SCATTERING OF MEDIUM-ENERGY IONS IN THIN LAYERS

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We have studied the scattering of ions by thin layers of metal atoms deposited on a substrate. The energy spectra of ions scattered by a thin target at a given angle differ sharply from the corresponding spectra obtained in massive targets. If certain conditions are satisfied, these spectra are similar to the spectra obtained in a gaseous target. Experiments with thin layers of variable thickness permit identification of the single-scattering peak in the energy spectra of particles scattered by a solid target. In a number of cases the scattering of heavy ions of medium energy can be used to determine the surface impurities in quantities as low as 10^{-2}–10^{-3} atomic layer.

1. INTRODUCTION

THE principal source of reliable quantitative information on the interaction potentials in ion-atom collisions at the present time consists of experiments in which the angular characteristics of the scattering are investigated. The current theory of atomic collisions does not permit calculation of the interaction potential in all of the cases necessary in practice. Accurate calculations are possible only for the simplest atomic systems. In the remaining cases, various approximations are used.

Most scattering experiments have been performed with gaseous targets (as a rule, inert gases or hydrogen), where it is easy to realize the condition of single binary collisions between the incident particle and the target atom.[1,2] Nevertheless, in order to explain a number of important and interesting questions, for example, the effect of electron-shell structure on the scattering characteristics,[3] it is necessary to extend considerably the set of partners involved in collisions. It is therefore disappointing that such investigations are not possible with the atoms of most metals, especially refractory metals. In this connection, attempts have recently been undertaken to study scattering by atoms belonging to the crystal lattice of a solid material.[4,5] In the energy spectra of ions scattered at a given angle, sharp single-scattering peaks are actually observed, similar to those which occur with gas targets, but the shape of the peak indicates the presence of a substantial number of ions scattered into the same solid angle as the result of multiple collisions with the target atoms. Thus, the energy spectrum of the multiple component overlaps the single-scattering peak.

If the aim of the experiment is reduced to determination of the peak location, a sufficient reduction in the multiple-scattering contribution can be achieved by use of a single-crystal target with a definite orientation.[5] However, it has not been possible to remove by this means the discrepancy between the calculated and experimental angular distributions of scattered ions due to multiple scattering.[4,6]

The presence of multiple scattering is the unavoidable consequence of the fact that the effective target thickness is much greater than the mean free path of the ion. It appears to us that from this point of view it is desirable to study the scattering of ions in thin layers of matter. In experiments of this type it is possible to achieve conditions under which the mean free path of the ion will be much greater than the target thickness. In this case we should expect a sharp decrease in the role of multiple scattering, and dominance of single processes.

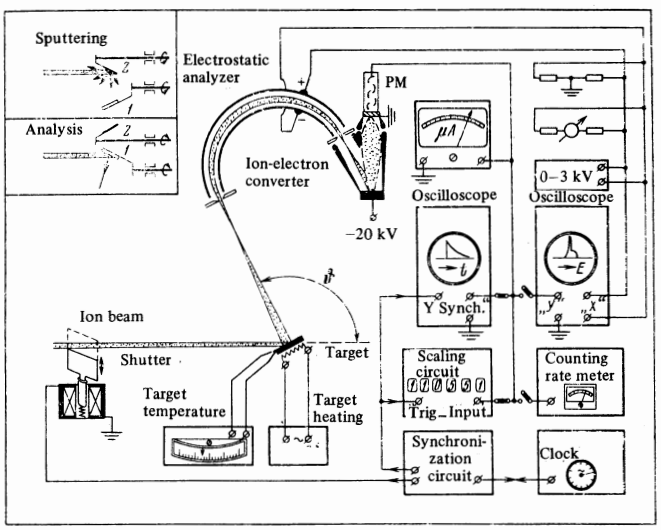

FIG. 1. Diagram of apparatus for study of ion scattering by thin layers. Upper left—location of substrate (1) and auxiliary target (2) during sputtering and during energy analysis.

Scattering of medium-energy ions in thin targets has not been studied up to the present time. We were therefore faced with the problem of designing and constructing appropriate apparatus. The experimental results turned out to be substantially different from those which are usually obtained in massive targets. We have, incidentally, considered the possibility of using the ion-scattering process to observe microquantities of foreign material on the target surface.

