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Surface Atomic Structure Analysis by Impact-Collision Ion Scattering Spectroscopy (ICISS)

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The characteristics of impact-collision ion scattering spectroscopy (ICISS) as a powerful method for surface atomic structure analysis are discussed in comparison with conventional low-energy ion scattering spectroscopy (ISS), and a list of recent studies made by using ICISS is given. As an example of surface atomic structure analysis by ICISS, a recent study on $CaF_2(111)$ is briefly reviewed. The outermost layer of this surface is formed by F ions, and no remarkable surface relaxation is observed.

§1. Introduction

Ion scattering spectroscopy is now recognized as a poerful technique for analyzing the atomic structure of solid surfaces. Ions with kinetic energies larger than a few hundreds of eV have de Blogli wave lengths of less than 10^{-2} Å, so that they behave as classical particles in their scattering processes. Ion scattering spectroscopy therefore yields real-space information directly, eliminating the necessity of a Fourier transform which is required in all the k-space techniques using quantum particles such as electrons and photons.

Ion scattering spectroscopy is classified into low-energy ion scattering spectroscopy (ISS)¹⁻⁵⁾ and Rutherford backscattering spectroscopy (RBS).⁶⁾ The apparent difference between ISS and RBS is only that the ion energies in ISS and RBS are of the orders of keV and MeV, respectively. This quantitative difference, however, gives rise to the following important quantitative difference.⁴⁾ Roughly speaking, ISS determines the positions of surface atoms relative to those of other surface atoms, while RBS analyzes the positions of surface atoms with respect to those of subsurface atoms.

Impact-collision ion scattering spectroscopy (ICISS) discussed in this paper is a specialization of ISS. In conventional ISS, the laboratory scattering angle θ_L is taken at 90° or less to obtain high counting rates of scattered ions by ensuring large scattering cross sections. The angular dis-



Fig.1 Schematic figure depicting the difference between (a) ICISS and (b) conventional ISS.

tribution of scattered ions is observed as a function of the polar and azimuthal angles of the ion incidence direction, usually by rotating the sample and keeping θ_L fixed. It is not straightforward to analyze surface atomic structures from such experimental data for the following reasons: (i) Shadowing and blocking effects both contribute simultaneousely to the angular distribution of scattered ions in this experimental geometry. (ii) The large scattering cross sections due to small θ_T increase the probability of troublesome

multiple scattering.

(iii) It is certainly not impossible to analyze surface atomic structures from such experimental data by calculating the angular distributions (or the energy spectra) of scattered ions for various surface structure models and by optimizing the agreement of the calculations with the experimental data, but such calculations (usually Monte Carlo simulations) are extremely costly in computer time. (iv) The scattering potentials required in the calculations mentioned above are not precisely known.

In order to solve these problems, the authors and co-workers $^{7,8)}$ introduced ICISS several years ago.

In ICISS, θ_{T} is taken as close to 180° as possible. Since ions detected in the ICISS mode have backscattered along such a trajectory that nearly retraces the incident trajectory, only the shadowing effect is observed. The possible largest $\boldsymbol{\theta}_{\tau}$ minimizes the contribution of troublesome multiple scattering. ICISS "sees" the center of each atom since the impact parameter is nearly zero owing to the large $\boldsymbol{\theta}_{_{T}}$, so that at the onset of a shadowing effect observed in the ICISS mode, the edge of the shadow cone of a shadowing atom necessarily passes the center of a concealed atom to a good approximation (see Fig.la). To recognize this characteristic of ICISS is a breakthrough, since it is indicated that surface atomic structures can be analyzed quantitatively by measuring the critical angles of shadowing effects. Note that such geometrical simplicity does not exist in the case of conventional ISS (see Fig.1b).

Finally, it is possible to know the scattering potentials by ICISS, since the shape of shadow cones can be determined by ICISS using the characteristic mentioned above.

So far, the authors and co-workers analyzed the atomic structure of TiC(111)-(1×1), ⁷⁻¹¹⁾ TiC(100) -(1×1), ⁴,9,12) Si(100)-(2×1), ¹³) Si(111)-(7×7), ¹⁴,15) Si(111)-(1×1)Te, ¹⁵) Si(111)-($\sqrt{3}\times\sqrt{3}$)Ag, ¹⁶,17) Si(111) -(3×1)Ag, ¹⁷) and Ag(111)-(1×1) ¹⁷) by ICISS. Recently, several groups have applied ICISS to study the atomic structures of many other surfaces, i.e., Cu(110)-(1×1), ¹⁸⁻²¹) Cu(110)-(2×1)0, ¹⁸⁻²⁰) Pt(111) -(1×1), ²²,23) Si(111)-($\sqrt{3}\times\sqrt{3}$)Au, ²⁴) Ni(100)-(1×1), ²⁵) and Au(110)-(2×1). ²⁶)

In this paper, we show how are surface atomic structures analyzed by ICISS, taking a recent study on $CaF_2(111)$ as an example.²⁷⁾ CaF_2 is of importance in connection with the fabrication of three-dimensional integrated circuits, since this compound is an insulator whose lattice constant is close to that of Si.

