Energy spectra of helium ions scattered from the (100) surface of a PbS crystal

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The energy spectra of helium ions, with initial energies up to 1 keV, scattered from the (100) surface of a PbS single crystal are obtained by the electrical differentiation method. The binary collision model is found valid for primary-ion energies beginning at about 100 keV. Carbon and oxygen atoms adsorbed on the PbS (100) surface are detected by elemental analysis.

Recent studies[1,2] have shown that the elemental composition of the surfaces of solids can be determined by analyzing the energy spectra of ion-ion emission on the basis of the binary collision model, which describes satisfactorily many characteristics observed in the scattering of inert-gas and alkali-metal ions from solid surfaces. According to this model the scattering process is governed by the collisions of the bombarding ions with atoms on the solid surface. The rest of the crystal lattice plays only a small role, because in the cases of bombarding-ion energies from 10^2 to 10^4 eV the intersection time is of the order of 10^{-16} sec, which is very much smaller than the thermal vibration period (10^{-12} sec) of the lattice. Moreover, it is known from quantum mechanics that scattering can be studied from the point of view of classical mechanics without considering the wave properties of particles when the de Broglie wavelength of the incident particle is much smaller than the lattice constant. Therefore, according to this model the scattering process should not depend appreciably on the structure of the solid.

Arifov et al.[3] assume that the lower limit for applying the binary collision model is 400 eV in the case of incident alkali-metal ions; according to Smith[1] this limit is 100 eV for inert-gas ions. The energy E of ions scattered by atoms of a solid as the result of binary collisions is related to the bombarding-ion energy E_0 by

$$\frac{E}{E_0}=\frac{M_1^2}{(M_1+M_2)^2}\left\{\cos\theta+\left(\frac{M_2^2}{M_1^2}-\sin\theta\right)^{1/2}\right\}^2, \qquad (1)$$

where M_1 and M_2 are the respective masses of the primary ion and lattice atom, and θ is the scattering angle.

The maximum energy that the scattered ions can possess (at θ = 90°) is obtained from the relation

$$E=E_0\frac{M_2-M_1}{M_2+M_1}. \qquad (2)$$

The minimum energy (at θ = 180°) is given by

$$E=E_0\left(\frac{M_2-M_1}{M_2+M_1}\right)^2. \qquad (3)$$

Therefore, according to the binary collision model the energy spectrum of the ions scattered at a given detection angle should consist, in its high-energy portion, of a series of peaks corresponding to the masses of the atoms that are located on the target surface and participated in the scattering. Inert-gas ions which are scattered from atoms in the interior (bulk) of the target emerge from the latter with such a very large energy loss that they cannot be regarded as having been scattered elastically, or, as is very likely, they are neutralized and therefore will not be detected. The probability of neutralization is especially high when the primary-ion is under 1 keV.[1,2] The spectra of alkali-metal ions scattered from solids are considerably more complicated. Their neutralization probability is quite small in virtue of their low ionization potential; therefore the secondary-ion spectrum can contain a considerable number of ions scattered by interior atoms and having a continuous range of energies. This leads to the aforementioned complexity of the spectra and can to a considerable degree hinder the identification of the peaks representing scattering from surface atoms.

The most encouraging results regarding the elemental composition of the surface were obtained in experiments with inert gases. Smith also showed[1] that with this technique one can determine, in addition to the elemental composition of the surface, the orientation of adsorbed molecules by comparing the heights of peaks for individual elements in the scattered-ion energy spectrum. The present investigation was undertaken to determine the applicability of the binary collision model to the case of helium ions scattered from lead sulfide, and to evaluate the suitability of this technique for detecting impurities on solid surfaces.