2. METHOD

A diagram of the apparatus is shown in Fig. 1. After extended evacuation and heating of the entire system, the vacuum in the apparatus attained a level of (1–2) $\times 10^{-7}$ torr (with the traps filled with liquid nitrogen). We will discuss briefly the design of the principal parts of the equipment.

1. **Target.** The following procedure was used to ob-

tain thin-layer targets. A mechanical device was used to move into the ion beam an auxiliary target consisting of a metallic plate of high purity. A fraction of the auxiliary target atoms, sputtered by the beam, were deposited on a beryllium substrate which formed the working target. For a given geometry the thickness of the sputtered layer can be evaluated on the basis of the sputtering coefficient, the bombardment time, and the ion current. By changing the duration of the sputtering (1–5 sec), it is easy to obtain layers of the desired thickness. The usual range of thicknesses studied was $(1-5)\times10^{15}$ atoms/cm^2. Before each sputtering of a thin-layer target, the surface of the substrate was cleaned by intense ion bombardment. After formation of a layer of a given thickness, the ion beam was interrupted by means of a fast magnetic gate, the auxiliary target was moved to one side, and the working target was placed in the beam path in front of the analyzer. The equipment was then completely ready for measurements.

We note that with the vacuum used the time of formation of a monomolecular layer of the residual gas is 10–20 sec. Thus, during the formation of the target and its movement into the beam, which occupied two seconds, an adsorbed gas film more than 0.2–0.4 molecular thick could not be formed on the target. The temperature of the substrate and auxiliary target was 400–500° C.

2. **Ion source.** The ion source was a beam similar to that described earlier.[7] The time of operation of the magnetic gate mentioned above was 1 msec. A system of two centered diaphragms (diameter 2 mm) selected the central, most uniform part of the beam. At 20 kV the current of krypton ions was ~ 50 μA, which corresponds to a current density in the vicinity of the target ~ 0.5 mA/cm^2. A stabilized power supply provided an ion energy constant within 0.01%, i.e., $\Delta W/W = 10^{-4}$. The angular divergence of the beam did not exceed 1–2°.

3. **Analyzer.** To analyze the scattered ions in energy we used an electrostatic analyzer with spherical plates and 180° deflection. The equilibrium trajectory of the ions had a radius of 250 mm. The slit widths at the entrance and exit of the analyzer could be varied between 0.3 and 3 mm. The distance from the target to the entrance diaphragm of the analyzer was 30 cm. The stability of the voltage on the analyzer plates was 0.01% or better.

The principal difficulty in experiments with thin targets lies in the fact that, in addition to the weak flux of ions which undergo scattering in the thin layer of target atoms, the entrance diaphragm of the analyzer also receives an intense flux of particles (fast neutral atoms and ions) arising as the result of scattering of beam ions in the massive substrate. These particles are multiply scattered by the internal surface of the analyzer plates and hit the secondary-emission detector, being recorded by it and producing a substantial background. In order to reduce the background to an acceptable level, the outer plate of the analyzer was made of a metallic grid with a transparency greater than 95%.

4. **Detectors.** In the work with massive targets the scattered-ion flux was rather high, and the measurements were made with an ordinary Faraday cup connected to an electrometer amplifier. An oscillographic method was used to record the spectra.[7]

In the work with the thin targets, the scattered-ion flux is much smaller. In addition, it is not constant with time as is the case with a massive target, but drops rapidly as the result of destruction of the target under the action of the ion bombardment. The decay time constant is 10^{-1}–10^{-2} sec.

In the thin-target experiments, the detectors were open electron multipliers and ion-electron converters. Each of these types of detectors allowed us to detect particles either by counting of individual particles or by measurement of current. The detection of particles in these detectors is based on the phenomenon of secondary ion-electron emission. The secondary emission coefficient, and consequently the ion detection efficiency, naturally depends on the incident ion energy. Therefore the current at the detector exit depends not only on the number of ions which entered the detector but also on their energy. However, since the energy spectra being studied consist of narrow peaks with a relative half-width not more than 10%, no correction was made for this dependence. For the same reason it was not necessary to take into account the energy dependence of the analyzer dispersion. Therefore we have presented below as energy distributions of scattered ions simply the experimental curves of signal strength (current or counting rate) at the detector output as a function of the potential difference between the analyzer plates.

