Ion Scattering Studies of the Structure and Chemical Composition of Surfaces

Edmund Taglauer

Max-Planck-Institut für Plasmaphysik, EURATOM Association
D-85748 Garching bei München, Germany

(Received: Jan. 31, 1997 Accepted: Feb. 20, 1997)

Abstract

Within the arsenal of surface analytical techniques surface analysis by low-energy ion scattering has become a well established method due to its particular features. This report first gives a brief introduction to the basic principles of the method and the relevant physical processes that provide the possibility to identify the atomic species present on the outermost atomic layer of a surface. In the subsequent sections the problem of quantification is considered and surface composition analysis of supported oxide catalysts and metallic alloys is discussed. In the final section the principles for obtaining structural information by ion scattering are introduced and applications to surface reconstruction, the structure of ordered adsorbates and thin film growth are presented. The related technique of direct recoil spectroscopy offers the possibility to detect atomic species with low masses such as hydrogen isotopes. The potential of the method for these various analytical problems is demonstrated by showing a number of typical results.

1. Introduction

For surface analysis by low-energy ion scattering 'low' refers to primary kinetic energies in the range of about 500eV to 5 keV. The ion species used most frequently are the rare gas ions He^+ and Ne^+ and the alkali ions Li^+ and Na^+. In this energy range, the fairly large scattering cross sections in combination with the high neutralization probability ensure that backscattered ions predominantly arise from interactions with the top one or two atomic layers of the surface under analysis. Therefore the energy and angular distributions of backscattered ions convey information about the composition and structure of the outermost atomic layers of the studied specimen. It turns out that the ion-surface interaction process can be described with sufficient accuracy by one binary collsion or a sequence thereof. Consequently, the concepts of data interpretation are in principle rather simple. Quantitative compositional analysis is not always that easy (mainly due to the neutralization process) and requires proper calibration. Also detailed structural analysis frequenly must be accompanied by numerical model calculations. The effect of the ion beam on the bombarded surface is not generally negligible, but 'static' analysis (i.e. without significant perturbation of the analysed surface) is possible and on the other hand the sputtering action of the ion beam can also be used for obtaining near-surface composition depth profiles.

Surface analysis by low-energy ions was first reported by D.P. Smith [1] and named 'Ion Scattering Spectroscopy', ISS. He used noble gas ions and an electrostatic energy analyser. Later applications included alkali ions and time-of-flight methods for neutral particle detection.

The acronym LEIS for Low-Energy Ion Scattering has also become commonly used. For recent reviews of the field see e.g. refs. [2-4].

In the following sections we first consider some principles of the method and experimental aspects, subsequently surface chemical composition analysis by ion scattering is discussed in view of successful applications such as the analysis of oxide and catalyst surfaces and the analysis of alloy surfaces with respect to segregation. Using ISS it is also possible to obtain mass selective structural information and that is demonstrated for adsorbate structures, surface reconstruction and thin film growth.

2. Basic Principles

The principle of ISS is the binary scattering process between an incoming ion and a target surface atom. According to collision kinematics, the kinetic energy E of the projectile after the collision process is a function of the mass ratio $A = M_2 / M_1$ of the projectile (M_1) and target (M_2) atomic masses:

$$\frac{E}{E_0} = \frac{1}{(1+A)^2}\left[\cos\vartheta_1 \pm \sqrt{A^2 - \sin^2\vartheta_1}\right]^2 \quad (1)$$

where E_0 is the primary ion energy and ϑ_1 the experimentally given laboratory scattering angle (the positive sign holds for $A \geq 1$, both signs for $A<1$). An energy spectrum of the scattered ions therefore yields a peak for each atomic mass present on the surface, the peak height being a measure of its abundance.

In a typical scattering arrangement a beam of noble gas ions is directed onto the sample surface, the currents being of the order of 10^{-8} to 10^{-7} A. Backscattered ions can be energy analysed by using electrostatic fields, e.g. in a spherical sector analyser or a cylindrical mirror analyser (CMA).

