MAX-PLANCK-INSTITUT FÜR PLASMAPHYSIK

GARCHING BEI MÜNCHEN

ION SCATTERING AND SURFACE ANALYSIS

IONENSTREUUNG UND OBERFLÄCHENANALYSE

W. Heiland

IPP 9/11 Mai 1973

A short version of this paper was presented at the International Symposium "Moderne Verfahren der Oberflächen-Analyse" am 4. und 5. Dezember 1972 in Frankfurt.

Die nachstehende Arbeit wurde im Rahmen des Vertrages zwischen dem Max-Planck-Institut für Plasmaphysik und der Europäischen Atomgemeinschaft über die Zusammenarbeit auf dem Gebiete der Plasmaphysik durchgeführt.

IPP 10/10

W. Heiland

Ion Scattering and Surface Analysis

May 1973

ABSTRACT

By means of ion scattering in the energy range 0.5 to 1000 keV it is possible to detect on surfaces quantities of substances equivalent to 1/10 to 10^{-4} of a monolayer. Generally speaking, the sensitivity for heavy masses is high, while He and H practically cannot be detected. Whereas the composition of the top-most atomic layer can be determined by ion backscattering at low energies (< 5 keV) at energies in the MeV range it is possible to utilize the large penetration depth of the ions for analyzing the depth distribution of foreign atoms in a matrix. Backscattering at low energies can be used to determine the arrangement of foreign atoms on a surface. Ion scattering is generally influenced by single crystal effects, ion yield, radiation damage, sputtering, and vacuum conditions. Not all of these effects are sufficiently well known to allow a reliable quantitative analysis. For this purpose calibration is necessary in most cases, and so quantitative surface analysis becomes only possible by suitable application of two methods.

1. INTRODUCTION

About twenty years ago particle scattering was first applied as an analytical tool [1]. Since then high energy (MeV) ion scattering has been widely used to study the kind and especially the depth distribution of atoms in solids. Five years ago D. P. Smith [2] showed that at relatively low energies (keV) noble gas ion scattering can be used for surface analysis in which only the topmost layer of a solid is examined.

2. ION BOMBARDMENT OF SOLIDS

If a beam of ions interacts with a solid the impinging ions can encounter different processes, as scattering from surface atoms, backscattering from the bulk and entrapment. The extent to which these processes occur depends on energy, mass and atomic number of the ions and on mass, structure, composition and the atomic number of the solid. This subject has been treated in a number of monographs [3-7]. Generally speaking the scattering cross section for the interaction of an ion with an atom in the gas phase or in the solid state increases with decreasing energy. Therefore, at high energies the majority of the particles of an ion beam impinging on a surface penetrates into the solid. There they lose their energy mainly in small angle collisions with the electrons of the solid. If an ion is backscattered from the solid it can be assumed that only one "large angle" nuclear collision has taken place. Up to the collision and on the way back to the surface the particle transfers energy to the electrons, so that its energy on emerging from the solid is a measure of the depth at which the collision centre is located. These relationships can be used for depth analysis [8-11]. With protons and α-particles in the MeV-range the depth range is about 10.000 Å with a resolution of a few 100 Å. Surface analysis in that energy range means then an analysis of the first 30 to 100 atomic layers of a solid.

With decreasing energy of the ions scattering from the surface becomes dominant, electronic energy losses can be neglected, but the charge state of the backscattered particles has to be taken into account since at energies of a few keV and less only ions can be easily detected. This is demonstrated in the energy spectra of backscattered ions for three different

primary energy regions given in Fig. 1. At 150 keV a broad backscattering spectrum is observed, where the highest energy is related to scattering from the surface. In this energy region most of the backscattered particles are ions. At 15 keV the increasing cross sections and the increasing neutralization probability causes the intensity of the ions to decrease with decreasing energy. Finally below a few keV only ions scattered back from surface atoms can escape neutralization in an appreciable amount and therefore a distinct peak in the energy spectrum is observed.

It follows from these general considerations that two phenomena are important especially for surface analysis in the monolayer region: the collision process and the charge exchange at the surface. The mass resolution will be given by the collision kinetics, the sensitivity will be given by the cross section and the neutralization probability.

3. BINARY SCATTERING

The interaction of an ion beam with a solid is most simply described as two mass points undergoing an elastic collision. The interesting quantity is the energy of the projectile mass after collision. From the conservation of energy and momentum it follows that:

$$E = E_o \cdot f(\vartheta, A)$$

where E_o is the initial energy, ϑ the scattering angle in the laboratory system, and A the ratio of the target mass M_2 to the projectile mass M_1. This yields:

$$E = E_o \cdot \frac{1}{(1 - A)^2} \left\{ \cos\vartheta \pm \left[A^2 - \sin^2\vartheta\right]^{1/2} \right\}^2 \qquad (1)$$

for $A > 1$ the + sign and for $A \leq 1$ both signs are valid, the scattering angle is limited to $\vartheta \leq \arcsin A$ in the second case.
For a scattering angle of $\vartheta = 90^\circ$ we then get:

$$E/E_o = (M_2 - M_1)/(M_2 + M_1) \quad \text{for } M_2 > M_1$$

This binary collision is observed in a wide energy range (Fig. 1). According to formula (1) the target mass can be determined by measuring the energy at a given primary energy and projectile mass.

