In situ real-time study of chemical etching process of Si(100) using light scattering

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We report the development of an *in situ* real-time light scattering technique to study the wet chemical etching process of Si(100). Based on a simple scattering theory, the number of etch pits and other statistical parameters such as correlation length and interface width on a pitted surface are extracted from the scattering profile. The time evolution of the surface morphology can be interpreted by a simple rate equation. © *1996 American Institute of Physics.* [S0003-6951(96)02528-4]

Real-time monitoring of the growth/etch front morphology of thin films is an extremely important task. Real-time measurements would allow us to obtain fundamental knowledge of the growth/etch front dynamic behavior. With this knowledge one can then better control the growth/etch front morphology by controlling the deposition/etching parameters. A variety of methods using electron, atom, or optical beams are now available for *in situ* study of thin-film growth. Among these techniques, optical beams are particularly promising for use in a hostile environment such as chemical vapor deposition or chemical etching of a surface. Examples of optical techniques are spectroscopic ellipsometry (SE) and various versions of reflectance spectroscopies (RS).[1] Information such as growth rate and average interface rms (root-mean-square roughness) can be obtained in real time. However, one can only obtain one statistical parameter of the rough surface from some of these techniques, e.g., the volume fraction from SE, and the rms from RS. The lateral information (correlation length) and the degree of roughness (roughness exponent) are not available. Light scattering has the advantage of providing all these roughness parameters simultaneously.[2] In this letter, we report the use of the light scattering technique to monitor the surface pit formation during the chemical etching of a Si(100) surface. It is shown that the dynamics of pit formation can be studied quantitatively.

A schematic illustration of the experimental setup is shown in Fig. 1. The light scattering system was previously described in detail.[2] The detector array, which consists of 1024 photodiodes, has a resolution of 10^{-7} Å^{-1} in momentum space (k space). The range of momentum transfer parallel to the surface, $k_{\parallel}$, can be measured up to 10^{-4} Å^{-1}. Here $k_{\parallel}=(2\pi/\lambda)\sin\gamma$, where γ is the in-plane scattering angle and λ is the wavelength of the laser. Each scattering profile can be obtained within 30 ms. The sample used was a commercial p-type Si(100) wafer with a resistivity in the 10–20 Ω cm range. It was degreased with organic solutions in an ultrasonic bath, followed by a rinse in deionized (DI) water, and then dipped into HF(49%) solution for 1 min to remove the native oxide. Finally, it was placed at the bottom of a homemade Teflon container with the polished surface facing upward. The etching experiment was performed in a HNO_3–HF–CH_3COOH solution [HNO_3(69%–71%):HF(49%):CH_3COOH(99.7%)=1:2:7] at room temperature. The average etch rate was determined to be 0.1 μm/min by measuring the mass loss after etching for a long time.

To avoid the direct light scattered from the air/solution interface getting into the detector array, the wafer was tilted away from the horizontal level as shown in Fig. 1, so that the reflected beam from the air/solution interface and the scattered beam from the silicon wafer can be separated spatially. The setup was mounted on an optical table with isolators. The peak shift and the intensity change in the light scattering profile due to the vibration of the liquid surface were measured to be in the order of 10^{-7} Å^{-1} and 1%, respectively. The bubbles on the silicon surface created by the etching reaction were blown away by using a Teflon dropper during the light scattering measurement while the etching continued.

Figure 2 shows four representative light scattering profiles collected at various etching times: 0, 20, 40, and 80 min.

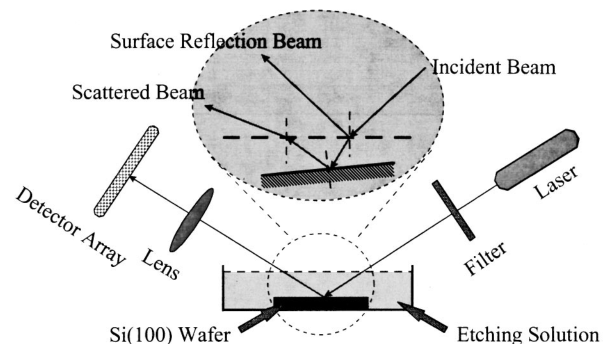


FIG. 1. A schematic of the experimental chemical etching setup.