EXPERIMENTAL TECHNIQUE

We employed a spherically symmetric glass chamber, described in[4], that was used for the observation of slow-electron diffraction. The evacuated chamber was filled with the inert gas helium, which was thoroughly purified by chemical purifiers, by freezing out of impurities in a liquid-nitrogen trap,[5] and by a molybdenum getter. The helium pressure in the chamber when sealed off from the vacuum apparatus, was regulated by means of the apparatus described in[6]; during the measurement procedure this pressure was about 10^{-5} Torr. The ion beam was generated in an ion-electron gun.[7]

To obtain the energy spectra of the secondary ions we used a scheme, similar to that described by Shul'man et al. in[8], for the electrical differentiation of the delay curves of ion current to a collector. The (100) surface of the lead sulfide single crystal was obtained by cleavage in a vacuum. The density of ion current to the target was 2–3 μA/cm^2.

EXPERIMENTAL RESULTS

Figure 1 shows the energy spectra of the secondary ions in the scattering of helium ions, with E_0 = 25–175 eV, on the (100) face of a lead sulfide single crystal. In the case of 25-eV incident helium ions the scattering spectrum is peaked at 8 ± 2 eV with a weak maximum at about 13 ± 2 eV. For 50-eV ions the spectrum has two pronounced peaks near 17 ± 2 and 28 ± 2 eV. For 75 eV ions, in addition to the inelastic scattering peak at 17 ± 2 eV there are peaks at 48 ± 2 and 72 ± 2 eV, which according to (3) can be attributed to scattering on sulfur

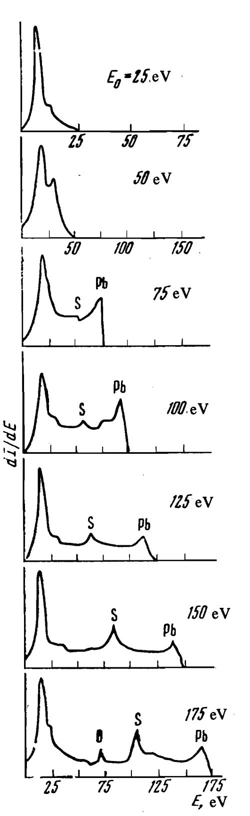

FIG. 1.

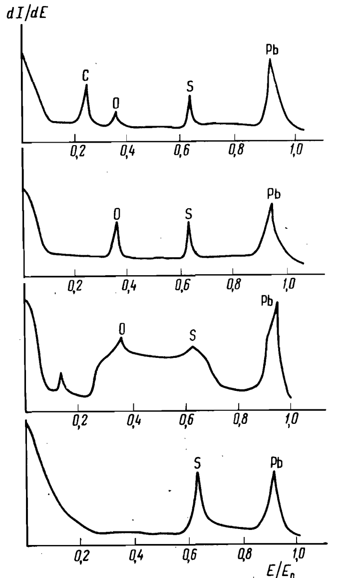

FIG. 2.

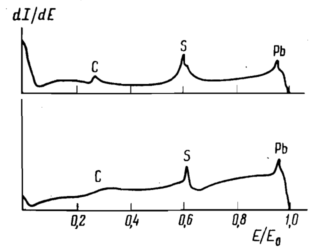

FIG. 3.

FIG. 1. Energy spectra of helium ions scattered from the (100) face of lead sulfide for E_0 from 25 to 175 eV.

FIG. 2. Energy spectra of helium ions scattered from the (100) surface of lead sulfide, for E_0 = 530, 650, 750, and 950 eV (starting at the top).

FIG. 3. Energy spectra of helium ions scattered from the (100) surface of lead sulfide heated to 400°C, for E_0 = 750 eV (above) and 930 eV (below).

and lead. For 100 eV the low-energy portion of the secondary-ion spectrum has about the same form as the spectra at the incident energies 25, 50, and 75 eV, i.e., a sharp peak at 17.0 eV and a faint peak at 31 ± 2 eV. The peaks corresponding to scattering from sulfur and lead are very clearly distinguished in the high-energy portion. A similar pattern is seen in the energy spectra of ion-ion emission from lead sulfide bombarded by 125-, 150-, and 175-eV helium ions. As the energy of the primary helium ions increases from 25 to 175 eV, the following changes are observed in the secondary-ion spectrum: The low-energy peak is shifted approximately from 10 eV to 17 eV; the relative number of fast scattered ions increases, while the fraction of low-energy secondary ions is reduced. The height of the highest-energy peak in the spectra from lead sulfide is reduced when the bombarding energy increases from 100 to 175 eV; on the other hand, the height of the preceding peak is enhanced; peaks are observed that require additional investigations for their interpretation. Specifically, the steps and peaks at about 31, 37, 41, and 51 eV for 100-, 125-, 150-, and 175-eV bombarding ions can be attributed, hypothetically, to doubly-charged helium ions scattered from sulfur atoms. Also, in the 175-eV spectrum the observed peak at 67 eV probably represents scattering from oxygen.

