

Energy dependent studies of anisotropic atomic sputtering of Ni(111)

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The anisotropic ejection of atoms sputtered from a Ni(111) surface by Ar⁺ ions of 1.1 keV was investigated by angle- and energy-resolved secondary neutral mass spectrometry (SNMS). The angular distribution of sputtered atoms exhibits three different peaks which correspond to a preferred emission along the close packed [111]-, [110]- and [100]-directions of the crystal, respectively. The intensity as well as the location of the "spots" are shown to depend strongly on the ejection energy E of the sputtered atoms. Also, the energy distributions measured in and outside of the spot directions are found to differ significantly. The results are reproduced at least qualitatively by a molecular dynamics simulation using a many-body embedded atom interaction potential.

1. Introduction

It has been known since long that the sputtered particle flux from ion bombarded single crystal surfaces contains anisotropic contributions [1]. In particular, distinct maxima of the differential sputter yield are detected for certain ejection angles ("Wehner spots") which are attributed to a preferred ejection along closely packed crystallographic axes of the sample. Although a considerable number of investigations has been devoted to the experimental determination of angular distributions, most of this work was performed without the possibility to mass or energy select the detected particles [3]. Especially the latter, however, is of particular importance, since it was known very early that the energy distribution of particles ejected along "spot" directions differs from that measured outside the spots [2]. One reason for the apparent lack of energy resolved angular distribution data is, of course, that the majority of the particles sputtered, for instance, from clean metallic samples are neutrals, and hence, have to be post-ionized prior to mass and energy analysis. Only very recently, energy resolved angular distributions of neutral particles sputtered from metal single crystals [4,5] have been reported. In the present work, we studied the anisotropic emission of neutral atoms sputtered from a Ni(111) surface by energy-resolved secondary neutral mass spectrometry (SNMS). Particular emphasis has been put on how the measured spatial distributions depend on the selected ejection energy of the particles. The experimental results are compared to a molecular dynamics simulation

of the sputtering process using a many-body embedded-atom interaction potential.

2. Technical

As mentioned above, the present work includes both experimental and theoretical work. Consequently, this paragraph is divided into two subsections describing the experimental details and the molecular dynamics calculations separately.

2.1. Experimental

The setup used in the present study is essentially identical to our energy resolved SNMS system described earlier [6]. In short, a low pressure rf Ar plasma resonantly excited by electron cyclotron waves (ECWR) serves both as a primary ion source delivering a parallel 1.1 keV, 0.3 mA Ar⁺ ion beam, and as an effective post-ionization medium. Sputtered neutral particles are ionized by the electron component of the plasma and subsequently energy and mass selected by means of a twin parallel plate energy analyzer and a quadrupole mass filter. The energy and mass resolution were set at $\Delta E = 1.5$ eV and $\Delta m = 1$ amu (FWHM), respectively. Details of the energy analysis and the procedure to correct the measured spectra for instrumental effects are given elsewhere [6]. The target is mounted outside the plasma chamber on a rotatable sample holder equipped with a flip mechanism to enable any orientation of the target in space. The angular

resolution given by the solid angle accepted by the detection system and by the reproducibility of the sample orientation is estimated to be 1° . In contrast to the setup described in ref. [6], the sputtered neutrals now enter the plasma backstream through the ion optics extracting the Ar^+ ion beam. Hence, the direction under which the particles are detected is identical with the direction of the impinging primary ions (in the following called "direction of analysis"). This "backward detection" scheme implies two important consequences: First, the incidence and analysis angles are always the same and can only be varied simultaneously. Second, since the detected neutral particles are only sputtered after the momentum originally imparted to the solid by the impinging primary ion is completely turned around, the measured intensities are likely to reflect the flux of particles sputtered due to the "isotropic part" of the collision cascade which is not expected to change drastically as a function of the primary ion impact angle. Hence, the disturbing influence of sputter yield changes due to the (in principle unwanted) variation of the bombarding angle is essentially restricted to channeling effects, which reduce the sputter yield if the primary ion beam is aligned with a low index crystal axis. Due to the relatively low bombarding energy employed here, however, we expect these variations to be small.