3. EXPERIMENTAL RESULTS

We recorded first of all the energy spectra of krypton ions for a number of massive targets for various scattering angles. These measurements were made in order to choose the spectra in which the single-scattering peak and the shoulder in the high-energy slope of the peak appear particularly distinctly. The most characteristic spectra are obtained at scattering angles of about 30–50° and for large and close together values of bombarding-ion and target-atom masses. Some of the spectra obtained are shown in Fig. 2. Sharp peaks are observed at the calculated energy values corresponding to single scattering of a krypton ion by a target atom. The presence of several isotopes of krypton leads to an additional broadening of the peak, in comparison with the instrumental broadening.

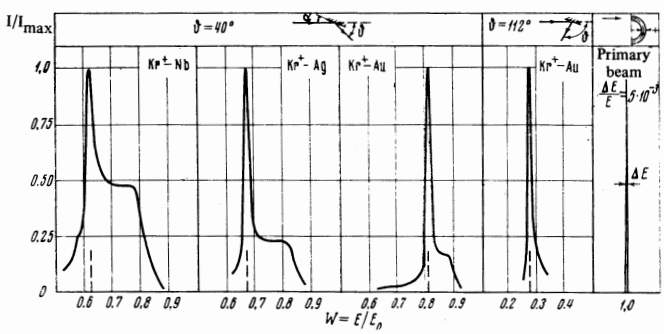

FIG. 2. Characteristic energy spectra in scattering of ions by massive targets of different materials. E_0 = 20 keV, α = 20°.

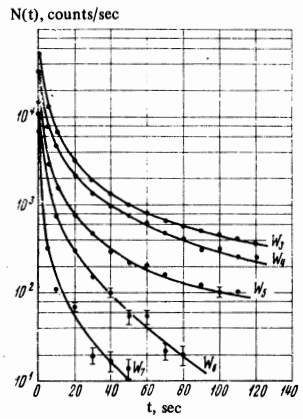

FIG. 3. Typical curve of scattered-ion current as a function of bombardment time (thickness) of the thin layer. Silver target ($n = 10^{15}$ atoms/cm^2) on beryllium substrate, bombarded by krypton ions; E_0 = 20 keV, $\vartheta = 40°$, $\alpha = 20°$. The energy values W_i correspond to the values in Fig. 4.

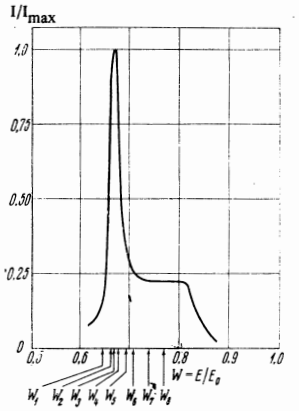

FIG. 4. Energy spectrum of krypton ions scattered by a massive silver target ($\vartheta = 40°$). The arrows show the energy values at which scattering by a thin silver layer has been studied. E_0 = 20 keV, $\alpha = 20°$.

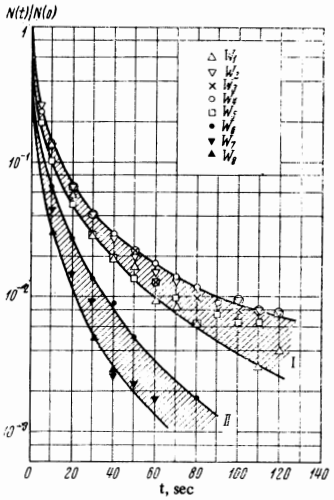

FIG. 5

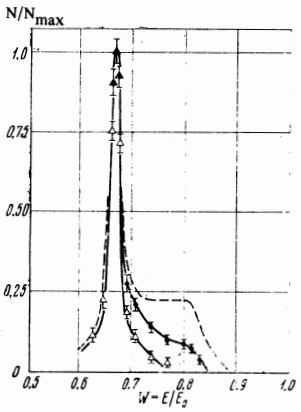

FIG. 6

FIG. 5. Normalized curves of scattered-ion current versus time corresponding to the energy values W_i in Fig. 4.

