

Sputtering and Surface Science

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Synopsis

Sputtering and surface science are intimately related, both historically and scientifically. While the knowledge and techniques which have been acquired in the discipline of surface science have been helpful and indispensable in understanding fundamental processes in the sputtering of elemental and multicomponent material, sputtering phenomena themselves have had a decisive share in the dramatic boom in surface science in the last decades. Sputtering has become an ubiquitous tool in experimental surface science work for cleaning, microsectioning, depth profiling etc. Powerful methods for the analysis of surface composition and crystalline surface structures are based on sputtering processes. Moreover, the sputtering of solids and the concurring surface phenomena have become an active field of research in their own right. Via sputtering new routes can be followed in fundamental surface research, e.g. by using atomic resolution microscopy techniques to study the kinetics and processes by which a (sputtered) surface relaxes to its thermodynamic equilibrium. Several aspects demonstrating the importance of sputtering for surface science are discussed.

1 Introduction

Sputtering and surface science are intimately related to each other in the sense that sputtering is both goal and vehicle in surface research. Sputtering, i.e. the release of atoms from a surface due to ion bombardment, is important in a vast field of applications as well as for basic understanding of dynamical processes on solid surfaces (Behrisch, 1981). Some of these aspects are discussed in the following.

In a typical situation in this context a surface is bombarded by Ar^+ ions with a kinetic energy of about one keV whereby atoms are set in motion in a near-surface region through a collision cascade.

Such an ion has a projected range in the solid of the order of 10 nm and the resulting collision cascade typically extends to dimensions of about 20 nm (Winterbon et al., 1970; Eckstein, 1991). The lifetime of the cascade is of the order

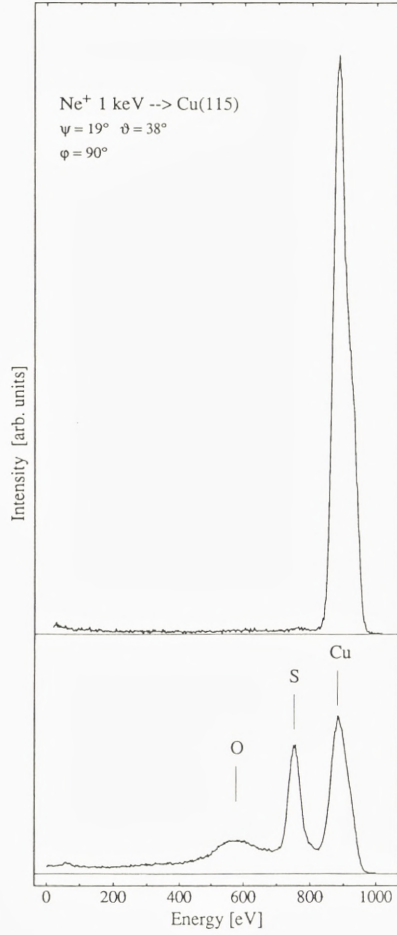


Figure 1. Ne⁺ ion scattering signal before (bottom) and after (top) sputter-cleaning of a Cu(115) surface (Liegl, 1992).



Figure 2. Daguerrotype photograph before (a) and after (b) cleaning in a glow discharge by 'physical' and 'chemical' sputtering (courtesy of W. Poschenrieder).

of 1 ps and only a small fraction of the atoms within a cascade are in motion at any time, i.e. in the situations considered here we are in the linear cascade regime (Sigmund, 1981). Those atoms which are eventually ejected from the surface as a result of the collision process originate predominantly from the first and second atomic layer (Sigmund et al., 1989; Harrison, 1983). This whole scenario demonstrates the surface sensitivity of the sputtering process. Consequently, sputtering is important in various surface related aspects, such as

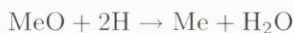
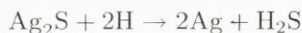
- surface preparation which includes surface cleaning and preparation of non-equilibrium surfaces,
- surface etching, i.e. the generation of sputter-depth profiles and the sputtering of adlayers,
- surface analysis by detecting sputtered particles, either ions or neutrals including directly recoiling particles, and
- the investigation of surface interactions such as preferential sputtering of compound material, radiation enhanced diffusion and segregation, and annealing kinetics of bombarded surfaces.

