Ion-induced roughening and ripple formation on polycrystalline metallic films

T Škereň¹, K Temst¹, W Vandervorst¹,² and A Vantomme¹,³

¹ Institut voor Kern- en Stralingsfysica, KU Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium
² IMEC, Kapeldreef 75, B-3001 Leuven, Belgium
E-mail: Andre.Vantomme@fys.kuleuven.be

New Journal of Physics 15 (2013) 093047 (20pp)
Received 25 May 2013
Published 30 September 2013
Online at http://www.njp.org/
doi:10.1088/1367-2630/15/9/093047

Abstract. We present a study of nanopattern formation on polycrystalline Ni surfaces upon low energy Ar ion bombardment. At low angles of ion incidence an isotropic, rough morphology develops on the surface while at grazing incidence a ripple structure parallel to the ion beam direction is formed (so-called perpendicular mode ripples). To explain this behavior we propose a model which is based on a combination of (a) surface roughening due to sputter yield variation between different crystalline grains and (b) anisotropic nonlinearity resulting from the oblique angle bombardment. By computer simulations we show that the combination of these two phenomena excellently reproduces the experimental behavior, in particular the dependence of the surface morphology on the ion incidence angle. Importantly, the formation of ripples at grazing incidence does not involve any linear instability, in strong contrast to the present model of the ripple formation process.
1. Introduction

The irradiation of surfaces with a broad ion beam often leads to the formation of quasiperiodic height modulations on the surface [1]. The formation of two dimensional dot or pit arrays and one dimensional ripples has been observed on a large variety of surfaces and upon a broad range of irradiation conditions [2–4]. In the recent past, this technique has been attracting increasing attention as a powerful tool for modification of the surface properties at the nanometer scale [5]. However, the physics behind this phenomenon is still not well understood and many aspects remain unexplained [6–12].

The patterning behavior is known to be strongly dependent on the target material (besides other parameters). Crystalline structure of the material is known to play an important role. One large and important group are the amorphous (and amorphizable) materials. These include some of the widely studied surfaces, such as Si or SiO\textsubscript{2}. These surfaces typically exhibit ripple formation by ion irradiation at moderate angles (around 60–70°, measured from the surface normal) with an orientation perpendicular to the ion beam projection on the surface (so-called parallel mode ripples (PaMR) since the \textit{wavevector} is parallel to the ion beam), while at grazing incidence the ripples become parallel to the ion beam [1, 13–16] (so-called perpendicular mode ripples (PeMR)). A second major group of materials are metals. In contrast to the previous group, metals remain crystalline even after irradiation with a substantial ion fluence. Formation of surface ripples at grazing angle irradiation is typically observed on these surfaces, with an orientation parallel to the ion beam (PeMR). In contrast to the amorphous materials, the formation of PaMR has been observed only in a few specific cases [17, 18].

Metallic surfaces can be further divided to polycrystalline (PC) and single-crystalline (SC) ones. Multiple studies on SC metals indicate that the role of the crystallinity in these systems is associated with the presence of the Ehrlich–Schwoebel (ES) barrier [3, 19–24].

On the other hand, in the case of PC metals the role of the crystalline structure in the pattern formation process is not very well understood. Pattern formation on different PC metals has been studied, e.g. Ag [25–27], Au [25, 27], Co [18, 28], Fe [18, 29] and Ni [18, 29]. Toma et al [30] and Colino et al [28] showed that the initial surface morphology influences the features of the ion-induced nanopattern. In particular, if the initial surface morphology has a specific
quasiperiodic wavelength, the ripple pattern formed by grazing incidence bombardment was shown to inherit this wavelength [30]. This observation suggests an indirect link between the material grain structure (which has a strong effect on the initial film morphology) and the pattern morphology. However, the role of the PC structure (other than via the initial morphology) in the patterning process has not been explicitly discussed.

The formation of periodic ripples is usually discussed in the context of the Bradley–Harper (BH) linear instability theory [6]. By analyzing the erosion process in the context of the Sigmund sputtering theory [31], BH found that the erosion speed should locally depend on the surface curvature (i.e., the local sputter yield is a function of the second derivatives of the surface topography). Specifically, the tops of the surface protrusions are eroded slower than the bottoms of valleys, which leads to an increase of the surface roughness upon the ion erosion. This roughening is counteracted by surface diffusion which acts as a smoothening term. The evolution of the surface topography is then described by a linear differential equation

$$\frac{\partial h(x, y, t)}{\partial t} = \Gamma_x(\theta) \frac{\partial^2 h}{\partial x^2} + \Gamma_y(\theta) \frac{\partial^2 h}{\partial y^2} - B \nabla^4 h,$$

where $h$ is a function describing the surface topography, $B$ is a coefficient describing the surface diffusion and $\Gamma_{x,y}$ are coefficients describing the dependence of the erosion speed on the surface curvature—these coefficients depend on the angle of incidence $\theta$. This linear differential equation can be easily analyzed by a Fourier transform and Bradley and Harper showed that it is always unstable—the amplitude of certain Fourier modes of the surface topography is expected to grow exponentially in the erosion process. The fastest-growing mode dominates the surface topography and determines the pattern wavelength and orientation. Since the coefficients $\Gamma_{x,y}$ depend on the angle of ion incidence $\theta$, the pattern periodicity and orientation is also expected to depend on the angle. In particular, the BH theory predicts that for low angles of ion incidence a ripple pattern perpendicular to the ion beam (PaMR) should form while for grazing incidence a ripple pattern should become parallel to the ion beam (PeMR). This angle-dependent change of the ripple orientation is indeed observed on many amorphous surfaces, whereas for metals only ripples parallel to the ion beam (PeMR) are typically present. The relevance of this mechanism for metallic surfaces has been challenged previously [22].