The maximum mass resolution is obtained at $\vartheta = 180^{\circ}$ for fixed energy resolution $E_1/\Delta E_1$. The mass resolution, as obtained from eq 1 :

$$\frac{M_2}{\Delta M_2} = \frac{E_1}{\Delta E_1} \cdot \frac{2A}{A-1} \qquad \text{for } \vartheta = 90^{\circ}. \qquad (2)$$

The mass resolution for a scattering angle of 90° and an energy resolution of $E_1 / \Delta E_1 = 100$ is presented in Fig. 2 as a function of the target mass for the three rare gases He, Ne, and Xe as projectiles. Best mass resolution is obtained for good mass match between target and projectile. For high mass resolution in the case of heavy target atoms it is necessary to have good energy resolution. If this is not possible for reasons of intensity, heavy ions have to be used. We constrict the discussion to the rare gases, since with reactive gas ions chemical reactions between target and incorporated gas lead to complications.

4. Sensitivity of ion scattering analysis

From similar simple considerations it is possible to obtain the relative mass sensitivity of ion scattering since under equal conditions the back-scattered intensity is proportional to the scattering cross section. For high energies (above 100 keV) the Rutherford scattering cross section is valid, that is, the intensity is proportional to Z_2^2 (atomic number of the target atoms). At lower energies good approximations of the scattering cross sections are obtained from screened Coulomb potentials, or the Born-Mayer potential. Figure 3 shows the differential scattering cross sections for He^+ as a function of the target mass at 1 keV and a laboratory scattering angle of 90°. For masses between 100 and 200 the variation is less than a factor of two, but between mass 12 and 100 the cross section changes by more than two orders

of magnitude. As in the high energy range the sensitivity for the detection of light elements is very low compared to the heavier elements. Generally speaking there is an intensity problem in the low mass range (Fig. 3) and a resolution problem in the high mass range (Fig. 2).

5. Neutralization

As shown in Fig. 1, the neutralization process exerts a strong influence on the yield of backscattered ions. In other words, the intensity of the backscattered ions is proportional to the number of scattering centers $N(cm^{-2})$, the cross section $d\sigma/d\Omega$ $(cm^2 sr^{-1})$ and the ion escape probability P. The intensity measured in a solid angle $\Delta\Omega$ is thus:

$$I \propto N \cdot \frac{d\sigma}{d\Omega} \cdot P \cdot \Delta\Omega \qquad (3)$$

Whereas formula (1) is sufficient for qualitative analysis the cross section and also the ion yield have to be known for quantitative analysis. Actually the neutralization process limits the absolute mass sensitivity of the ion scattering method. The cross section can be calculated with sufficient accuracy but the neutralization process is not yet properly understood. For low energies a theory for rare gas ions was developed by Gobas and Lamb [12] and by Hagstrum [13], and for high energies a theory was recently formulated by Brandt and Sizmann [14].

In the low energy range the probability of an ion remaining in its charge state after collision with the surface is given by $P = \exp -\frac{A}{a v_\perp}$, where $v_\perp$ is the velocity of the ion perpendicular to the surface and A (s^{-1}) and a (cm^{-1}) are constants depending on the ion-metal combination. The basic process is an Auger-type transition where electrons from the conduction band of the metal

tunnel to the ground state (or exited states) of the ion. The potential energy gain leads to the production of a second electron which may transport the energys as kinetic energy through the surface barrier.

The emitted electrons therefore afford information on the density of states of the electrons close to the surface. Hagstrum[15] has developed a deconvolution technique to yield this information. This method is unique in revealing surface molecular orbitals of adsorbed species on metal surfaces [16]. Very recently, Hagstrum [17] combined ion neutralization spectroscopy (INS) with photoemission spectroscopy (PES). This experiment demonstrates the extreme sensitivity of the INS technique to the electronic properties of a surface.

For the ion scattering technique at low energies (< 5 keV) the conclusion from Hagstrum's work is that different ion yields for different ion-metal combinations are generally very likely. For backscattering from adsorbed species it has also yet to be proved that the ion escape probability is not different for scattering from substrate atoms and from adsorbed atoms.

At high ion energies (100 keV) T. Buck et al. [18] demonstrated, in agreement with the theory [14], that the ion yield is a universal function of the ion velocity and is independent of the kind of adsorbed species on the same substrate (Au, Fe, Ni on Si). At very high energies (MeV) charge exchange processes play only a minor role since the ion yield approaches unity. Furthermore, at high energies the energy of both neutrals and ions can be measured with sufficient resolution by means of solid state detectors, whereas at low energies electrostatic analyzers have to be used, so that only the charged reflected particles can be detected.

6. Analysis by ion scattering

The following examples are chosen to demonstrate the potential of ion scattering, to show the difference between the high and low energy range and to give examples of calibration methods and surface sensitivity in the low energy range. Fig. 4 shows a set of typical high energy spectra from a metal semi-conductor contact and its behaviour during a heat treatment [11]. Initially there is a sharp boundary between Si and Pt indicated by the sharp edge of the Si signal. At 300 to 350°C a Si-Pt interphase appears indicated by the step in the Si and the Pt signal. Finally in Pt Si layer with twice the thickness of the original Pt film is formed.

He backscattering from the polar faces of a II-VI semiconductor (Fig. 5) show the differencies in backscattered intensities expected from the noncentrosymmetric crystal structure [2]. Quantitative evaluation is difficult because the faces are not plane in an atomistic scale, and so the contribution of the second layer is hard to estimate. Brongersmaa and Mul[19] argued that each Si atom on a (111) silicon single-crystal face has only one bond to become saturated by an adsorbed Br atom. Provided there is enough Br pressure above the Si surface, this will be covered by exactly one monolayer of Br (Fig. 6). From this experiment the ultimate sensitivity can be estimated to be 3×10^{-3} monolayer of Br on Si. Similarly ordered sorption can be used for the purpose of calibration since it can be checked by LEED[20] (Fig. 7). The (2x1) O structure on a Ni (110) face contains half a monolayer of oxygen[21]. Since the probing He beam also senses the second layer of the Ni surface under the given experimental conditions (plane of scattering perpendicular to the surface parallel to the [110] direction in the surface). The measured intensity ratio Ni to O of 35:1 has to be reduced according to the relative abundance of 3:1 to about 12:1. This is in fairly good agreement with the ratio of the scattering cross sections which is 15 :1. It may be concluded that for this example the neutralization probability is the same for scattering from Ni and O. An estimate of the sensitivity leads to a detection limit of less than 1/10 of a monolayer of oxygen on Ni.