Figure 1 shows as an example a series of energy spectra of an Al_2O_3 sample which is covered by about a monolayer of Rh (due to the roughness of the surface the nominal amount for a monolayer does not imply complete coverage)[5]. Several essential features of ISS can be recognized in this example: the binary collision model is obviously applicable to calculate the peak positions for each atomic mass on the surface. Detailed analysis shows (see e. g. ref. 2) that these distinct peaks are due to the fact that the vast majority of the detected backscattered ions has undergone collisions with atoms in the topmost layer, whereas ions which penetrate further into the solid are backscattered as neutrals and not detected. Figure 1 further demonstrates that the method can be applied to insulating material if electrons are offered for charge neutralization.The presence of contaminants with low atomic mass (hydrogen, hydrocarbons) has the effect that there is almost no backscattered ion yield at the beginning of the bombardment. The sputtering action of the ion beam removes this contamination layer and can also be used for etching through the deposited Rh layer. The ion beam is therefore suitable to measure the kind and amount of atomic species present on the surface and due to the sputtering effect also to obtain near surface concentration profiles [6].

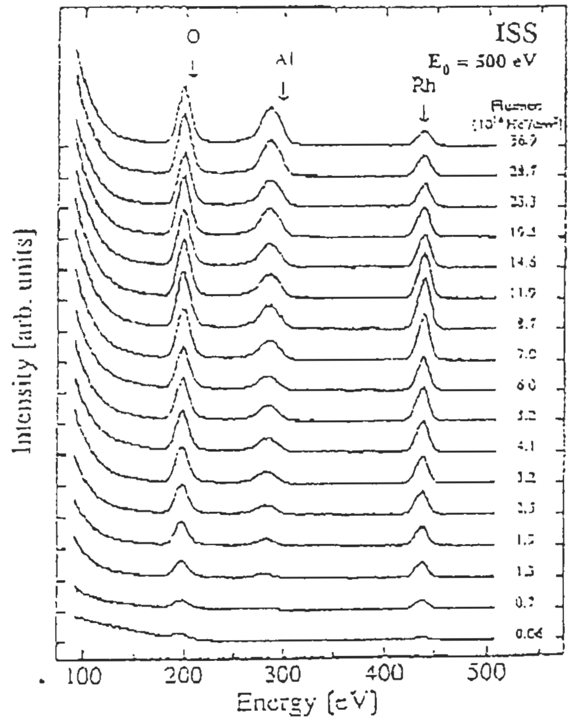

Fig. 1 ISS spectra (500 eV He^+, scattering angle 137°) of an alumina film formed by oxidation in air, with an overlayer of rhodium. At the right side the ion fluence at the beginning of each spectrum is noted. The arrows indicate the peak positions calculated with eq.1[5].

3. Quantification Aspects

In the scattering model mentioned so far, a linear dependence of the scattering signal on the surface density N_i of species i could be expected and would be desirable for quantitative analysis. This has in fact been observed for various surfaces, but it cannot be generally assumed. For the scattered ion intensity I_i^+ the following expression can be written:

$$I_i^+ = I_0^+ K N_i \frac{d\sigma_i}{d\Omega} \cdot \Delta\Omega \cdot P_i \qquad (2)$$

Here I_0^+ is the primary current, K a factor for the apparatus transmission, $d\sigma / d\Omega$ is the differential scattering cross section and $\Delta\Omega$ the acceptance solid angle of the detector. P_i describes the probability that an ion is backscattered as an ion and not neutralized, its value is generally of the order of a few percent for noble gas ions scattered from surface atoms and at least an order of magnitude less for scattering from deeper layers. Auger neutralization has been identified as the dominating process [7-10].