In this paper, we investigate the evolution of the ion-induced morphology on PC metallic surfaces. We focus on a particular system—PC Ni—and we study its morphology after 5 keV Ar ion beam irradiation at different angles of incidence.

We propose a mechanism for the formation of the surface morphology which does not involve the erosive linear instability but is based on substantially different phenomena—local variation of the sputter yield due to (i) the crystalline orientation of grains and due to (ii) local ion incidence angle. By computer simulations we show that this mechanism explains all the experimental observations. The simulated morphologies are qualitatively and quantitatively in excellent agreement with the experimental ones.

2. Experimental

50 nm thick PC Ni films were grown on SiO$_2$ substrates by molecular beam epitaxy (MBE) at room temperature with a deposition rate of 0.15 Å s$^{-1}$ and a base pressure lower than 1 × 10$^{-9}$ mbar. Ni(001) films with a thickness of 50 nm were prepared by MBE growth on MgO substrates. Prior to the growth, the MgO substrates were outgassed in ultra high vacuum.

New Journal of Physics 15 (2013) 093047 (http://www.njp.org/)
conditions at 600 °C for 30 min and cooled down to the growth temperature of 180 °C. The deposition rate and base pressure were identical to the PC film deposition conditions. After growth the Ni(001) samples were annealed to 700 °C for 1 h. The PC samples were not subjected to any post-growth thermal treatment. X-ray diffraction analysis of Ni(001) films confirmed that the films are highly oriented with Ni(001)||MgO(001) and Ni[100]||MgO[100] (in agreement with the results of Sundgren et al [32]). The crystalline structure of the PC Ni films is discussed in section 3.4.

In situ scanning tunneling microscopy (STM) was performed with Omicron room temperature ultra-high vacuum STM/AFM tool directly after the preparation of the films which were then taken out of the vacuum and cut in smaller pieces for the ion bombardment experiments. Ion beam irradiation of the samples was performed at room temperature with a 5 keV Ar⁺ ion beam produced by an electron ionization gun. The ion beam with a typical current of 4 µA and a diameter of about 1 mm was scanned over an area of 9 × 9 mm. The base pressure of the irradiation chamber was below 5 × 10⁻⁹ mbar, while during the irradiation it increased to about 8 × 10⁻⁸ mbar. The morphology of the eroded surfaces was investigated by an in situ STM at room temperature. The root mean square (rms) roughness of the surfaces was extracted from the STM topographs, error bars represent statistical spread between several different areas.

3. Results

3.1. Experimental results

The STM of the surface topography of an as-grown PC Ni film is depicted in figure 1(a). Individual grains can be roughly recognized by the ‘caps’ visible on the topograph. Their lateral size is approximately 15 nm, which is much less than the thickness of the film (50 nm). Internally, the film has a lamellar structure with grains propagating through the whole film thickness—a natural result of the film growth [33].

The topographs of the PC Ni films eroded at different angles of ion incidence are presented in figures 2(a)–(d). The general trend is a gradual transition from an isotropic rough structure to a strongly anisotropic rippled surface as the angle of incidence increases. At 50° incidence we observe a granular structure with different grains having a different height and some of the grains protruding significantly from the mean surface plane. At 60° incidence, the surface looks

New Journal of Physics 15 (2013) 093047 (http://www.njp.org/)
Figure 2. (a)–(d) Surface morphologies of PC Ni films eroded with 185 ions nm$^{-2}$ of 5 keV Ar$^+$ ions at different angles of incidence, (e)–(h) simulated surface morphologies with irradiation conditions and length scale corresponding to (a)–(d) respectively, (i) and (j) SC Ni(001) surface eroded at identical conditions as (a) and (d) respectively. The ion beam was incident from the top side of the images.

Similar, but certain grains appear to have a short ‘tail’ down the ion beam direction. This trend continues for 70° but the granular structure is less obvious and the surface evolves into a short ripple-like morphology. Finally, for 80° we find a pronounced ripple structure parallel to the ion beam direction (PeMR).

Figures 2(i) and (j) show the surface morphology of a SC Ni(001) surface eroded at 50° and 80° incidence and an identical ion fluence as in the case of the PC film. Similarly, an isotropic mound structure can be observed at low angles of incidence while a pronounced ripple structure is formed at grazing incidence.

Figure 3 shows the evolution of the rms roughness as a function of ion fluence for both a Ni(001) and a PC Ni film and for two angles of incidence (45° and 80°). For the PC film, we observe an initial decrease of the rms roughness followed by an approximately linear increase.
3.2. Physical mechanism

For low angles of ion incidence, an isotropic roughness develops on the PC Ni surface. The roughening of PC films by ion erosion has been previously reported (often in the context of depth profiling) and is generally attributed to the variation of erosion rate between different grains due to their random crystalline orientations \[34, 35\].

It is useful to compare the situation to the case of SC surface. The PC roughening mechanism obviously cannot play a role in the SC metal roughening. In the SC case, roughening is attributed rather to the presence of the ES barrier which prevents the surface defects created by the ion bombardment from crossing descending steps and it introduces a linear instability \[19, 24\]. The ES barrier is in principle active even on a PC surface, however, in the current experimental situation, the relatively small size of the grains (not much larger that the characteristic length scale induced by ES instability on Ni(001) surface, figure 2(e)) in combination with their random orientation hinders its action as an effective surface instability. Moreover, the initial rounded shape of the grains translates into a tight spacing of the atomic terraces which hinders the nucleation of mounds/pits on the grain surfaces. Consequently, the dominant mechanism for the roughness formation is likely the erosion rate variation. This conclusion is also corroborated by the observation that the characteristic length scale of the morphology of the eroded PC film coincides with the initial grain size (see section 3.4).

Interestingly, the roughening of a SC surface is thus based on a thermally activated process and it is also known to cease at low temperatures \[2, 22\], while the roughening of a PC surface is of athermal nature and should remain active even at low temperatures.