2 Surface Preparation

The surface cleaning effect of the sputtering process has first been observed by Wehner (1957) in a glow discharge and has been introduced specifically to studying well defined surfaces by Farnsworth et al. (1958). Since then, sputter-cleaning of surfaces has become a standard procedure in any kind of surface investigation (Taglauer, 1990). Quite frequently, 1-3 keV Ar⁺ ion beams with current densities of microamps/cm² are used and allow the removal of many surface contaminants within a reasonable time, i.e. in the order of some 10³ seconds.

A typical situation is shown in fig. 1, in which a surface contamination of about half a monolayer of O and S on Cu(115) is reduced to less than a hundredth of a monolayer after 20 min Ne⁺ bombardment (Liegl, 1992). Situations as shown in fig. 1 are familiar to every experimenter in this field. It has to be mentioned that the radiation damage on the surface caused by sputtering generally has to be removed by annealing, a procedure which can again lead to surface contamination due to segregation. As a result, repetitive cycles of sputtering and annealing have been adopted in most cases in order to prepare clean surfaces. Recoil implantation is another process which can considerably reduce the cleaning effect of sputtering, particularly for heavier overlayers on light substrates (Targn and Wehner, 1972).

An enhanced cleaning effect can occur when in addition to the physical sputtering processes chemical reactions can take place. This occurs in glow discharge sputtering if reactive species such as hydrogen ions are involved. Such a combination is used in conditioning the inner walls of large fusion devices (Dylla, 1980) or also in semiconductor fabrication (Winters and Coburn, 1992). There is also an interesting application for cleaning precious silver objects, such as ancient altar figurines or Daguerrotype photographs (Roidl et al., 1987). Figure 2 shows the cleaning effect of a hydrogen glow discharge on such an early photograph. On these very thin and sensitive silver layers only little physical sputtering can be tolerated and this is controlled by operating close to the sputtering threshold (which is about 100 eV for H on Ag). In addition, chemical reactions like



take place (here MeO stands for any metal oxide). With the same procedure also 17th century angel figurines of the altar in Tschenstochau (Poland) were restored.

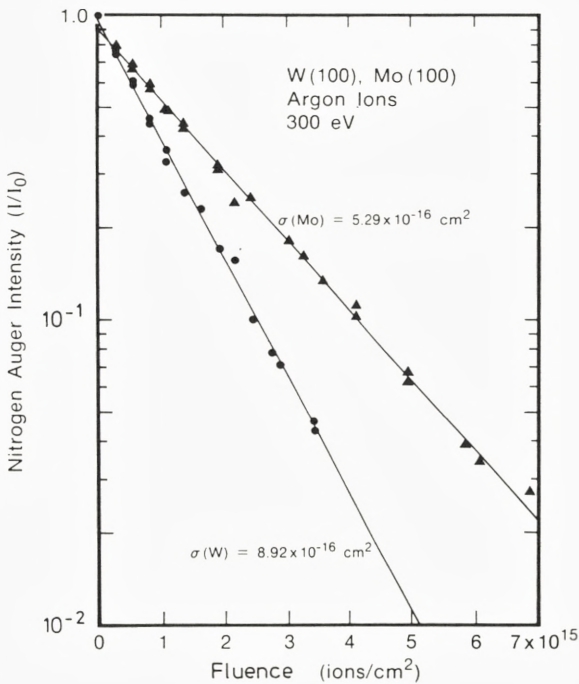


Figure 3. Sputter removal of nitrogen from W and Mo single crystal surfaces. Initial coverage about half a monolayer (Winters & Taglauer, 1987).

