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NANOSTRUCTURING SURFACES BY USING ION SPUTTERING

NANOSTRUKTURIRANJE POVR[IN S POMO^JO IONSKEGA JEDKANJA

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Surface etching by ion sputtering, besides producing equilibrium-oriented patterns similar to those obtained by Molecular Beam Epitaxy, can also be used to pattern the surface along non-equilibrium orientations, thus extending the possibilities of Molecular Beam Epitaxy. By tuning the competition between erosion at grazing angle and diffusion induced surface re-organisation, it is for example possible to pattern a substrate characterised by a square symmetry with a well ordered ripple structure running along any desired direction. Potential applications of such nanofabricated substrates can be found among others in the field of surface coatings because a control of the local roughness on the nanometric scale is expected to improve the adhesion as well the tribological properties of the films. The paper will discuss the use of sputter etching in material science as a powerful method which permits the in situ production of substrates with well defined vertical roughness, lateral periodicity and with a controlled step size and orientation.

Key words: ion sputtering, surface nanostructuring, equilibrium patterns, erosion, surface morphology, controlled nano roughness

Ionsko jedkanje povr{ine, ki ustvarja ravnote`ne oblike podobno kot pri molekularni epitaksiji (MBE), se lahko uporabi tudi za neravnote`no preoblikovanje povr{ine, kar pove~a mo`nosti MBE. Z uskalditvijo tekmovanja med erozijo pri vpadnem kotu ter reorganizacijo povr{ine zaradi difuzije, je na primer mogo~e oblikovati substrat kvadratne oblike z dobro urejeno valovito povr{ino vzdol` poljudno `elene smeri. Potencialna uporaba za tako nano-izdelane substrate je med drugim na podro~ju povr{inskih prevlek, kjer pri~akujemo izbolj{anje adhezije kot tudi izbolj{anje tribolo{kih lastnosti trdih prevlek. V ~lanku je obravnavana uporaba ionskega jedkanja kot mo~nega orodja na podro~ju znanosti o materialih, ki omogo~a *in situ* izdelavo substratov z dobro definirano vertikalno hrapavostjo, lateralno periodi~nostjo in s kontrolirano velikostjo in orientacijo stopnic.

Klju~ne besede: ionsko jedkanje, nanostrukturiranje povr{ine, ravnote`ne oblike, erozija, morfologija povr{ine, kontrolirana nanohrapavost

It is well known that when an off-normal incidence ion beam etches an amorphous solid a ripple topography can be observed. One of the first observations was done in 1956 by Navez et al. [1] by bombarding glass with an ion beam. They found that for incident angles close to the normal the ripple morphology is oriented in a direction perpendicular to the ion beam and that the ripple orientation is rotated 90° when the beam is close to grazing incidence. The authors did not find an accurate explanation at that time, but simply tried to find analogies with macroscopic phenomena like the ripple structures when air or water flows over a sand bed or the ripple formed during the sandblasting of solids[2]. An explanation of the mechanism was first proposed by Bradley and Harper [3]. They proved that, since the sputtering depends on the surface curvature, under certain conditions this dependence gives rise to a surface instability where the erosion is faster for the bottom of a trough than for the crest of a peak. This instability can be described by the continuum equation[3] reported in **figure 1** that describes the time evolution of the local surface height h (t). The derivative of h is proportional to the Laplacian of the surface height and the proportionality factor ν is the surface tension. Whenever the surface tension is negative it tends to maximize the surface in contrast to the surface tension that minimizes the surface.

It is the competition between this surface instability and the smoothing effect of diffusion that forms the ripple morphology. The periodic modulation occurs along the direction for which ν is negative and, in absolute value the largest one.

Experimentally those structures were observed on amorphous materials[4] and on semiconductors[5].

In the case of metals additional consideration should be done. The diffusion effects are not negligible and they introduce in equation[3] an additional term, which is again proportional to the Laplacian of the surface height. What happens if the atom diffuses on the island and approaches its edge from above? There is an additional potential barrier (Schwoebel barrier see **figure 2**) at the edge of the island that atom must overcome in order to descend, so the probability to be reflected is higher than the probability to jump off [6]. This contribution adds to equation[3] a term which is proportional to the Laplacian of h. In this case the coefficient in front of the Laplacian S is now depending from the crystallographic directions and from the surface temperature and is not related to the initial conditions of the ion beam (scattering angle, energy, penetration depth). The combination of the two effects induces the formation of a ripple for normal incidence[7] as shown in **figure 3**, in the case of a surface with a 110 symmetry, but produces for surfaces with a

