Temperature and high fluence induced ripple rotation on Si(100) surface

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Abstract
The topography evolution of Si(100) surface due to oblique incidence low energy ion beam sputtering (IBS) is investigated. Experiments were carried out at different elevated temperatures from 20 °C–450 °C and at each temperature, the ion fluence is systematically varied in a wide range from $1 \times 10^{18}$ cm$^{-2}$ to $1 \times 10^{20}$ cm$^{-2}$. The ion sputtered surface morphologies are characterized by atomic force microscopy and high-resolution cross-sectional transmission electron microscopy. At room temperature, the ion sputtered surfaces show periodic ripple nanopatterns where their wave-vector remains parallel to ion beam projection for the entire fluence range. With an increase of substrate temperature, these patterns tend to demolish and reduce into randomly ordered mound-like structures around 350 °C. A further rise in temperature above 400 °C leads orthogonally rotated ripples beyond fluence $5 \times 10^{19}$ cm$^{-2}$. All the results are discussed combining the theoretical framework of linear, non-linear and recently developed mass redistribution continuum models of pattern formation by IBS. These results have technological importance regarding the control over ion-induced pattern formation, as well providing useful information for further progress in the theoretical field.

1. Introduction
Recently, ordered patterns in the nanometer (nm) range on a semiconductor surface have been pursued for immense technological applications in semiconductor devices, optoelectronics, spintronics, etc [1, 2]. Large-scale fabrication of such nanopatterns with simultaneous control on their purity and uniformity demand a cost-effective and reproducible technique. In this respect, low energy ion beam sputtering (IBS) is known to be a promising method among other top-down and bottom-up approaches of nanostructuring [3]. By only varying the ion incidence angle, IBS can induce different nanoscale topographies, like one-dimensional ripples (oblique incidence) [4], two-dimensional dots (normal incidence) [5], cones or needle-shaped structures (grazing incidence) [6], etc within a very short time on a wide range of substrates in just one step, i.e. by simple exposure to ion beam. Depending on the ion incidence angle, the wave-vector of the ripples can appear in either the parallel or perpendicular direction of ion beam projection, and they are generally referred to as (i) parallel (observed in the range of incidence angle 45°–65°) and (ii) perpendicular mode (observed in the range of incidence angle 80°–85°) ripples, respectively [7]. The capability of the IBS technique to form nanopatterns falls short in an application perspective due to upper surface amorphization of the nanostructures. To get rid of this amorphization, sputtering at an elevated substrate temperature can be a key factor. Thus, the studies on temperature-induced morphological evolution during IBS is important from the technological point of view.

This study is important for theoretical understanding as well because the complete understanding of the pattern formation mechanism is still not clear. The evolution of ripple patterns by IBS was first explained by Bradley and Harper in 1988 and was named BH theory, where the self-organization between curvature-dependent ion erosion and diffusion-based surface relaxations is thought to generate the surface instability during sputtering [7–9]. BH theory is the most accepted continuum model so far which successfully explains several experimental results, e.g. the orthogonal rotation of ripples after a certain incidence angle, the
exponential increase of ripple amplitude with an increase of ion sputtering time, the increase of ripple wavelength with the increase of substrate temperature, etc. Later on, the non-linear terms were added to BH theory by Makeev et al [10] to explain the ripple coarsening phenomena or saturation of the ripple amplitude due to high sputtering time. One of the predictions of BH theory is the finite probability of obtaining ripples at all oblique incidence angles. Thus, it can not explain the experimental observation of smooth surfaces at near-normal ion incidences. This phenomenon is explained by Carter and Vishnyakov (CV model) [11] where BH instability is considered to be counteracted by a curvature-dependent smoothing term arising due to the diffusion of surface adatoms parallel to the local surface in the direction of the incident ions. Recently, Madi et al [12] have shown that the parallel mode ripple formation is also dominated by the mass redistribution of surface adatoms rather than the curvature-dependent BH instability, especially in the low energy (< 1 keV) regime of ion sputtering. Again, Norris et al [13], by adopting the crater function approach, have shown that ion erosion is not even necessary to create the surface instability during sputtering. The above-mentioned theories explain the pattern formation mechanism on an amorphized surface. The patterning mechanism is slightly altered on the crystalline surface, which is indeed interesting and has attracted attention recently [14–17]. On a monocrystalline metallic target, an additional instability arises from the Schwerdel barrier associated with the crystal type, symmetry and orientation [18]. When the semiconductor surface is irradiated above its recrystallization temperature, bulk defects are dynamically annealed and the surface defects, i.e. adatoms, vacancies and their clusters, tend to self-organize to form the nanostructures following the step edge dynamics of the crystalline surface. Thus, the temperature-dependent morphological studies on the semiconductor surfaces help us gain a deeper understanding of the pattern formation mechanism during IBS, which helps to improve the control of IBS techniques in order to fabricate the well-ordered patterns. Unfortunately, perhaps due to the experimental complexity or the possibility of having impurity contamination, only a few studies have reported on the high fluence and temperature-dependent nanopatterning on a Si(100) surface by low energy ion beam sputtering [19–21].

