Is Ion Sputtering Always a "Negative Homoepitaxial Deposition"?

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We present a scanning tunneling microscopy study of the direct comparison between homoepitaxial deposition and surface ion sputtering on the Ag(001) system. At a temperature of 200 K, sputtering results in mound formation similar to the epitaxy case, while at higher temperatures an erosive regime sets in with the appearance of regular square pits. Contrary to the conventional wisdom, which considers ion sputtering as a deposition of vacancies, the analysis of single ion impact events reveals that the process produces both adatom and vacancy clusters. The key parameter determining the temperature dependence of surface morphology turns out to be the mobility of the adatom clusters which exceeds that of vacancy clusters.

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Ion sputtering, i.e., the bombardment of surfaces by means of energetic ionized particles, is used in a large number of experimental techniques for the analysis and preparation of solid interfaces. For example, sputtering is employed for depth profile analysis in secondary ion mass spectroscopy and has been shown to improve the quality of thin films if used in combination with molecular beam epitaxy [1]. Recently, it was demonstrated that ion bombardment at low energies is also a powerful tool for surface nanostructuring: By simply changing a few experimental parameters such as substrate temperature or sputtering geometry, a large variety of self-assembled periodic structures was reported on metals [2], semiconductors [3], and amorphous materials [4]. According to this, GaSb quantum dots were produced by means of Ar^+ sputtering [5] and showed quantum confinement effects marked by photoluminescence properties.

In spite of the wide spreading of surface applications based on ion bombardment, a detailed understanding of the time-extended surface sputtering process is still lacking. In particular, while the effects of ion irradiation of solid materials have been extensively studied at the bulk level, surface modifications received only minor attention, being mainly focused on the damage process caused by the ion-substrate interaction, which ends in the first tens of psec after the impact [6,7]. On the other hand, especially for what concerns surface nanostructuring, a great importance is held by the later evolution of the surface, since the final morphology depends on how the surface defects created by the ion impact diffuse on the substrate and interact with each other. A continuum theory for surface sputtering has actually been developed [8] but, obviously, it gives only a coarse-grained description of the process, completely neglecting the atomistic aspects which, on the contrary, are fundamental for the full comprehension and control of this phenomenon. A simplifying assumption is often made by considering the sputtering process as equivalent to a "negative deposition" where adatoms are replaced by single atomic voids (monovacancies) (see, e.g., [9,10]). Experimental evidences supporting this picture have been reported in the case of low energy ion bombardment of Ge(001) [11]; moreover this statement has also been used in computational models which tried to simulate surface sputtering [12,13]. In order to achieve a better understanding of the sputtering phenomenon and to directly test the presumed equivalence between ion sputtering and negative deposition, we performed a temperature dependent comparison between the morphology of an ion-bombarded Ag(001) surface and the morphology which results from exposing the same surface to a thermal atomic beam. We chose this particular metallic substrate both for its simple crystalline structure and because surface diffusion is isotropic, which makes it an ideal model system. Moreover on this system single adatoms and vacancies have almost the same surface diffusivity [14,15], which in a simple guess should lead to specular surface morphologies if the negative deposition assumption were true.

The experiments were made by means of a variable temperature scanning tunneling microscope (STM) housed in an ultrahigh vacuum chamber with a base pressure of 1×10^{-10} mbar [16]. Ne^+ ions with an energy of 1 KeV were used for sputtering, while an electron-bombardment Ag source was employed for homoepitaxial growth. The direction of the ions was chosen normal to the surface, so to eliminate from the final surface morphology any effect caused by the curvature-dependent sputtering yield [8]. In order to make the comparison between sputtering and deposition more meaningful, the atom deposition rate was chosen to be equivalent to the rate of total displaced material during sputtering. In particular, the ion flux ($\Phi_{\text{sput}} = 2.5 \times 10^{12}$ ions $\cdot$ cm^{-2} $\cdot$ s^{-1}) was scaled down in respect to the deposition flux ($\Phi_{\text{dep}} = 8.8 \times 10^{13}$ atoms $\cdot$ cm^{-2} $\cdot$ s^{-1}) by the total number of atomic defects created by each impact (discussed later). In both experiments the surface was exposed for the same time ($t = 450$ s, corresponding to a nominal deposition of 33 monolayers) to the ionic or atomic beam and, immediately after turning off the particle source, the surface temperature was rapidly quenched to 130 K in order to avoid subsequent surface restructuring.