The reliability of quantification and the absence of matrix effects has been demonstrated in favourable cases, e. g. for the surfaces of binary alloys. Here it is justified to assume that the sum of the surface concentrations $c_i=N_i/N$ (where N is the the density of lattice sites on the surface) is unity:

$$C_A + C_B = 1 \qquad (3)$$

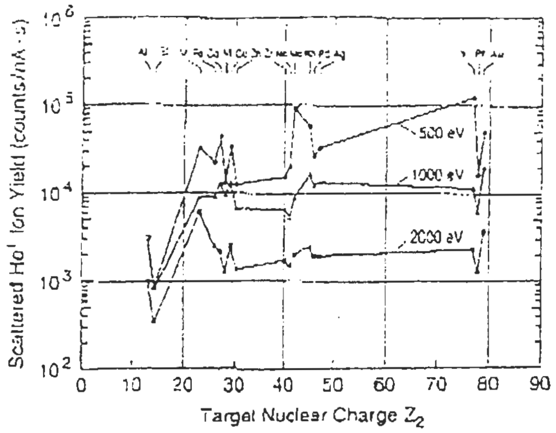

Fig. 2 Yield (counts/s) of He^+ ions scattered from various elemental surfaces, given in relation to the target current. Data taken with a cylindrical mirror analyzer (scattering angle 137°) at three different primary energies [12].

From the combination of eqs. 2 and 3 it follows that a linear relationship between the signals of the constituents A and B should be observed. This has been shown for CuPd alloys with varying surface concentrations [11].

Experimental results for scattered ion yields are given in fig.2. They show a general trend but deviations from a monotonous increase with target atomic number are obvious. These are due to the differences in the ion escape probabilities for the different elements.

The neutralization effect provides the exclusive surface sensitivity of ISS to the outermost atomic layer, but it also can cause problems for quantification because changes of the surface or scattering conditions can produce changes of the neutralization probability. In order to deal with this problem, alkali ions have been used [13-15]. Their ionization energy is close to the work function of most materials, i. e. about 4-5 eV, and therefore their neutralization probability is much lower than for noble gas ions. Another approach is the detection of neutral partices in time-of-flight systems [16-18], some of which offer the possibilty to measure with a scattering angle of or close to 180°. This is advantageous for structure analysis, as discussed below. Alkali ion scattering and neutral particle detection circumvent the neutralization problem to some extent, but generally the specificity to the outermost layer is lost. Their energy spectra can contain large contributions from multiple scattering and numerical simulations have to be made for data interpretation.

4. Oxide and Catalyst Surfaces

A field in which ISS has been very succesfully applied is the analysis of supported catalyst systems [11,19-21]. For the catalytic performance the composition of the outermost atomic layer is of decisive importance. Supported catalysts generally consist of oxide material (e.g. Al_2O_3, TiO_2, SiO_2) with a high surface area on which other metals or oxides are dispersed as the active components. These materials are highly insulating and therefore electron spectroscopies can generally not be used. Ion scattering, however, is applicable, because charging effects can be overcome by flooding the sample with electrons.

An illustrative example is the spreading of the oxides of group Vb,VIb, and VIIb metals on the support oxides mentioned above. It has been shown by ISS experiments that during heat treatment (calcination) spreading in the sense of monolayer dispersion can occur as a process of solid-solid wetting [22]. A result of that kind is plotted in fig. 3. The near-surface depth profile as a function of He^+ ion fluence shows a flat distribution for a physical mixture of molybdena and titania (slightly increasing due to preferential sputtering). The drastic changes in the Mo/Ti intensity ratios after calcination indicate the high dispersion of the molybdenum on the titanium oxide after that treatment: we observe a high Mo signal at the surface which decays with ion fluence with a value characteristic for sputtering of about one monolayer. This kind of ISS studies is particularly valuable if they are combined with other measurements, such as catalytic activity, laser Raman spectroscopy [22] or X-ray photoemission spectroscopy, XPS [23].