In this paper, we report the influence of temperature ranges 23 °C–450 °C on Si surfaces during 500 eV Ar+ ion irradiation at an incidence angle of 65° for ion fluence 1 × 1018 cm−2 to 1 × 1021 cm−2. The experimental results show an orthogonal rotation of ripple nanopatterns at 400 °C beyond ion fluence 5 × 1019 cm−2. The morphology of the modified surfaces was characterized by atomic force microscopy (AFM) and their microstructural and chemical compositions were investigated by high-resolution transmission electron microscopy (TEM). All the results are discussed within the framework of linear and non-linear continuum models of pattern formation during ion beam sputtering, including the recently developed mass redistribution model.

2. Theories of pattern formation by IBS

According to BH theory and its non-linear extension and mass redistribution model, the temporal evolution of height function h(x, y, t) on an amorphized surface can be numerically approximated by the anisotropic KS equation (1) [22, 23] which is:

$$\frac{\partial h}{\partial t} = -\nu_0 + \nu'_0 \frac{\partial h}{\partial x} + S_x \frac{\partial^2 h}{\partial x^2} + S_y \frac{\partial^2 h}{\partial y^2} + \lambda_x \left( \frac{\partial h}{\partial x} \right)^2$$

$$+ \lambda_y \left( \frac{\partial h}{\partial y} \right)^2 - K \nabla^4 h + \eta$$

(1)

The $S_{x,y}$ term represents the sum of curvature-dependent erosion [7] and mass redistribution co-efficients [12], i.e. $S_{x,y} = S_{x,y}^{\text{eros.}} + S_{x,y}^{\text{redist.}}$ in the parallel (x) and perpendicular directions (y) of the ion beam projection respectively [7, 12]. $\nu_0$ is the rate of material erosion from the surface at normal incidence and $\nu'_0$ contributes as the derivative of the angle-dependent sputtering yield [7]. $\lambda_{x,y}$ corresponds to the KPZ nonlinearities associated with tilt-dependent local erosion yield in the respective directions and $\eta$ is the noise term incorporating the stochastic nature of incident ions [10]. The term K denotes the diffusion co-efficient for different surface relaxation processes which can be of different origins, such as (i) thermally activated surface diffusion (TSD), which is generally used to explain the high temperature and ion flux dependence of a ripple wavelength during IBS [7]. Assuming TSD is an isotropic phenomena, $K^{\text{TSD}}$ can expressed as $D_i \frac{\nu_{00}}{T}$ where the surface self diffusivity $D_i$ follows Arrhenius law with a temperature as $D_i = D_0 \exp(-\Delta E/k_B T)$, here $D_0 = \text{const.}$, $\Delta E$ is the activation energy for surface diffusion, whereas $\gamma_s, \rho$ and $n$ designated as the surface tension co-efficient, the areal density of diffusing atoms and the target atomic density respectively. (ii) Ion-induced surface diffusion (ISD) $K^{\text{ISD}}$, which is basically the higher order expansion of the erosion process and mathematically equivalent to surface diffusion, means it just mimicks the surface diffusion and does not execute the real mass transport along
the surface [10]. It depends on the ellipsoidal distribution parameters of the deposited ion energy and exhibits no dependence on temperature. $K_{SD}^I$ is anisotropic in nature with respect to the ion beam direction and its details are given in [10]. (iii) Ion-enhanced viscous flow relaxation (IVF), which is driven by the surface tension within the thin ion damaged layer and depends on the defect concentration generated within the collision cascade [24–26]. $K_{IVF}^I$ is represented by $\frac{a}{\eta}$ where $a$ is the ion energy penetration depth, $\gamma$ and $\eta$ presents the surface tension and ion enhanced surface viscosity respectively. $K_{IVF}$ can be considered as temperature-independent phenomena as the exact dependence of its associated parameters on temperature is still not known. It also does not exhibit an anisotropic nature with respect to ion beam projection, and in addition, does not unveil any dependency on ion current density.

