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A New Insight into Atomic Scale Morphology of H-Terminated Si(100) Surfaces Studied by FT-IR-ATR and Scanning Probe Microscopies

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Using FT-IR-ATR and AFM and STM, we have systematically studied hydrogen terminated Si(100) surfaces. These surfaces were obtained by varying the solutions for removal of the chemical oxide grown during the SC1 clean step. We find that the smoothest surfaces are obtained by an acidic HF-solution containing an oxidizing component such as H_2O_2. Surfaces treated in, for example, an $HF:H_2O_2 = 1:9$ solution exhibited an FT-IR-ATR spectrum dominated by the asymmetric $=Si-H_2$ stretching mode while AFM and STM studies verified the formation of parallel steps on such surfaces. On the other hand, a basic solution such as NH_4F resulted in locally rougher surfaces. For such surfaces, we found a correlation between the observations of large amount of $-Si-H_3$ termination and round structures on the Si(100) surface.

1. INTRODUCTION

As MOS device dimensions are scaled down, control of the Si surface on an atomic scale during processing is becoming more and more important, especially for the gate oxidation step. Although the Si(100) surface is used extensively in CMOS manufacturing, control of its surface morphology has proven to be more challenging than for the Si(111) surface. Heyns et al. and Ohmi et al. have shown that reducing the concentration of NH_4OH in the SC1 cleaning solution reduces the roughness of Si(100)[1,2] and improves electrical properties such as the break-down voltage[2]. We would like to point out that basic solutions such as NH_4OH but also NH_4F and KOH all promote the formation of Si(111) facets. Therefore, the observed reduction in roughness in Refs. 1 and 2 were due to the reduction of the number and size of Si(111) facets formed during the SC1 cleaning step as the NH_4OH concentration was decreased. From these results we believe that in order to obtain smooth Si(100) surfaces, solutions containing high concentration OH^- must be avoided during the final treatment before oxidation. That leads one to consider acidic solutions such as dilute HF for removal of the chemically grown oxides. Once the oxide is removed and the Si surface exposed, different solutions might etch or oxidize the surface isotropically or anisotropically. The ideal solution for planarizing Si(100) would selectively etch or oxidize defects on the surface while not attacking the Si(100) planes. As an example, Hirose et al. found that adding H_2O_2 to the HF-based solution for oxide removal yields smoother surfaces as probed by FT-IR-ATR (Attenuated Total Reflection)[3].

In this study, we have investigated a range of solutions for removal of chemical oxides from Si(100) that yield significantly different FT-IR-ATR spectra in the region of $Si-H_x$ stretching vibrations. Most of these solutions contain acids but we have also included a base, NH_4F, which have proven to be the best solution for obtaining flat Si(111) surfaces[4]. In addition, we have studied the surface morphologies on an atomic scale by AFM and STM after treatment in same solutions, will also discuss correlations between FT-IR-ATR and scanning probe microscopy results.

2. EXPERIMENTAL PROCEDURES AND RESULTS

The Si(100) substrates used in this study were cut from 10 Ω-cm p-type CZ wafers. After cleaning in a low NH_4OH concentration ($NH_4OH:H_2O_2:H_2O$ = 0.15:3:7) SC1 clean at 80°C, the chemically grown oxide was removed in one of the following solutions: 40 % NH_4F, 50% HF, 0.1% HF, 0.1% HF + 1% H_2O_2, or $HF:H_2O_2 = 1:9$.

As is illustrated in Fig. 1, concentrated HF treatment results in an ATR spectrum dominated by a broad dihydride peak at 2108 cm^{-1} and a significant contribution from trihydrides around 2137 cm^{-1}. On the other hand, concentrated NH_4F yields a spectrum where the dihydride peak sharpens and shifts to 2104 cm^{-1} (symmetric dihydride stretching mode, D_{ss}). $HF(50\%):H_2O_2(30\%)$ = 1:9 results in a third characteristic spectrum, where a very sharp dihydride peak at 2114 cm^{-1} now dominates the spectrum (asymmetric dihydride stretch, D_{as}). At the same time, the trihydride peak at 2137 cm^{-1} is reduced significantly, while a monohydride peak appears at 2088 cm^{-1}. The narrower FWHM of the dihydride peak indicates that this treatment should result in a reduction of the surface

roughness compared to that of the other two treatments. In addition, since the H-atoms experience less repulsive forces in the asymmetric vibrational mode we would expect this mode to appear on smooth Si(100) surfaces.