FIG. 6. Comparison of energy spectra of krypton ions scattered by a massive silver target (dashed curve) and by a thin silver target on a beryllium substrate (●—1 sec, Δ—10 sec). E_0 = 20 keV, $\alpha = 20°$, $\vartheta = 40°$.

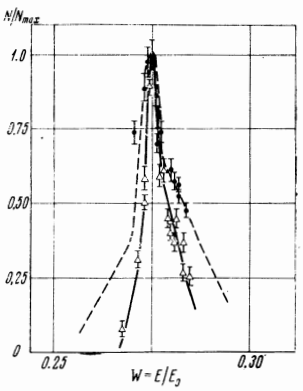

FIG. 7. Comparison of energy spectra of krypton ions scattered by a massive gold target (dashed line) and by thin gold targets on carbon (●—0 sec, Δ—10 sec).

Targets of gold and silver were used to study the scattering in thin layers, since these materials have high sputtering coefficients (see, for example, Almen and Bruce[8]) and the time for deposition of a thin layer turned out to be quite small. Use of niobium targets is difficult: because of the low sputtering coefficient, the target-formation time is comparable with the adsorption time for a layer of residual-gas molecules.

The rapid destruction of the target by ion bombardment makes it practically impossible to obtain an energy spectrum in one cycle of measurements. In practice the following procedure was used to obtain a spectrum: the target being studied was deposited to a chosen standard thickness on the cleaned substrate, and the time dependence of the current at the detector output was recorded in a given energy interval. Then a target of the same thickness was deposited again and the measurements were repeated in a new energy interval. Figure 3 shows some typical experimental curves for a silver target, obtained by the means described and plotted on a semilogarithmic scale. The values of W_i shown near each curve correspond to the ion energies denoted in the energy spectrum of Fig. 4. The background corresponding to scattering by the beryllium substrate was subtracted. The value of this background after 10 sec did not exceed 5%.

The rate of fall of the current at the detector output is different for different values of W_i, which becomes particularly noticeable after normalization of the curves to the initial value of counting rate, i.e., on replotting the curves of Fig. 3 in coordinates N(t)/N(0) = f(t), as has been done in Fig. 5. Furthermore, the curves in Fig. 5 are actually located in two distinctly bounded regions (I and II in Fig. 5). One of these regions contains all curves corresponding to the single-scattering peak and the other—curves corresponding to multiple scattering, i.e., the shoulder in the right-hand slope of the peak.

The rate of fall in region I is noticeably smaller than in region II. This means that the shape of the energy spectra changes with time, in other words, with decreasing target thickness. The curves shown in the Figs. 6 and 7 illustrate this effect. These curves were plotted from experimental curves similar to the curves of Fig. 3, and correspond to successive moments of time 0, 1, and 10 sec, i.e., to falling target thicknesses. It is apparent that initially the spectra obtained with the thin target are extremely similar to the spectra observed with massive targets. In the transition to thinner targets, the nature of the spectrum changes substantially: the right-hand shoulder completely disappears and the entire spectrum acquires the shape of a narrow symmetric peak.

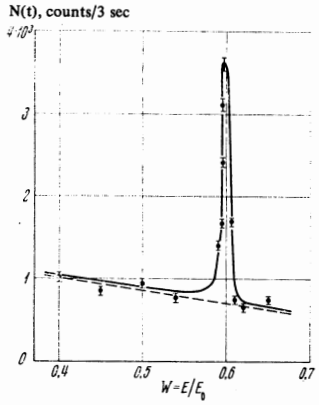

FIG. 8. Energy spectrum of argon ions scattered by uranium atoms (5×10^{-8} g/cm^2) deposited on a stainless steel substrate (ϑ = 118°). The dashed curve shows scattering in the stainless substrate.

4. DISCUSSION OF RESULTS

The experimental results obtained permit the following qualitative explanation.

In the first moments after the beginning of ion bombardment of a thin target, the concentration of sputtered atoms is still sufficiently large that, in addition to single scattering, ion multiple-scattering events occur. The situation is similar to that which exists in scattering by a massive target and, in addition to a sharp single-scattering peak, a shoulder on its right-hand slope is observed in the energy spectrum.