During oblique incidence ion irradiation, regardless of the respective smoothing mechanism, the alignment of the ripple wave-vector is determined by the larger absolute value between two co-efficients $-S_x$ and $-S_y$ [7, 12] and the ripple wavelength $\Lambda$ is expressed by:

$$\Lambda_{x,y} = 2\pi\sqrt{2K_{x,y}/S_{x,y}}$$

In the case of the isotropic surface diffusion process, $K_{xx}$ and $K_{yy}$ both reduce into $K$, the same term mentioned in equation (1).

3. Experimental

Ultrasonically cleaned $1 \times 1 \ cm^2$ p-type (boron doped, doping concentration $\sim 1.7 \times 10^{15} \ cm^{-3}$) single crystal Si(100) wafers of thickness 0.5 mm and conductivity 6–8 $\Omega \ cm$ were irradiated by 500 eV Ar$^+$ ions at an incidence angle of 65° (with respect to the surface normal) in a broad beam high current ion beam system (M/s Roth & Rau Microsystems GmbH, Germany) [16]. An inductively coupled RF plasma discharge ion source having a three-grid graphite optics system was employed to extract a homogeneous and collimated ion beam 3 cm in diameter. Also, a plasma bridge neutralizer was used during ion bombardment to reduce the beam divergence. Thus, the effects of ion beam angular distribution [27] is negligible in our system. During extraction of the ion beam, the chamber pressure was $\sim 10^{-4}$ mbar while usually the base pressure was of the order of $10^{-8}$ mbar. The crystallographic orientation of the Si(100) surface with respect to ion beam projection is represented by a schematic in figure 1. The ion sputtering was performed at elevated temperatures up to 450 °C using a radiation type heater placed at the top of the chamber. A thermocouple placed between the sample and the substrate chuck measured the substrate temperature. The sample stage was integrated with a He backside heat contact which excellently carried heat from the sample to the thermocouple while flowing He gas between them. On the other hand, the substrate chuck was equipped with water and a cryo-cooling facility which was used to cool the samples after ion bombardment at higher temperatures. The ion sputtering time varied from 6 min–9 h 30 min, corresponding to the ion fluence $1 \times 10^{14}$ to $1 \times 10^{20} \ cm^{-2}$ respectively for different temperatures where the current density was kept fixed around 1000 $\mu$A cm$^{-2}$. The ion sputtered modified surface was characterized using an ex situ Vecco MMSPM NanoScope IV atomic force microscope in ambient conditions, operating in tapping mode with Si cantilevers having a nominal tip radius of 10 nm. Quantitative information regarding amplitude, periodicity, and the wavelength of the surface features were extracted from the AFM images processed by Nanotec Electronica SL WSxM software (version 5.0 Develop 5.3) [28] and Gwyddion [29]. The microstructural analysis of the ion sputtered surfaces was carried out in a FEI, TECNAI G2 F30, S-TWIN
transmission electron microscope operated at 300 kV. To check whether the sample surfaces were contaminated with impurities or not due to ion sputtering, the chemical composition of the sputtered surfaces were examined by EDX attached with TEM and also by x-ray photoelectron spectroscopy.

4. Results and discussion

The experimental results are ordered as: initially, the temperature-induced morphological evolution of the Si(100) surface for different ion fluences are explored. In the next section, the experimental observations are discussed in the context of different continuum models of pattern formation.