T. Buck et al.[22] used neutron activation as calibration method for Au deposited on Si. With 2 keV He^+ backscattering a detection sensitivity of $5x10^{-4}$ monolayer has obtained. For Ar^+ at the same energy $1x10^{-4}$ may be possible. From the data in this section the monolayer scale in Fig. 2 can be deduced and, though it may be rather qualitative it does give a fair estimate of what can be achieved with present-day equipments.

6. Further aspects of low-energy ion scattering

A relatively general feature with respect to ion energy is the effect known as multiple scattering. It was first theoretically predicted[23] and then experimentally observed[24-26]. From the theory the effect is expected to be more pronounced at lower energies[23,27]. Below 1 keV Ne and Ar scattering indeed show impressive multiple scattering events, e.g. from an undisturbed single-crystal surface single binary scattering becomes impossible. Multiple scattering predominates when experimental conditions are chosen such that owing to the mutual shadowing of neighbouring atoms not all impact parameters are accessible for collision. Instead, the ion undergoes a sequence of binary collisions, which leads to final energies above the energy after a single binary collision for equal total deflection. Furthermore, the observed energies of the backscattered ions become dependent on the impact angle and the lattice parameter. Besides the possible disturbance of surface analysis, since multiple scattering gives rise to high-energy shoulders even in the case of polycrystals[22], the effect can be used to study surface structure[28,29].

Typical of the low-energy regime is the effect first observed by D. P. Smith[2] that due to the large cross sections sorption leads to effective shadowing of the underlying species. In the case of CO sorption on Ni the observed peak heights (carbon to oxygen approximately 1:5) are much smaller than expected from the ratio of the scattering cross sections. This leads to the interpretation

that the O atoms shadow the C atoms, which is in agreement with the observation that CO adsorbs with the C bonded to a Ni surface atom [31].

This shadowing effect has been applied to the case of the O (2x1) sorption on the Ni (110) surface [20]. By varying the angle of incidence relative to the surface and relative to the crystal orientation the reconstruction model proposed by Germer et al. [21] was confirmed.

7. Experimental aspects of ion backscattering techniques

The experimental requirements for surface analysis by ion scattering follow immediately from the points discussed in the previous sections. A concept for an experiment (Fig. 8) covering all energy ranges contains an ion source, beam forming system (accelerator, mass and energy analyzers, collimator), target, energy analyzer, and detector. The requirements imposed on the ion source and beam forming system are derived from formula (1). The energy spread and divergence of the beam have to be small relative to the postulated energy resolution. The same applies to the energy analyzer for the secondary particles.

The necessary primary beam densities are subject to a lower limit imposed, for one thing, by the detection sensitivity of the detection system. It should be noted here that in the high-energy range only about 0.1 % of the particles are backscattered, while at low energies almost all particles are backscattered, but only about 0.1 % of them as ions. With a total primary current of, for example, 10^{-8} A it can be estimated for 1 keV at a scattering angle of 90° that with a monolayer with 10^{15} particles/cm^2 and a cross section of 0.1 Å^2/sr only about 10^{-13} A is backscattered, assuming neutralization to be 10^{-3}. For an energy resolution of, for example, 1 % it is desirable to use a solid angle of detection of 10^{-3} sr, i.e. 10^{-16} A arrives at the detector when the transmission of the system is 1. That is of the order of 10^3 particles /s, i.e. counting methods have to be applied. With the cross section stated the monolayer sensitivity is

10^{-3} if 1 counts/s is assumed as lower counting limit, as indicated by previous studies (Fig. 2).

The primary current that can be applied is subject to an upper limit because certain ion current densities may not be exceeded for ion-optical reasons [32] (assuming the ion sources are capable of supplying so much current) without exceeding the requirements relating to, for example, the beam divergence. Furthermore, limits are prescribed by the object to be investigated because ion bombardment causes radiation damage and sputtering. The minimum requirement stipulates that the sample ought not to be changed during the measurement. The critical quantity is the measuring time (s) x primary current density ions/cm^2 s) x sputtering rate (atoms/ion) compared with the monolayer density (atoms/cm^2). (Similar considerations are valid for radiation damage at high energies). At 1 keV and 1 μA cm^{-2} it is possible to attain measuring times of 60 s. The sputtering rates for many metals are about 1 [3-7], however, and so 10^{15} atoms/cm^2 are sputtered, i.e. about 1 monlayer/measuring time. The sputtering rates for He are about 10^{-2}, which means that under the same conditions it is possible to perform non-destructive analyses.

The need for low current densities to avoid changes of target imposes the need for good vacuum conditions if the measurements are to be made independently of the residual gas pressure. In many cases this calls for UHV, as can be estimated by comparing the adsorption rate from the residual gas with the desorption rate due to ion bombardment [6].

We thus have two essential cost factors for analysis by ion bombardment, i.e. the vacuum system and particle detection system, which are valid for practically all energy ranges. In the high-energy range appreciable costs are entailed for the accelerator if one is not already available and spare capacitance can be utilized. Not to be neglected are personnel costs, especially since the insufficiently understood physical problems mentioned mean that misinterpretation of the results in many cases can only be avoided by providing suitable training.

