ABSTRACT

During a typical chemical etching process growth front morphology generally generates an isotropic rough surface. In this work, we show that it is possible to form a rippled surface morphology through a geometrical self-assembly process using a chemical oblique angle etching technique. We observe in our Monte Carlo simulations that obliquely incident reactive species preferentially etch the hills that are exposed to the beam direction due to the shadowing effect. In addition, species with non-unity sticking (etching) coefficients can be re-emitted from the side walls of the hills and etch the valleys, which at the end can lead to the formation of ripples along the direction of the beam. This mechanism is quite different than the previously reported ripple formation during ion-beam bombarded surfaces where the incident ions have much higher energies, and surface and subsurface bulk atoms are physically removed (sputtered) from the substrate. We investigate the ripple formation process in our simulated surfaces for a wide range of etching angle and sticking coefficient values.

INTRODUCTION

Although it is a key parameter in microfabrication and nanofabrication processes, morphological evolution during etching, where the material from the surface is chemically removed, has got less attention compared to that of thin film deposition [1]. Contrary to the common belief, it has been shown that [1] etched surfaces can remarkably get rougher due to the competition between “shadowing and re-emission effects”. In shadowing effect, obliquely incident etching molecules can preferentially remove the tops of “hills” due to their higher heights, while lower lying “valleys” get shadowed and stay intact. Therefore, shadowing has a smoothening effect during etching process. On the other hand, etching particles with non-unity sticking coefficient ($s$), which defines the probability of etching a surface atom (for example, $s = 1$ stands for 100% probability of etching the surface atom, and $s = 0.1$ for 10%), can bounce off from the first impact point, get re-emitted, and finally etch another surface point after such multiple re-emission processes. As illustrated in Fig.1, re-emission can lead to the removal of atoms at valleys, and therefore, it has a roughening effect as opposed to smoothening shadowing effect.

Unlike well studied oblique ion beam sputtering/erosion/etching process [2-4], where the material from the surface is “physically” removed (sputtered), to the best of our knowledge, no work has been reported yet for the morphological evolution of surfaces under the presence of an obliquely incident “chemical” etching beam. Boyd et al. has used an oblique reactive ion etching (RIE) flux incident on a patterned substrate in order to investigate the angular dependence of etching rate during RIE [5].

In this work, using Monte Carlo simulations, we investigate a new oblique angle chemical etching approach, in which unlike the conventional techniques (e.g. planar plasma etching), the beam of etching particles is highly directional and obliquely incident on the film surface. By controlling the shadowing effect through the angle of etching combined with optimized re-emission energetics, it can be possible to engineer surfaces having morphologies like ripples and mounds in nano or micro-scales.
In the past, ripple formation has been observed in obliquely ion-bombarded or sputtered/eroded surfaces, in which atoms are physically removed (sputtered) from the surface [2-4]. However the mechanism reported in these studies are quite different than the ones in our oblique angle etching process. In oblique angle ion-bombarding or sputtering, a highly energetic particle can penetrate beneath the surface and transfer its energy to other atoms leading to deformation, mobilization in the bulk, and eventually sputtering [2]. Ripple formation is believed to be mainly due to competition between roughening effects such as local surface curvature dependent preferential sputtering [6], stress induced mobility variations [7], and smoothening effects like surface diffusion, re-deposition [8], and surface viscous flow [9]; and is typically described using the Bradley-Harper (BH) continuum model [10].

MONTE CARLO SIMULATIONS

Oblique Angle Etching Simulations:

Monte Carlo simulation codes for oblique angle etching process were developed in an C++ environment. Simulation parameters such as lattice size, etching angle, sticking coefficients, substrate rotation speed, number of particles sent to the surface, and surface diffusion can be defined by the user. In this work, we didn’t include substrate rotation and surface diffusion effects. No overhangs were allowed. That is, etching can take place at any height of a lattice point reducing the total height by one. Re-emission direction was defined by a cosine distribution centered around the local surface normal. If a re-emitting particle does not collide with any lattice point after re-emission process, no etching process takes place.

The simulations were performed on a planar square lattice size of 512*512. The total number of particles sent for each simulation performed was $25\times10^7$. The incidence angle values of the etching particles were taken as $\theta = 0^\circ$ (normal incidence), $45^\circ$, $60^\circ$, $70^\circ$, and $85^\circ$ as measured from the surface normal. Sticking coefficient $s$ was non-unity for first interaction of etchant with the surface but was 1 for the second impact. Simulations were performed for sticking coefficients of 0.1, 0.3, 0.5, 0.7, and 0.9 for each incidence angle studied.
RESULTS AND DISCUSSION

Normal Incidence Etching:

At normal incidence ($\theta = 0$), the following surface morphologies shown in Fig. 2 corresponds to final etching topographies as a result of various sticking coefficients. It can be clearly seen that low $s$ values leads to rougher surfaces due to the re-emission effect, as explained before (also see Fig. 1). However, in general surfaces are isotropic and no periodic pattern formation has been observes, consistent with previous experimental reports [1].