4.1. Temperature- and fluence-dependent morphological behavior of a Si surface

Figure 2 represents $1 \times 1 \mu \text{m}^2$ AFM images of 500 eV Ar$^+$ ion sputtered Si(100) surfaces at different temperatures $T = 20\, ^\circ\text{C}, 200\, ^\circ\text{C}, 300\, ^\circ\text{C}, 350\, ^\circ\text{C}, 400\, ^\circ\text{C}$ and $450\, ^\circ\text{C}$ for low ion fluence $1 \times 10^{18} \text{cm}^{-2}$. At room temperature $\sim 20\, ^\circ\text{C}$, the surface morphology exhibits well-ordered parallel mode ripple nanopatterns. Parallel mode means the wave-vector of these ripples are aligned parallel to ion beam projection. This can be confirmed by the corresponding FFT (fast Fourier transform) image, where two first order bright spots are aligned symmetrically along the ion beam projection with respect to the central spot. As the temperature rises up to $300\, ^\circ\text{C}$, the ordering of the ripple patterns remains as it is and both the surface roughness and wavelength remain constant at around $1.04 \pm 0.08 \text{nm}$, $32.03 \pm 0.60 \text{ nm}$ (figures 5(c), (d)) respectively. The wavelengths of the ripples are determined from the first peak position of the corresponding PSD (power spectral density) functions shown in figures 5(i)–(c). The presence of sharp bright spots beside the center one in the FFT image or the peak in the PSD curves is the approval of periodicity on the sample surface. From $T > 300\, ^\circ\text{C}$, the ripple amplitude begins to fall (figure 6(c)) and the ripples start to lose their periodicity (figure 2). The mean surface roughness is found to decrease from 0.9 nm–0.3 nm with a rise in temperature from $300\, ^\circ\text{C}$–$450\, ^\circ\text{C}$. The loss of ripple ordering from $200\, ^\circ\text{C}$–$350\, ^\circ\text{C}$ can be confirmed by the corresponding FFT images where the first order bright spots (inset of figures 2(c)–(d)) show a gradual shrinkage of sharpness and simultaneously move closer towards the central spot. The corresponding PSD curves (figures 5(i) (d)–(e)) also show a relatively wider distribution of the peak. The broad width means less ripple periodicity because the FWHM of the peaks in PSD is inversely proportional to the correlation length or the surface periodicity. At $400\, ^\circ\text{C}$, the first bright spots finally merge with the central spot and FFT is left with an elliptical spot whose major axis lies along the parallel direction of the ion beam projection. This reveals a poor degree of ripple ordering. As a consequence, the corresponding PSD curve displays no peak (figures 5(i)(f)). A further increase of temperature up to $450\, ^\circ\text{C}$ leads only to a circular spot in the FFT image. This indicates the presence of no preferred pattern orientation on the surface. Consequently, the AFM image, figure 2(f), corresponding to $450\, ^\circ\text{C}$, also displays irregular modulations of very low amplitude surface heights.

Now, the effect of high fluence on the temperature-induced Si surface morphologies are demonstrated. The experimental conditions remained the same as described in the above paragraph, only the ion fluence was varied up to $1 \times 10^{20} \text{cm}^{-2}$. The surface morphologies at high fluence and at high temperatures are quite different to that observed for low fluence $1 \times 10^{18} \text{cm}^{-2}$. Some representative AFM images of temperature-influenced surface patterns at high fluence $1 \times 10^{20} \text{cm}^{-2}$ are shown in figures 3(a)–(f). The ion fluence-dependent ripple
morphological behaviors at room temperature are shown elsewhere [4]. Figure 3(a) shows that the ripples as a result of very high fluence $1 \times 10^{20} \text{cm}^{-2}$ retain the same orientation with respect to ion beam projection at room temperature as in the low fluence regime (figure 2). In addition, a larger corrugation in wavelength is observed on the surface, together with the parallel mode ripple nanopatterns which develop beyond fluence $2 \times 10^{19} \text{cm}^{-2}$ (the AFM images are not shown here) [4]. This sort of roughness looks similar to that also reported on Si(100) subject to IBS patterning at room temperature by Keller et al [30]. The corresponding PSD curve represented by figure 5(ii)(a) shows a peak which gives a wavelength value 36 nm for short length scale ripples. Weak ordering in large wavelength corrugation corresponds to no peak in the PSD function. Thus, the periodicity in a large length scale is calculated by taking the average of the peak to peak distance of the surface profile extracted from the corresponding AFM image which gives a value around $450 \pm 60$ nm. But as the temperature increases, the parallel mode ripples start to lose their ordering from $300 \degree C$, similar to the low-fluence regime, and reduce to randomly ordered mound-like structures around $350 \degree C$. The larger corrugation in wavelength is also degraded with an increase of substrate temperature and completely disintegrates at $350 \degree C$. This scenario is supported by the broadening of the peak in the corresponding PSDs. At $T \geq 400 \degree C$, orthogonally rotated ripples evolve where their wave-vector is oriented along the perpendicular direction of ion beam projection (figures 3(e)–(f)). These kinds of ripples are generally addressed as perpendicular mode patterns. This can be confirmed by the corresponding FFT image represented by figure 3(e) which clearly displays the ellipsoidal distribution of the central spot along the perpendicular direction of the ion beam projection. A further rise in temperature (450 $\degree C$) leads to more pronounced perpendicular mode patterns.

The evolution of perpendicular mode patterns at a temperature of 450 $\degree C$ as a function of ion fluence is presented in figure 4. The signature of perpendicular mode patterns is primarily observed for fluence $2 \times 10^{19} \text{cm}^{-2}$, although the pattern’s alignment is not clearly visible from the AFM image (figure 4(d)) but realizable from the corresponding FFT image. These patterns become prominent with an increase of ion fluence, as can be seen from figures 4(e) and (f) respectively.