3 Sputtering of Adsorption Layers

For well defined adsorption layers (in contrast to the uncontrolled contamination layers considered in the previous section) the relevant physical sputtering processes have been studied in detail and experimental results can be well reproduced by theoretical estimates. Under the influence of an ion flux F the surface density of an adsorption layer, N_A , decreases according to the relation

$$\frac{dN_A}{dt} = -\sigma \cdot F \cdot N_A \quad (1)$$

in which σ is the sputtering cross section. For the purpose of comparison σ can be related to a sputtering yield Y through the monolayer density N_{ML} , $\sigma = Y/N_{ML}$. The exponential decrease following from eq. (1) has been observed for some adsorption systems, an example is given in fig. 3 (Winters and Taglauer, 1987). Here, the sputtering of N from single crystalline Mo and W surfaces is well represented by an exponential decay. Frequently, a deviation from the initial slope is observed

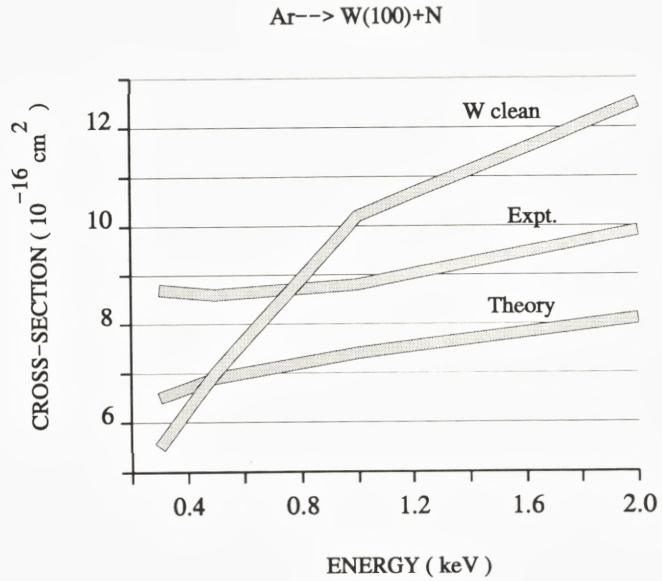


Figure 4. N-Sputter cross sections for Ar⁺ in bombardment of W(100) + N and W-sputter cross section for clean W (data from Winters & Taglauer, 1987).

after sputtering of about 90% of the adsorption layer, this deviation is attributed to recoil implantation. Obviously this is not the case for the system shown in fig. 3. Probably recoil implanted N segregates back to the surface. The slope of the straight lines in the figure yields the sputtering cross section. Such cross sections were calculated by Winters and Sigmund (1974) and in more detail by Yamamura and Kimura (1987). Important parameters in these calculations are the surface binding energy of the adsorbate, the reflection coefficient for the primary projectiles and the total energy transfer to the substrate lattice which determines the substrate sputtering yield. Figure 4 shows the comparison of these calculations with experiments for N on W(100) and also the sputtering yield for Ar on clean W. Without a fitting parameter the theory reproduces the experimental data quite well, particularly also the fairly flat energy dependence which deviates from the much steeper metal sputtering yield. It also shows that for low energies the adlayer sputtering yield can significantly surpass the substrate sputtering.

The removal of the surface adlayers by sputtering brings the second (and following) atomic layers to the surface and thus quite naturally allows the analysis of the layering of the various constituents of a multicomponent structure by using appropriate surface analytical techniques. Therefore sputter-etching of surfaces has

