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Non-monotonic roughening at early stages of isotropic silicon etching

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Isotropic etching using a mixture of HF, HNO_3 and CH_3COOH was carried out for single crystalline Si surfaces for different times and the resulting morphologies were investigated using atomic force microscopy. The acquired data were analyzed using dynamic scaling theory. It was found that for each surface, there exists two roughness exponents which correspond to two different length scales. Moreover, the local roughness properties undergo a reversal between these two length scales before and after an etching time of 120 s. The power spectra density (PSD) curves of the analyzed images also show a reversal in the overall trend before and after 120 s. It is further noted that the PSD spectra of the surfaces resembles more that of a superstructured surface which is a distinct departure from the self affine nature of the surfaces investigated. The deviation is by far the largest for the 120 s etched surface. The morphology evolution in the present scenario does not follow the dynamical model of progressive hardening of the solid surface. Hillock flooding analyses of the AFM images exhibit the percolation nature of the process.

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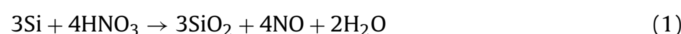
1. Introduction

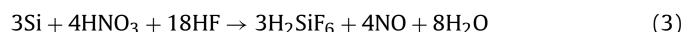
In the present day world of miniaturization of devices, development of electronic device technology toward nanometer scale relies largely on the substrate properties upon which the device is fabricated. Generally, such substrates fulfill two basic properties, namely, they should be of high crystallinity with low defect density and should be appropriate for integrating processes with Si based electronics [1]. It is due to the latter, that the structural and electronic properties of Si surfaces are extensively studied. Moreover the production of clean and smooth surfaces plays an increasingly important role in the microelectronic industry since the presence of defects and impurities degrade the electronic properties of materials. Silicon surface texturing also plays a key role in the solar cell fabrication industry [2,3]. Several etching processes are thus widely used for structuring and modifying silicon surfaces [4]. The orientation independent isotropic etching or the orientation dependent anisotropic etching are the key methodologies used for bulk micromanufacturing of silicon [5]. Isotropic etching plays a key role in a number of applications such as liquid handling devices, removing rough and sharp corners after anisotropic etching, delineation of electrical junctions, etc. [6,7]. It has been found that an acidic etched surface can absorb 0.5–1% more incident light than an alkaline etched surface thus proving to be a better harvester of solar energy [2]. The texturing, however, is found to depend largely on the original surface morphology of silicon [3]. An anisotropically etched Si surface has been proven to absorb more incident light when it is pre-etched in an acidic mixture owing to the increased number of pyramid density on the surface. Hence, the morphology study of acidic etched Si surfaces warrants a detailed attention in the light of the above.

The most common acidic agent used for isotropic etching of Si is a combination of HF, HNO_3 and CH_3COOH, commonly known as HNA. The first comprehensive study of the mechanism of isotropic etching of Si by HNA was done by Robbins and Schwartz [8–10]. The combination of these acids in HNA exhibits three areas of general interest: the high HNO_3 region, the high HF region and the region in the vicinity of maximum etch rate [9]. In the high HNO_3 region, HF plays a kinetically important role and vice versa. In the region near the maximum etch rate, however, both reagents play an important kinetic role [9]. The etching of Si in HNA is regarded as a two-step process, the first of which is the oxidation of Si to SiO_2 by HNO_3 (Eq. (1)). This is followed by the subsequent dissolution of the formed SiO_2 by HF (Eq. (2)). The overall reaction is given by Eq. (3).



$$3Si + 4HNO_3 \rightarrow 3SiO_2 + 4NO + 2H_2O \quad (1)$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \quad (2)$$



$$3Si + 4HNO_3 + 18HF \rightarrow 3H_2SiF_6 + 4NO + 8H_2O \quad (3)$$

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The above equation can be diffusion or etch rate limited depending upon the relative concentration of HNO_3 and HF [7]. For high HF and low HNO_3 the reaction is etch rate limited and is controlled by the rate of oxidation, so that it tends to be orientation dependent and affected by dopant concentration, defects and catalysis. In this regime the temperature influence is more pronounced. For low HF and high HNO_3, on the other hand, the reaction is diffusion limited and the etch rate is controlled by the ability of HF to remove the SiO_2 as it is formed. Here the temperature changes are less important. Etches in this regime are isotropic and truly polishing, producing a bright surface with anisotropies of 1% or less when used on ⟨1 0 0⟩ wafers. Studies have also shown that under this regime, with glacial acetic acid as dilutent, the etching solution is the major concern in etching with the type of etched semiconductor playing only a minor role [11].

Sapoval and his group has proposed a model for chemical etching of a solid where a complex dynamics plays a vital role at the solid–solution interface [12]. According to their study, the weakest sites are eroded first, thereby rendering the solid to be harder with erosion time. Additionally, the surface tends to get rougher and rougher uncovering the critical spatial correlations typical of percolation. The distribution of debris produced by the etching process can be regarded as a chemical fragmentation process. The dependence of surface roughness on the corrosion front velocity has been modeled in a study by Tu et al. (KLT model) [13]. In their model, the eroding system is characterized by fluctuations which are quenched random variables. The fluid interface moving through a random medium is given by the equation

$$\frac{\partial h}{\partial t} = F + \nu \nabla^2 h + \eta(x, t) \tag{4}$$

where F is the pushing force, ν is the surface tension and $\eta(x, t)$ represents the quenched noise. This model has been found to be typical for percolation scenarios [13].