Based on fluence-dependent changes in surface roughness $\omega$ up to 350 $\degree C$, the fluence range can be divided into two regimes: (1) the first one is from $1 \times 10^{18} \text{cm}^{-2}$ to $1 \times 10^{19} \text{cm}^{-2}$ and (ii) the second one is from $1 \times 10^{19} \text{cm}^{-2}$ to $1 \times 10^{20} \text{cm}^{-2}$ and are shown in figure 6(a). For the first regime, the surface roughness increases with the growth exponent $\beta = 0.23 \pm 0.01$ and remains almost constant in the second regime. For temperatures $400 \degree C$ and $450 \degree C$, initially $\omega$ remains constant, then with fluence it follows a power law behavior with exponent $0.31 \pm 0.01$ and $0.56 \pm 0.02$ respectively and saturates later on. On the other hand, figure 6(b) shows the ion fluence-dependent behavior of ripple wavelength $\Lambda$ at different substrate temperatures from $20 \degree C$–$450 \degree C$ where $\Lambda$ increases for ion fluence $1 \times 10^{18} \text{cm}^{-2}$ to $1 \times 10^{19} \text{cm}^{-2}$ and beyond that, it shows saturation. At room temperature, $\Lambda$ shows a very slow increase from 33–36 nm with coarsening exponent $n = 0.03 \pm 0.01$ and with the rest of the temperatures, it coarsens with exponent $n = 0.11 \pm 0.01$. The temperature-dependent surface morphological behaviors at different fluences are illustrated in figures 6(c) and (d). Irrespective of ion fluence, surface roughness is found to remain constant up to $350 \degree C$ and then falls at higher temperatures. On the other hand, for fluences $>1 \times 10^{19} \text{cm}^{-2}$, $\Lambda$ shows an initial increase with $T$ up to $100 \degree C$, and after that it becomes constant for higher $T$.

In order to investigate the geometrical shape and crystallinity of temperature-induced ion irradiated surface morphologies, cross-sectional TEM is performed for the samples sputtered at highest ion fluence $1 \times 10^{20} \text{cm}^{-2}$ and at temperatures $T = (i) 20 \degree C$, (ii) $350 \degree C$ and (iii) $450 \degree C$. The results are presented in figure 7. The TEM
image corresponding to figure 7(a) shows the ion sputtered Si surface at room temperature. The rippled surface profile does not exactly follow the sinusoidal nature but looks like a sawtooth wave with an average peak to peak separation of 35 nm, one side of which facing the ion beam (front slope) is steeper than the other (rear slope). The magnified TEM image (figure 7(b)) reveals a thin amorphous layer on crystalline Si which possesses unequal thickness on the front (2.3 nm) and rear slope (1.1 nm) of the sawtooth ripples. The sawtooth shape of the ripples and the inhomogeneity in the amorphous layer is attributed to the shadowing effect arising due to the grazing incidence (65°) of ions for a long irradiation time. Due to grazing incidence, ions can easily reach one face of the rippled surface while the other gets blocked due to shadowing. Thus, the surface which faces the ion beam is eroded faster, becoming steeper than the other, and due to long-time exposure, it results in an asymmetric surface profile (sawtooth shape). At the same time, as more ions hit the front face, it bears a thicker amorphous layer. The presence of the amorphous layer on crystalline Si is expected for ion irradiation at a fluence $\sim 1 \times 10^{19} \text{ cm}^{-2}$ which is sufficiently higher than the amorphization threshold [31], and the extent of the amorphous layer depends upon the depth of the ions on target. According to SDTrimSP V5.05 [32], the penetration depth for 500 eV Ar$^+$ ions on the Si surface is $\sim 2$ nm, which is in agreement with the experimental results obtained at room temperature. In comparison to room temperature, the TEM study of the surface, which is sputtered at 350 °C (figure 7(c)), shows quite low ordered and low amplitude height modulation in a large lateral scale ($\sim 46$ nm), which supports the morphologies revealed by the AFM image of figure 3(d). Simultaneously, the HRTEM image (figure 7(d)) confirms that there is a narrower amorphous layer than at room temperature but it still shows non-uniformity in thickness at two slopes, i.e. 1.5 nm and 0.7 nm for the front slope and rear slope respectively. At a further higher temperature $T = 450$ °C (figure 7(e)), the surface becomes flat and it is hard to distinguish any amorphous layer, even from the HRTEM image (figure 7(f)). The outcome of these TEM studies on temperature-treated ion sputtered surfaces reveals one more interesting finding—that the crystalline damage in the near-surface region increases with an increase of the substrate temperature, although the extent of the damage is not uniform from the surface to inside the bulk direction. In the case of 450 °C, the damage is extended up to a maximum of 8 nm, which is quite surprising with respect to the penetration depth of $\sim 2$ nm for 500 eV Ar$^+$ ions on the Si surface. This may be due to the high temperature-driven surface crystallinity, where the ions can be channeled accidentally through some crystal sites, propagating up to a greater extent than their range and causing inhomogeneous damage in the crystalline planes near the surface [33].