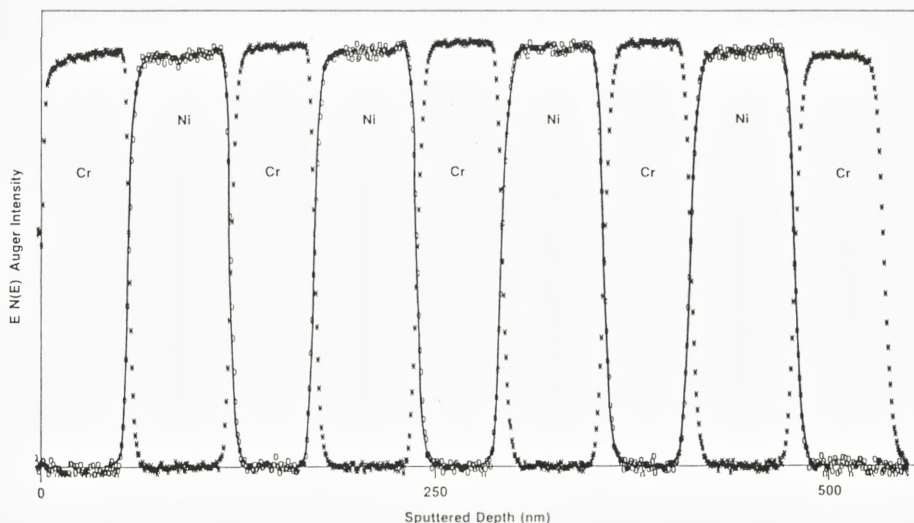


Figure 5. Sputter depth profile of a Ni-Cr multilayer structure using a 1 keV rastered argon ion beam. The average film thickness is 50nm for Cr and 63nm for Ni (Fine & Navinsek, 1985).

become a very common method for determining concentration depth profiles. For coverages of the order of a monolayer, i.e. the situation described above, this application is e.g. important for the analysis of supported catalyst systems (Brongersma & van Leerdam, 1991; Taglauer, 1991). These catalysts consist of high surface area supports (e.g. transition metal oxides) that carry the active components. For the performance of the catalyst (activity, selectivity etc.) the geometric position of the outermost atomic layers is decisive and 'monolayer depth profiles' are therefore very helpful in studying catalysts.

In many cases the depth distribution of the constituting elements is of interest to much larger depths, say several hundred nanometers. This is a range which is not usually comprised in the field of surface science, but the analytical techniques, i.e. ion or electron spectroscopies are quite often taken from the surface science arsenal. A nice example is given in fig. 5 which shows the result of a Ni-Cr multilayer structure, sputtered with 1 keV Ar^+ ions and analysed by Auger electron spectroscopy (AES) (Fine & Navinsek, 1985). Up to the ninth layer a sharp interface was obtained here. This raises the question of the limitations of sputter depth profiling, i.e. to which extent does the experimental result really represent the initial concentration profile? This question has been investigated by many researchers and can only be marginally touched here. The examined sample

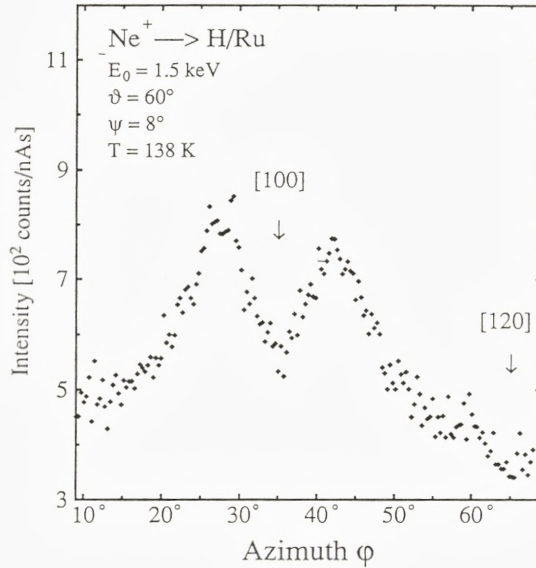


Figure 6a. Azimuthal distribution of H^+ recoils from $Ru(001)$ under Ne^+ bombardment: Experiment (Schulz et al., 1992).

is changed by the impinging ion flux mainly due to atomic mixing (i.e. relocation of sample atoms due to collision processes), there is no ‘layer-by-layer’ removal of atoms and therefore a broadening of the depth distributions must be expected. Furthermore, different atomic species have different sputtering yields and therefore the flux of sputtered particles leaving the surface has an elemental composition that differs from that of the surface. This preferential sputtering effect (Betz & Wehner, 1983) has important consequences on depth profiling. The analysis of the sputtered particle flux or the surface composition can lead to quite different results (Coburn, 1976). The relevance of the various effects of course depends on the experimental parameters, i.e. mass, energy and angle of incidence of the probing particles and also the target properties such as chemistry, temperature, roughness, etc. (Wittmaack, 1968). Figure 5 nevertheless demonstrates that very satisfactory results can be obtained by sputter etching.