The remaining question is what mechanism causes the formation of ripples at high angles of incidence? The increasing surface roughness is naturally accompanied by increasing variation of the local surface slopes and consequently local angle of ion incidence. This also introduces a variation in the local erosion rate due to uneven flux and sputter yield angular dependence. This
variation is particularly pronounced at high angles of incidence where the sputter yield becomes more sensitive to the local impact angle and we can expect that it introduces a certain anisotropy to the morphology evolution. The detailed action of this anisotropy is, however, difficult to predict analytically and we investigate its behavior numerically in the following section.

The mechanism we are proposing here is thus based on roughening (due to uneven erosion of different grains) and nonlinearities resulting from the oblique angle bombardment. However, the ripple formation on metallic surfaces is often ascribed to the BH instability [18, 30, 36]. Let us make the following consideration: In the case of SC surfaces it has been observed that ripple formation ceases at low temperatures [2, 22]. This indicates that the patterning process (or its crucial component) is thermally activated. This is inconsistent with the BH instability, which should remain active even if all thermal processes freeze, i.e. even if thermal diffusion is removed from the BH equation, the curvature dependent erosion should remain active and lead to the pattern formation. Consequently, the BH instability is also unlikely to play a role in the ripple formation on PC surfaces since its strength is expected to be the same as on the SC surface.

Additionally, the BH theory predicts the formation of both PaMRs and PeMRs, but only PeMRs are typically observed on both SC and PC metals. Interestingly, the general applicability of the BH theory to the formation of PeMRs at grazing incidence has been already questioned by the authors themselves in the original BH publication [6] since at grazing incidence additional phenomena come into play which are not accounted for by the BH theory.

Moreover, in the current experiments, the initial decrease of the rms roughness in the case of 45° angle of incidence bombardment of PC Ni (figure 3(a)) is also not consistent with the presence of the BH linear instability—such instability predicts amplification of the existing roughness rather than decay.

These arguments show that the BH theory does not provide a consistent description of the pattern formation on metallic surfaces. Nevertheless, it is difficult to conclusively disprove the existence and importance of the BH instability, but, as we show below, the ripple formation observed in the current case can be successfully explained without the BH instability.

3.3. Model

In the following we formulate a mathematical description for the surface morphology evolution based on the two aforementioned phenomena—sputter yield variation due to random grain orientation in a PC film and sputter yield variation with the local angle of ion incidence.

3.3.1. Erosion of polycrystalline films. In order to simulate the erosion of a PC film, we need to account for the grain structure which introduces the inhomogeneity in the erosion rate. We assume that the PC film has a lamellar structure with grains propagating through the whole thickness of the film in a parallel manner (figure 1(d)). We estimate the grain density of the 50 nm Ni films by counting the number of grain caps on several STM images of an as-grown surface. Although this method is only approximative, it gives us a reproducible grain density of 220 grains per 200 × 200 nm² image area with a statistical spread of ±20 grains.

An estimate of the sputter yield variation can be done based on the angular dependence of the sputter yield of a SC target, where dips in the sputter yield are typically present around low-index directions [37]. These directions coincide with crystal channeling directions and the two phenomena are not unrelated. By analyzing these dips for the different low-index directions,
Table 1. Widths and depths of the main fcc Ni channels for 5 keV Ar⁺ bombardment. The last column indicates the number of channels according to the crystal symmetry.

| Channel | Width (°) | Depth (rel.) | Number |
|---------|-----------|--------------|--------|
| ⟨110⟩  | 18        | 0.39         | 12     |
| ⟨100⟩  | 12        | 0.55         | 6      |
| ⟨111⟩  | 12        | 0.55         | 8      |
| ⟨112⟩  | 15        | 0.58         | 24     |

we can extract the angular width and the relative decrease of the sputter yield (i.e. depth of the dip). To the best of our knowledge, no data are available for the particular case of 5 keV Ar⁺ bombardment of SC Ni and, instead, we used the data for 5 keV Ar⁺ bombardment of a Cu(001) surface [37]. Since Ni and Cu are both face-centered cubic (FCC) metals with very similar atomic numbers and lattice constants, we assume that also their sputter yield variation with crystalline orientation is comparable. We extracted the widths (represented by the full width at half maximum (FWHM) of the sputter yield dip in degrees, approximated by a Gaussian function) and relative depths (ratio of the sputter yield local minimum and sputter yield at the edges of the dip) of the four most pronounced sputter yield dips in the Ni crystal (table 1). This analysis is rather approximative, since the sputter yield value is also influenced by the varying angle of incidence and by the presence of higher order channels and additional crystalline effects [35]. However, the data provide reasonable starting values for the estimation of the sputter yield variation. Based on these data and taking into account the position of the channels we obtained a sputter yield variation as a function of the two spherical angles (figure 4(d)). This function can be interpreted in the following way: if a (flat) surface is bombarded at a given angle of incidence, the sputter yield for a grain with a particular crystalline orientation is given as the product of the mean sputter yield for the given angle of incidence and the value of this function for the particular crystalline orientation of the grain. The angular dependence of the sputter yield for a PC Ni surface is presented in figure 4(a) along with the reconstruction of the sputter yield angular dependence for a crystalline Ni(001) target along two incidence planes obtained by the described model. The SC yield for specific directions can be larger than the PC sputter yield, since the PC yield for each point is a mean value of the random portion and the ‘channeled’ contribution.