8. Summary

By means of ion scattering in the energy range 0.5 to 1000 keV it is possible to detect on surfaces quantities of substances equivalent to 1/10 to 10^{-4} of a monolayer. Generally speaking, the sensitivity for heavy masses is high, while He and H practically cannot be detected. Whereas the composition of the topmost atomic layer can be determined by ion backscattering at low energies (< 5 keV) at energies in the MeV range it is possible to utilize the large penetration depth of the ions for analyzing the depth distribution of foreign atoms in a matrix. Backscattering at low energies can be used to determine the arrangement of foreign atoms on a surface. Ion scattering is generally influenced by single crystal effects, ion yield, radiation damage, sputtering, and vacuum conditions. Not all of these effects are sufficiently well known to allow a reliable quantitative analysis. For this purpose calibration is necessary in most cases, and so quantitative surface analysis becomes only possible by suitable application of two methods.

Acknowledgement:

Tanks are due to E. Taglauer for many helpful discussions and critical reading of the manuscript.

References

1) S. Rubin, V.K. Rasmussen; Phys. Rev. 78, 83 (1950)

2) D.P. Smith; Surf. Sci. 25, 171 (1971)

3) G. Leibfried; "Bestrahlungseffekte in Festkörpern", Stuttgart 1965

4) M.W. Thompson; "Defects and Radiation Damage in Metals", Cambridge 1969

5) G. Carter, J.S. Colligon; "The Ion Bombardment of Solids", London 1968

6) R. Behrisch; Sputtering by Ion Bombardment", Ergebnisse der exakten Naturwissenschaften 35, 295 (1964)

7) M. Kaminsky; (Atomic and Ionic Impact Phenomena on Metal Surfaces ", Berlin-Heidelberg-New York 1965

8) J.W. Mayer, Z. Erikson, J.A. Davies; "Ion Implantation in Semiconductors", New York 1970

9) J.A. Davies, J. Denhartog, L. Erikson, J.W. Mayer; Can. J. Phys. 45, 4053 (1967)

10) E. Bøgh; Can. J. Phys. 46, 653 (1968)

11) M.A. Nicolet, J.W. Mayer, I.V. Mitchell; Science 177, 841 (1972)

12) A. Gobas, W.E. Lamb Jr.; Phys. Rev. 65, 327 (1944)

13) H.D. Hagstrum; Phys. Rev. 96, 336 (1954)

14) W. Brandt, R. Sizmann; Phys. Letters 37 A, 115 (1971)

15) H.D. Hagstrum; Phys. Rev. 150, 495 (1966)

16) H.D. Hagstrum, G.E. Becker;Phys. Rev. 22, 1054 (1969)

17) H.D. Hagstrum; Paper pres. at the AVS-Symposium Chicago 1972

18) T.M. Buck, S.H. Wheatley, L.C. Feldmann; private communication

19) H.H. Brongersmaa, P.M. Mul; Chem. Phys. Letters 13, 380 (1972)

20) W. Heiland, E. Taglauer; J. Vac. Sci. Tech. 9, 620 (1972)

21) L.H. Germer, A.U. McRae; J. Appl. Phys. 35, 2923 (1962)

22) D.J. Ball, T.M. Buck, D. Macnair, G.H. Wheatley; Surf. Sci. 30, 69 (1972)

23) E.S. Parilis; Proc. VIIth Int. Conf. Phen. Ion. Gases, Belgrad 1965

24) E.S. Mashkova, V.A. Molchanov; Can. J. Phys. 46, 713 (1968)

25) P. Dahl, N. Sandager; Surf. Sci. 14, 305 (1969)

26) W.F. van der Weg, D.J. Bierman; Physica 38, 406 (1968)

27) E. Taglauer, W. Heiland; Surf. Sci. 33, 27 (1972)

28) S.H.A. Begeman, A.L. Boers; Surf. Sci. 30, 134 (1972)

29) W. Heiland, E. Taglauer; Rad. Effects to be published

30) D.P. Smith; J. Appl. Phys. 38, 340 (1967)

31) R.L. Park, M.E. Farnsworth; J. Chem. Phys. 40, 2354 (1964)

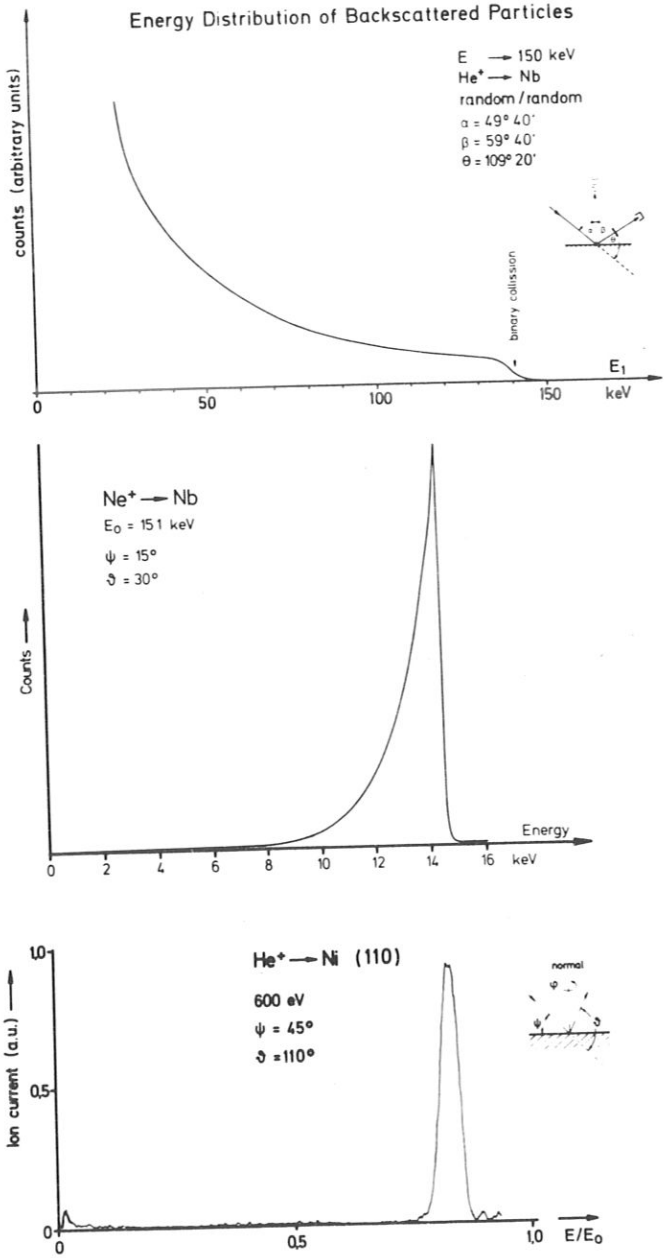
32) M. von Ardenne "Tabellen zur angewandten Physik", Berlin 1964

