Effect of surface diffusion algorithm on nanostructure formation in a semi-empirical Monte Carlo model of sputter erosion of materials

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Abstract. A semi-empirical ion sputtering model (SEISM) was extended for clearer ripple profiles on material surfaces on which atoms self-organise into rippled topography. The improvement was by way of modifying the sputter erosion algorithm with implementation of the curvature dependence of sputter yield and the avoidance of shadowing effect. And by way of modifying surface relaxation through adaptation of a surface diffusion algorithm that is popular in Monte Carlo simulations of material growth by particle deposition (growth of thin films) as a replacement for the surface reorganisation algorithm of the SEISM. Prior to these extensions, the SEISM model exhibited some characteristic properties of sputtered surfaces but gave indistinct ripples. With the extensions, the model gives a clearer indication of distinct ripple topographies. Specifically, surface stability was improved when the original surface reorganisation algorithm of the SEISM was replaced.

1. Introduction
Ion beam surface sputtering is a versatile tool of surface morphology analysis and surface topography fabrication, with a vast range of applications [1, 2, 3, 4, 5].

In sputtering experiments, apart from rough surfaces, nanopatterns are observed on substrates at certain angles. These nanostructures are important in the field of nanotechnology, thin film deposition and semiconductor manufacturing. For this reason, there is a need for an accurate model for performing computer simulations of processes of interest so as to provide valuable information on viable prospects and minimise wasteful expenditures on experimental projects that would likely not yield meaningful or useful results. Thus, in this paper, a promising semi-empirical ion sputtering Monte Carlo model of sputtering has been further developed [6].

This semi-empirical ion sputtering model (SEISM) [6] is useful for simulating the surface morphology of target substrates during energetic ion-beam sputtering. With this model, computer simulation of sputtering process is achieved through three algorithms: an Ion Beam Surface Erosion Algorithm (IBSEA), a Redeposition of Eroded Material Algorithm (REMA) and a Surface Reorganisation Algorithm (SRA). In addition, incorporation of experimental values of the sputter yield to the surface erosion algorithm (IBSEA), and addition of REMA which allows the number of particles of the target material to be conserved, making this model similar to Monte Carlo models [6,7].
In this Paper, we improved SEISM in three ways. Firstly, we implemented curvature-dependence of sputter yield, a condition that is critical to, and without which there can be no, clear (ripple) pattern formation. Secondly, we introduced a condition that prevents shadowing effect, which is an anomaly (similar to overhangs) of computer simulations of surface growth or alteration by particle flux. In the course of this work, we found the surface relaxation algorithm of the original SEISM weak in surface particle reorganisation when compared to another relaxation algorithm which is popular in Monte Carlo simulations of surface growth. Hence, thirdly, we replaced the SRA with this surface relaxation algorithm.

2. Continuum Theory Background
The continuum theory describes surface morphology by particle bombardment with deterministic and stochastic partial differential equations, the solution of which gives experimentally observed profiles. The continuum equation provides a great deal of insight to, and understanding of, the dynamical evolution of sputtered surfaces. They, therefore, inform the elemental and critical processes which the more pertinent discrete models must include in their algorithmic composition. In this section, we briefly review the basic and pioneering continuum models as a fundamental background to our discussions.

2.1. Bradley-Harper Theory
The Bradley-Harper theory was developed from the Sigmund’s theory [8]. According to [9], ripples are often produced on the surface of amorphous solids due to ion bombardment at off-normal incident angles. The ripple wavelength is of the order of 0.1 to 1 µm, however, wavelengths of 250 Å have been observed. The ripple wave vector is parallel to the component of the ion beam in the surface plane for incidence angles \( \theta \) less than the critical angle \( \theta_c \), from the normal whereas it is perpendicular to this component for incidence angles close to grazing. Curvature dependence of the sputtering yield is required for ripples to be formed on material surfaces. This requirement together with the effect of surface self-diffusion was combined to derive a linear equation for surface morphology evolution which is given in equation 1