For both types of experiments the final surface morphology is marked by quite regular three-dimensional

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nanostructures with a square symmetry, whose aspect resembles, respectively, that of pyramidlike mounds for homoepitaxy or both mounds and pits for sputtering. A quantitative characterization of such structures is obtained by computing from the STM images the morphological parameters of surface roughness W and correlation length Λ, which are related, respectively, to the vertical and lateral dimensions of the surface nanostructures [17]. The results of such an analysis, conducted as a function of T on a large number of STM data, are reported in Figs. 1(a) and 1(b), and clearly reveal a strong difference between sputtering and homoepitaxy. In particular, in both cases a bell-shaped dependence of W on T [Fig. 1(a)] is observed with very similar values of the maximum roughness, but the two curves are mutually shifted by almost 100 K, indicating that, for example, at room temperature sputtering still produces high-roughness 3D structures, while homoepitaxial growth already proceeds smoothly. These differences are also reflected by the temperature dependence of the lateral dimension of the surface nanostructures in Fig. 1(b). In fact, for both processes, the $\Lambda(T)$ curves follow an Arrhenius behavior $\Lambda \propto \exp(-E_{\mathrm{eff}}/kT)$, which is typical of activated diffusion processes, but a significantly higher effective energy barrier E_{eff} is found in the case of the sputtered surface. Since the evolution of the nanostructures results from several elementary diffusion processes which involve single atoms or monovacancies and above all a concerted motion of the whole cluster, the value of E_{eff} cannot be directly associated with a particular atomic movement.

In order to simplify the picture and to understand which processes are really important in determining the surface morphology, we studied the single ion impact event by sputtering the surface at extremely low ion fluxes and doses (flux 10^{11} ions $\cdot$ cm^{-2} $\cdot$ s^{-1}, dose 10^{11} ions $\cdot$ cm^{-2}). A characteristic pattern is shown in Fig. 2 where a vacancy cluster (central depression) is surrounded by several adatom clusters (bright islands) which are found in a radius of a few nanometers around the impact site. We notice that since the experiment of Fig. 2 is done at a low temperature, diffusion induced cluster restructuring can be ruled out. A similar behavior was observed on Pt(111) by Michely *et al.* [18]. A more detailed analysis of the patterns in Fig. 2 shows that the adatom and vacancy clusters are one atomic layer high/deep. On average each