33) A.A. Abrahamson; Phys. Rev. 178, 76 (1969)

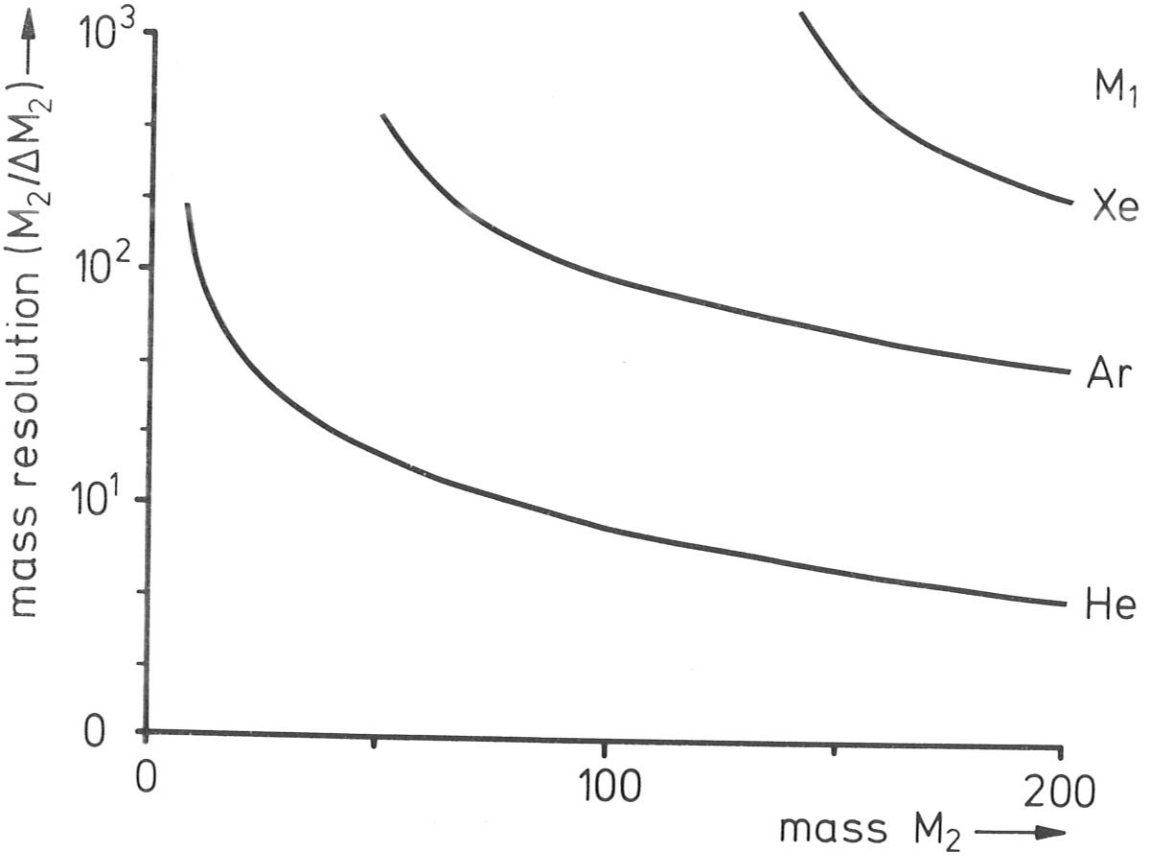
34) M.T. Robinson; ORNL Laboratory Report 4556, Oak Ridge 1970