\[
\frac{\partial h}{\partial t} = -v_0(\theta) + v_1(\theta) \frac{\partial h}{\partial x} + \xi_x \frac{\partial^2 h}{\partial x^2} + \xi_y \frac{\partial^2 h}{\partial y^2} - B \nabla^2 h
\]

where \( v_0(\theta) \) is the rate of erosion of the unperturbed planar surface, \( h(x, y, t) \) is the surface height,

\[
\xi_x = \frac{f a}{n} Y_0 \Gamma_1(\theta)
\]

\[
\xi_y = \frac{f a}{n} Y_0 \Gamma_2(\theta)
\]

\[
B = \frac{D \nu}{n^2 k_B T}
\]

\( f \) is the flux, \( \xi_x \) and \( \xi_y \) are the effective surface tension, \( Y_0 \) is the sputter yield. \( D \) is the surface diffusion constant induced by thermal diffusion, \( n \) is the number of atoms per unit volume in the amorphous solid, \( \Gamma_1 \) and \( \Gamma_2 \) are dimensionless quantities that describe the curvature dependence of the sputter yield. It is however important to note that this theory is not suitable for incidence angles close to the grazing angle [10].

According to [1] it was stated that the ripple wavelengths and orientation predicted by [9] agreed with experimental results. However, the theory could not account for the stabilization of the ripples and for kinetic roughening and it also failed to explain ripple formation at low temperatures since the only smoothing mechanism it considered is thermally activated. It was further maintained that the Bradley-Harper theory has been improved to include thermally activated anisotropic surface diffusion found in metallic substrates like Cu(110)
2.2. Makeev, Cuerno and Barabasi Theory
In [1] a linear theory was developed which explained the phenomenon of ripple formation at high temperatures in the symmetric case. This theory introduced a third order differential equation with a noise term and is given by equation 5

\[
\frac{\partial h}{\partial t} = -v_0 + \gamma \frac{\partial h}{\partial t} + v_x \frac{\partial^2 h}{\partial x^2} + v_y \frac{\partial^2 h}{\partial y^2} + \Omega_1 \frac{\partial^3 h}{\partial x \partial y^2} + \Omega_2 \frac{\partial^3 h}{\partial y^3} - k \nabla^4 h + \eta(x, y, t) \tag{5}
\]

The term \(v_0\) represents the erosion velocity of a flat surface which does not affect the formation of ripples but the erosion rate and it depends on the angle of incidence, \(\theta\). The terms \(\Omega_1\) and \(\Omega_2\) influence only the ripple propagation, \(\gamma\) only affects its velocity while the orientation and wavelength of the ripples is as a result of the terms \(v_x\) and \(v_y\) and for normal incidence, \(\gamma = 0\). It was further stated that the noise term represents the haphazardness of the ion arrival to the surface and has a mean value of zero and that it is also uncorrelated, that is, equations 6 and 7 respectively.

\[
\langle \eta(x, t) \rangle = 0 \tag{6}
\]

\[
\langle \eta(x, t) \eta(x', t') \rangle = J \delta(x - x') \delta(t - t') \tag{7}
\]

The third order differential terms only made corrections to the ripple velocity so that the mode velocity is given as

\[
\omega = -\gamma k_x + \Omega_1 k_x^3 + \Omega_2 y k_y^2 \tag{8}
\]

and the ripples travel parallel to the ion beam direction with velocity

\[
v_r(\lambda_x, \lambda_y) = -\gamma + 12\pi^2 \frac{\Omega_1}{\lambda_x^2} + 4\pi^2 \frac{\Omega_2 y}{\lambda_y^2} \tag{9}
\]

and the growth rate

\[
r = -(v_x q_x^2 + v_y q_y^2 + K (q_x^2 + q_y^2)^2) \tag{10}
\]

The ripple wavelength is given as

\[
l_x = 2\pi \sqrt{\frac{2K}{|v_x|}} \tag{11}
\]

and

\[
l_y = 2\pi \sqrt{\frac{2K}{|v_y|}} \tag{12}
\]

in the \(x\) and \(y\) direction respectively where \(K\) is a positive constant.