Figure 2 shows spectra of ions scattered from the (100) face of lead sulfide when the primary helium-ion energies were in the range 500 to 1000 eV. The abscissa is $\eta = E/E_0$ (the energy ratio of the secondary and primary ions). According to the binary collision model the peaks for E_0 = 530 eV can be identified as representing helium ions scattered by atoms of carbon (η = 0.26), oxygen (η = 0.37), sulfur (η = 0.60), and lead (η = 0.93).

The values of η calculated on the assumption that scattering occurs mainly at θ close to 180°, i.e., in accordance with (3), are 0.25, 0.359, 0.603, and 0.920, respectively. The peak attributed to helium ions scattered by carbon atoms was surprisingly tall, but the peak from sulfur atoms was much smaller than that from lead atoms. At E_0 = 650 eV no peak from carbon is observed, but distinct peaks are seen from oxygen (η = 0.39), sulfur (η = 0.60), and lead (η = 0.95). The peaks corresponding to scattering by oxygen and lead atoms grew sharply, but there was no change in the height of the peak from sulfur. At E_0 = 750 eV the background level was considerably higher, but peaks of scattering by oxygen, sulfur and lead atoms are seen. In addition, there are a distinct peak at η = 0.11 and a shoulder in the background of the lead peak at η = 0.84. In the case of E_0 = 950 eV, peaks are observed at η = 0.13, η = 0.60 (from sulfur), and η = 0.94 (from lead).

Figure 3 shows energy spectra of ions scattered from the (100) surface of lead sulfide that had been heated to 400°C. Here the low-energy peak is much shorter than at room temperature. At E_0 = 750 eV the secondary-ion distribution includes approximately equally tall peaks of the basic material (sulfur and lead), a peak at η = 0.27, which can be attributed to scattering by oxygen, and a broad peak at η = 0.16. With E_0 = 930 eV, peaks are seen for scattering by atoms of sulfur, lead, and possibly carbon (η = 0.26).

DISCUSSION OF RESULTS

The absence of peaks for helium ions scattered elastically from the (100) surface of lead sulfide in the cases of incident ions up to 75 eV probably indicates inelastic potential interaction in this energy interval. It should be noted that the structure of energy spectra corresponding to the binary collision model can be strongly distorted by the dependence of the probability of inelastic interactions on the energy of the bombarding ions;[10] this probability varies sharply at low energies. Accordingly, we can account consistently for the shift of the low-energy peak and the variation of the heights of the high-energy peaks in Fig. 1, as the bombardment energy is changed. In accordance with (3), the high-energy peaks, beginning at 75—100 eV, can be attributed to elastic scattering of helium ions from surface atoms (particularly sulfur and lead atoms). It is probably significant that the binary collision model is applicable in this case beginning with primary ions of about 100 eV, i.e., as soon as high-energy elastic-scattering peaks appear. It is also important that the quadratic expression (3) is valid, which corresponds to the scattering of the light helium ions by heavy atoms in the direction θ = 180°.

A comparison between the experimental and calculated positions of the peaks in the secondary-ion spectra indicated that the elemental composition of the target surface was determined very reliably. From the fact that the patterns of slow-electron diffraction observed in a helium atmosphere contain no reflections besides those corresponding to a clean surface, while the energy spectra of secondary ions include peaks resulting from scattering on atoms of carbon and oxygen impurities, we conclude that the spectra of scattered ions are more highly sensitive to the presence of surface impurities than is the case in slow-electron diffraction.