2.2. Description of the calculation

The molecular dynamics simulations have been discussed in detail elsewhere [7]. In the present work, we used a many-body potential describing the atom-atom interaction in a nickel solid which was developed by Foiles et al. [8] using the embedded-atom method (EAM). Similar to the procedure described in ref. [9], this potential was splined to a Molière potential at

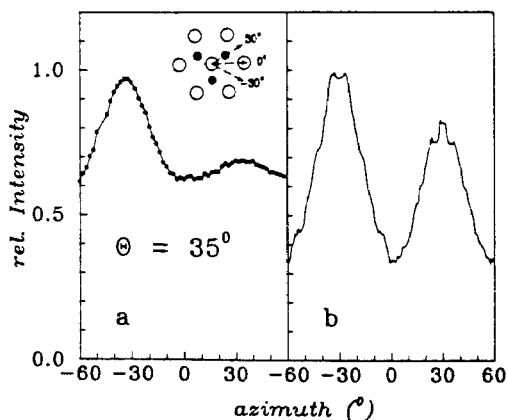


Fig. 1. Azimuthal distribution of neutral atoms sputtered from Ni(111) for fixed polar angle $\Theta = 35^\circ$ and ejection energy $E = 10$ eV; (a) experiment; (b) molecular dynamics simulation.

small internuclear distances ($< 2 \text{ \AA}$) in order to include a sufficiently repulsive interaction in this regime. 1000 trajectories were run for Ar^+ ions of 1 keV normally incident on a Ni(111) surface, yielding a total of 3160 sputtered atoms which were then analyzed with respect to their ejection angle and energy.

The energy resolution used in the histogramming procedure was chosen to be compatible with the experimental value. Unfortunately, due to the limited statistics of the calculation, this was not possible for the angular resolution. Instead, values of $\Delta\Theta = \pm 5^\circ$ and $\Delta\phi = \pm 7.5^\circ$ were used to produce the results displayed in figs. 1 and 5 (Θ : polar ejection angle with respect to the surface normal, ϕ : ejection azimuth measured in the surface plane).

3. Results and discussion

3.1. Angular distributions

In order to visualize the anisotropic ejection of atoms sputtered from the Ni(111) surface under investigation, fig. 1a shows the relative intensity variations of post-ionized Ni atoms versus the analysis azimuth ϕ while the polar ejection angle was kept fixed at $\Theta = 35^\circ$. The zero of the azimuth was arbitrarily chosen as depicted in the inset of fig. 1. A corresponding plot obtained from the computer simulation is displayed in fig. 1b. It is seen that the experimental observation of a major and a minor peak is reproduced by the simulation, which even yields peak widths similar to the experiment. It is also apparent, however, that, presumably due to the variation of the bombarding angle in the experiment, the relative peak heights predicted by the MDS differ from the experimental results. The two "spots" observed in fig. 1 have been reported earlier and are commonly attributed to preferred ejection of atoms along the closely packed [110] (large maximum) and [100] (small maximum) crystallographic axes [1]. Fig. 2 depicts polar angle distributions measured at $\phi = -30^\circ$ for two different pass energy settings of the detector. It is apparent that the polar angle distribution strongly depends on the ejection energy E of the sputtered atoms. For $E = 10$ eV the [110] spot is detected under the crystallographically expected angle of $\Theta = 35^\circ$, and a second peak around $\Theta = 0^\circ$ becomes visible which corresponds to a preferred ejection along the [111] axis. For $E = 25$ eV both peaks appear with comparable intensities. A similar energy dependence of the (111) spot has been observed by Winograd et al. [10] for Rh atoms sputtered from a Rh(111) surface. In principle, two mechanisms may cause a preferential emission along the [111] direction, namely, (i) a surface atom may be struck by a head-on collision from an underlying fourth layer atom, or (ii) a second layer

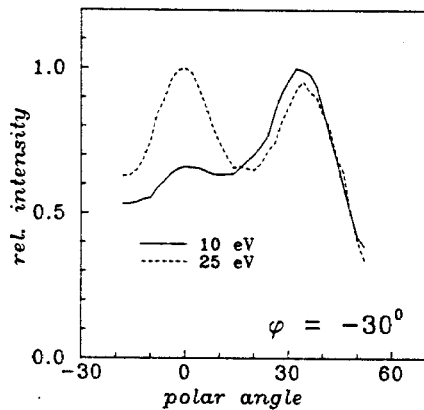


Fig. 2. Polar angle distribution of neutral atoms sputtered from Ni(111) measured in the $\phi = -30^\circ$ azimuthal plane. Parameter is the ejection energy of the sputtered atoms.