In order to explore whether the temperature-induced surface morphologies are not induced by impurity contaminants, high-angle-annular-dark field analysis, which essentially gives Z-contrast imaging, is performed. The spectrum of elemental mapping by energy dispersive x-ray spectroscopy (EDX) over a domain (marked in figure 7(e)) of ion sputtered surface topography at 450 °C shows strong Si lines with weak signals of C and O at the background shown in figure 7(e), and no evidence of any metal species or any other impurities [34] are found. This observation is also supported by the spectrum of elemental mapping obtained from the XPS study (not shown here). The presence of a very small fraction of C is probably due to the exposure of the bombarded sample in the air.

4.2. Theoretical discussions on surface morphological behaviours

Some of the experimental results described above can be fitted well to the prediction of the existing theoretical framework based on BH theory [7], whereas some other results cannot. The detail of BH theory has already been
discussed in section 2. In the present experiment, the energy (500 eV) of incident Ar$^+$ ions exceeds 35 times the energy threshold for defects' production in Si. Thus, the incidence ion beam produces a large number of defects on the surface in the form of adatoms and vacancies which act as perturbation to create initial surface instability during ion sputtering. One of the most recent concerns in the field of ion beam nanopatterning is to understand the pattern formation mechanism in terms of curvature-dependent ion erosion and mass-redistribution of the near-surface adatoms. To reveal this, the BH-coefficients $S_{x,y}^\text{eros}$ and mass-redistribution coefficients $S_{x,y}^\text{redis}$ are calculated by ellipsoidal ion energy distribution parameters, average depth $d = 1.38$ nm, lateral and longitudinal widths of energy distribution $\sigma = 1.19$ nm and $\mu = 0.87$ nm respectively, and their angle-dependent variations are shown in figure 8. The parameters $a$, $\sigma$ and $\mu$ for 500 eV Ar$^+$ ion irradiation on the Si surface are extracted using the code SDTrimSP V5.05 [32]. The larger absolute value between ion erosion $-S_{x,y}^\text{eros}$ and mass-redistribution $-S_{x,y}^\text{redis}$ co-efficients determine the formation of the nanopattern and its orientation with respect to ion beam projection, where $x$ and $y$ signifies the same direction as described earlier. Figure 8 shows that $S_{x,y}^\text{redis}$ exhibits a larger negative value for $\alpha_{\text{ion}} = 65^\circ$. This predicts the evolution of anisotropic patterns with its wave-vector along the $x$ direction which matches the experimental results, and the pattern formation is dominated by the mass redistribution of near-surface adatoms rather than the curvature-dependent erosion.