35) B.M.U. Scherzer; private communication

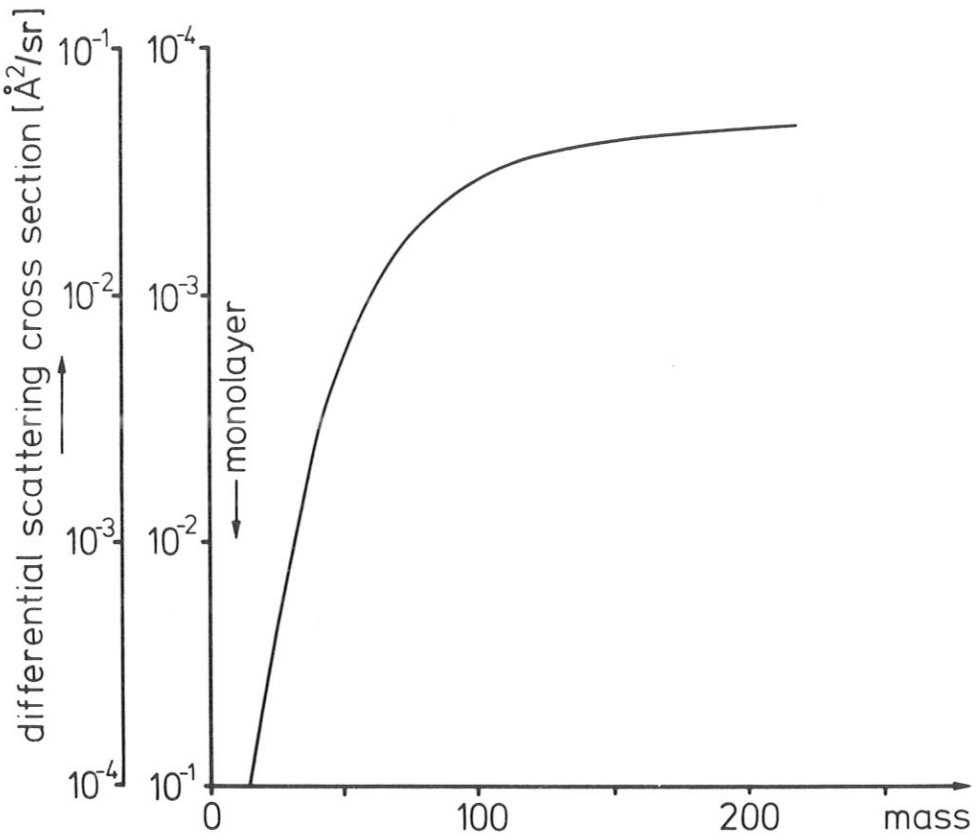
36) W. Eckstein, H. Verbeek; J. Vac. Sci. Tech. 9, 612 (1972)



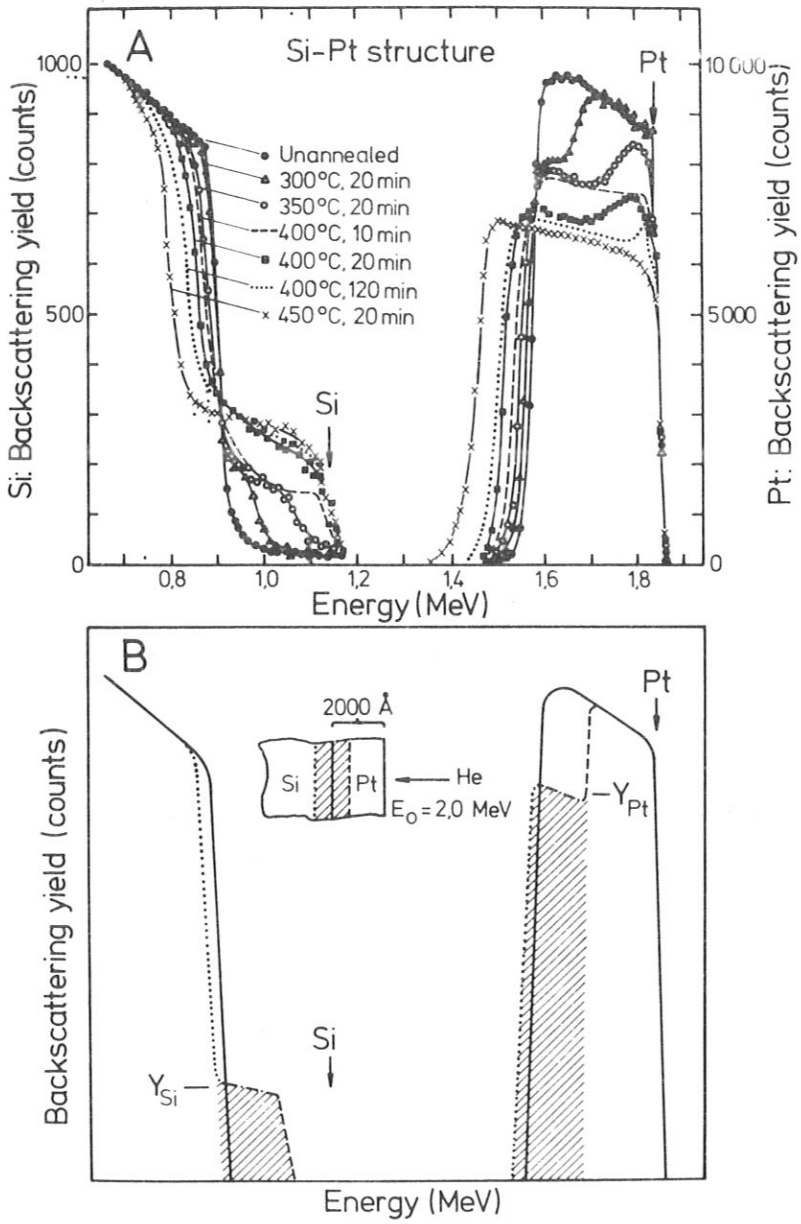
1) Rare gas ion backscattering spectra at 150 keV (ions and neutrals are measured)[35]„ 15 keV (only ions are detected)[36] and 0.6 keV (only ions).