One of the important features of the ion-scattering technique for the elemental analysis of solid surfaces is the feasibility of determining the composition of both a surface and the gas in the scattering chamber, because active components of the gas are adsorbed on the surface and are identified as impurities. This probably occurs when on the surface of lead sulfide we find carbon and oxygen atoms; the latter indicate adsorption of carbon monoxide that is a contaminant of the helium in the chamber.

In presenting our results we noted that carbon and oxygen are observed on lead sulfide when $E_0 = 530$ eV, but that at $E_0 = 650$ and 750 eV carbon is not observed, while at 950 eV both elements are absent (Fig. 2). After the bombardment with helium ions in the range 530—950 eV we used 530-eV ions again and the carbon peak reappeared. Carbon and oxygen peaks were also observed in the spectrum for 780 eV. It is quite difficult to account for the disappearance of peaks simply as the result of changing experimental conditions; the bombardments and recording of the spectra were performed continuously, the primary-ion currents were steady, and the amplification factor was constant. The absence of carbon peaks in spectra at some primary energies and their presence in other cases can be attributed to variation in the probability of inelastic collisions as a function of the incident-ion energy. At a certain velocity an ion transfers energy to the crystal and is included among those scattered inelastically. Accordingly, we may expect that at certain ion energies the peaks of the intrinsic crystal elements will also disappear. Something like this is observed at $E_0 = 750$ eV, when the sulfur peak is seen as only a "conjecture" against the high general background.

An alternative explanation of the observed results has been devised as follows. Carbon monoxide is adsorbed in such a way that carbon atoms mainly shadow lead atoms, while oxygen atoms shadow sulfur atoms. This can account for the enhanced lead peak that accompanies disappearance of the carbon peak, while the sulfur peak remains unchanged as the bombardment energy is increased. When at some incident energy no "oxygen" peak is observed the sulfur peak grows sharply. The hypothesis that carbon and oxygen atoms are desorbed is supported by the appearance of a peak in the region $\eta = 0.13$—0.14 of spectra at $E_0 = 750$ and 950 eV; this peak is related to the onset of sputtering of the target material. Peaks of this nature, with fluctuating positions and heights, have been observed by Panin,[9] and Smith,[1] and Ball et al.[2]

By assuming that for helium ions scattered from atoms of a given species the peak height is proportional to the surface density of these atoms multiplied by the cross section for scattering of the primary ions from the same atoms, subject to the condition that there is no difference in charge exchange, we can evaluate quantitatively the surface-elemental composition of the target, as was done in[1,2]. From this point of view it is not surprising that the lead peak is considerably taller than the sulfur peak, because, as a calculation shows, the differential cross section for scattering from lead is about 6.8 times larger than for scattering from sulfur. The measured heights of peaks resulting from the scattering of the primary ions by oxygen and carbon atoms indicate that their ratio on the surface could be represented by $C_{3.3}O$. This is consistent, in general, with the hypothesis that the surface of lead sulfide holds carbon that is not combined chemically with oxygen, and enables us to explain why some spectra include peaks only due to carbon or only due to oxygen. The presence of carbon atoms on the surface of lead sulfide heated to 400°C indicates the possibility of carbon diffusion to the surface from the interior. And since it is postulated that carbon atoms emerging at the surface will shadow lead atoms, it becomes understandable why the lead and sulfur peaks are of comparable heights, despite the large difference between the respective differential scattering cross sections.

Investigations using slow-electron diffraction to detect defects created in lead sulfide by helium ions have shown that the probability of inelastic interaction between ions and a solid surface is peaked at certain energies of the incident ions.[10] On this basis we consider that the first explanation given for the disappearance of peaks such as those due to carbon in the scattered-ion spectra is more realistic. Since the heights of the peaks vary depending on the primary-ion energy, the numerical ratio of the elements on the surface can evidently be determined only in an energy range where the interaction cross sections are constant; in the general case the latter depend on the energy of the interacting particles. This must also obviously be taken into account in determining the orientations of adsorbed molecules.

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