§2. Structure Analysis of CaF₂(111) by ICISS

The authors recently analyzed the atomic structure of $\operatorname{CaF}_2(111)$ by ICISS.²⁷⁾ A $\operatorname{CaF}_2(111)$ surface was obtained by cleavage in air and subsequent heating for cleaning at about 1000°C in ultrahigh vacuum. The surface treated in this way, which exhibited a 1×1 low-energy electron diffraction (LEED) pattern, had an ideal bulk-like atomic structure as will be discussed below, but a Ca-rich surface is obtained when the heating was done at lower temperatures as a result of the preferential evaporation of F atoms. All the ICISS and ISS experiments described in this paper were made for the former surface, using a beam of He⁺ with an energy of 979 eV. Charging effects of the insulator sample were compensated by an electron flood gun.

Figure 2 shows typical ISS spectrum of $\operatorname{CaF}_2(111)$ The peaks at 523 and 734 eV are due to surface F and Ca ions, respectively. Shown in Figs.3a and b are the angular dependences of the intensities of the F and Ca peaks, respectively, where α and ϕ are the polar and azimuthal angles of the ion incidence direction; α is measured from the surface, and ϕ is measured with respect to [$\overline{121}$]. As we see in Figs.3a and b, the intensity of the F peak shows no remarkable ϕ dependence even at small α 's such as 12°, whereas that of the Ca peak exhibits noticeable ϕ dependences at α 's as large as 30°. This indicates that the outermost layer of CaF₂(111) is formed by



Fig.2 Typical ISS spectrum of CaF₂(111).



Fig.3 Angular variations of the intensities of He⁺ scattered from (a) F and (b) Ca at CaF₂(111). The top figure shows the experimental geometry.

F ions; the noticeable intensity variations observed for the Ca peak are due to such shadowing effects that F ions in the outermost layer shadow Ca ions in an underlying layer. By analyzing Figs.3a and b in more detail, we come to the conclusion that CaF_2 (111) has the atomic structure shown in Fig.4. The outermost layer is formed by F ions as mentioned above, and the second layer is formed by Ca ions. The atomic arrangement is essentially the same as in the bulk.

Since the surface interlayer distance is in general different from the corresponding bulk interlayer distance, we measured the distance between the outermost F layer and the second Ca layer of CaF2(111) by ICISS in the following way. Shown in Fig.5a are the intensity variations of the Ca peak measured against a in different azimuths <A>, , and <C> indicated in Fig.5b. In each azimuth, the intensity of the Ca peak decreases to zero as α decreases beyond a critical value due to a shadowing effect in which F ions in the outermost layer shadow Ca ions in the second layer. The shadowing critical angles are 22±1° in azimuth <A>, 38±1° in azimuth , and 14±1° in azimuth <C>. Since we already know the shape of the shadow cone of a F ion for He of 979 eV via preliminary ICISS experiments (not shown), we can draw the situations at the onset of the shadowing effects as shown in the side views in Fig.5b. In the drawings, the distances parallel to the surface between a surface F ion and adjacent Ca ions in the second layer are the same as those in

the bulk since a 1×1 LEED pattern is observed for the surface, and the edge of the shadow cone of a surface F ion necessarily passes the center of an adjacent Ca ion in the second layer at the onset of each shadowing effect observed in the ICISS mode. From the drawings, we can readily determine the distance between the outermost F layer and the second Ca layer to be 0.80 ± 0.08 Å, which is close to the corresponding bulk value, 0.79 Å.

§3. Summary

The characteristics of ICISS as a powerful tool for surface atomic structure analysis were discussed in comparison with conventional ISS. As



Fig.4 Structure of $CaF_2(111)$ determined by ISS and ICISS. The outermost layer is formed by F ions, and the second layer by Ca ions. The atomic arrangement is the same as in the bulk.



Fig.5. (a) Angular variations of the ICISS intensity of He⁺ scattered from Ca at $CaF_2(111)$ in different azimuths. Arrows show the critical angles of shadowing effects. (b) Situations at the critical angles of the shadowing effects observed in (a).

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an example of surface atomic structure analysis by ICISS, a recent study on CaF₂(111) was briefly reviewed. The atomic arrangement of the surface is the same as that in the bulk, and no remarkable surface relaxation exists. The outermost layer of the surface is formed by F ions.

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