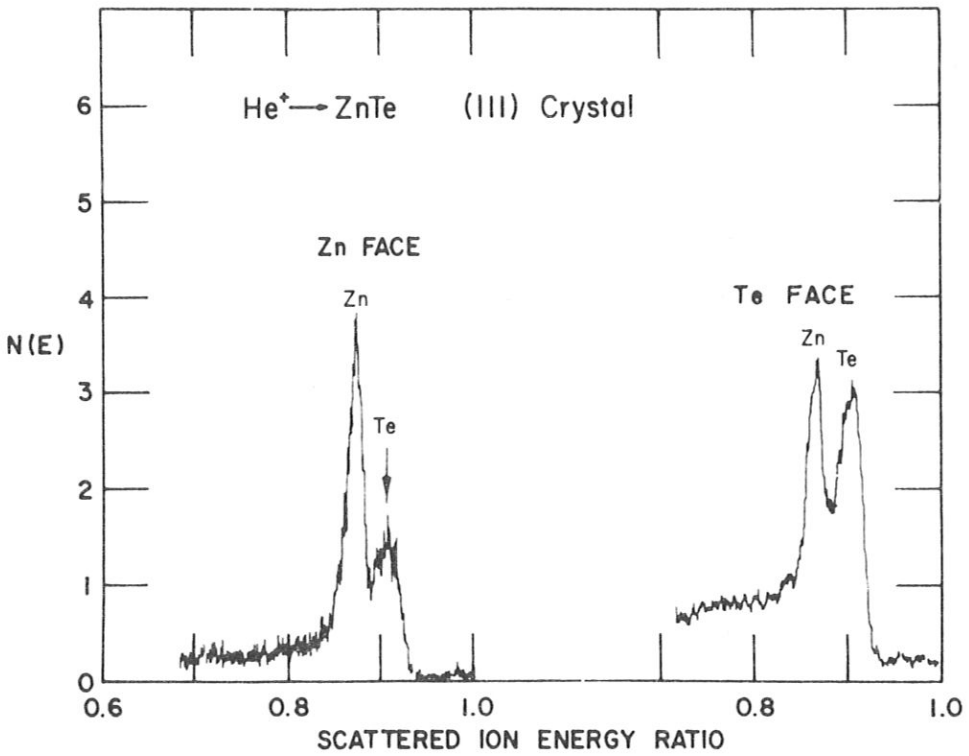
2) Binary scattering: Mass resolution $M_2 / \Delta M_2$ as a function of the target mass M_2 for He, Ar and Xe as probing ions (mass M_1) for a laboratory scattering angle of 90° and an energy resolution $E_1 / \Delta E_1 = 100$. E_1 is the energy of the reflected ions.



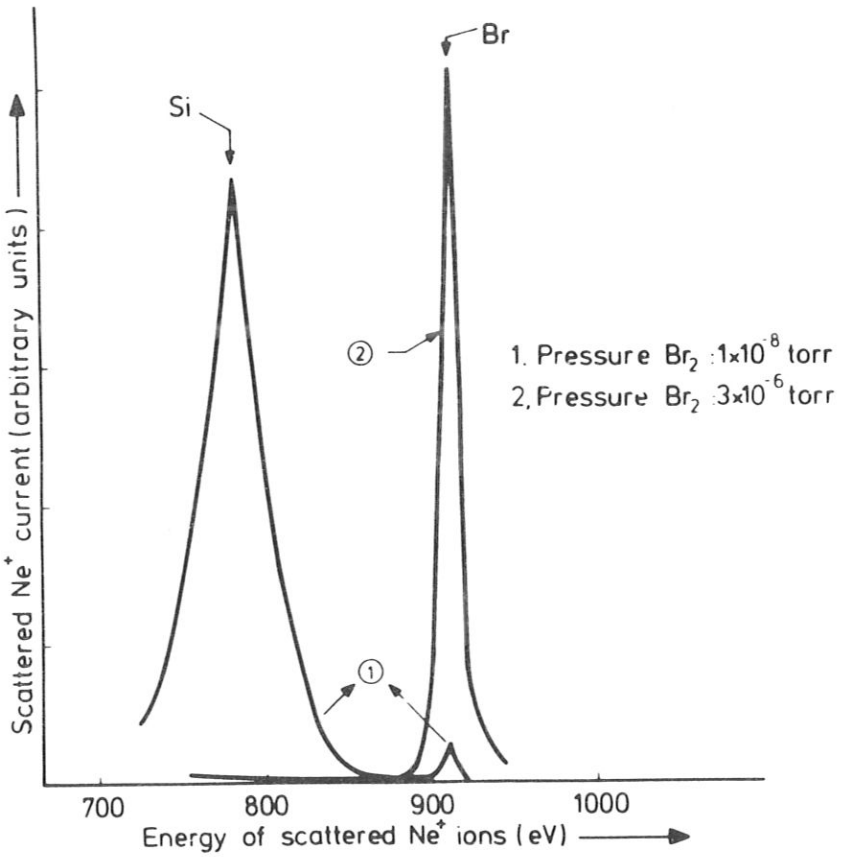
3) Differential scattering cross section for 1 keV ions at a laboratory scattering angle of 90° as a function of the target mass for Born-Mayer potential ($V(r) = Ce^{-r/a}$) with constants C and a according to Abrahamson[33] using the table work of Robinson[34]. The monolayer scale is extrapolated from experiments and an estimate of the sensitivity taking into account cross section, primary current, neutralization probability and detector sensitivity.