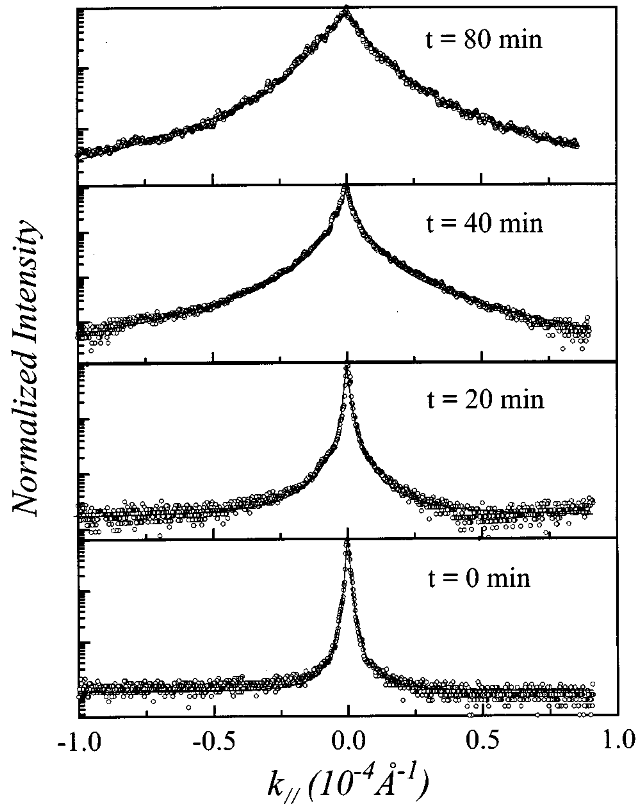


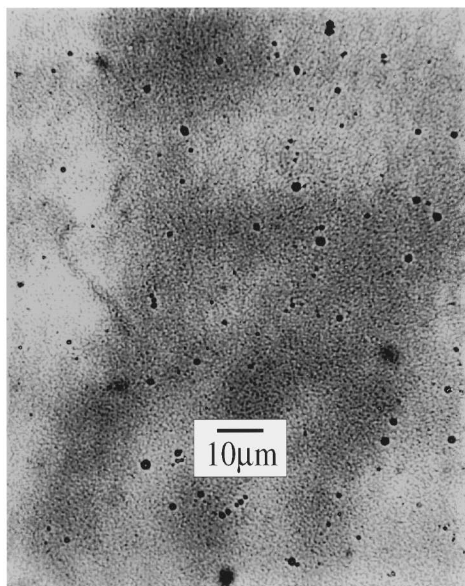
FIG. 2. Time dependent light scattering profiles during chemical etching of Si(100) surface: open circle: experimental data; solid curve: best fit by two Lorentzian shapes, one of them has a fixed width of 5×10^{-7} Å^{-1}, due to the instrumental broadening.

The initial profile ($t=0$) has only one sharp peak, with a full-width-at-half-maximum (FWHM) of 5×10^{-7} Å^{-1}, which corresponds to the instrumental broadening. However, as the etching proceeds, a diffuse profile gradually appears which superposes onto the sharp peak. With increasing etch time the diffuse profile becomes more and more prominent. This kind of profile is believed to result from surface roughness[3,4] caused by the etching process.

It is well known that the roughness of an etched surface is mainly due to etched pits.[5] In Fig. 3 we show the optical micrographs of surfaces of different samples etched under identical conditions. Figures 3(a) and 3(b) were taken from the samples etched for 15 and 45 min, respectively. Note that the square shape of pits at 45 min is similar to the crystal symmetry of Si(100). The time dependent light scattering profiles, therefore, can be ascribed to the contribution from the pits. The kinetics of pit formation can be described in terms of the rate of pit formation, and the rate of growth of these pits. The favorite sites on the surface for pit creation are lattice defects, such as vacancies, impurities, and dislocations.[5] The pits are distributed randomly over the surface. We describe the light scattering profiles approximately by a diffraction theory developed by Pimbley and Lu for a random distribution of two-dimensional islands (pits).[6] The random pit size distribution was assumed to be a geometric distribution with an average size of *l*. An explicit formula for the 2D island formation [Eq. (11) in Ref. 6] was given. However, for our experimental setup, each diode acts like a ''slit'' detector, and the formula appropriate for the scattering profile is reduced to one dimension:[2]

$$I(k_{\parallel})=2C\pi[1-2P(1-P)(1-\cos k_{\perp}d)]\delta(k_{\parallel})+4CP(1-P)(1-\cos k_{\perp}d)\frac{1}{1+k_{\parallel}^2l^2}, \quad (1)$$

where C is a constant, P is the pit coverage, d is the depth of the pits, $k_{\perp}=(4\pi/\lambda)\cos\theta$ is the momentum transfer perpendicular to the surface, θ is the incident angle with respect to the normal of the surface, and l is the average distance between two pits (or correlation length). The diffuse profile



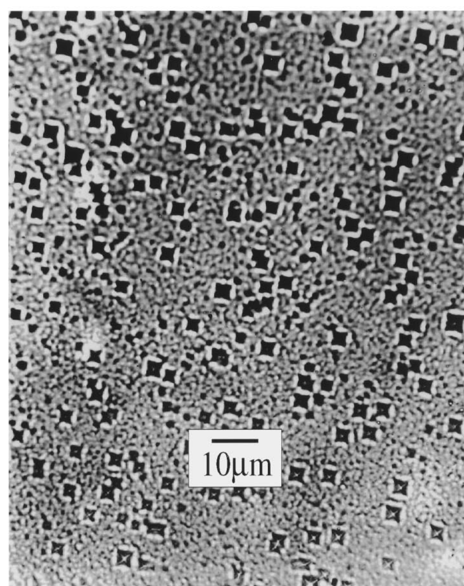


FIG. 3. *Ex situ* optical micrographs of etched Si(100) surface: (a) etch time $t=15$ min; (b) etch time $t=45$ min.