3. Low Energy Sputtering and Surface Morphology
From the experiments carried out by [2] silicon substrates through low energy (1.2 keV) ion-beam sputtering (IBS), they were able to produce results that agree with the predictions of [9]. However, their model could not explain some observed features due to the linear form of the model. It was observed that a hexagonal array of nanodots was produced for normal incidence angle. The nano-ripple and sawtooth-like morphology have wavelengths in the ranges of 30 - 50 nm and 200 - 700 nm respectively while their amplitudes were in the ranges of 2 - 5 nm and 50 - 100 nm respectively. The diameter of the nanodots formed was in the range of 40 - 50 nm with a height of approximately 6 nm. It was also argued that residues present on the surface of substrates do not lead to the formation of nanodots. It was further maintained that the surface morphology of the substrate is as a result of the interplay of the surface curvature and surface diffusion which in turn affects the sputtering yield.

The experiments of [11] investigated effect of contaminant on the surface morphology of silicon target. Molybdenum was as the contaminant (Seed) with Argon ion beam of energy 1 keV. It was reported that with the presence of Molybdenum as contaminant, with normal ion incidence...
angle, nanodots structure were observed whereas in the absence of contaminants only a rough surface was observed. This result does not agree with the work of [2] in which they observed nanodots without the presence of any seed, although, the silicon target was cleaned before sputtering, the atoms sputtered on the wall of the vacuum chamber might have caused contamination leading to the formation of nanodots. It was also reported by [12] that when pure silicon substrate was rotated and bombarded at a grazing angle of 75°, nanodots were observed. According to [13], experiments with Argon ions have been to produce ripples only at some angles. It was further stated that there is a critical angle \( \theta_c = 45^\circ \) such that below and above this value, the surface remained at flat and exhibited ripples respectively. Table 1 [13] shows ions different ions and energies with their corresponding critical angle, \( \theta_c \).

| System                  | \( \theta_c \) |
|-------------------------|-----------------|
| \( \text{Ar}^+ \rightarrow \text{Si} \ (250 \text{ eV} - 1 \text{ keV}) \) | 48°             |
| \( \text{Ar}^+ \rightarrow \text{Si} \ (300 \text{ eV} - 1.1 \text{ keV}) \) | 45° - 50°       |
| \( \text{Kr}^+ \rightarrow \text{Si} \ (2 \text{ keV}) \) | 60°             |
| \( \text{Ar}^+ \rightarrow \text{Si} \ (500 \text{ eV} - 1 \text{ keV}) \) | 46°             |
| \( \text{Xe}^+ \rightarrow \text{Si} \ (500 \text{ eV} - 1 \text{ keV}) \) | 58°             |
| \( \text{Kr}^+ \rightarrow \text{Ge} \ (1 \text{ keV}) \) | 62°             |
| \( \text{Xe}^+ \rightarrow \text{Ge} \ (1.2 \text{ keV}) \) | 70°             |

**Table 1.** Various ions and energy ranges with corresponding experimental critical angles for Silicon and Germanium ion beam.

4. Simulation Models

The foregoing sections show the diversity and complexity of surface of morphology by ion beam sputtering, which makes the phenomena notoriously difficult to be wholly captured by any single model, continuum or discrete. Nonetheless a number of characteristics are more pertinent which, if captured by a model, may suffice for practical purposes tailored for device fabrication. It is for ease of reference for practical purposes that the SEISM was devised. The sputter yield calculations of SRIM and TRIM [14] could have been used but a yield formula would make the model more flexible and self-contained.

Hence, the approach of Seah [15] was adapted, instead, for the relevant yield parameter of the model. Moreover, we do not suppose that SRIM and TRIM accounts for surface diffusion, which could lead to exponentially increasing surface gradients and, therefore, different yield to the yield given by practical sputtering in which the growth of the surface gradients is moderated by surface diffusion. We suppose the latter case, which includes influence of surface diffusion, is captured by the empirical values of the yield fitted to the formula of Seah.