On the other hand, the surface smoothing mechanism during the sputter-induced pattern evolution process is also quite complex. Details of the different smoothing mechanisms have already been discussed in section 2. To identify the smoothing mechanism, we analyze the slopes ($m$) of the PSD curves (figure 5) for high-$k$ ($k \gg k_0$) values corresponding to different temperatures for both low and high fluxes. The estimated value of $m$ for the temperature range $T = 20$°C–350 °C, say region I, is found to be equal to $-4.1 \pm 0.2$ and for $T > 400$ °C, say region II, $m$ is around $-2.0 \pm 0.1$. The scaling comes from the wave-number $k$ in PSD, which helps us to recognize the dominating relaxation process associated with the $K$-term in equation (1). Frost et al [35] have shown that PSD $\propto k^{-4}$ can correspond to TSD, effective ISD or IVF. Again, PSD $\propto k^{-2}$ corresponds to the ion-induced ballistic smoothing [11]. For region I, at room temperature, TSD ($K_\text{TSD} = 4 \times 10^{-8}$ nm$^4$ s$^{-1}$) contributes only a negligibly small amount, whereas ISD ($K_\text{ISD}^\text{ESD}$) gives the ripple wavelength (using equation (2)) one order less than the experimental value. By considering IVF ($K_{\text{IVF}}$) as the smoothing mechanism, the estimated ripple wavelength for parameters $n_{\text{Si}} = 4.31$ nm$^2$ s$^{-1}$, $\gamma = 6.74$ eV nm$^{-2}$ and $N = 49.77$ atom nm$^{-2}$ is found close to the experimentally obtained value. Thus, $K_{\text{IVF}}$ can be concluded as the dominant surface relaxation mechanism during IBS at room temperature. For higher temperatures, $K_{\text{TSD}}$ increases following the Arrhenius law but its contribution in pattern formation up to 300 °C ($\sim 3.6$ nm$^{-1}$ s$^{-1}$) is too small. A further rise in temperature obviously makes TSD stronger but somehow the experimental results do not follow the obvious BH behavior, i.e. the increase of ripple wavelength with temperature [7]. In contrast, the experimental results show the degradation of parallel mode ripples as the temperature is increased. Another smoothing mechanism, i.e. $K_{\text{ISD}}$, exhibits no dependency on temperature. On the other hand, the scaling from PSD reveals IVF can be a possible smoothing mechanism for the temperature range up to 350 °C. Thus, IVF for $T = 20$ °C–350 °C and ion-induced ballistic smoothing for $T \geq 400$ °C can be concluded as the dominant smoothing mechanism. In the ballistic smoothing process, an atomic flux diffuses parallel to the local surface with a momentum in the direction of the incident ion which gives rise to a curvature-dependent
smoothing term and compensates the curvature-dependent surface roughening. Carter and Vishnyakov [11] introduces this smoothening phenomena to explain the flat and stable surfaces at near-normal incidence of ion sputtering [11]. In our case, ballistic smoothening plays a role during near-grazing incidence \( \sim 65^\circ \) ion sputtering but after a certain substrate temperature \( 350^\circ C \). Thus, the fall of surface roughness beyond \( 350^\circ C \) is influenced by the ion-induced ballistic smoothening.

One of the other possibilities behind the decrease in surface roughness with an increase of substrate temperature may be the strain fields developed among the crystal planes during the reconstruction of the amorphized layer [36]. The strain can either be compressive or tensile, which may increase or decrease the surface diffusion depending on whether the surface stress is under compression or tension [37]. Gago et al [21] had confirmed the presence of compressive strain in the near surface region for ion irradiated surfaces at an elevated temperature through GID (grazing incidence diffraction) measurements. The increase in crystalline strain is observed in our case also, as a result of which the defects in the near surface crystalline planes are found to increase with an increase of temperature (figure 7).

