Energy Distributions of Alkali Ions Sputtered from Alkali-Halide Crystals with Energetic Rare Gas Ion Bombardment

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Relative energy spectra of sputtered alkali ions from three alkali-halide crystals (LiF, NaCl, and KCl) were measured by bombarding the energetic rare gas ions (He^+ and Ar^+) whose energies ranged from 10 keV up to 100 keV. It was found that the energy spectrum of K^+ ions from a KCl crystal were in close agreement with the energy spectrum of sputtered ions from the metal surface in both respects of the shape and the peak position, whereas Na^+ ions from an NaCl crystal were likely to fit to the energy spectrum of neutral atoms rather than that of ionic one, and Li^+ ions sputtered from an LiF showed also neutral spectrum with slightly different asymptotic behaviors in the higher energy region.

1. Introduction

Although numerous investigations have been carried out up to now to measure the energy spectra of sputtered atoms from metal surfaces,¹⁻⁴⁾ only a few experiments have been made of measuring ionic energy distributions from the ionic crystals. This is mainly due to the charge build up on the surface of the crystal by the ion bombardment which prevents us from measuring the energy of sputtered ions exactly.

Stein⁵⁾ measured the angular distributions of the sputtered atoms from a KCl crystal bombarded by neutral Ne and Ar atoms with energy of 200 ~ 400 eV. Campbell and Cooper⁶⁾ bombarded a KBr

crystal with Ar^+ and Xe^+ ions in the energy range from 25 to 180 eV, in which they observed a relatively strong signal of Br^- ions sputtered from the target. Abroyan and Lavrov⁷⁾ sputtered several alkali-halide targets with K^+ ions in the energy range from 40 eV to 7 keV. They found positive alkali ions, negative halide ions, and molecular ions of alkali-halide compounds. As sputtering experiments concerning alkali-halide crystals at somewhat higher ion energies, Kelly and Peterson⁸⁾ measured the angular distribution of K^+ ions sputtered from a KCl target bombarded with 30 keV Ar^+ ions.

Miyagawa⁹⁾ reported the energy spectrum of sputtered Na^+ ions from an NaCl

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crystal using a time-of-flight technique, in which he showed the energy distributions of Na^+ were very similar to those of sputtered neutrals from the metal surfaces. For K^+ ions sputtered from a KCl crystal, Arikawa et. al.¹⁰⁾ found a different result from Na^+ ions. In that experiment, the energy analysis was made by an electrostatic energy analyzer of 127° bending type. No mass analysis was attempted, since the majority of sputtered ions were considered to be K^+ ions on the ground of the data obtained by the ion microscopic analysis.^{11,12)} The energy distributions were in close agreement with the ionic spectra from metal surfaces rather than the neutral spectra in both respects of the shape and position of the peaks.

In this paper we will present the relative energy spectra of positive alkali ions ejected from three alkali-halide crystals, LiF, NaCl and KCl. In order to discriminate sputtered alkali ions from other background ions, an RF-quadrupole mass filter was installed at back of the energy analyzer. In the next section a brief description of the apparatus in association with

experimental procedures will be given. The experimental results and some discussion will be presented in the last section.

2. Experimental Apparatus

A main part of the apparatus is similar to that described in the previous paper,¹⁰⁾ and it consists of an ion source, a mass separator, an accelerator, a sputtering chamber which houses a target assembly, the electrostatic energy analyzer and the RF-quadrupole mass filter as shown in Fig. 1.

The incident ions were produced with the RF ion source which was operated at 40 MHz with 300 watts. Ions were then extracted and accelerated with a pre-accelerator to an energy appropriate for mass separation. After being deflected by the 15° bending mass-analyzing magnet, ions of interest were focused to the entrance slit of the main accelerator where ions were further accelerated by a series of electrostatic tube lenses to their final energies ranged from 10 keV to 100 keV. Argon and helium ions were used as projectile ions. All ions were considered

Fig. 1. A schematic view of the experimental apparatus (not to scale).

to be in their electronical ground states. The ion beam from the accelerator was then positioned vertically or horizontally by two pairs of parallel plates and was introduced into the sputtering chamber.

The target crystal was attached to a copper target holder and was mounted on the turn table in the sputtering chamber. The target crystal was heated to about 200°C so as not to suffer from surface charge build up during the ion bombardment. It is generally accepted that the temperature of the target has very little direct influence on the sputtering yield.^{13,14} Much attention should be taken of removing surface charge, because such surface charge would have a marked influence on the measured energy of sputtered ions and causes a systematic error in the measurement of their energy distributions. As a target three single crystals of alkali-halide, LiF, NaCl and KCl were employed.