In the introduction of SEISM [6], much attention was not paid to details of topographic morphology by certain statistics of surface evolution such as height profile data and roughness data. The model satisfied intuitive expectations for these data but the preliminary topographies obtained were not clearly defined. In this work, we extend the model, as earlier mentioned, to address surface topography evolution; in particular, rippled topography. We mentioned, to address surface topography evolution; in particular, rippled topography. We make two extensions to the erosion model, which are exclusion of shadowing effect, and accounting for the curvature dependence of the sputter yield. Although, curvature dependence of the sputter yield could be a factor in the experimental values of sputter yield, where the stabilising effect of surface diffusion should manifest in the moderation of the destabilizing effect of surface erosion, yet there is no
way of knowing how it varies locally over the surface. Hence, we suppose the experimental yields adapted to SEISM are average values and extend SEISM to include local variations in the yield, due to curvature dependence, in the simulated erosion process for sweeps through the lattice, so as to have clear ripple pattern formation.

4.1. Modifications to the Sputter Erosion Algorithm

The SEIS model makes use of the sputter yield parameter Υ(θ, E) as one of its important control parameters because it incorporates the angular and energy dependence, attributes of the projectile and the target material, and other sputtering characteristics [6]. In [9], it was stated that the yield is curvature dependent. This means that the troughs (depressions or valleys) are eroded in preference to the crests during the surface erosion. Also, surface profiles coarsen with time. This means for ripple topography, the amplitude grows. However, this growth tends to be somewhat different in simulations where some parts on the surface that would normally have been eroded are screened by the surface protrusions between it and the incoming ion beam. This is known as shadowing effect. Such is not a normal occurrence in reality where the tips of such protrusions could have been knocked off by the ion beam before it leads to shadowing (another example is a surface overhang). The possibility of tip knock-off in reality, but which is not simulated here, is what makes the shadowing effect an anomaly. We suppose that simply introducing a cut-off length as done in this work should be more economical in computer simulation algorithm and time than actually implementing the tip knock off, in which case one has to consider the most realistic projection and redeposition of the knocked off material. Both of these conditions are now incorporated into the erosion model, in the simple cut-off algorithm, to make it more realistic as regards pattern formation.

The curvature dependence of sputter yield was implemented by comparing the surface height at the chosen site with those of neighbouring sites (nearest neighbours) and eroding the site with the lowest height among them all while the avoidance of showing effect was implemented by introducing a cut-off surface gradient whose value was set to some constant. Thus, in addition to curvature-dependent erosion, the erosion process in the vicinity of a chosen site was required to stop when the height gradient becomes equal to the cut-off. Several simulations carried out with these modifications, for different variations of the yield and cut-off length, gave rough surfaces with no clear pattern.

4.2. Surface Reorganisation/Stabilising Models

Surface reorganisation algorithm (SRA) of the SEIS model was introduced in [2]. Details of the simulation algorithm of the Hamiltonian model, which was used to simulate surface diffusion as replacement for existing surface reorganisation algorithm, are as follows. This model employed thermal energy as its major criterion for the diffusion process which depends on the number of the nearest neighbours and is represented on a two-dimensional lattice. For each Monte Carlo step, a random site (i, j) is selected such that it has at least one nearest neighbour site (m, n) which is selected at random as well. A trial move is first done to determine the probability that a move will be accepted. Thus, when an atom moves from a site (i, j) to the nearest neighbour site (m, n), the surface height changes as moves from a site (i, j) to the nearest neighbour site (m, n), the surface height changes as

\[ h(i, j) = h(i, j) - 1 \]

and

\[ h(m, n) = h(m, n) + 1 \]

respectively. The surface energy is calculated before and after the hop as given in equation 13

\[ E = \frac{\Phi}{2} \sum_{i,j} |h(i, j) - h(m, n)|^2 \]  (13)