5. Alloys

The investigation of alloy surfaces is also a field of very successful applications of ISS methods. This is mainly due to two reasons: Firstly, the composition of the first and second atomic layers are often very different (and also different from the bulk), particularly if strong segregation occurs, and it is to these first layers that ISS is particularly sensitive. Secondly, quantification has been shown to be reliably applicable for metal surfaces, either by using elemental standards or by scattering from single crystal surfaces under various scattering conditions. Consequently, ISS has been applied to a number of studies of surface segregation and preferential sputtering of alloys [24-27].

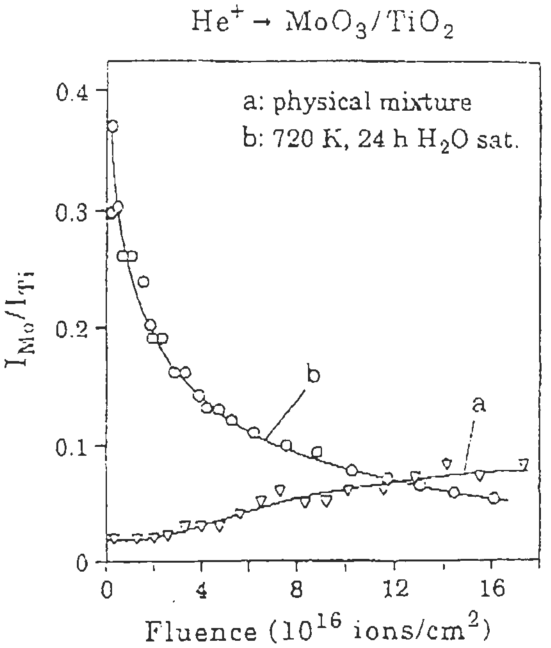

Fig. 3 Scattered He$^+$ ion intensity ratios Mo/Ti as a function of ion fluence for a MoO_3/TiO_2 mixture: (a) physical mixture; (b) after calcination for 24h in H_2O-saturated O_2 [22].

If elemental standards are used, the concentration of species A of a binary system with components A and B is given by

$$c_A = \left(1+\frac{I_B N_B I_A^\infty}{I_A N_A I_B^\infty}\right)^{-1} \qquad (4)$$

here N_i are the respective surface densities and I_i^∞ the signals from the related elemental standards. The validity of this expression has been proven in several cases. For a series of PdPt alloys it could be verified by analyzing samples which were prepared by milling in UHV, a treatment that is expected to produce the bulk composition on the surface [25].

A good example for alloy investigations is the copper-gold system. It is a classical case of an ordering alloy with a negative enthalpy of mixing and undergoes a bulk first order phase transition, the critical temperature depending on the composition. With respect to surface segregation and its relation to the order-disorder transition particularly the Cu_3Au alloy was studied with several methods including ISS [24]. For the (001) surface Au segregation (59%) was found in the top layer and only Cu in the second layer. For the complementary system Au_3Cu complete Au segregation to the first layer and close to 100% Cu in the second layer were observed on the (001) surface [27]. ISS was also used to study details of the structure and segregation kinetics of that system. Figure 4 shows energy spectra from the (001) surfaces of these two alloys. The scattering contributions from the first layer alone ($\Phi = 0$) and from the first plus second layer ($\Phi = 45°$) can be well distinguished. This is a nice example for the mass and layer specific information obtainable by ISS which is probably a unique feature of the method.