4 Surface Analysis

One of the major connections of sputtering to surface science is that it offers the possibility of determining the chemical composition and the structure of surfaces

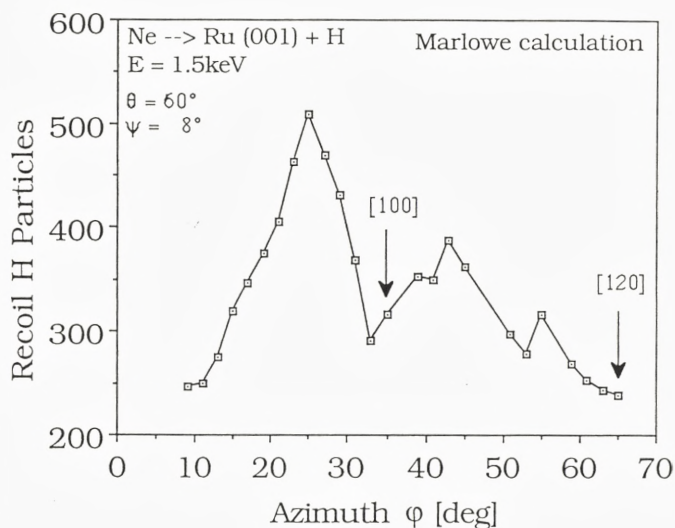


Figure 6b. Same as figure 6a: MARLOWE calculation

by analyzing sputtered particles. For instance, understanding of adsorbates can be gained if directly recoiling species are detected from the bombarded surface (Rabalais, 1991; Niehus et al., 1993). These recoils can be identified by their kinetic energy and thus by variation of bombardment and detection geometry a mass specific, structure dependent signal is obtained.

Figure 6 shows as an example the azimuthal distribution of H^+ recoils from a H/Ru(001) surface sputtered with 1.5 keV Ne^+ ions (Schulz et al., 1992). From the azimuthal distribution it can be deduced that hydrogen adsorbs in a threefold coordinated position on this surface, about 1 Å above the top Ru layer. These findings are corroborated by numerical simulations using the binary collision code MARLOWE (Robinson & Torrens, 1974). In this program only collisional but no charge exchange processes are taken into account. The similarity between experiment and calculation proves that H^+ species are representative for all recoils under these conditions. In the calculation the adsorbed H was only placed in fcc lattice sites, and the resulting asymmetry on both sides of the [100] direction is more pronounced than in the experiment. This is probably due to domain formation.

A related technique is the angle resolved secondary ion mass spectrometry (Winograd & Garrison, 1991) in which the structural information again arises from the detection geometry but the sputtered species are identified with a mass spectrometer. With such measurements e.g. detailed analyses of Cl on Ag (100) were