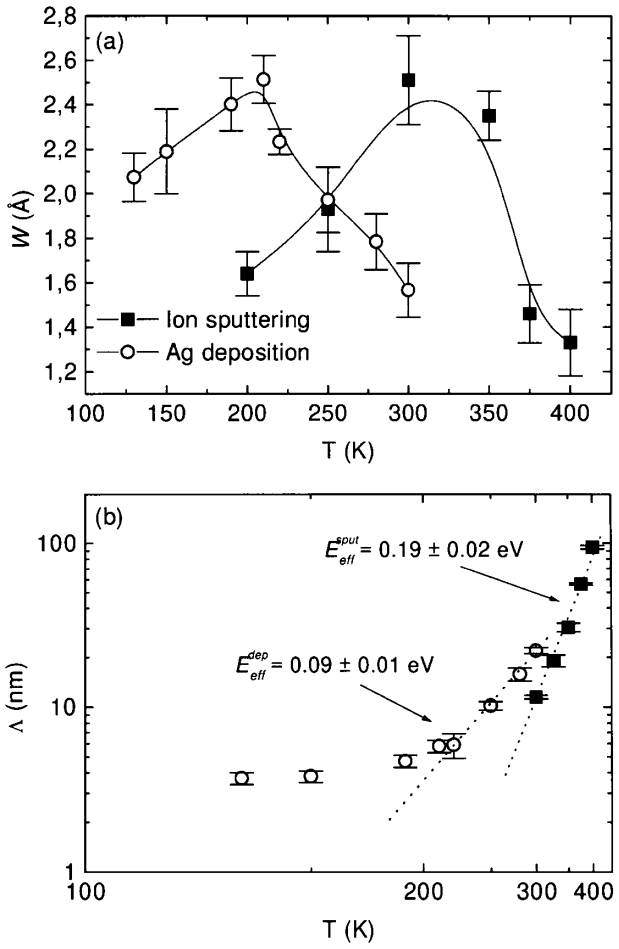

FIG. 1. Temperature dependence of the morphological parameters W and Λ for ion sputtering (full squares) and homoepitaxial deposition (open circles) on Ag(001). (a) Surface roughness W versus T. The continuum lines serve only as guides to the eye. (b) Lateral dimension Λ versus T. The dotted lines represent Arrhenius best fits to the experimental data and are obtained by excluding the lowest temperature values. In both panels the experimental error bars show the statistical uncertainties derived from averaging over a large set of STM topographies.

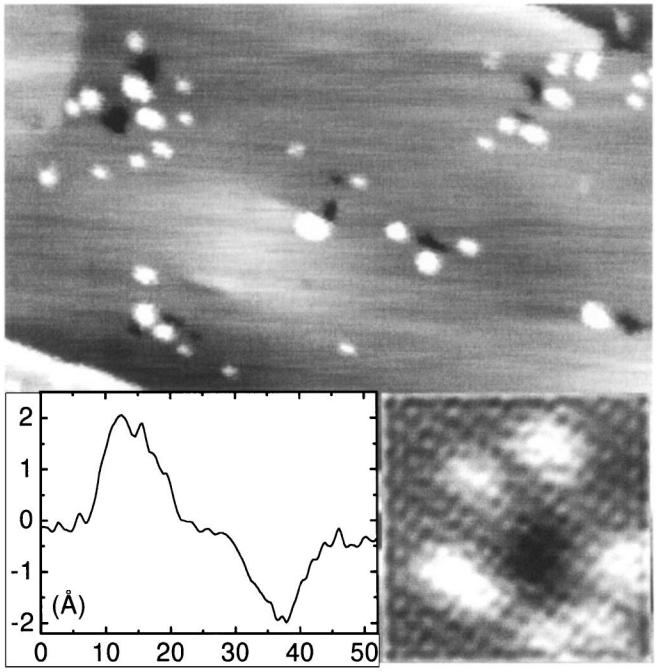

FIG. 2. Top: Typical surface morphology after single ion impact experiments at $T = 115$ K (scan area 40×23 nm^2). Bottom right: high resolution scan of a single ion impact pattern with software superposition of an atomic resolution image. Such images were used in order to determine the dimension of adatom and vacancy clusters. Bottom left: typical linear scan through an adatom and a vacancy cluster, demonstrating their monatomic height/depth of about 2 Å.

pattern extends over an area of about 12 nm^2 and is composed by one vacancy cluster of 8–10 monovacancies and 3–4 adatom clusters of 6–7 atoms each [19]. Assuming a sputter yield of about 5 atoms per ion [20], in order to satisfy mass conservation, we have to consider the formation of bulk vacancies as was reported in the case of Pt(111) [18]. In our case, surface diffraction measurements [2] demonstrate that the crystalline quality of the top layers is not affected by the presence of such bulk defects. This behavior is common to other metal systems as reported in the case of Pt(111), where the diffusivity of such bulk vacancies is very low, so that they can be considered to be essentially immobile in the temperature range of the present experiment.