To the extent that a part of the sputtered atoms are removed from the substrate as the result of ion bombardment, the average distance between neighboring atoms increases. This leads to a gradual decrease in the probability of multiple collisions to a negligibly small value. Here the probability of single collisions also decreases, as is indicated by the drop in intensity of the main peak with time. It is easy to see that this drop should occur at a slower rate, which is confirmed by experiment. Thus, as time passes the experimental conditions become more and more similar to those with which we are dealing in the case of a gaseous target, and the energy spectrum degenerates into a narrow symmetric single-scattering peak. The unique difference from the ordinary gaseous target is the plane geometry which occurs in the experiments described here.

The similarity with gaseous targets, which have repeatedly and successfully been used in scattering experiments, permits us to suggest the technique described above for determination of the interaction potentials of atomic systems. In a number of cases, especially in work with refractory metals, this technique is more suitable than construction of a target of metallic vapor. Of course, the plane geometry of the target and the presence of the substrate necessarily introduce certain features into the process of investigation, which will appear to the greatest degree for grazing incidence of the bombarding ions and in analysis of the secondary ions emitted at small angles to the target surface.

In conclusion we will dwell on one further question. The decay of the signal with time in the detector circuit is explained by the decrease in the target thickness, but an open question remains as to why the rate of decrease gradually slows down. For a thin target the signal strength for a constant primary-ion flux is obviously proportional to the number of scattering centers. If destruction of the target as the result of ion bombardment occurs and this is the only cause of its change in thickness, then the signal will fall with an exponential law. However, here it is tacitly assumed that the current density at the target surface is constant. Nevertheless, the current distribution has a maximum in the center and falls off toward the outside. Therefore at first a comparatively rapid depletion of the central portions of the target occurs and then a slower destruction of the periphery. The specific form of the I(t) curves should depend on the beam intensity and the current density distribution over the target surface.

5. POSSIBLE APPLICATIONS

In conclusion, let us consider the possible application of the ion-scattering process to the determination of small concentrations of surface impurities. For this purpose we have performed experiments with targets containing impurities whose concentration was measured previously by an independent means. The targets used in this series of experiments were metallic disks on which an extremely thin and uniform layer of uranium had been deposited. The quantity of deposited uranium atoms was measured in the usual way from the α activity. The technique of the probing ion beam experiments was similar to that described in Sec. 2, with the difference that instead of sputtering new layers before taking each point in the energy spectrum, here we used different portions of the same uniform target.

The experiments performed showed that ion scattering can be successfully applied to measurement of surface concentrations down to 10^{-2}–10^{-3} atomic layer. As an illustration we have shown in Fig. 8 the energy spectrum of argon ions scattered by uranium atoms located on the surface of a stainless steel substrate. The surface concentration of uranium atoms was 5×10^{-8} g/cm^2 or 10^{-1} monolayer.

Let us compare the proposed method with some other corpuscular methods of measuring surface concentrations.

A number of experimental studies of the concentration of foreign atoms on a metal surface and determination of the chemical composition of surface layers have used the scattering of protons or α particles with energies of 1–5 MeV.[9, 10] In proton probing the measurement time is several minutes (in the case of concentrations equivalent to tenths of a monolayer) to several tens of minutes and requires use of rather bulky equipment (a Van de Graaff accelerator). In the experiments described by us, a simple ion source was used, and the measurement time did not exceed several tenths of a second in the case of the smallest concentrations.

In measurements based on analysis of the Auger spectra of secondary electrons or on analysis of the characteristic x rays arising in bombardment of a target by fast heavy particles,[11, 12] sensitivities of about 10^{-1}–10^{-2} atomic layer have been achieved. Use of these methods requires, however, extremely good vacuum conditions: the pressure in the apparatus must be in the range 10^{-9}–10^{-10} torr, and an oil-free vacuum must be used. In probing with ions of medium energy we have used ordinary oil diffusion pumps.

An exclusively high sensitivity is characteristic of methods based on ion-ion emission with subsequent mass-spectrometric analysis.[13,14] Here in some cases it has been possible to observe a covering of the order of 10^{-6} atomic layer. A complete comparison of these results with those of our experiments is difficult at the present time because of the great difference in the experimental conditions.

We note further that the technique described by us can be used also to detect atomic beams which are variable in time.

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154