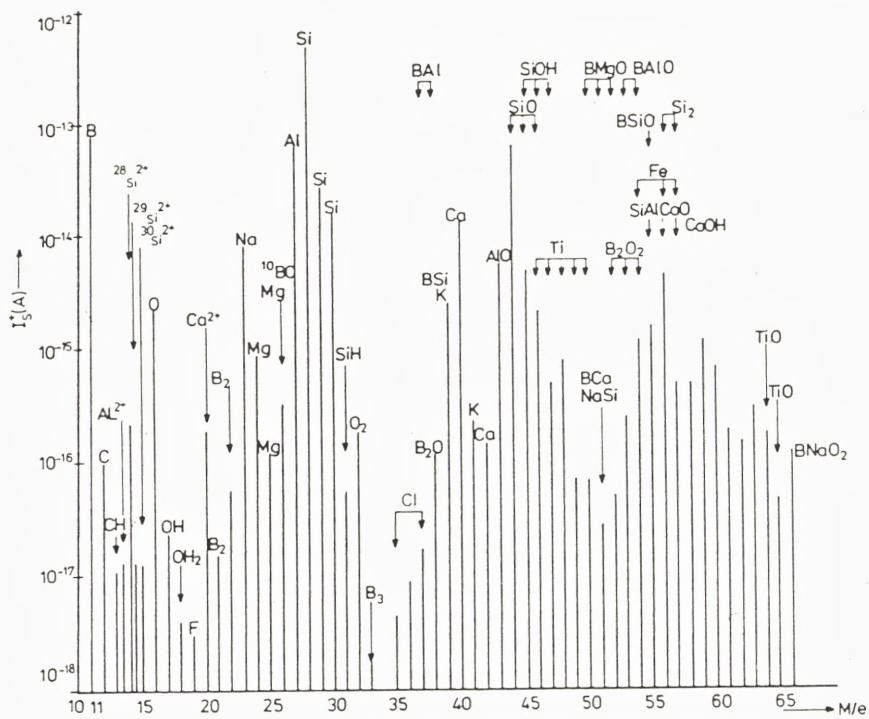


Figure 7. Positive SIMS spectrum from a glass standard (NBS 93) using 14.5 keV O^- ions, $0.2 \mu\text{A}$ (Morgan & Werner, 1987).

obtained.

Secondary ion mass spectrometry (SIMS) is certainly the most widespread surface analysis technique related to sputtering (for a comprehensive reference see e.g. Benninghoven et al. (1987)). In this technique secondary ions (positive or negative) emerging from a bombarded surface are analyzed using a mass spectrometer. It is thus possible to analyze elemental and molecular species, their depth distribution (by sputter etching) and their lateral distribution (on a micrometer scale) using scanning or imaging techniques. The main advantages of the technique are the excellent mass resolution, the possibility to detect molecular species (from hydrogen to large organic molecules) and the high sensitivity which also results in an extraordinary dynamical range of the detection signal. Some of these features can be observed in fig. 7 which shows a positive-ion mass spectrum from a glass bombarded with 14.5 keV O^- ions (Morgan & Werner, 1987). The spectrum exhibits a large variety of ionic species which can be exploited for information about the surface chemistry, but they also make quantitative analysis difficult. The spectrum also indicates the high sensitivity for trace analysis, which is in the ppm range for SIMS, and a dynamical range of about six orders of magnitude. As already mentioned, the main limitation of SIMS lies in the quantification problem. This is not only due to the multielemental molecular species but even more so due to the large variations in ion yields, which sensitively depend on the chemical composition of the surface (matrix effect). The secondary ion yield Y^+ (secondary ion/primary ion) can vary by orders of magnitude if the surface composition changes, experimental values for 3 keV Ar^+ bombardment are e.g. 0.02 for clean Al and 2.0 for oxidized Al; 3×10^{-4} for clean Si and 10^{-2} for oxygen covered Si. These problems can partly be compensated by using electronegative species (oxygen ions or gas stream) for positive SIMS and electropositive ions (Cs^+) for negative SIMS, but this is not always compatible with the analytic situation. Another approach consists in post-ionization of sputtered neutrals (consequently abbreviated by SNMS) either by an electron beam, a plasma discharge or laser radiation (see e.g. Benninghoven et al., 1987). These methods require a large technical effort and are not yet as widespread as SIMS, but they are under rapid development and offer substantial new analytical possibilities.

5 Surface Interactions

The effects of ion bombardment on near-surface compositional changes are of fundamental interest and also important for many applications such as depth profiling, ion implantation and material modification. Particular preferential sputtering effects on metallic alloys have obtained considerable attention, also in view of the