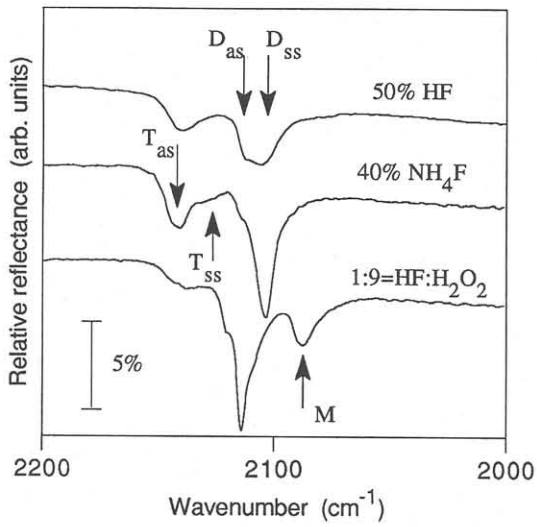

Fig. 1. Three characteristic ATR spectra from H-terminated Si(100).

The growth of the asymmetric dihydride stretching mode was studied in more detail by comparing treatments in 0.1% HF, 0.1% HF + 1% H_2O_2, or HF:H_2O_2 = 1:9 as shown in Fig. 2, where we notice a clear correlation between the sharpness of the dihydride stretching mode and the growth of the monohydride peak around 2088 cm^{-1}.

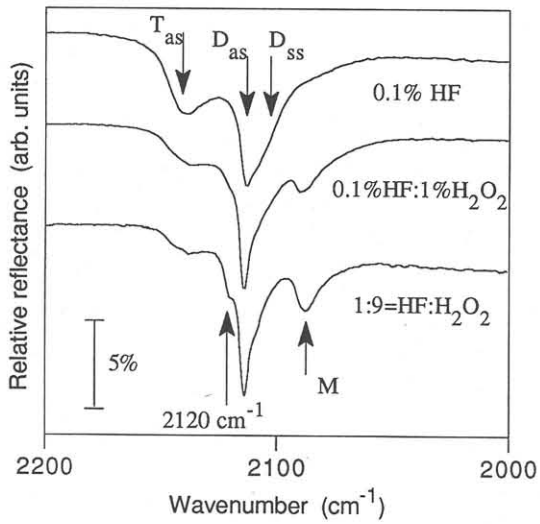

Fig. 2. ATR spectra showing the evolution of the dominant asymmetric dihydride mode.

When the above surfaces were studied by AFM and STM we found no significant differences in the roughness measured over a 5x5 μm^2 scan area. However, we did observe differences when the scan area was reduced. As Fig. 3 shows, surfaces that have significant trihydride and symmetric dihydride modes showed the formation of round pits and islands but no atomic scale step features. These observations were confirmed by STM in UHV, showing 0.5 - 1 nm tall round islands of diameter less than 10 nm.

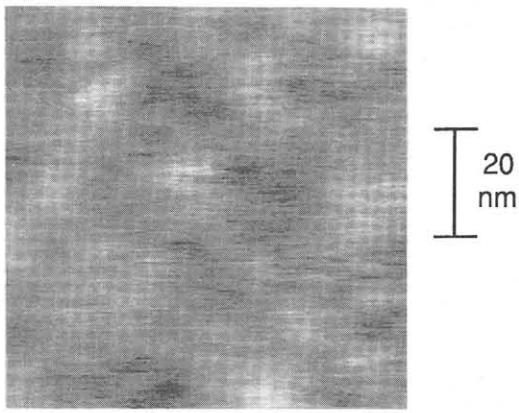

Fig. 3. AFM image of NH_4F treated Si(100).

In contrast, parallel steps were observed on HF:H_2O_2 = 1:9 treated surfaces for scan areas less than 100x100 nm^2, which is illustrated in Fig.4. Also, when the scan area was reduced to 25x25 nm^2, we were able to observe atomic scale step features on the same surfaces that exhibit a sharp asymmetric dihydride stretching mode in the ATR spectrum in Fig. 2. Again, this observation was confirmed by STM, showing the formation of parallel steps less than 10 nm apart. This terrace width corresponds to a miscut angle of more than 0.8° although the wafers were guaranteed to be within 0.5° of the (100) direction. Therefore, the local miscut angle is larger than global one and the surface appears to be corrugated.

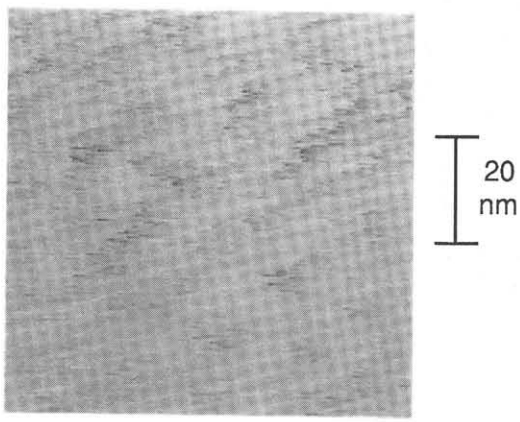

Fig. 4. AFM image of 1:9=HF:H_2O_2 treated Si(100).