Finally, if we assume that the orientation of the grains in the film is random (see discussion below), we can evaluate the statistical distribution of the sputter yields of a large set of grains (figure 4(b)). This distribution is normalized to its mean value and the statistical spread of this distribution (standard deviation) is 0.15, i.e. the sputter yield variation in a randomly oriented set of grains is ±15%. Interestingly, this distribution is strongly asymmetric, the right-hand peak corresponds to the random orientation while the left-hand tail corresponds to the channeling alignment. This is in agreement with an experimental observation—a height histogram of a Ni surface eroded by ion bombardment (conditions from figure 2(a)) is presented in figure 4(c) and it also exhibits a visible asymmetry—a small portion of the grains protrudes from the surface because of their alignment while a major part of the surface lies in the peak on the left hand side. Finally, in the simulations we neglect the shape of the distribution and we simply assume
Figure 4. (a) Angular dependence of the sputter yield for various Ni surfaces obtained by our erosion model. (b) Statistical distribution of the sputter yield for random grain orientation as obtained by the channeling model and a corresponding uniform distribution used in the simulations. (c) Height histogram of a Ni surface sputtered by 5 keV Ar$^+$ ions to a fluence of 185 ions nm$^{-2}$ and 50° angle of incidence. (d) Polar plot of the sputter yield variation function as obtained by our erosion model.

that the sputter yield of a particular grain is a random number from a uniform distribution with the standard deviation estimated above, i.e. 0.15 (red line in figure 4(b)). This approximation preserves the quantitative evolution of the rms roughness but it has some minor impact on the surface morphology. Most notably, in figures 2(a)–(c) a small number of grains protrudes exceptionally from the mean surface plane which is not visible in the corresponding simulations (figures 2(e)–(g)).

Further, we generated the grain boundaries in the simulation area as Voronoi cells of a given number of grain seeds randomly distributed inside this area (corresponding to the grain density estimated from the STM topographs). In other words, we first randomly generated the specific number of points (seeds) and to each seed we assigned a region of points which are closer to this seed than to any other. To each such region (which represent one crystalline grain) we randomly assigned a coefficient from the uniform distribution described above. Via this procedure, we obtained the function $G(x, y)$ that describes the local variation of the sputter yield due to the random grain orientation. Figure 1(c) shows an example of this function for
an area corresponding to the STM topograph in figure 1(a). The meaning of this function is as follows: if the surface is eroded by an ion beam at a specific angle of incidence, the function $G(x, y)$ provides a correction factor for the sputter yield in the point $(x, y)$, due to the specific orientation of the grain which is present in this point. The value of $G(x, y)$ thus oscillates around 1—if it is more than 1, the particular grain is eroded slightly faster than average. If it is less than 1 the grain is eroded slightly slower than average which physically represents a grain oriented in a channeling direction.

For the simulations where initial surface morphology has been taken into account we generated the as-grown morphology by imposing a parabolic cap on each grain seed (figure 1(b)) and normalizing the Z-scale to obtain the rms roughness corresponding to the experimental surface (0.85 nm).

3.3.2. Film texture. In the above estimation of the sputter yield variation we assumed that the grain orientation is fully random, i.e. in a large set of grains all orientations are equally populated. However, the growth of PC thin films is typically accompanied by formation of texture, i.e. a specific crystallographic grain orientation is preferred in the growth process [38]. This can have an impact on the sputter yield variation and we discuss this influence in the following paragraphs.

Generally, if an amorphous substrate is used for the growth (as in the current case) the in-plane orientation of the grains is fully random. Certain out-of-plane orientation can be selected via a number of distinct processes [38]. In an extreme case this results in a perfect fiber texture—all grains have precisely the same out-of-plane orientation (they face the substrate with the same crystallographic plane) and are randomly oriented in-plane. In reality, the situation is typically somewhere in between—a certain out-of-plane grain orientation is preferred and the grains are oriented around this direction within a distribution with a finite width.

For fcc metals (such as Ni) the film growth typically leads to a preferential (111) out-of-plane grain orientation [38] (we confirmed this by comparing the intensities of the different diffraction peaks in specular geometry ($\theta - 2\theta$ scan) with powder diffraction intensities). The distribution of the grain orientations (texture profile) can be estimated by measuring the intensity of the (111) x-ray diffraction peak as a function of the sample angle $\omega$ (rocking curve). The result of such a measurement for the 50 nm PC Ni film is presented in figure 5(a). The rocking curve shows a very wide distribution with a FWHM of about 20° (due to such a large distribution width, this measurement is biased by geometric effects of the x-ray diffractometer, nevertheless, the measured width provides a lower limit for the real texture profile width [39]).

The impact of the texture on the ion erosion model presented above can be illustrated by first assuming a film with a perfect fiber texture. If a (111) fiber-textured film is eroded at a specific angle of incidence, the sputter yield variation between differently oriented grains is given by a statistical spread of the sputter yield variation function on a circle with a specific diameter (figure 5(b): the diameter corresponds to the angle of ion incidence, the circular shape results from the random in-plane grain orientation). For comparison, in the case of a fully random film, the statistical spread is calculated from the entire area of the polar plot. Clearly, at normal incidence, all grains are eroded along the same crystalline direction and no roughening is expected to occur for a film with a fiber texture. For oblique angles of incidence, the degree of sputter yield variation would depend on the amount of channels that the particular circle intersects (figure 5(b)). This degree would depend on the angle of incidence, but a certain variation is always expected. In simple words, the $\pm 15\%$ variation estimated above would not
Figure 5. (a) Texture profile of a 50 nm thick PC Ni film used in the erosion experiments. (b) Polar plot of the sputter yield variation centered around the [111] direction with red lines/areas indicating the distribution of the ion-irradiation directions for different ion incidence angles for a film with perfect (111) fiber texture and (c) for a film with a texture profile approximately corresponding to our samples.

be quantitatively correct for a fiber textured film and the precise value would depend on the angle of incidence.

If the film has a finite texture profile width, the ion impact directions for different grains would form a ‘blurred’ circle distribution with a width corresponding to the texture profile width (figure 5(c)). As figure 5(c) indicates, the 20° texture width of the PC Ni samples used in our experiments is large enough to cover multiple channels of the crystal and the statistical spread is only weakly angle-dependent and approximately equal to the value estimated from the random grain orientation—±15%.