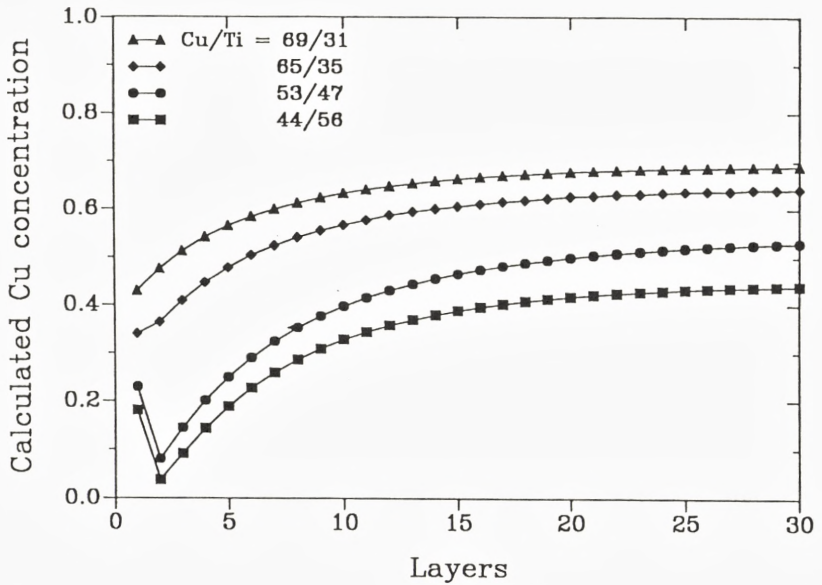


Figure 8. Calculated steady state Cu concentration profiles (using ISS and AES data) for bombardment of various CuTi alloys with 2 keV Ar^+ ions (van Wyk et al., 1991).

concurring effects of surface segregation and radiation-enhanced diffusion (Betz & Wehner, 1983; Lam & Wiedersich, 1987). Preferential sputtering results in an altered layer below the surface, whose composition is different from the bulk due to the difference in sputtering yields of the components. The depth of this altered layer corresponds to the range in which the kinetic energy of the primary ions is deposited (Baretzky et al., 1992). The depletion of one constituent can be counteracted by surface segregation if this minimizes the surface free energy (Kelly, 1985). Segregation is a true surface phenomenon, leading to a concentration jump between the top and the second atomic layer. Analysis of these effects therefore requires methods with appropriate information depths, as e.g. given by ion scattering spectroscopy (ISS) with an exclusive first-layer sensitivity (Niehus et al., 1993) and AES with an information depth of about 5 atomic layers. From the combination of both methods the near-surface concentration profile can be deduced. In steady state the sputtered flux is balanced by the diffusion flux and thus the segregation energy and the radiation-enhanced diffusion coefficient can be obtained from such measurements. Figure 8 shows as an example steady-state concentration profiles calculated with ISS and AES data for various amorphous CuTi alloys bombarded with 2 keV Ar^+ ions (van Wyk et al., 1991). The depth of the altered layer corre-

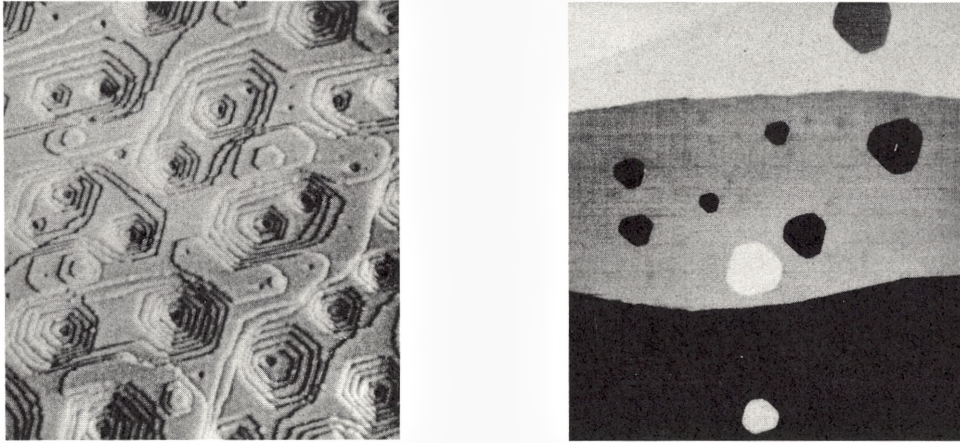


Figure 9. STM micrograph ($825 \text{ \AA} \times 825 \text{ \AA}$) of a Pt(111) surface sputtered at 625 K (a) and at 910 K (b) ($3300 \text{ \AA} \times 3300 \text{ \AA}$) with 600 eV Ar^+ ions (courtesy of Michely & Comsa).

sponds to the range of the defect distribution caused by the argon ions.