The projectile ions were focused onto the cleavage surface of the target crystal with the incident angle of 60° for experimental conveniences. Sputtered ions from the target crystal with the ejecting angle of 60° with respect to the surface plane were passed through an angle-defining slit, and their energies were measured by the cylindrical electrostatic energy analyzer whose energy resolution was designed to be about 60, which was sufficient for the measurement of such a low energy ion. Ions emerging from the energy analyzer were accelerated to 20~30 eV appropriate for the subsequent RF-quadrupole mass filter.

A channel multiplier was located just behind the exit slit of the mass filter.

The output signals from the channel multiplier were fed into a charge-sensitive preamplifier which served for the reduction of the effect of stray capacitance of the cable from the channel multiplier to the preamplifier. Output pulses were shaped to a convenient form for the subsequent discriminator and were amplified by a linear amplifier which was followed by an electronic counter and a digital recorder.

Evacuation was made separately for the ion source chamber, the main accelerator, the scattering chamber and the sputtering chamber. A typical vacuum pressure inside the sputtering chamber was maintained as lower than 1×10^{-6} Torr during the experiment.

3. Experimental Results and Discussion

Relative energy distributions of the sputtered alkali ions from the LiF, NaCl and KCl single crystals were measured by bombarding Ar⁺ and He⁺ ions whose energies ranged from 10 keV up to 100 keV.

Sputtering processes of alkali-halide crystals are less obvious than those of metals, and no reliable theory is available at present to compare with experiments. So the experimental data were fitted to the theoretical curve based on the collision cascade model derived for metal by Sigmund,¹⁵⁾ though there is no extensive physical meaning to fit the data to the theory for metals. The energy distribution of sputtered particles, from the metal surface, either ionic or neutral species, was derived by Gries and Rüdenauer¹⁶⁾ in a compact form as given by

$$\frac{dN^+}{dE} = A_i \frac{B^2 E (E + B/2)^{1/2}}{(E + B)^3} \quad (1)$$

for ionic species, and

$$\frac{dN^0}{dE} = A_n \frac{E}{(E + B)^3} \quad (2)$$

for neutral species, where N^+ and N^0 denote the numbers of sputtered ionic species and neutral species respectively. E is the energy of sputtered species and B is the surface binding energy of the target material. Coefficients A_i and A_n are a function of several parameters which are specified by the incident species and target materials such as the mass ratio of the target atom to the incident ion, the cross section for elastic collision between incident ions and target atoms, ionization energy and work function of the target material.¹⁷⁾ In the present experiment, however, we only aim at the relative energy distribution of sputtered species, dependence of these coefficients on the energy distribution is not necessary to be taken into account.

According to Eq. 1, the peak of the energy distribution curve for ionic species should appear at $E = 0.768 B$, and the energy distribution exhibits the $\sim E^{-3/2}$ dependence at energies sufficiently large compared with the surface binding energy. On the other hand, from Eq. 2 the peak should appear at $E = B/2$ and the energy dependence approaches $\sim E^{-2}$ at higher energies for neutral species.

The energy distribution curve for the sputtered Na^+ ions from the NaCl single crystal is shown in Fig. 2a in which the incident energy of bombarding Ar^+ ions is 70 keV. Theoretical curves of the ionic

and neutral distributions for metals are also presented to compare with the experimental plots. Relative data are normalized to the theoretical curve at the peak position. As is apparent from the figure, the experimental peak appears around 4 eV, and the plots are well fitted to the neutral distribution as a whole. Other plots obtained from different bombarding energies ranging from 10 keV to 100 keV also show an excellent agreement with the curve for neutral distribution. In the case of He^+

Fig. 2. Energy distributions of sputtered Na^+ ions from NaCl crystals (A) and Li^+ ions from LiF crystals (B). Experimental data ($\circ$) are well fitted to the theoretical curve derived for neutral species sputtered from metal surfaces (—). The theoretical curve for ionic species from metal (---) is also shown for comparison.

ion bombardment, the plots are also seen to be neutral distribution as is the case of Ar^+ ion bombardment.

For the value of surface binding energy of NaCl, we adopt the cohesive energy U_0 as is usually done in most sputtering calculations. U_0 is the energy necessary to disperse a pair of atoms in the crystal into its component atoms. Therefore, the average binding energy of a surface atom can be regarded as being equal to U_0 . For the NaCl crystal the cohesive energy U_0 is 7.92 eV. If we take this value as a surface binding energy of NaCl, the peak should appear at $E=3.96$ eV for the neutral distribution and $E=6.08$ eV for the ionic distribution. The experimental peak appears at 4 eV, the value of which is very close to that of the neutral distribution, and the asymptotic energy distribution curve also exhibits E^{-2} dependence with a slight undulation. It is surprising that the energy distribution of sputtered ion from the alkali-halide crystal fits well to Eq. 2 which is derived for a metal. In any case as far as the NaCl crystal is concerned, the present experimental result seems to support the previous data of Miyagawa,⁹⁾ and strongly suggests that the process would reflect the mechanism of the neutral sputtering from the metal surface.