In conclusion, the texture of the samples studied in this work is not expected to have a large impact on the ion-erosion behavior. However, in the case of ‘narrower’ fiber texture or in the case of an additional in-plane texture, the quantitative description of the erosion process would require proper treatment of the texture.

3.3.3. Oblique incidence irradiation. In order to take into account the variation of the sputter yield due to the local angle of incidence, we use the Yamamura formula [40]

\[ Y(\theta) = Y_0 \cos^{-f} \theta \exp \left( f \left( 1 - \cos^{-1} \theta \right) \cos \theta_{\text{opt}} \right) \]

(2)

where \( \theta \) is the local incidence angle, \( Y_0 \) is the sputter yield at normal incidence, \( f \) is a dimensionless coefficient describing the shape of the angular dependence and \( \theta_{\text{opt}} \) is the angle of the maximal sputter yield. For 5 keV Ar\(^+\) ions on a Ni surface we use the following values: \( Y_0 = 3.3 \text{ atoms ion}^{-1}, f = 1.95, \theta_{\text{opt}} = 70° \) [40] and the dependence is presented in figure 4(a).

We describe the evolution of the surface upon ion irradiation with a differential equation

\[ \frac{\partial h}{\partial t} = E + K, \]

(3)

where \( h(x, y, t) \) is the surface height function and the terms \( E \) and \( K \) stand for the contribution from the ion erosion and surface diffusion respectively. The ion erosion term can be expressed.
as a function of the local incidence angle and the local sputter yield coefficient \( G(x, y) \) defined above:

\[
E = -\Omega \phi \frac{\cos \theta_{\text{loc}}}{\cos \theta_{\text{off}}} G(x, y) Y(\theta_{\text{loc}}),
\]

where \( \Omega \) is the volume of a Ni atom in the Ni lattice (\( \Omega_{\text{Ni}} = \frac{1}{9\Omega_1^2} \text{nm}^3 \text{atom}^{-1} \)) and \( \phi \) is the ion flux in a plane perpendicular to the ion beam direction. \( \theta_{\text{loc}} \) is the local incidence angle, which can be expressed in terms of the local surface derivatives as

\[
\cos \theta_{\text{loc}} = \frac{\sin \theta_{\text{nom}} \partial_x h + \cos \theta_{\text{nom}}}{\sqrt{\left(\partial_x h\right)^2 + \left(\partial_y h\right)^2 + 1}}.
\]

where \( \theta_{\text{nom}} \) is the nominal ion bombardment angle (measured from the normal of the mean surface plane). \( \theta_{\text{off}} \) in (4) is the angle between the local surface normal and the normal of the mean surface plane

\[
\cos \theta_{\text{off}} = \frac{1}{\sqrt{\left(\partial_x h\right)^2 + \left(\partial_y h\right)^2 + 1}}.
\]

The coefficient \( \cos \theta_{\text{loc}} \) in (4) reduces the flux \( \phi \) by the cosine of the local incidence angle and the coefficient \( \cos \theta_{\text{off}} \) accounts for the fact that the surface is eroded in the direction perpendicular to the local surface plane (rather than vertically downwards).

The term 4 thus describes the erosion of the PC film and can be divided in two contributions. The variation of the sputter yield with the position on the surface due to the crystalline orientation of the underlying grains (described by \( G(x, y) \)) and the variation of the sputter yield due to surface topography (described by \( Y(\theta_{\text{loc}}) \), \( \cos \theta_{\text{loc}} \) and \( \cos \theta_{\text{off}} \)). The former introduces uneven erosion to the surface, hence roughness formation, whereas the latter is a high-order nonlinear function of the local surface derivatives \( \partial_x, \partial_y h \) and it introduces the anisotropy (and eventually causes ripple formation) at high angles of incidence.

The diffusion term \( K \) in (3) accounts for the smoothening of the surface and for the stochastic nature of the erosion process and is given by

\[
K = \Omega \phi \cos \theta_{\text{loc}} \left(-B \nabla^4 h + N \eta(x, y)\right),
\]

where \( B \) is the surface diffusion coefficient and \( \eta(x, y) \) is a uniform random noise from interval \((-\frac{1}{2}, \frac{1}{2})\) and \( N \) is a coefficient. \( K \) is proportional to the local ion flux \( \phi \cos \theta_{\text{loc}} \) because the thermal population of surface defects is negligible at room temperature (otherwise the patterns would decay spontaneously which is not observed). The following coefficients have been used in the simulations: \( B = 3.75 \text{ and } N = 37.5 \). However, these terms do not substantially influence the pattern formation process and even if they are removed, the general trends remain the same but the morphology evolution is more realistic with them. These terms in the simulations are e.g. responsible for the rounding of the tops of the grains which otherwise remain flat.

### 3.4. Comparison of the results

We integrated (3) for four different incident angles \( \theta_{\text{nom}} \) starting with an initially flat surface. The role of the initial surface morphology and the shadowing effect will be discussed later. The comparison of the experimental morphologies with the simulated ones after the same ion fluence is presented in figure 2. The simulations show the same general trend as observed
in the experiments—at 50° incidence an isotropic rough structure develops and as the angle of incidence increases an anisotropy develops on the surface which turns into a clear ripple pattern at 80°. Qualitatively speaking, the simulated morphologies reach an excellent degree of correspondence to the experimental STM topographs.

The simulated rms roughness evolution for the four angles is presented in figure 3(b). The initial stage of the simulated rms roughness evolution differs from the experimental data since these simulations do not account for the initial surface morphology. After this initial discrepancy, the simulated and experimental data show a good agreement. For the 50° and 60° angles of incidence, the simulated evolution follows almost the same path, since the morphology evolution is dominated by the sputter yield variation between different grains. For larger angles of incidence we can see a significant drop in the simulated rms roughness, which is caused by the increasing importance of sputter yield variation with the local incidence angles. This decrease is also present in the experimental data—the rms roughness is substantially smaller for 80° incidence than for 45°.