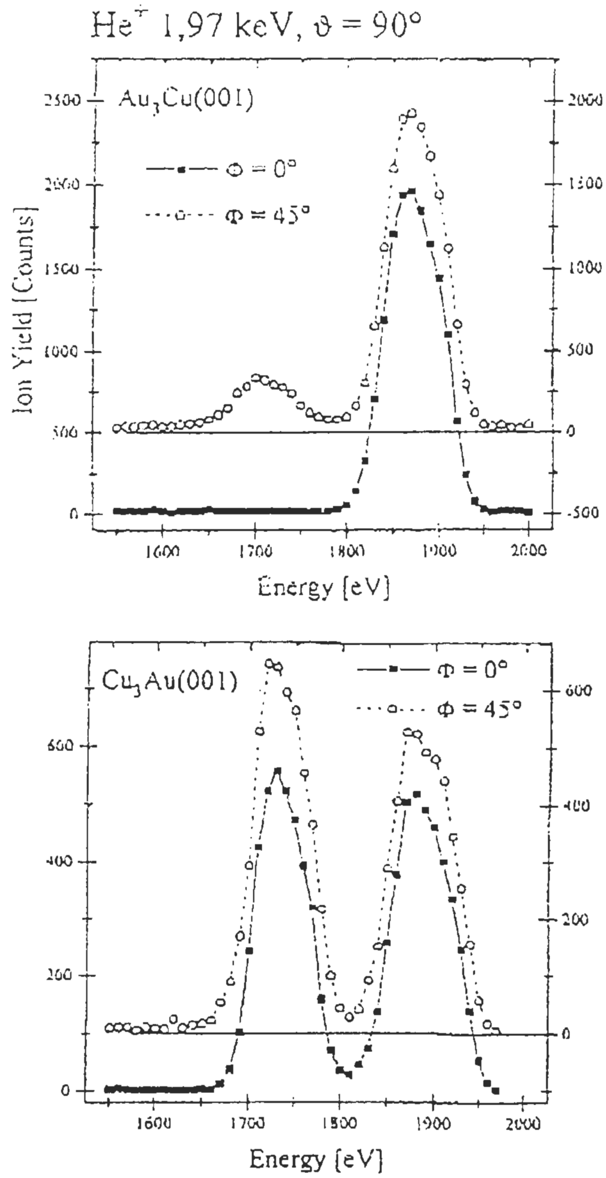

Fig. 4 ISS spectra from the (001) surfaces of Au_3Cu (top) and Cu_3Au (below) alloy single crystals. The angle of incidence is 45°, the scattering angle 90°; $\Phi = 0°$ corresponds to a scattering plane parallel to the [100] direction, $\Phi = 45°$ to scattering parallel to the [110] direction [27].

6. Structure Investigations

The basis for obtaining structural information by ion scattering consists in the concept of the shadow cone. It describes the flux distribution downstream of a target atom on which a flux of primary ions impinges. The radial flux distribution f(R) behind the scattering atom exhibits strong flux peaking at the edge of the cone. For a Coulomb potential the radius R_S of the shadow cone at distance d from the scatterer is

$$R_S = 2\left(Z_1 Z_2 e^2 d / E\right)^{1/2} \tag{5}$$

There is a square root singularity at $R = R_S$ that is smeared out by beam divergence and by the thermal vibrations of surface atoms. If the peaked flux of the shadow cone edge is directed onto a neighbouring atom (i.e. at the appropriate impact parameter), a peak in the scattered ion intensity is observed. This situation can be created by gradually increasing the angle of incidence of the ion beam on the surface until the shadow cone edge hits a neighbouring atom. The technique has been called Impact Collision Ion Scattering Spectroscopy, ICISS [28] and allows to measure interatomic distances on a surface. If the shadow cone radius $R_S(d)$ is known, either by calculation or by calibration using a known surface structure, the interatomic distance d is found from the critical angle ψ_c for which the maximum scattering intensity is observed:

$$d = R_S / \sin\psi_c \tag{6}$$

Using this technique the local arrangement of surface atoms can be measured with an accuracy of about 0.1 Å. In order to determine a crystallographic surface structure, e.g. in the frequent case of surface reconstruction, structural models have to be considered (usually deduced from low-energy electron diffraction (LEED) patterns). Ion scattering then provides the possibility to unambiguously determine which of various models of the same symmetry exists on the surface. For multicomponent material it is particularly useful that ISS provides a mass sensitive signal, i.e. the positions of the various constituents can be identified. A nice example in the literature is e.g. the confirmation of the missing row model for the reconstructed Ni(110)-O(2x1) surface [29,30].