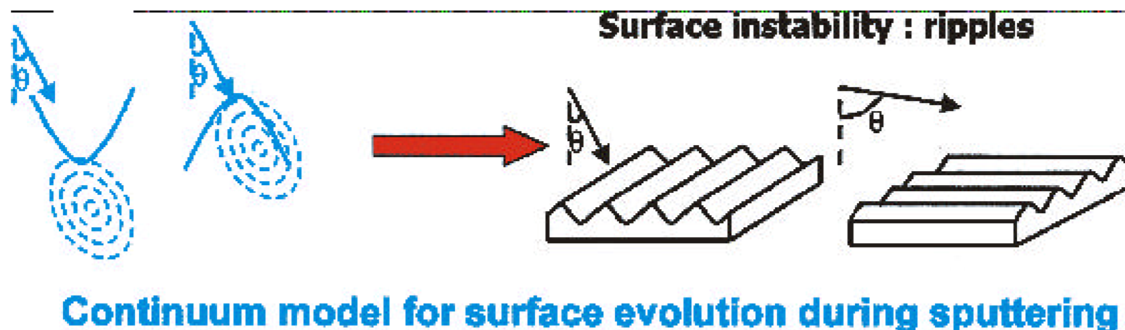

Figure 1: The figure describes the effect of the ion erosion, which is faster for the bottom of a trough than for the crest of the peak because of the curvature dependence of the sputtering. In the continuum equation that describes the surface evolution during sputtering, h and ν depend on ion flux and incident angle θ, D is the diffusion coefficient and takes into account of the stochastic arrivals of atoms. ν is the surface tension. The periodic modulation set in along the direction for which ν is negative and in absolute value, the largest one

Slika 1: Prikazan je vpliv ionske erozije, ki je hitrej{e za dno brazde kot za greben vrha, zaradi odvisnos ti ionskega jedkanja od ukrivljenosti. V zvezni ena~bi, ki opisuje nastanek povr{ine med ionskim jedkanjem sta h in ν odvisna od gostote ionskega toka in od vpadnega kota θ, D je difuzijski koeficient, ki upo{teva stohasti~no prihajanje atomov in n je povr{inska napetost. Periodi~na modulacijska smer je vzdol` strani, za katero je n negativna in absolutno najve~ja

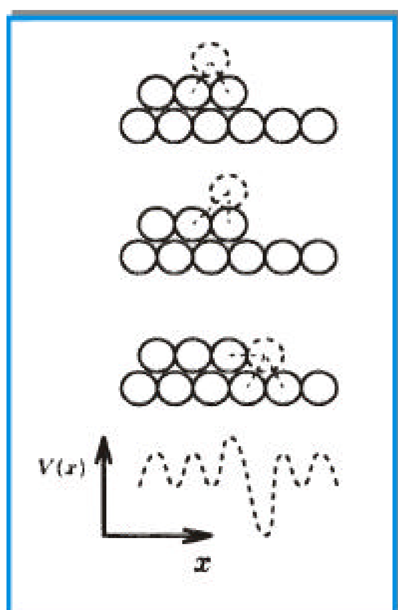

Figure 2: Schematic view of the Schwoebel barrier at the edge of an island

Slika 2: Shemati~en pogled na Schwoebel oviro na robu otoka

100 symmetry nice and regular checkerboard patterns. In the case of an amorphous material one is expecting a rough surface without any periodic structure.

But if one sputters at grazing angles the erosion mechanism becomes again dominant and both (100) and (110) **(see figure 3)** surfaces present a well defined ripple morphology, which depends from the beam orientation and not from the crystallographic directions.

The peculiar role played by the Schwoebel barrier is also illustrated clearly in **figure 4** where a (110) surface is reported after ion bombardment of Ar+ for different temperatures. At low temperature (180 K) the surface is rough and no ripple structures are present since the adatoms mobility is low. At T= 250 K, diffusion sets in along <1-10> but the temperature is too low to overcome the Schwoebel barrier in this direction and thus a ripple is formed along the <100>. By increasing the temperature, atoms start first to diffuse also along <100> (T=320 K) and then start to descend the edge of the islands along the <100> stops thus forming a clear ripple structure along the <1-10>. For higher temperatures the adatoms descend the edges of the islands along both direction <100> and <1-10> thus forming a flat surface. The effect is known as ripple rotation and was first reported in ref. [8].

The application of ion sputtering techniques in producing novel structures on the nanometer scale may be of great interest for future applications.

Quite recently Facsko et al. [9] produced with this method crystalline dots 35 nanometers in diameter, in a regular hexagonal lattice on gallium antimonide surfaces demontrating that this method is useful in device fabrication.

The capability of controlling the defect on a surface can be an other example of future application of this method for modifying the catalytic properties of a surface. Quite recently[10] it has been in fact demonstrated that by tuning the orientation of the ripple on a substrate Ag (001) it is possible to change the density of defects onto the surface (in particular kinks) allowing for