Therefore these observations demonstrate that surface restructuring by ion sputtering cannot be simply attributed to a deposition of vacancies, but is determined by a temporally and spatially correlated deposition of two-dimensional *adatom and vacancy clusters.* In order to understand the temperature shift between the sputtering and deposition experiments, the difference in diffusivity of such clusters must be taken into account and not the diffusivity of monovacancies and adatoms. A simple bond counting argument suggests that the diffusion energy barriers of adatom clusters are lower than those of vacancy clusters; moreover a direct experimental evaluation of cluster diffusion on Ag(001) exists [21] which shows that the diffusion rate of adatom clusters exceeds by about an order of magnitude that of vacancy clusters. We checked this statement by means of annealing experiments of the surface morphologies corresponding to Fig. 2 (data not shown). By gradually increasing the substrate temperature, first ($T \approx 180$ K) the adatom clusters begin to diffuse and coalesce, while the vacancy clusters still remain stuck (the number density of the former decreases, while that of the latter remains almost unchanged). Only at higher T does the vacancy cluster also begin to diffuse ($T \approx 250$ K), while the adatom ones completely disappear from the terraces, being probably incorporated at ascendant step edges. Finally, upon a further increase of T, the surface terraces appear almost free from defects, meaning that the diffusivity of vacancy cluster has increased to the point at which they quickly migrate at descendant step edges where they become incorporated.

Based on these experimental evidences, it becomes possible to formulate a temperature dependent model for the surface sputtering process in which two reference temperatures are present: an activation temperature for adatom cluster diffusion, $T_{ad} \approx 180$ K, and one for vacancy cluster diffusion, $T_{vac} \approx 250$ K, with $T_{ad} < T_{vac}$. In particular, for $T_{ad} < T < T_{vac}$ the surface morphology will be dominated by the diffusion and coalescence of adatom clusters (the vacancy ones being practically neglected because of their immobility) and thus, similarly to the homoepitaxial case, it will be characterized by moundlike structures such as those shown in Fig. 3(a) which correspond to a substrate temperature $T = 200$ K. For $T > T_{vac}$, the diffusion and coalescence of vacancy clusters will be the leading process, because the adatom clusters are quickly incorporated at step edges. In this case, pitlike structures like those of Fig. 3(b) ($T = 300$ K) will characterize the surface morphology.