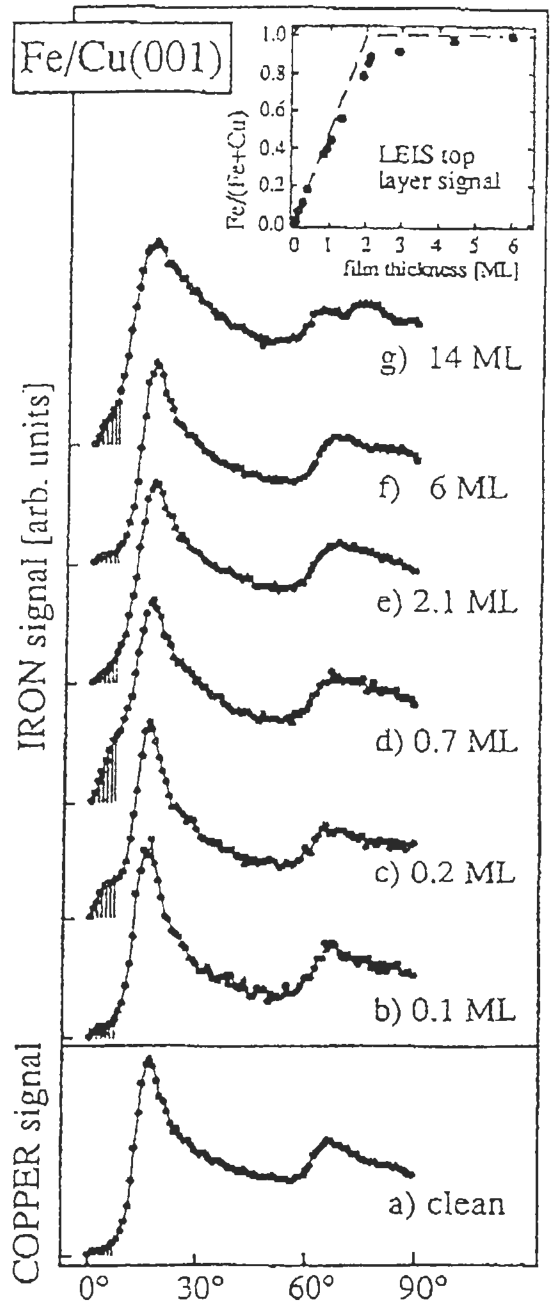

Fig. 5 ICISS spectra for the clean surface and various Fe films on Cu(001), azimuth [100]. All spectra are normalized to the same maximum height. Insert: Fe signal at an angle of incidence of 40° where only the top layer is probed [31].

As an illustrative example that demonstrates the potential of ion scattering for structural investigations we consider an ISS study of the growth of ultrathin iron films on Cu(001) [31]. Figure 5 shows ICISS spectra obtained in the way described above using 5keV Ne^+ ions at a scattering angle of 160°. As a function of the angle of incidence (measured relative to the surface) the first peak relates to scattering from the topmost atomic layer, the second peak (at 63°) to scattering from the second layer. Both peaks are observed for the clean Cu surface, for the lowest Fe coverage of 0.1ML and for the continuous film at about 6ML. This demonstrates that the films do not grow layer-by-layer, but Fe is incorporated into the original Cu surface from the beginning, the Cu substrate being at room temperature during evaporation. The insert in fig. 5 shows that at a coverage of 1ML there is still 50% Cu on the surface and the iron signal only saturates after deposition of 2 monolayers (1ML=$1.53\cdot10^{15}$ atoms/cm^2). The subsequent growth resembles more the layer-by-layer growth of an ordered iron film. This can also be seen from the scattering intensity at very low angles of incidence (hatched area). There should be no scattering at all into this angular region from a completely ordered surface due to the shadow cone position. The intensity observed is therefore an indication of defects and adatoms on the surface and it becomes a minimum at a coverage of about 2ML. The results shown in fig. 5 also demonstrate that the ineratomic distance (peak positions) is the same for the Cu substrate and the Fe films, (within an accuracy of 0.1 Å), i.e. these films grow in the fcc structure. Only after depositon of more than 10ML a phase transition from fcc (001) to bcc (110) can be observed (see fig. 13g). This structural development is also correlated to the magnetic properties of these films: no ferromagnetism up to 2ML, ferromagnetism between 5 and 10ML, only surface layer ferromagnetism above 10ML [32]. Studies of that kind demonstrate the assets of low-energy ion scattering for probing surfaces, i.e. sensitivity to the topmost atomic layer, to the structure of the surface and to the masses of surface atoms. It should be noted that generally such experiments can be done with low enough current density to avoid considerable damage or sputtering of the surface, although this point has always to be kept in mind.