The temperature-induced experimental observations of this study, i.e. the evolution of grains at low ion fluences and the orthogonal rotation of ripples at high ion fluences for \( T \geq 400^\circ C \) are quite surprising as these are not predicted by any existing continuum models of ion beam nanopatterning. According to existing theories, the fluence-dependent ripple rotation is only predicted at room temperature by the non-linear extension of BH
theory. The negative sign of the product of non-linear terms \( \lambda_x \) and \( \lambda_y \) predicts the rotation of the ripple by an angle \( \theta = \tan^{-1}(\lambda_{xy}/\lambda_{yx}) \) after a prolonged sputtering time \( t_s \approx \frac{K}{\lambda_{xy} V_{inc}} \ln \frac{S_{xy}}{S_{yx}} \) [37]. At high temperatures, as we discussed before in the introduction, if the irradiation is performed near or above the surface re-crystallization temperature, then the pattern formation is driven by an additional instability arising due to the presence of an ES barrier, which is an inherent property of the crystalline surface. The Schwoebel barrier-induced biased diffusion of surface adspecies, i.e. the vacancies or adatoms on terraces, across terrace steps and kinks, gives rise to a diffusion current which generates regular and faceted structures on the surface. As the diffusion takes place along the preferred crystallographic direction of the sample surface, thus the pattern’s shape and orientation follows the crystal symmetry. Recently, Ou et al have shown the inverse square pyramids on a Si (100) surface when 500eV Xe\(^+\) ion irradiation is performed at normal incidence and at an elevated temperature of 530 °C for ion fluence \( 3 \times 10^{19} \text{ cm}^{-2} \) [38] whose well-defined edges run along the \( \{110\} \) and \( \{110\} \) crystallographic directions. The ES barrier-induced diffusion bias of the surface vacancies are found to generate those surface structures. Generally, low energy (\( \leq 1 \text{ keV} \)) ion irradiation creates both adatoms and vacancies on the surface, but as the mobility of the adatoms is high, they can easily be knocked out by the incident beam, which consequently increases the population of vacancies and acts as a major carrier for surface diffusion. In the presence of an ES barrier, the vacancies do not ascend the steps but prefer to stick at lower terraces and result in a net downhill diffusion current which generates regular and faceted structures on the surface. As the diffusion takes place along the preferred crystallographic direction of the sample surface, thus the pattern’s shape and orientation follows the crystal symmetry. Recently, Ou et al have shown the inverse square pyramids on a Si (100) surface when 500eV Xe\(^+\) ion irradiation is performed at normal incidence and at an elevated temperature of 530 °C for ion fluence \( 3 \times 10^{19} \text{ cm}^{-2} \) [38] whose well-defined edges run along the \( \{110\} \) and \( \{110\} \) crystallographic directions. The ES barrier-induced diffusion bias of the surface vacancies are found to generate those surface structures. Generally, low energy (\( \leq 1 \text{ keV} \)) ion irradiation creates both adatoms and vacancies on the surface, but as the mobility of the adatoms is high, they can easily be knocked out by the incident beam, which consequently increases the population of vacancies and acts as a major carrier for surface diffusion. In the presence of an ES barrier, the vacancies do not ascend the steps but prefer to stick at lower terraces and result in a net downhill current, which leads to surface instability in the form of depressions. In our case, instead of surface re-crystallization at 450 °C (see the TEM results), we observe a random height modulation at low ion fluences and ripples at high fluences whose ridges are aligned parallel to the \( \{110\} \) direction and perpendicular to ion beam projection respectively. This can be qualitatively explained by the curvature-dependent erosion kinetics rather than the ES barrier-induced biased surface diffusion where the growth of surface structures are dictated by the incident ion beam direction rather than the symmetry of the crystal face. These types of observations were obtained earlier by Valbusa [18, 39] on an ion irradiated metal surface at elevated temperatures. Recently, we reported the same phenomena on a GaAs surface [40] where the pattern formation at high temperatures is determined by the crystal symmetry up to 65°, and beyond that, it depends on the incident beam direction. On the other hand, the orthogonal rotation of ripples was shown by only one group, Erlebacher et al [20, 41], both on Si(100) and Si(111) surfaces. For Si(100), 750 eV Xe\(^+\) ion bombardments were performed for substrate temperatures of 500 °C–600 °C at an ion incidence angle of 67.5°, whereas for Si(111), 500 eV Ar\(^+\) ion irradiation was performed at an incidence angle of 60°, and for ion fluences 8.4 × 10^{18} \text{ cm}^{-2} to 4.8 × 10^{19} \text{ cm}^{-2} for a fixed substrate temperature of 657 °C. This report clearly indicates that the formation of perpendicular mode ripples at high temperatures and high fluence is not influenced by the bombarded surface crystallography but driven by the incident ion beam direction with respect to the surface normal. Moreover, the evolution of the perpendicular mode ripple patterns is not as strong in our studies as observed in [41] and [19, 20]. This may be attributed to the lower temperature range of 20 °C–450 °C used in our experiments compared to the reported value of 657 °C in [41] and 500 °C–600° C in [19, 20] respectively.
5. Conclusion

The present work describes a systematic study on the temperature-induced morphological evolution of an ion sputtered ripple surface for low to high fluence regimes. For the low fluence regime, a self-organized parallel mode ripple is found to flatten with temperature, but the ripples are orthogonally rotated at higher temperatures ($T \gtrsim 450 \, ^\circ C$) at high ion fluences. 350 $^\circ C$ is identified as the transition region of pattern orientation for an entire fluence range. The EDX study confirms that the surface morphologies are not induced by impurities or any other metal contamination. TEM studies of an ion sputtered surface at room temperature for high ion fluences reveal a sawtooth surface profile of ripples with a thicker amorphous layer on its front slope than its rear one. The TEM studies also show a decrease in thickness of the amorphous layer with an increase in substrate temperature for fixed ion fluence. The experimental results are discussed in the framework of existing continuum models dealing with the morphology evolution of ion sputtered surfaces. The ion beam induced pattern formation is found to be dominant by the mass-redistribution of surface adatoms rather than the curvature-dependent ion erosion. On the other hand, IVF acts as a dominant smoothing mechanism during pattern evolution within the temperature range $T \sim 20 \, ^\circ C$ and $350 \, ^\circ C$, whereas ion-induced ballistic smoothing is identified as a smoothing mechanism for $T \gtrsim 450 \, ^\circ C$. The temperature-induced ripple rotation for high ion fluences can be attributed to the curvature-dependent erosion kinetics arising due to the grazing incidence of ion sputtering. Some of the results presented here are surprising and demand further theoretical progress for clear understanding of the ion-induced pattern formation mechanism, which in other ways helps to improve the control of the IBS technique on surface nanopatterning.

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