4. DISCUSSION

As mentioned above, surfaces that have significant trihydride and symmetric dihydride modes showed the formation of round pits and islands in the AFM images.

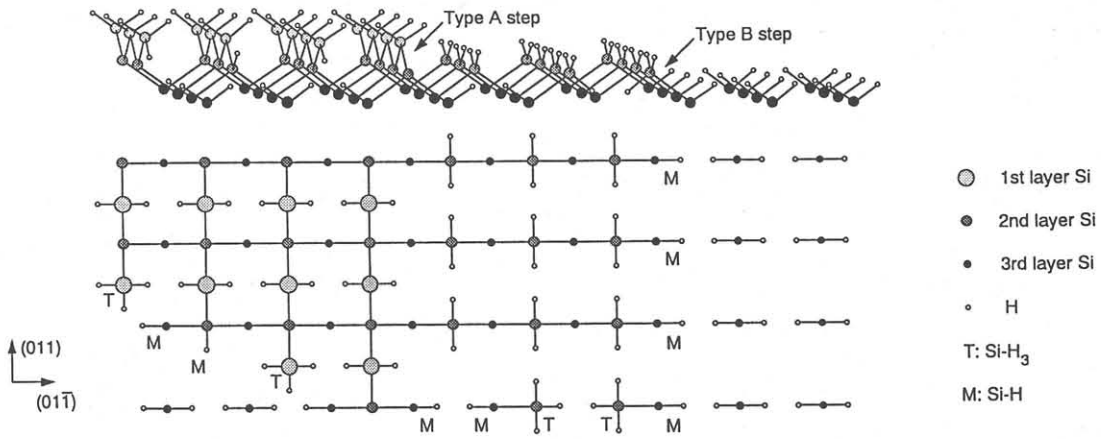

Fig. 5. Side and top view of H-terminated Si(100).

This is explained by the model structure of the H-terminated Si(100) surface in Fig. 5, which illustrates that trihydrides will be observed if the surface exhibits at least double-height steps that are neither parallel nor perpendicular to the rows of ideally dihydride terminated Si-atoms on the terraces. Therefore, any round structures in the plane of the surface of more than a single-height step will yield the highest density of trihydrides than structures of any other shape.

In contrast, we found correlations between the growth of the asymmetric dihydride stretching mode and observations of parallel steps for AFM scan areas less than 100x100 nm^2. On the same surfaces, we also observed a sub-peak around 2120 cm^{-1} (see Fig. 2), whose peak height was proportional to that of the monohydride peak. We interpret this mode as dihydrides coupled to neighboring monohydrides which results in the observed blue-shift. As illustrated in Fig. 5, there are several defect sites where monohydrides will be observed in the neighborhood of dihydrides. The one thing in common for all these sites is that atoms are missing from the surface layer of a Si(100) terrace, for example, at the so-called type B steps in the (011) or (01$\bar{1}$) directions, which we believe is the most probable site for the coupled mode. These monohydrides will always be observed on ideally stepped Si(100) surfaces and their density relative to that of the dihydride termination depends on the local roughness of the corrugated surface, i.e., the density of type B steps. We should point out that Chabal et al. and Watanabe et al. have preliminary assigned a coupled mode between dihydride and monohydride on the Si(111) surface in the neighborhood of the trihydride mode, i.e., 2137 cm^{-1} [5-6]. However, we believe this shift is too large while the peak we observed at 2120 cm-1 is shifted only 6 cm^{-1} from the asymmetric dihydride mode. Other monohydride sites are at steps in any direction that is neither parallel nor perpendicular to the rows of ideally dihydride terminated Si-atoms, or at single atom height defects on the terrace.

On the other hand, trihydrides can only be observed if atoms are missing from the second silicon layer. Therefore, the presence of trihydrides indicates an atomically rougher surface compared to one exhibiting monohydrides together with the dominating asymmetric dihydride peak. Our results show that a mixture of HF and H_2O_2 yields monohydride termination together with the predominant asymmetric stretch of the dihydride mode, indicating a smoother surface than that of the other treatments.

5. CONCLUSIONS

By varying the solutions for removal of the chemical oxide grown during cleaning of Si(100), we have observed changes in the H-termination as probed by FT-IR-ATR spectra and the corresponding surface morphology as probed by AFM. Surfaces that have significant trihydride and symmetric dihydride vibrational modes showed the formation of round pits and islands in the AFM images. This correlation between FT-IR-ATR and AFM results for NH_4F treated surface was predicted since trihydrides will be observed if the surface exhibits at least double-height steps that are neither parallel nor perpendicular to the (011) or (01$\bar{1}$) directions. In addition, we found correlations between the growth of the asymmetric dihydride stretching mode and observations of parallel steps by AFM on surfaces treated in mixtures of HF and H_2O_2.

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