An alternative method followed to study the surface morphology is to use the dynamic scaling approach (discused in the following section). Although scaling analyses have been extensively used for studying the morphology of surfaces eroded by physical means [16,17], one can only find a handful of such studies applied to surfaces eroded by chemical etching processes [18]. Scaling studies were done by Dotto and Kleinke for Si(1 0 0) surfaces etched by NaOH under different conditions [19]. Their results indicated that etched Si surfaces in saturated ambient can be described by KLT percolation model. Etching in their case was however performed with a small drop of NaOH for increasing concentration gradient and for generating interfacial turbulence near the surface. Similarly in 2004, Wisz et al. had studied fractal evolution in case of Si(1 0 0) etched with HF:HNO_3 in the ratio 10:1 [20]. Samples in their case were prepared from p-type and n-type Si(1 0 0) and the morphology was studied for an etching time of 15 s. The present work deals with morphological characterization of the erosion dynamics of HNA etched Si(1 0 0) system under the framework of dynamic scaling theory. The etching was performed with a finite solution of HNA which was supposed to increase the surface roughness monotonically with time according to the model proposed by Sapoval [12]. In the current study, diffusion limited regime of HNA etching was chosen by taking a low HF and high HNO_3 concentration. The etching process was monitored with respect to time using the scaling theory approach. Our findings were also discussed in the light of percolation concepts.

2. Material and methods

Si samples of the size of 10 mm × 10 mm cut from undoped Si(1 0 0) single crystal wafers were cleaned and rinsed using deionized water ($\rho \sim 18.2\,M\Omega$) from a Milli-Q Gradient water purification sysytem (Millipore). Before etching, all samples were cleaned by sonicating with isopropyl alcohol for 15 min each. Etching solution of HF, HNO_3 and glacial CH_3COOH in the ratio 2:3.5:5.5 (by volume) (5M:5.3M:8.7M by molar conc.) was prepared and ultrasonicated in order to ensure homogenity of the etching solution. Samples were etched for 30 s, 60 s, 120 s, 240 s, 360 s, 480 s and 600 s respectively along with ultrasonication. After etching, samples were thoroughly rinsed with DI water and dried. The samples were thereby imaged in ambient by Atomic Force Microscopy (AFM) using a Multimode 8 Scanning Probe Microscope (SPM) equipment operating in the tapping mode. A large number of AFM images each having a resolution of 512 × 512 pixels were acquired over different regions of each sample. This was done for better statistical averaging of quantities obtained from the AFM data.

The AFM data were statistically analyzed using the dynamic scaling approach. In this formalism, the steady state morphology and dynamics of a rough surface can be characterized by the fluctuations of surface height $h(r, t)$, around its mean value $<h>$, through the root-mean-square (rms) roughness or interface width defined as $w(r, t) = <(h(r, t) - <h>)^2>_r^{1/2}$, where t is the erosion time and $<>_r$ denotes average over all r in a system of size L and $r \le L$. A similar correlation function used in the scaling arguments is the height–height correlation function defined as $H(r, t) = <(h(x+r, t) - h(x, t))^2>$, where $h(x+r, t)$ and $h(x, t)$ denotes the surface height with respect to the substrate at a position $(x+r)$ and x respectively on a surface at time t [14]. In the absence of any characteristic length in the problem, growth processes are expected to obey power-law behavior of the correlation functions in space and time and the Family-Vicsek dynamic scaling law $w(L, t) = t^{\alpha/z} f(L/\xi(t))$ holds, where α is the roughness exponent and ξ is the lateral correlation length. The dynamic exponent z is defined as α/β where β is the growth exponent describing the surface roughening process in time through the power law behviour of $w \sim t^{\beta}$. Beyond the short range lateral correlation of a surface, even though surface heights are not significantly correlated, they may exhibit a periodic behavior on all length scales larger than the lateral correlation length. In order to determine this long-range behavior, the structure factor or power spectral density function (PSD) of the interfacial fluctuations is taken into consideration. This is defined as $\mathrm{PSD}(k, t) = \langle H(k, t) H(k, t) \rangle$, where $H(k, t)$ is the Fourier transform of the surface height in a system size L, with k being the spatial frequency in reciprocal space [15].

3. Results and discussion

Fig. 1 shows the morphology evolution of HNA etched Si surfaces obtained by using AFM. Fig. 1a shows the pristine Si surface before etching. After etching for about 30 s, globular structures appear on the Si surface (Fig. 1), almost similar to what was found in the study by Wisz et al. [20]. However, in their case, the size of each globule was approximately 10 μm while in our case it is about 50 nm. This contrast is primarily due to the differences in choice of the pristine Si wafer and concentration of the etching solution accompanied with sonication. The size of the globules, however starts decreasing with etching time until 120 s of etching. After this a macroscopic morphology evolves on the Si surface which in turn influences the globular morphology obtained earlier. This effect is further noticed in samples etched for 480 s and 600 s.

In order to study the roughening process quantitatively, a dynamical scaling approach was used. Roughness was calculated for all possible length scales for all scanned AFM images using a Fortran program. These values were then averaged over identical length scales. A large number of images from different regions of a particular etched surface were used to find the average behavior of each scaling parameter for all etching times. Fig. 2 depicts a typical

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