A comparison of the simulated and experimental evolution of the surface morphology for 80° incidence is presented in figure 6. We can again observe an excellent qualitative agreement between the experiment and the simulation. The experimental topograph in the first frame is still mildly affected by the initial surface morphology and the rms roughness is somewhat larger than in the simulation, nevertheless, the general agreement is very good. A parameter which is seldomly discussed in the context of ion-induced ripples is the length of the ripples. However, as both experimental and simulated topographies indicate, the development of the morphology during the ripple formation apparently consists mainly of the increase of the ripple length, or ‘stretching’ of the surface morphology in the direction of the ion beam.

For 45° angle of incidence we simulated the evolution of the surface taking into account the initial surface morphology (similar to figure 1(b)). The overview of the rms roughness evolution
Figure 7. (a), (c) Surface morphology of the as-grown and eroded PC Ni film respectively, (b), (d) corresponding simulated surface morphologies and (e) simulated evolution of a line profile for the same conditions.

is presented in figure 3(b). From the proposed mechanism of the roughness formation during the ion erosion it is apparent that the nature of the eroded surface topography should be different from that of an as-grown surface. In simple words, the eroded surface roughness is caused by different height of different grains, whereas the as-grown surface roughness is mainly given by the rounded shape of each particular grain, while the variation between the height of individual grains is not so pronounced and important. This can be demonstrated by the larger characteristic length scale of the eroded surface roughness than that of an as-grown surface—the eroded surface appears coarser (figure 7).

As a consequence, the initial surface topography is not ‘supported’ by the erosion roughening mechanism and it rather decays due to smoothening effects of surface diffusion, redeposition, etc. This initially leads to a decrease in the rms roughness value, but after a certain crossover time, the erosion induced topography becomes the dominant component of the roughness and a linear roughness increase follows (figure 3). A mild initial decrease of the rms roughness is also present in the simulations but a better quantitative agreement would probably require a more rigorous treatment of the smoothening terms. Finally, as the surface becomes progressively rougher and slopes become steeper, the nonlinear effects resulting from the slope dependence of the sputter yield slow down the increase of the rms roughness. The transition from the as-grown surface topography to the eroded topography is presented in figure 7 for both experimental and simulated situations. The decay of the as-grown grain topography and build-up of the erosion-induced roughness is further demonstrated by a simulated line profile evolution in figure 7(e).

3.5. Shadowing effect

The as-grown PC Ni surface used in our experiments has a substantial initial rms roughness (∼0.85 nm). At oblique ion incidence it is possible that some steep surface protrusions cast a
The early stage of surface morphology evolution of a PC Ni surface eroded at 80° angle of incidence. The highlighted pixels represent the areas with slopes higher than the ion incidence angle (i.e. areas ‘behind the corner’). The percentage represents the ratio of these areas to the total surface. The arrows indicate the direction of the ion beam.

The role of the shadowing effect has been previously discussed in the context of the patterning of PC metallic films [30, 41]. Since we do not account for this effect in the simulations we would like to estimate its impact on the morphology evolution. We investigated the initial stage of the pattern formation for 80° angle of incidence (figure 8). For each pixel in the topographs we analyzed the direction of the surface normal. The pixel is considered 'shadowing' if the angle between the local surface normal and the ion beam direction is obtuse. In figure 8 we showed the geometric ‘shadow’ and prevent the irradiation of some neighboring areas. This effect is non-local—the evolution in a specific point of the surface can be affected by a shadow casted by a distant protrusion. We do not account for this effect in our numerical model but since we use a flat surface as an initial condition this does not introduce problems. The only case when we use a non-flat initial morphology in the simulations was for 45° angle of incidence (figure 7). In this case, due to the low angle of incidence there was no shadowing effect present (the way this was checked is explained below).

Figure 8. Early stage of surface morphology evolution of a PC Ni surface eroded at 80° angle of incidence. The highlighted pixels represent the areas with slopes higher than the ion incidence angle (i.e. areas ‘behind the corner’). The percentage represents the ratio of these areas to the total surface. The arrows indicate the direction of the ion beam.
such pixels are highlighted and represent the surface areas which are ‘behind the corner’ and cast a geometric shadow downstream the ion beam.

As is apparent from figure 8, the shadowing areas disappear already after a rather low ion fluence, even before a pronounced ripple pattern is formed. Also, the initial decrease of the rms roughness (figure 3(a)) is unlikely linked to the shadowing effect, since (i) the roughness decrease seems to last at least until a fluence of 64 ions nm$^{-2}$ according to figure 3, while according to figure 8 the shadowing areas virtually vanish already for a dose of 32 ions nm$^{-2}$ and (ii) a qualitatively similar decrease of the rms roughness is present during the bombardment at 45° angle of incidence where no shadowing is present even in the beginning of the erosion process. In conclusion, a non-local shadowing effect is present in the very early stage of the erosion process discussed here. However, it probably does not play a crucial role in the ripple pattern formation because its importance diminishes after a rather low ion fluence. It is worth noting that this conclusion only encompasses the non-local shadowing, i.e. it does not disprove the role of the initial morphology as such, which may still be important [28, 30].

Additionally, the shadowing analysis revealed an interesting feature present in the STM topographs. Figure 9 shows an example of a Ni surface eroded at 75° angle of incidence where several shadowing areas are clearly visible. Such areas are consistently observed in our STM topographs and do not disappear within the fluence range studied here. The fact that these areas are present is counterintuitive: if a particular area of the surface is shadowed, there is no ion flux and hence no erosion. During the ion irradiation, the rest of the surface is being eroded and at some point the shadowing areas should shrink and disappear.