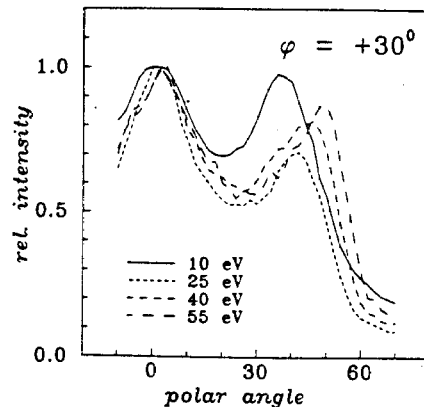


Fig. 3. Polar angle distribution of neutral atoms sputtered from Ni(111) measured in the $\phi = +30^\circ$ azimuthal plane. Parameter is the ejection energy of the sputtered atoms.

atom may be ejected and focused as it moves upward through the threefold hollow site above. In fact, both mechanisms are indistinguishable here as they both require a particle with sufficient energy to overcome the energy barrier connected with the passage through a threefold focusing ring (some 20 to 60 eV [7,11]). Therefore only particles with relatively high ejection energies contribute to this peak. This is presumably the reason why the [111] spot has not been detected by experiments in which no energy selection of the sputtered particles was performed [12].

It should be mentioned that the data of Gnaser and Hofer [5] do not agree with the present results. For Ni atoms ejected from a Ni(111) surface they found a more pronounced ejection along the surface normal (relative to the [110] peak height) if the particle energy was decreased from 10 to 4 eV. The only apparent difference between their experimental setup and ours is the "forward" detection scheme employed in ref. [5] as opposed to our backward detection described above. In particular, if their instrument is tuned to the [110] spot, sputtered atoms are detected exactly in the direction of specular reflection of the primary ion beam. It has been shown that particles ejected along this direction exhibit higher average ejection energies than those sputtered in a "random" direction [13,14]. Hence, we suppose that the corresponding results in ref. [5] may primarily reflect the enhancement of the [110] spot rather than a suppression of the [111] spot with increasing energy.

The polar angle distribution measured along the $\phi = +30^\circ$ direction is shown in fig. 3 for different ejection energies E . The curves were arbitrarily normalized to the same height of the [111] spot and, hence, the variation of the relative peak heights merely reflects the energy dependence of the [111] spot described above. The important observation made in fig.

3 is the strong dependence of the [100] spot (cf. fig. 1) on the particle ejection energy. While for $E = 10$ eV this spot is detected under roughly the same polar angle as the [110] spot (fig. 2), it shifts towards the crystallographically expected value of 54.7° when E is increased. An energy dependence of this type has been predicted by calculations of Robinson [11] estimating the influence of "surface scattering", i.e. the deflection of an atom originally ejected along a crystal axis towards the surface normal by the surrounding surface atoms. The corresponding calculations for Cu atoms sputtered from a copper (111) surface reveal shifts of the [100] peak which are in quantitative agreement with our measured data (cf. fig. 3.12. in ref. [11]).

The concept of surface scattering is further supported by comparing the energy dependent angular distributions measured for the different spots: As seen from fig. 2, the [110] spot exhibits no noticeable peak shift between $E = 10$ and 25 eV, while at the same time the [100] spot is shifted by as much as 6° . This reflects the fact that due to the smaller angle between the [110] axis and the target normal (35.5°) the influence of the neighboring surface atoms is largely reduced for the [110] spot.

Table 1
Polar angle θ_{\max} for maximum of the [100] peak vs ejection energy E of sputtered Ni atoms

E [eV]	θ_{\max} [deg]	
	exp.	calc.
10	36.3	39.0
25	42.3	40.4
40	45.8	42.5
55	49.4	44.3

Table 1 displays the energy dependent peak positions of the [100] spot ($\phi = +30^\circ$) extracted from the MD simulation in comparison with the corresponding experimental values. It is seen that, although the magnitude of the peak shift is somewhat smaller in the simulation, the results are in qualitative agreement with the experimental finding of larger maximum polar angles at higher ejection energies. Similar results were obtained by earlier MD simulations (using pair potentials) performed on rhodium [10]. On the other hand, we state that the experimental results presented here are quite in contrast to recent MARLOWE simulations performed for 600 eV He⁺ ions normally incident on Au(111) [15]. In this work, no shift of the maximum with increasing ejection energy was found. The reason for this apparent discrepancy remains unclear at the present time.