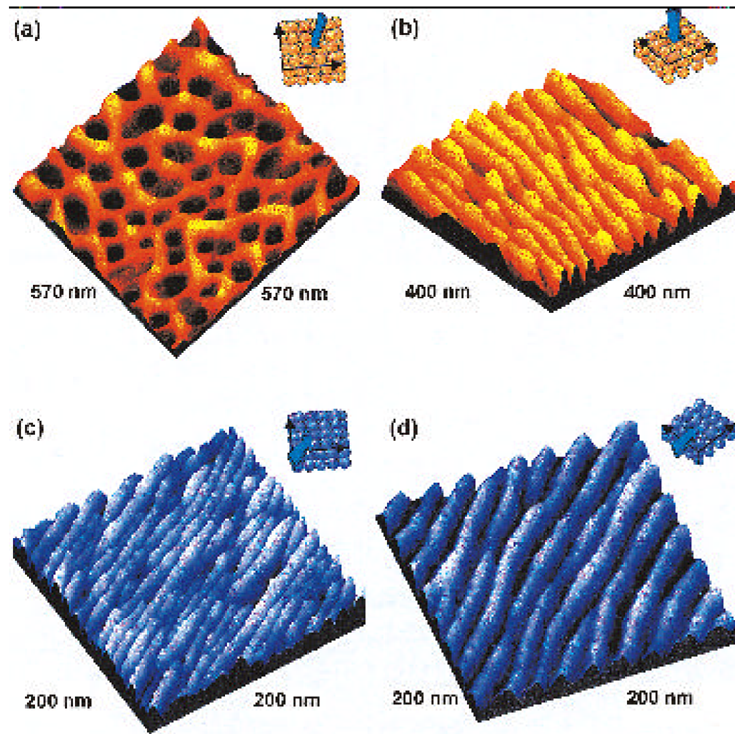

Figure 3: Ag (001) and Ag(110) after sputtering with Ne $^+$; a) is Ag (001) sputtered in conditions where the diffusion mechanisms are dominant 570 nm^2, b) is Ag (110) sputtered in conditions where the diffusion mechanisms are dominant 400nm^2, c) is Ag (001) sputtered in conditions where the erosion is dominant 200 nm^2, d) is Ag (110) sputtered in conditions where the erosion is dominant 200 nm^2 (From ref. 7)

Slika 3: Ag(001) in Ag(110) po jedkanju z Ne+; a) Ag (001) ionsko jedkan v pogojih, ko prevladuje difuzijski mehanizem, 570 nm^2; b) Ag (110) ionsko jedkan v pogojih, ko prevladuje difuzijski mehanizem, 400 nm^2; c) Ag (001) ionsko jedkan v pogojih, ko prevladuje difuzijski mehanizem, 200 nm^2; d)Ag (110) ionsko jedkan v pogojih, ko prevladuje difuzijski mehanizem, 200 nm^2 (po referenci 7)

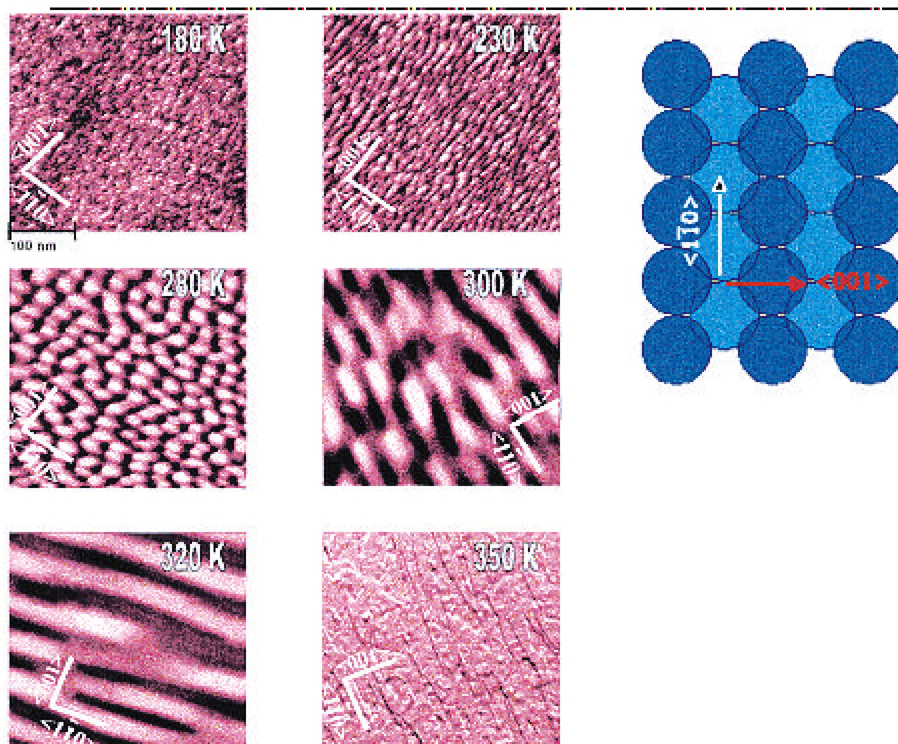

Figure 4: Ripple formation on Cu (110) as function of temperature. The inset reports the unit cell. Ripple rotates 90° by increasing temperature (From ref. 8)

Slika 4: Oblika valov na Cu (110) v odvisnosti od povr{ine. Vstavki so merilo mre`ne celice. Valovi se obrnejo za 90° pri pove~anju temperature. (Po referenci 8)

Oxygen dissociation at low temperature while this mechanism is not allowed on a clean and flat surface.

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