It is unlikely that this observation is just an artifact caused by the STM tip shape (the measured slope should always be smaller or equal to the real one). One possible explanation would be the drift during the STM measurement, however, the effect has been observed consistently on a multitude of images and different samples and it is unlikely that all of them would suffer from the drift.

Figure 9. (a) PC Ni surface eroded at 75° angle of incidence (from the top) with the areas casting a shadow highlighted. (b) Side view illustration of the grain transparency phenomenon.
Taking into account the mechanism of the roughness formation, it is, however, tempting to speculate that this effect is a real consequence of the nature of the roughening process. The shadowing areas are generally located on the downstream side of highly protruding grains. According to our model, these grains are protruding from the surface, because their sputter yield is lower than average, which is caused by the orientation of these grains—they should be aligned with a low-index direction toward the ion beam. These grains are thus irradiated in an open direction and because of ion channeling they may be partially transparent for the ions. Some ions may thus channel through these grains and still cause erosion on the downstream side and support the formation of these paradoxical morphologies.

Whether this scenario is possible depends on the penetration depth of the channeled ions in Ni crystal. We are not aware of experimental data for the particular conditions discussed here (5 keV Ar\(^{-}\) \(\rightarrow\) Ni) but we can get a crude estimation based on the findings of Redinger et al [42]. In [42] low energy ion channeling in Pt was studied—5 keV Xe\(^{+}\) ions could channel as far as 40 nm in Pt. In our case, this would be sufficient to travel through the PC grains and still cause sputtering on the other side.

4. Discussion

The mechanism we propose for the ion-induced morphology formation on PC surfaces can be summarized in a simple description. The variation of the sputter yield between different grains results in the progressive increase of the surface roughness. This roughening is a dominant term in the morphology evolution for low angles of incidence (below \(\sim 50^\circ\)). The oblique ion bombardment of a rough surface leads to a variation of the flux and sputter yield due to varying local incidence angle, which imposes an anisotropy to the surface morphology evolution. For moderate incident angles, this anisotropy reveals itself by the formation of tails on the downstream slopes of the protruding grains. For a sufficiently large angle of incidence (80° in our case) the morphology turns into a pronounced ripple pattern with the ripples oriented parallel to the ion beam direction. Numerical simulations of the morphology evolution based on the above described mechanism lead to an excellent agreement with the experiments.

The input parameters of the current model are the angular dependence of the sputter yield and the dependence of the sputter yield on the crystalline orientation of a particular grain (orientation dependence). We estimated the orientation dependence by a simple model based on the data from a SC target erosion, but a more precise input could be possibly obtained by a dedicated computer simulation of the sputtering process. This mechanism substantially differs from the erosive linear instability which is often cited as the cause of ion-induced pattern formation on various materials including PC metals.

The nature of the current mechanism implies several general predictions for pattern formation on PC films:

(i) Both the angular and orientation dependence of the sputter yield are temperature independent effects. Although the model includes a thermal diffusion term it is not an essential part of the pattern formation mechanism. As a result, this pattern formation mechanism for PC metals is not expected to have a low temperature limit, in contrast to SC metals where pattern formation is known to cease at low temperatures. On the other hand, sufficiently high temperatures can lead to both smoothening or roughening of the surface
or even grain recrystallization. The high temperature limit of the mechanism remains to be explored experimentally.

(ii) A crucial component of the pattern formation mechanism is the orientation dependence of the sputter yield. This dependence is characterized by the presence of ‘open’ directions which have a finite acceptance angle. In the current study, a scanning ion beam from an electron ionization gun has been used. This beam is highly collimated (angular spread of less than $\sim 2^\circ$) and given the typical acceptance angles indicated above, it can be considered parallel. However, particularly for broad ion beams, the beam angular dispersion can play a role in the roughening of the surface (by dispersion we mean the internal variation of the ion direction in a specific point on the surface, not the variation of the nominal ion direction across the beam). It is expected that for a highly dispersive beam (an extreme case of which would be an omnidirectional plasma etching), the sputter yield variation between different grains will be suppressed and the roughening will be slowed down.

(iii) For the PC films with parallel lamellar structure, the rms roughness for normal (or low angle) ion irradiation should increase linearly with ion fluence. More precisely, the rms roughness at a given point is directly given as a product of the eroded depth and the variation of the sputter yield. This prediction is not valid in the very early stage of the evolution when the initial morphology plays role.

(iv) The sputter yield orientation dependence (i.e. the widths and depths of the channels) is also expected to depend on the ion energy. In [37] a comparison between 5 and 0.5 keV bombardment of copper is presented and the sputter yield variation becomes significantly suppressed for the 0.5 keV case. Consequently, in the energy range typically employed in ion beam pattern formation (from $\sim 100$ eV to $\sim 10$ keV) the roughening rate is expected to depend on the ion energy.

(v) The lateral scale of the ion-induced pattern is clearly correlated with the size of the crystalline grains in the film. This correlation was indeed observed experimentally [30]. However, it is expected that this behavior is only present if the grains are rather small compared to the diffusion length of the surface defects. If the grains are large enough their surface can be seen as a SC surface where other roughening mechanisms can be active (e.g. ES instability) and a pattern with a smaller characteristic scale than the grain size can be dominant on the surface [30, 43].

5. Conclusions

We studied the formation of the ion-induced morphology on a PC Ni surface. We propose a model to describe the erosion process of PC films which is based on (i) the sputter yield orientation dependence (i.e. sputter yield variation due to random crystalline orientation of the grains) and (ii) sputter yield angular dependence. The first effect is mainly responsible for the roughening of the surface and the second one leads to the formation of strongly anisotropic ripple morphology by grazing incidence irradiation. By numerical simulations we showed that this model explains all the experimental trends and the simulated surface morphologies are in excellent qualitative and quantitative agreement with the experiments.