3.2. Energy distributions

From the preceding section it is already evident that the energy distribution of sputtered atoms strongly depends on the direction under which the particles are detected. Fig. 4 shows energy distributions of sputtered neutral Ni atoms ejected along the different "spot directions". For comparison, the energy spectrum measured on a polycrystalline Ni foil is included in the figure. It is seen that in all three spots the energy distributions are broader and peak at higher energies than in the polycrystalline case. Apparently, the distributions measured for the three spots are different in so far as the maximum shift is largest for the [110] spot and the high energy tail is most pronounced for the [111] spot. These results are completely analogous to the measurements of Winograd and coworkers on Rh atoms sputtered from Rh(111) [10]. On the other hand,

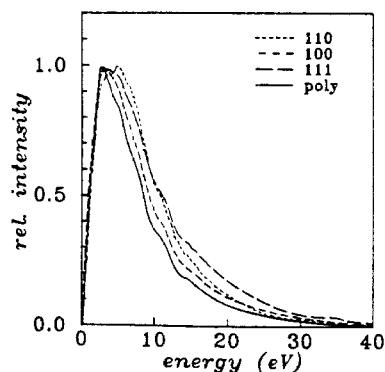


Fig. 4. Energy distribution of neutral atoms sputtered from Ni(111) measured for various ejection angles Θ and ϕ . [110]: $\Theta = 35^\circ$, $\phi = -30^\circ$; [111]: $\Theta = 0^\circ$, [100]: $\Theta = 35^\circ$, $\phi = +30^\circ$; the solid line represents the spectrum measured for a polycrystalline Ni target ($\Theta = 0^\circ$).

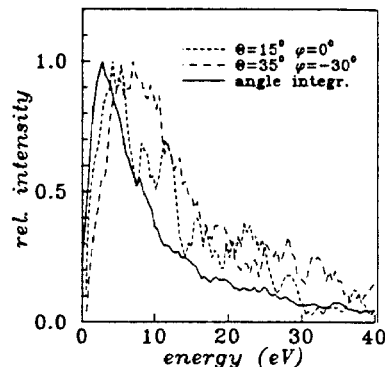


Fig. 5. Energy distribution of atoms sputtered from Ni(111) calculated for various ejection angles Θ and ϕ . The solid line represents the spectrum integrated over all ejection angles.

if the single crystal is analyzed in a direction as far outside a spot as possible^{#1}, the energy spectrum is found to be identical with the one obtained from the polycrystalline sample within the experimental error.

Similar ejection angle dependences have been reported several times in the literature [2,5,16,17]. They clearly indicate that the flux of particles sputtered along a spot direction contains a considerable "anisotropic" fraction of atoms ejected with high average kinetic energy being superimposed to a "random background". As shown in ref. [17], this finding appears to be consistent with the Silsbee model [18] of focusing collision sequences leading to the anisotropic ejection of particles. Also, due to the recent availability of many-body potentials, the experimental results obtained on rhodium can be reproduced by molecular dynamics computer simulations [7]. For the present case, fig. 5 shows the energy distribution of atoms calculated for the [110] spot and the off-spot direction by the MD simulation. Despite the relatively large statistical scatter, it is seen that in particular the maximum shift observed experimentally is qualitatively reproduced by the simulated results. Comparing the theoretical energy distributions to the experimental curves, one finds that the calculated angle integrated distribution nicely agrees with the spectrum measured on the polycrystalline sample.

4. Conclusions

It is shown that the angular distributions of neutral atoms sputtered from Ni(111) depend strongly on the kinetic energy E of the ejected particles. In particular,

^{#1} We chose the twofold local minimum at $\Theta = -15^\circ$, $\phi = 0^\circ$ of both the polar and azimuthal ejection angle distribution displayed in figs. 1 and 2 for this purpose.

the [100] spot is found to occur at markedly lower polar ejection angles with decreasing E . In agreement with theoretical estimates this effect is attributed to surface scattering. The measured energy distributions reveal a higher average kinetic energy of atoms ejected along a spot direction than those sputtered into off-spot directions. Both results are qualitatively reproduced by the MD simulation. There are several possible reasons why the agreement between experiment and theory is only limited. First, the EAM interaction potential used in the simulation may of course not be sufficiently realistic to allow a quantitative description of all details of the sputtering process. As shown for instance in ref. [7], the calculated results may depend strongly on only small variations of the potential. Secondly, however, it should be recalled that (i) our measured angular distributions do not necessarily reflect the true angular distributions since the bombarding angle is varied simultaneously with the ejection angle, whereas the calculations were always done for normal incidence of the primary ions, and (ii) the experimental results were obtained in the limit of large primary ion fluence ($> 10^{19} \text{ cm}^{-2}$), i.e. are representative for a target that may have been subject to radiation damage and surface roughening^{#2}, whereas the simulation was performed for an ideal crystal. Regarding these difficulties, we consider the agreement between experimental and computational results obtained in the present work quite satisfactory.

^{#2} The results of ref. [12], however, show no significant influence of pre-irradiation on the measured angular distributions.

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