Sputtering of surfaces is generally associated with the development of a variety of surface structures (Carter et al., 1983). From the basic physics point of view, structural studies with high lateral resolution are of particular interest. Early investigations with atomic resolution were performed with field ion microscopy (e.g. Vernickel, 1966). The recent development of the scanning tunneling microscope (STM) opened new possibilities for obtaining real-space information about sputtered surfaces and their annealing behavior. This is of basic interest concerning the equilibrium morphology of surfaces. A beautiful example in this context is a study of the sputtering of a Pt(111) surface with 600 eV Ar^+ ions at various temperatures (Michely & Comsa, 1991). Figure 9a shows an STM micrograph for sputtering at 625 K. Ordered pit formation on the surface can clearly be seen, up to ten terraces or more can be distinguished. This result indicates that under these conditions intralayer diffusion obviously takes place (hexagonal pits) but interlayer diffusion is prohibited. This occurs at higher temperatures and results in a quasi layer-by-layer removal of surface atoms as shown in fig. 9b. On one terrace only vacancy clusters (dark hexagonal structures) with monoatomic depth or equivalent adlayer islands (bright structures) are found. The apparent rotation of these two structures can be understood from the crystallographic orientation of $\langle 110 \rangle / \{111\}$ steps and $\langle 110 \rangle / \{100\}$ steps. Application of the Wulff construction to this equilibrium form allows the determination of the ratio of the free energies of these steps. It could also

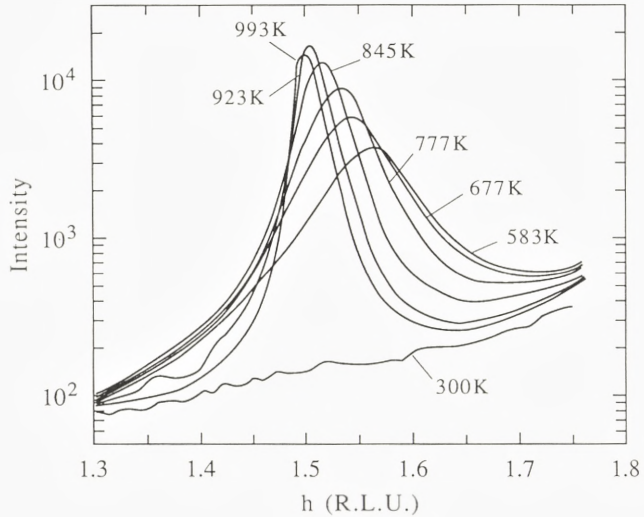


Figure 10. Half-order diffraction peaks of a sputter-roughened Pt(110) surface after annealing at various temperatures. The direction of h (in reciprocal lattice units) is along the [001] surface direction (Kern et al., 1992).

be shown that temperature-dependent equilibrium morphology of sputtered metal surfaces (pit formation, layer-by-layer removal; vacancy islands) is analogous to crystal layer growth (3D island growth; layer-by-layer growth; adatom islands). A further example along these lines is the investigation of the ‘smoothing’ kinetics of a sputter-roughened surface by time-resolved X ray diffraction (Kern et al., 1992). The interest is the expectation that the kinetic behavior of various systems can be classified by universality classes analogous to equilibrium phase transitions. In a study of a sputter-roughened Pt(110) surface the roughness was characterized by the step density measured by the shift (and broadening) of a half order diffraction peak, see fig. 10. Flattening of this surface proceeds with a power law dependence on time, the exponent depending on the temperature. A detailed theoretical understanding of this behavior is presently not yet available.

The purpose of showing these examples is that sputtering, apart from its very important and widely used application as an indispensable means of surface analysis and etching, also has a decisive role in research activities concerning the fundamental behavior of solid surfaces. Thus, particularly at the advent of new techniques and applications sputtering will certainly continue to be an important aspect of surface investigations.

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