An attractive variety of ISS is the direct recoil spectroscopy (DRS). It refers to the detection of those atoms or ions which are released from the surface in one single collision (as opposed to the collision cascade which is effective in sputtering). For these particles a similar expression as eq. 1 holds:

$$\frac{E}{E_0}=\frac{4M_1M_2}{(M_1+M_2)^2}\cos^2\vartheta_2 \qquad (7)$$

ϑ_2 being the recoil angle relative to the incident beam.This technique is particularly useful for the detection of light particles such as hydrogen isotopes. For them scattering is restricted to small scattering angles (arcsin ϑ <A) and the scattering cross section is relatively small, whereas the recoil cross sections can be much higher [3,33].

DRS can also be used in connection with the shadow cone technique described above. It has e.g. been applied to determine the position of H adsorbed on Ru(001), where adsorption in a threefold coordinated hollow site at a distance of 1.01 A° ± 0.07 A° above the topmost Ru layer was found [34], see fig.6. This result again demonstrates the mass selective structural sensitivity of ion scattering and recoiling techniques.

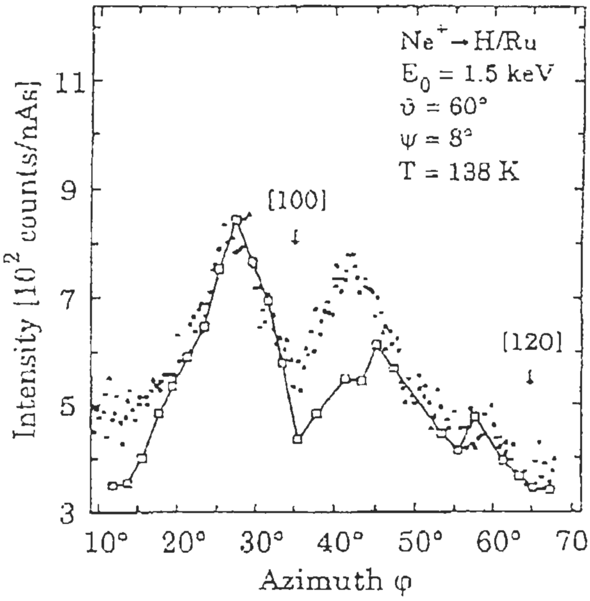

Fig. 6 Azimuthal intensity distributions of direct H$^+$ recoils for Ne$^+$ bombardment of H adsorbed on Ru(001). Experimental results are given by black dots, open squares connected by the solid line correspond to numerical simulations with H only in fcc positions [34].

Acknowledgement

Support by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 338, by the European Community through HCM project no. 94-0479 and also by NRIM, Tsukuba, is gratefully acknowledged.

References

1. D.P.Smith, J.Appl.Phys.18, 340 (1967), and Surf.Sci.25 (1971) 171.
2. H. Niehus, W. Heiland, and E. Taglauer,

Surf. Sci. Rep. **17** (1993) , 213.