where \( \Phi \) is a coupling constant through which the nearest neighbor interacts, \( h(i, j) \) and \( h(m, n) \) are the height variables at the two dimensional lattice sites (i, j) and (m, n) respectively. The value \( k_B/\Phi = 2 \) was used in the simulation, where \( T \) and \( k_B \) are the substrate temperature Boltzmann's constant respectively. The energy change \( \Delta E \) between the initial and final state was also determined.
Furthermore, the Metropolis Algorithm was used to determine whether or not the hop is accepted. If the resulting change in energy is less than zero, the hop is accepted, otherwise, the hop is accepted using the Gibbs probability,

$$P \sim \exp \left( \frac{-\Delta E}{k_B T} \right)$$

(14)

This was implemented by generating a pseudo-random number $r$ such that if $r \leq P$, the hop is accepted otherwise, the hop is rejected. This algorithm allowed hops to degenerate sites to be accepted always.

5. Results and Discussion

In furtherance to the recommendation of [2] that SRA was only a preliminary representation of surface relaxation which needs to be fine-tuned to become a realistic model, the effect of SRA of the SEISM as a surface relaxation algorithm was analysed. This was done by studying the number of hops (diffusion of a surface atom from one lattice site to another) per unit time, where, for square lattice of size $L$, a unit time is a MC step per lattice site (MC step/L). This is shown in Fig. 1 (a). As can be seen from these figures, the number of particles disturbed by the sputtering process to relocate or reorganise to a neighbouring site appears to be fairly constant at about 0.965 with an increase in sputtering time having a peak value of 1.

A wide utilised surface diffusion algorithm in MC simulations of surface growth, known as the Hamiltonian model of surface diffusion [16, 17, 18, 19], was then employed and its effect analysed as shown in Fig. 1 (b). From these figures, the number of hops was also fairly constant but at a lesser value of about 0.52 with a peak value of about 0.75. These indicate that the hopping rate, or reorganisation rate, is lower with the Hamiltonian model.

Next, we studied the difference in erosion rates due to the two different surface stabilising models by analysing the number of eroded particles with sputtering time, starting with SRA. This is shown in Fig. 2 (a) as a linear relationship between the number of eroded particles and the sputtering time. This figure showed a remarkable similarity with the result of Fig. 2 (b). However, the erosion rate is lower in Fig. 2 (b), thus indicating that the reorganisation processes of the Hamiltonian model increase the stability of the surface and reduce (relative to SRA) the occurrence of loose surface particles that can be more easily eroded. This agrees with the result in Fig. 1 where the number of hops per unit time was higher with the use of SRA than the Hamiltonian model. Also, a comparison of the erosion rate of both surface stabilising models is shown in Fig. 2 (c), where the rate of surface diffusion was faster than that of surface reorganisation by a factor of about 2 obtained from the gradients of the plots.
Figure 1. Graphs showing hops per lattice site with time for (a) SRA with curvature dependence (b) Hamiltonian model with curvature dependence
Figure 2. Graphs showing the number of eroded particles versus sputtering time for (a) surface diffusion model, and (b) surface reorganisation model. (c) comparison of results of both models.

6. Conclusion
From the results obtained, the use of the Hamiltonian model of the surface diffusion compared to the SRA showed that the number of hops per unit time and the erosion rate were lower and faster (double) respectively. Thus, the Hamiltonian model was found to have a more stabilising effect and reduces the occurrence of loose particles that can be more easily eroded.

However, it was not certain whether the surface reorganisation algorithm is not effective although in this research it was found to be slow. This SRA was actually devised to study whether any relaxation mechanism is sufficient for nanostructure formation or whether the Hamiltonian and Arrhenius mechanisms are particularly crucial, especially since the HM algorithm was found to yield cauliflower-like structures, instead of the known sputter-induced topographies, for certain values of its parameters.

Research is still ongoing to further investigate the effectiveness of the surface reorganization algorithm and Hamiltonian model of diffusion for the SEISM and also the effect of the latter on surface morphology.

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