The surface binding energy of the LiF crystal is 10.5 eV, the value of which is larger than that of NaCl by 2.58 eV. Here again we use the cohesive energy of LiF as the surface binding energy. The peak position is expected to shift to the higher energy side with a little wider maximum by the amount of the increment of the surface binding energy. From Eqs. 1 and 2, the

peak of the energy distribution curve should appear at 8.06 eV or 5.25 eV, according to whether the sputtering process reflects the ionic distribution or neutral distribution. A typical example is shown in Fig. 2b. Experimental plots show fairly good agreement with the theoretical curve for the neutral distribution especially in the neighbourhood of the peak. The sputtering behavior is much the same as the NaCl crystal, i. e., the shape and the position of the peak are little affected by the projectile species and the bombarding energy over the wide range from 10 keV to 100 keV. An asymptotic behavior is, however, slightly different from that of the NaCl crystal. A relatively wide undulation is superimposed on the monotonically decreasing function above 10 eV, and the amplitude of this undulation seems to be slightly dependent on the incident energy. Apart from these slight differences in the asymptotic behaviors, sputtering processes of both cases of NaCl and LiF may be considered as neutral-like.

The energy distribution of K^+ ions sputtered from the KCl crystal shows different aspect from above two cases as pointed out in the previous paper¹⁰⁾ in that the energy distribution curve is in close agreement with the ionic spectrum from the metal surface. Typical examples are shown in Fig. 3. Experimental plots apparently fall on the theoretical curve for the ionic distribution. As mentioned above, mass analysis of the sputtered ions was not performed in the previous experiment. In order to make clear if such difference comes from the background ions, mass analysis was attempted. However, results

Fig. 3. Energy distributions of sputtered K^+ ions from KCl crystals with 90 keV Ar^+ ion bombardment (A) and with 40 keV He^+ ion bombardment (B). Experimental data (O) are well fitted to the theoretical curve derived for ionic species from metal surfaces (---) in both cases of Ar^+ ion and He^+ ion bombardment. The theoretical curve for neutral species from metal (—) is also shown for comparison.

were in excellent agreement with those measured without mass separation. Therefore, if we assume that Eq. 1 stands for the sputtering processes of KCl, the expected position of the peak is calculated to be 5.52 eV from Eq. 1 taking the value of the surface binding energy of KCl as 7.19 eV. The calculated peak position is indeed very close to the experimentally obtained peak position that appears near 6 eV. Moreover, the asymptotic behaviors

on the higher energy side are also in close agreement with the $E^{-3/2}$ dependence on the average, though a broad undulation is also seen on the asymptotic curve above 10 eV as is the case of LiF. It may be said, therefore, that the energy distribution function for sputtered K^+ ions from KCl crystals is very similar to that for ionic emission from metal surfaces, in contrast to the cases of LiF and NaCl. The situation is almost the same as is the case of He^+ ion bombardment as shown in Fig. 3. The relative energy distribution function seems to be little influenced by the projectile species used and the bombarding energies from 10 keV to 100 keV.

A small undulation observed on the monotonically decreasing function of the energy spectrum may be interpreted qualitatively as caused by a symmetric charge changing collision between a recoiled alkali atom and an alkali ion in its lattice site at the surface. An incoming energetic particle will collide at first with the ions in the crystal, thereby transferring to them more energy than the binding energy at the lattice site to create a primary recoil ion. Recoiled ions will further collide with other target ions distributing the energy through a successive collision cascade. A part of such recoiled ions will be converted to neutral atoms in the course of collisions, and finally at the surface the resonant charge changing collision will take place between recoiled atoms and the ions at the lattice site. During the collision electrons are considered to be transferred back and forth between collision partners, which results in a oscillatory structure in the energy distribution function. Such a process

is a very common phenomenon in a low energy symmetric ion-atom collision,¹⁸⁻²¹⁾ and can be described in terms of an interference between two waves scattered from symmetric and antisymmetric potentials of a pseudo molecular ion. On the assumption that the undulation in the energy distribution function is attributed to the resonant charge exchange, the oscillation peaks should be approximately equally spaced when plotted against inverse relative velocity. Figure 4 shows the inverse

Fig. 4. Relative K^+ ion yield sputtered from KCl crystal versus inverse velocity calculated from Fig. 3A. Arrows indicate the positions of the oscillation peak.

velocity plots. As can be seen from the figure, peaks seem to be equally spaced, though oscillation peaks are not so prominent as is usually observed in a gas phase collision. From these spacings an average area between symmetric and antisymmetric potentials $\langle ER \rangle$ can be estimated approximately.²²⁾ Here E and R denote the potential difference and the inter-atomic distance, respectively. For the case of K_2^+ the quantity $\langle ER \rangle$ is calculated to be 8.67 eV

$\text{\AA}$, the value of which is not so unreasonable. However, further experimental and theoretical investigations of these points should be needed to resolve the many uncertainties remaining.

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Keywords

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