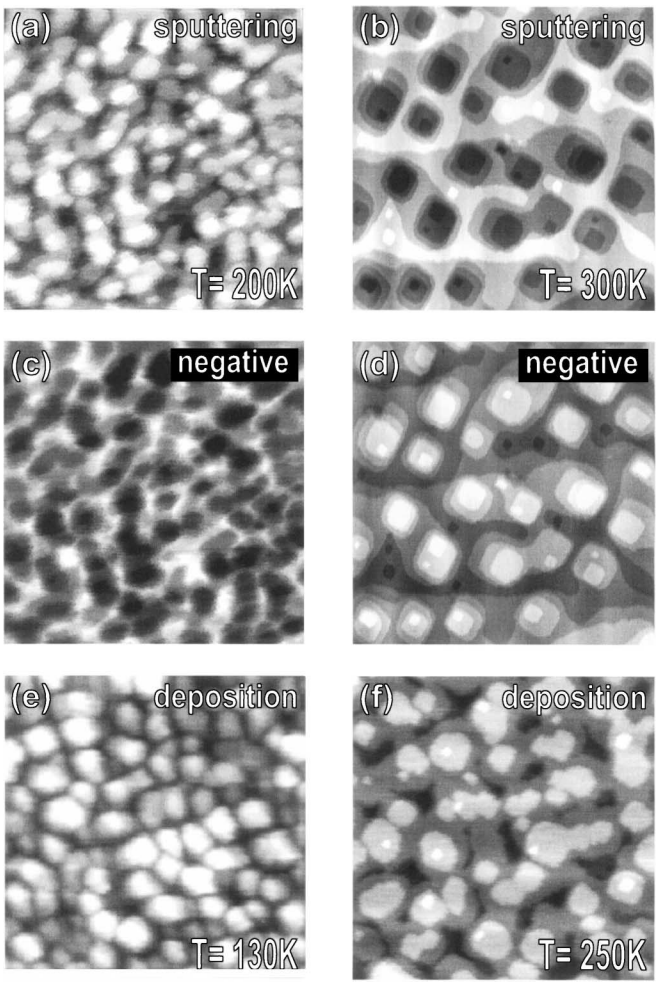

FIG. 3. Gray scale images representing the Ag(001) surface after Ne^+ sputtering (upper row) and Ag deposition (lower row) at low temperatures (left column, scan area 40×40 nm^2) and high temperatures (right column, scan area 63×63 nm^2). The shown temperatures are such that the sputter induced nanostructures in (a) and (b) have the same lateral extension of the corresponding homoepitaxy induced ones in (e) and (f). Images (c) and (d) in the middle row are the "photographic negatives" of the corresponding sputtering images (a) and (b).

On the contrary, independently on substrate temperature, homoepitaxy experiments always lead to mound structures [Fig. 3(e), $T = 130$ K, and Fig. 3(f), $T = 250$ K], since in this case adatoms are the only diffusing surface defects. Figures 3(c) and 3(d) (central row) are the "photographic negatives" of the respective sputtering images (upper row) and, because of the gray scale representation of the STM data, correspond to the mirror reflections of the morphologies in Figs. 3(a) and 3(b). Following our initial discussion, since this image treatment is equivalent to the substitution of heights with valleys and vice versa, if sputtering were equivalent to a deposition of vacancies,

sputtering morphologies should be directly transformed into homoepitaxy ones. Thus the data in Fig. 3 are a further demonstration that this picture is wrong: The "negative" sputtering morphologies in the higher temperature regime [Fig. 3(d)] are actually very similar to the positive deposition ones [Fig. 3(f)], but this is absolutely not true at lower temperatures [compare Fig. 3(c) with 3(e)], because sputtering produces unexpected mound-like structures such as those of Fig. 3(a). Moreover, independently on the details of the model, these mound morphologies cannot be interpreted by any theoretical scheme for ion sputtering that involves only vacancies.

Finally let us notice that for a complete description of the temperature dependence of the sputtering process, the two extreme temperature regimes have to be considered. For $T < T_{ad}$, both adatom and vacancy clusters are immobile, thus a random surface morphology characterized by a high step density occurs. In this case, a lowering of surface roughness is observed thanks to athermal processes such as sputter induced diffusion [4] or local surface heating due to ion impacts. The very high temperature regime is on the contrary characterized by very quick motion of adatom and vacancy clusters so that they do not meet anymore, but migrate to step edges immediately after having been created by ion hits, and erosion takes place almost by step flow. As a consequence, both extreme temperature regimes are characterized by a small number of exposed layers as can be seen from the bell shape of the $W(T)$ curve for sputtering in Fig. 1(a). Notice that very similar temperature regimes can be found for homoepitaxial growth [see Fig. 1(a) and [17,22]].

We expect that the validity of the above model is not restricted to our particular choice of sputtering conditions and target substrate, since we consider only the nature of surface defects created by ion bombardment (adatom/vacancy clusters) and their temperature dependent diffusion coefficients. On the contrary, this model should be applicable whenever the damage mechanism induced by ion impacts cannot be simply described by a linear cascade of binary collisions into the solid, but involves a local surface melting and a viscous flow of melt material onto the surface. In fact, while the first case generates only isolated point defects (see, for example, Ref. [11]), the second one, as demonstrated in [7], has larger surface effects with a high probability for the formation of surface clusters of adatoms and vacancies. As a consequence, our model should describe the sputtering of targets with high atomic densities and low melting temperatures (e.g., noble metals), which happens in the so-called thermal spike regime [23].

In conclusion, we have made a direct comparison between the surface morphologies induced by ion sputtering and homoepitaxial deposition on the model system Ag(001). The results of such an analysis show that a realistic description of the ion sputtering process must consider that the most relevant surface defects produced by ion impacts are two-dimensional adatom and vacancy clusters instead of isolated monovacancies. Basing upon single ion impact experiments, the temperature dependence of the morphologies generated by low temperature ion sputtering is attributed to the lower activation temperature for adatom cluster diffusion compared to vacancy clusters.

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