![Surface morphology evolution at different sticking coefficient values](image)

Oblique Angle Etching:

Morphological evolution of obliquely etched surfaces for sticking coefficient values $s = 0.1, 0.3, 0.5, 0.7, 0.9$ are presented as a function of simulation time, at various incident beam angles $\theta = 45^\circ, 60^\circ, 70^\circ$ and $85^\circ$ in Figs. 4, 5, 6, and 7, respectively. A visual comparison indicates that the surface morphology moves towards a rippled structure elongated in the beam direction as the sticking coefficient $s$ is increased. The ripple formation seems to be more dominant for high etching angles larger than $60^\circ$, and for a certain range of sticking coefficients. For angles at $45^\circ$ and $60^\circ$, surfaces show an anisotropic morphology especially for sticking coefficient values at $0.7$ and $0.9$, but not a clear ripple structure. On the other hand, at higher oblique etching angles of $70^\circ$ and $85^\circ$, we can clearly see a ripple formation for sticking coefficient in the range $0.5 \leq s < 1$. Aspect ratio of the ripples along X direction (i.e. ratio of ripple height to width) at $\theta = 70^\circ$ for $s_0 = 0.9$ is around 1/8 to 1/20 and for $s_0 = 0.5$ it is around 1/10. For $\theta = 85^\circ$ the aspect ratio is in the range of 1/4 to 1/6 in the X direction for $s_0 = 0.9$. For $s_0 = 0.5$, typical values for X direction vary from 1/7 to 1/15.

Interestingly, the ripple formation direction is found to be along the oblique etching beam direction. We believe this directional selection is caused by the direction of the oblique incidence flux but the development of ripples is through re-emission and shadowing effects. Initially particles begin etching a perfectly smooth surface, randomly leaving tiny “valleys” and “hills” on the surface. These structures initiate the shadowing effect on the system and play a key role in the development of directionality of ripples. Due to shadowing effect the side of a hill facing towards the instant beam (front side) will be etched faster compared to its opposite shadowed side (back side). However due to the cosine distribution of re-emitted particles along the surface normal, the back sides will also experience etching through the particles being reflected from the front sides. In this process front and back sides of hills will be etched more efficiently compared to their sidewalls, which are parallel to the incident beam. This will lead to an elongated valley. Over time, the hills separating these valleys can be etched combining these to form even longer valleys that will eventually lead to the formation of ripples. In addition, re-emitted particles can also start etching sidewalls which will result in the
widening of valleys and eventually merging two neighboring ripples. This effect is qualitatively observable at high angle simulations shown in Figs. 6-7.

Figure 4: Morphological evolution for etching angle $\theta = 45^\circ$ for sticking coefficient values $s = 0.1, 0.3, 0.5, 0.7, \text{ and } 0.9$ are shown.

Figure 5: Morphological evolution for etching angle $\theta = 60^\circ$ for sticking coefficient values $s = 0.1, 0.3, 0.5, 0.7, \text{ and } 0.9$ are shown.
Figure 6: Morphological evolution for etching angle $\theta = 70^\circ$ for sticking coefficient values $s = 0.1, 0.3, 0.5, 0.7,$ and 0.9 are shown.

Figure 7: Morphological evolution for etching angle $\theta = 85^\circ$ for sticking coefficient values $s = 0.1, 0.3, 0.5, 0.7,$ and 0.9 are shown.
The ripple formation is strongly correlated to the etching angle and re-emission parameters. As seen from the Figs. 4 to 7, at lower incidence angles ($\theta = 45^\circ$ and $60^\circ$) we observe anisotropic morphology however shadowing effect is not strong enough to produce a clear ripple structure. At high angles, the ripple formation is also weaker at smaller sticking coefficients $s = 0.1, 0.3$ and $0.5$. The main reason for this is believed to be due to the loss of directionality as re-emission dominates over shadowing effect at smaller sticking coefficients. Enhanced re-emission will lead to a more uniform and isotropic etching hindering the ripple formation.

In summary, simulation results indicate that self-assembled periodic structure formation by oblique angle etching can be possible through adjustment of shadowing effect and re-emission parameters. We observed that in the range of sticking coefficients $0.5 \leq s < 1$ it is possible to produce rippled surface structures. The ripple formation is also enhanced at high etching angles $\theta > 60^\circ$.

**CONCLUSIONS**

As a new technique, oblique angle etching, where obliquely sent etching particles interact with surfaces under shadowing and re-emission processes, shows promising results for self-assembly process and nano-pattern formation. From our Monte Carlo simulation results, we found that at high etching angles and for a range of sticking coefficients, shadowing and re-emission effects can lead to the formation of a rippled surface morphology. Material removal in this process reflects a chemical etching and mechanisms of ripple formation is different than that observed during ion sputtered/eroded surfaces where surface and subsurface bulk atoms are physically removed by high energy particles.

**REFERENCES**