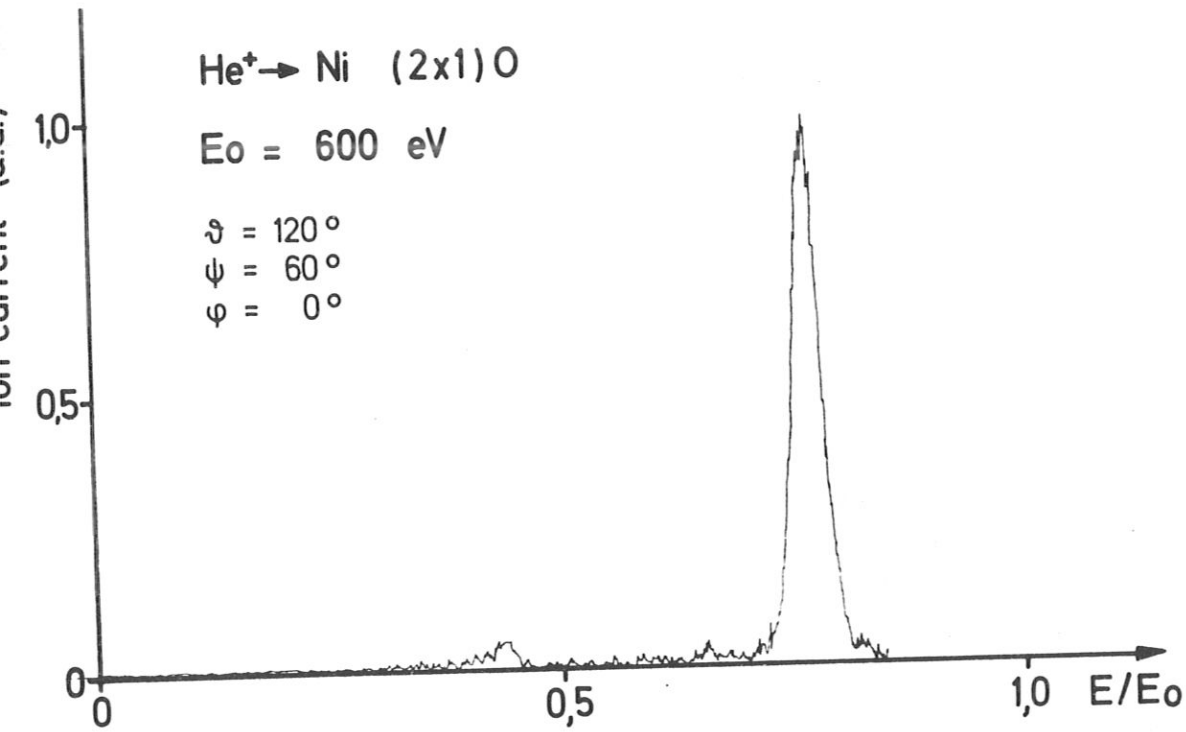
4) Thin film analysis by Nicolet, Mayer and Mitchell [11] by 2 MeV ions. Si covered with a 2000 Å Pt layer, before, during and after heat treatment . The composition of the intermediate layer (Pt_2Si) and the final layer (Pt Si) follows from the ratio of the backscattering yields Y_{Si} and Y_{Pt} and the known values of the scattering cross sections and the stopping power for Si and Pt.
(With courtesy of the authors [11]).



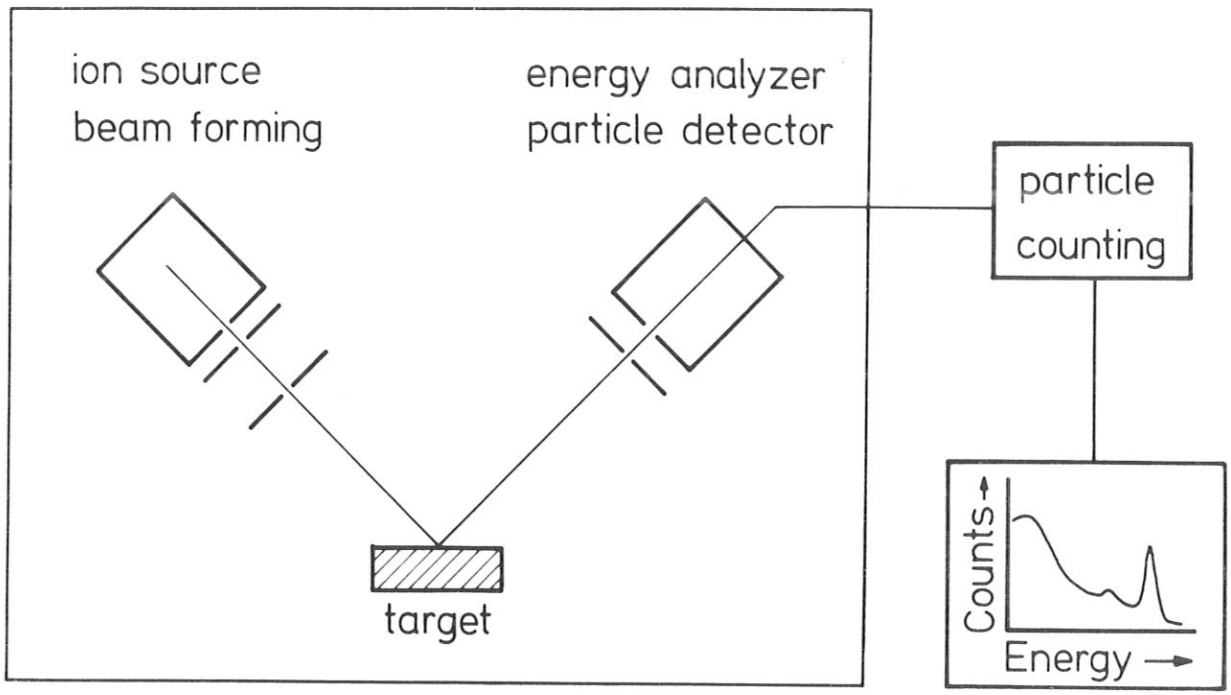
5) He backscattering at 1.5 keV from the polare faces of a ZuTe crystal [2].
(With courtesy of the author)



6) Ne backscattering at 1.5 keV from Si (111) covered with Br [19].
(With courtesy of the authors).



7) He backscattering at 0.6 keV from Ni (110) covered with the (2x1)O structure



8) Scheme of an ion scattering experiment.