resulting from the scattering of the randomly distributed pits is a Lorentzian function with a width equal to the inverse of *l*. As the etching proceeds, the average distance *l* between two pits also varies with the change of the number of pits *n(t)*. The relation between *l* and the number of pits *n(t)* is $n(t) \propto l^{-2}$. In Fig. 4 we plot the width 1/*l* of the diffuse profile as a function of etch time *t*. As *t* increases, the diffuse profile becomes broader and broader, indicating that the average distance *l* between two pits shrinks with time. The best curve fit for $t \geqslant t_0$ shows that $l^{-1} \propto (t-t_0)^{1/2}$, where $t_0 = 24.5$ min. Since $n(t) \propto l^{-2}$, the pit number *n(t)* is a linear function of the etch time, as shown in the inset of Fig. 4.

The non-zero value of t_0 is related to the limitation of the light scattering technique, i.e., the signal to noise ratio and dynamic range of the detector system.[2] If the pit coverage *P* is low and the pit depth *d* is very small, then the relative contribution of the diffuse profile in the total profile will also be very small, as seen from the second term on the right-hand side in Eq. (1)

$$\frac{I_D}{I_{\text{total}}} = 2P(1-P)(1-\cos k_\perp d), \tag{2}$$

where I_D is the integral of the diffuse profile over $k_\parallel$, and I_{total} is the integral of the whole scattering profile. In the initial stages, the number of pits as well as the size of the pits are both very small, so their contribution to the scattering profile is too small to be detected. Also the average distance *l* between pits is very large which implies that the diffuse profile is very narrow. Therefore, I_D will be buried in the noise, and one cannot resolve the diffuse profile for $t<20$ min. After time t_0, the surface has sufficient pit coverage *P* and pit depth *d* to contribute significantly to the scattering, so the detector array can resolve the diffuse profile.

Under thermal equilibrium, the number of lattice defects is a constant, n_0, and the number of potential pit-forming sites is constant. Assuming that the rate for forming a pit is the same for all n_0 sites, then

$$\frac{dn}{dt} = r[n_0 - n(t)], \tag{3}$$

and

$$n(t) = n_0(1-e^{-rt}), \tag{4}$$

where *n(t)* is the number of pits formed at time *t*, and *r* is the rate constant. The number of pits that contributes to light scattering and can be detected is

$$n'(t) = n(t) - n(t_0) = n_0(e^{-rt_0} - e^{-rt}) \approx n_0 r(t-t_0),$$
$$(\text{for } rt \ll 1). \tag{5}$$

This simple kinetic model is consistent with the experimental results shown in Fig. 4.

From Eq. (1) it is not possible to extract the value of *P* and *d* independently. However, it is well known that for small $k_\perp w$, where *w* is the interface width, the ratio I_D/I_{total} can be approximated by $(k_\perp w)^2$ based on a general diffraction theory (scalar) for a random rough surface.[3] Therefore, from Eq. (1), we can extract the interface width $w = [P(1-P)]^{1/2} d$ from the measured I_D/I_{total} for small $k_\perp w$ or small $k_\perp d$ regime. For example, from 20 to 40 min the interface width of the etched Si surface grew from 161 to 186 nm as calculated from the measured I_D/I_{total}. This method does not apply for $t>60$ min because $k_\perp w$ becomes too large.

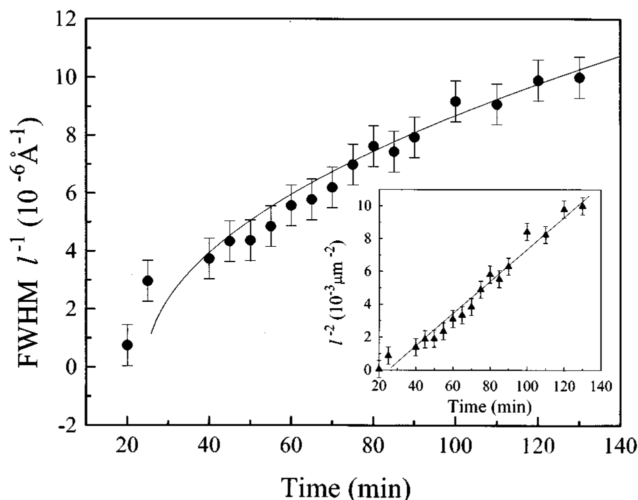


FIG. 4. The FWHM l^{-1} of the diffuse profile is plotted as a function of the etch time *t*. Inset: the number of pits l^{-2} vs *t*. The solid curve $(t-t_0)^{1/2}$ and the straight line are fits for FWHM and pit number, respectively.

In conclusion, we report the development of a real-time light scattering technique which is used as an *in situ* probe to study the wet chemical etching process of Si(100). Based on a simple scattering theory, the number of etch pits and other statistical parameters such as correlation length and interface width on the pitted surface can be extracted from the scattering profile. The time evolution of the surface morphology can be interpreted by a simple rate equation.

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