1. The first column lists seven different HF solutions with different PH values. The next four columns list the results of XPS analyses of the Si wafers etched by the eight prepared HF solutions for different times |
|-----------------------------------------------|----------------|----------------|----------------|----------------|
| pH   | 1 min | 5 min | 10 min | 20 min |
| C₆ No final HF-etching                        |               |      |       |       |
| C₁ 27.5M HF                                   | < 1           | 6.5% | 3.8% | 1.0% |
| C₂ 0.5M HF                                    | ~ 2.0         | 10.5%| 11.8%| 1.9% |
| C₃(NH₄F:HF = 7:1) + HCl)                      | ~ 2.0         | 0.8% | 0    | 0.4% |
| C₄(NH₄F:HF = 7:1)                            | ~ 4.0         | 0    | 1.6% | 1.8% |
| C₅ 28.6 wt% NH₄F ~ 6.2                        | ~ 7.8         | 9.9% | 12.8%| 12.2%|
| C₆ 40 wt% NH₄F ~ 7.8                          | ~ 9.0         | 0.63 ML | 0.87 ML | 0.85 ML | 0.42 ML |
| C₇ (NH₄F:H = 7:1) + NH₂OH                     | ~ 9.5         | 36.8 | > 1 ML |       |
| C₈ (NH₄F:NH₂OH = 1:1.6)                       | ~ 9.5         | > 1 ML |       |       |