Importantly, our model departs substantially from the conventional paradigm where the ion-induced pattern formation is attributed to the presence of a linear instability. In particular,
according to our model, the ripple pattern formation at grazing incidence irradiation is caused by the nonlinear terms resulting mainly from the sputter yield angular dependence and it is a fundamentally nonlinear process. We believe that these results clarify the physics behind the pattern formation on PC metal surfaces.

Acknowledgments

This work was funded by the FWO, Vlaanderen, the KU Leuven (GOA/09/006 and GOA/14/007) and the European Commission through the SPIRIT (Support of Public and Industrial Research using Ion beam Technology, contract no. 227012) projects.

References

[1] Navez M, Sella C and Chaperot D 1962 C. R. Hebd. Seances Acad. Sci. 254 240
[2] Valbusa U, Boragno C and de Mongeot F B 2002 J. Phys.: Condens. Matter 14 8153
[3] Chan W L and Chason E 2007 J. Appl. Phys. 101 121301
[4] Facsko S, Dekorsy T, Koerd t C, Trappe C, Kurz H, Vogt A and Hartnagel H L 1999 Science 285 1551
[5] Buatier de, Mongeot F and Valbusa U 2009 J. Phys.: Condens. Matter 21 224022
[6] Bradley R M and Harper J M 1988 J. Vac. Sci. Technol. A 6 2390
[7] Madi C S, Anzenberg E, Ludwig K F and Aziz M J 2011 Phys. Rev. Lett. 106 066101
[8] Norris S A, Samela J, Bukonte L, Backman M, Djurabekova F, Nordlund K, Madi C S, Brenner M P and Aziz M J 2011 Nature Commun. 2 276
[9] Hossain M Z, Das K, Freund J B and Johnson H T 2011 Appl. Phys. Lett. 99 151913
[10] Le Roy S, Søndergård E, Nerb ø I S, Kildemo M and Plapp M 2010 Phys. Rev. B 81 161401
[11] El-Atwani O, Allain J P and Suslova A 2012 Appl. Phys. Lett. 101 251606
[12] Cuerno R, Castro M, Muñoz García J, Gago R and Vázquez L 2011 Nucl. Instrum. Methods Phys. Res. B 269 894
[13] Chason E and Mayer T M 1993 Appl. Phys. Lett. 62 363
[14] Keller A, Rolfbach S, Facsko S and Möller W 2008 Nanotechnology 19 135303
[15] Keller A, Facsko S and Möller W 2009 Nucl. Instrum. Methods Phys. Res. B 267 656
[16] Macko S, Grenzer J, Frost F, Engler M, Hirsch D, Fritzschke M, Mücklich A and Michely T 2012 New J. Phys. 14 073003
[17] Mishra P and Ghose D 2006 Phys. Rev. B 74 1
[18] Ghose D 2009 J. Phys.: Condens. Matter 21 224001
[19] Ehrlich G 1991 Surf. Sci. 246 1
[20] Costantini G, Rusponi S, Buatier de Mongeot F, Boragno C and Valbusa U 2001 J. Phys.: Condens. Matter 13 5875
[21] Rusponi S, Costantini G, Boragno C and Valbusa U 1998 Phys. Rev. Lett. 81 2735
[22] Hansen H, Redinger A, Messlinger S, Stoian G, Rosandi Y, Urbassek H M, Linke U and Michely T 2006 Phys. Rev. B 75 235414
[23] Malis O, Brock J D, Headrick R L, Yi M S and Pomeroy J M 2002 Phys. Rev. B 66 035408
[24] Rusponi S, Costantini G, Boragno C and Valbusa U 1998 Phys. Rev. Lett. 81 4184
[25] Gailly P, Petermann C, Tihon P and Fleury-Frenette K 2012 Appl. Surf. Sci. 258 7717
[26] Mishra P and Ghose D 2008 J. Appl. Phys. 104 94305
[27] Toma A, Chiappe D, Massabo D, Boragno C and Buatier de Mongeot F 2008 Appl. Phys. Lett. 93 163104
[28] Colino J M and Arranz M A 2011 Appl. Surf. Sci. 257 4432
[29] Zhang K, Uhrmacher M, Hofsaess H and Krauser J 2008 J. Appl. Phys. 103 83507
[30] Toma A et al 2008 J. Appl. Phys. 104 104313

New Journal of Physics 15 (2013) 093047 (http://www.njp.org/)
[31] Sigmund P 1969 Phys. Rev. 184 383
[32] Sundgren J, Greene J E and Madsen L D 1999 Surf. Sci. 429 206
[33] Petrov I, Barna P B, Hultman L and Greene J E 2003 J. Vac. Sci. Technol. A 21 S117
[34] Batic B S and Jenko M 2010 J. Vac. Sci. Technol. A 28 741
[35] Wang J Y, Hofmann S, Zalar A and Mittemeijer E J 2003 Thin Solid Films 444 120
[36] Kim J S J H, Ha N B, Kim J S J H, Joe M, Lee K R and Cuerno R 2011 Nanotechnology 22 285301
[37] Behrisch R and Eckstein W 2007 Top. Appl. Phys. 110 125–6
[38] Thompson C and Carel R 1995 Mater. Sci. Eng. B 32 211
[39] Vaudin M D, Rupich M W, Jowett M, Riley G N and Bingert J F 2011 J. Mater. Res. 13 2910
[40] Yamamura Y 1984 Radiat. Eff. Defects Solids 80 57
[41] Toma A, Chiappe D, Setina Batic B, Godec M, Jenko M and de Mongeot F 2008 Phys. Rev. B 78 153406
[42] Redinger A, Standop S, Rosandi Y, Urbaske H M and Michely T 2011 New J. Phys. 13 013002
[43] Qian H X, Zhou W, Fu Y Q, Ngoi B and Lim G C 2005 Appl. Surf. Sci. 240 140