3. E.Taglauer, in 'Methods of Surface Characterization', Vol.2, Eds. A.W. Czanderna and D.M. Hercules, Plenum 1991, p.363.
4. M. Aono, Nucl. Instr. Meth. Phys. Res. **B2** (1984) 374.
5. Ch. Linsmeier, H. Knözinger and E. Taglauer, Surf. Sci. **275** (1992) 101.
6. S. Hofmann, Appl. Surf. Sci. 70/71 (1993) 9.
7. H. D. Hagstrum, Phys. Rev. **96** (1954) 336.
8. R. J. MacDonald and D. J. O'Connor, Surf. Sci. **124**, (1983) 423.
9. M. Beckschulte and E. Taglauer, Nucl. Instr. Phys. Res. **B78** (1993) 29.
10. M. Aono and R. Souda, Nucl. Instr. Meth. Phys.Res. **B27** (1987) 55.
11. H.H.Brongersma, G.E.van Leerdam, in 'Fundamentals of Heterogeneous Catalysis studied by Particle Beams', Eds. H.H.Brongersma, R.A. van Santen, Plenum Press, New York (1991) p. 283.
12. E. Taglauer, Appl. Surf. Sci. **13** (1982) 80.
13. E. Taglauer, W. Englert, W. Heiland and D. P. Jackson Phys. Rev. Lett. **45** (1980) 740
14. J. Los and J. J. C. Geerlings, Phys. Rep. **190** (1990) 133.
15. S.H.Overbury, D.R.Mullins, M.T.Paffet, B.E.Koel, Surf.Sci. **254** (1991) 45.
16. T.M.Buck, Y.S.Chen, G.H.Wheatley, W.F.van der Weg, Surf.Sci. **47** (1975) , 244.
17. H. Niehus, Appl. Phys. **A 53** (1991) 388.
18. M. Aono, M. Katayama and E. Nomura, Nucl. Instr. Mezh. Phys. Res. **B64** (1992) 29.
19. E. Taglauer, in 'Fundamentals of Heterogeneous Catalysis studied by Particle Beams', Eds.H.H.Brongersma, R.A. van Santen, Plenum Press, New York (1991) p.283.
20. P. Bertrand, J.-M. Beuken, and M. Delvaux, Nucl. Instr. Meth. **218** (1983) 249.
21. E. Taglauer and H. Knözinger, phys. stat. sol. (b) **192** (1995) 465.
22. J.Leyrer, R.Margraf, E.Taglauer, H.Knözinger, Surf.Sci. **201** (1988) 603.
23. J.-P- Jacobs, L.P.Lindfors, J.G.H. Reintjes, O. Jylhä and H.H. Brongersma, Catal.Lett. **25** (1994) 315.
24. T. M. Buck, in: Chemistry and Physics of Solid Surfaces IV, Eds. R Vanselow and R. Howe (Springer Berlin, 1982) p.435.
25. J.du Plessis, G.N.van Wyk and E.Taglauer, Surf.Sci.**220** (1989) 381.
26. I. Katayama, K.Oura, F. Shoji and T. Hanawa, Phys. Rev. **B38** (1988) 2188.
27. S. Schömann and E. Taglauer, Surf. Rev. Lett (1997) in print.
28. M.Aono, C.Oshima, S.Zaima, S.Otani, Y.Ishizawa, Jpn. J. Appl. Phys.**20**, (1981) L829.
29. H.Niehus and G.Comsa, Surf.Sci.**151** (1985) L171.
30. C.D. Roux, H. Bu, and J.W. Rabalais, Surf. Sci. **259** (1991) 253.
31. N. Memmel and Th. Detzel, Surf. Sci. 307-**309** (1994) 490.
32. Th. Detzel, N. Memmel and Th. Fauster, Surf. Sci. **293** (1993) 227.
33. W.Eckstein, Nucl. Instr. Meth.**B27** (1987) 78.
34. J.Schulz, E.Taglauer, P.Feulner, D.Menzel, Nucl. Instr. Meth. **B64** (1991) 588 .