Chemical Analysis of Surfaces by Total-Reflection-Angle X-Ray Spectroscopy in RHEED Experiments (RHEED-TRAXS)

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A new method for chemical analysis of surfaces by total-reflection-angle X-ray spectroscopy in RHEED experiments (RHEED-TRAXS) has been developed. When the X-ray take-off angle is set to be the critical angle for total reflection of the characteristic X-ray emitted from the deposited atoms on surfaces, the detection efficiency for the deposit becomes drastically higher owing to the refraction effect of the X-ray. This enhancement of surface sensitivity is demonstrated with Ag on Si(111). The smallest detectable amount of Ag is about 0.01 monolayer or less. This sensitivity is comparable to or higher than that of AES.

For chemical analysis of solids by an electron beam, two competing processes are of special interest: the generation of characteristic X-rays, used in X-ray microanalysis (XMA), and the generation of Auger electrons, used in Auger electron spectroscopy (AES). Because the escape depth of Auger electrons from the surface generally ranges from 5 to 30Å,[1] AES is effective for the chemical analysis of the several atomic layers of a surface. On the other hand, since the escape depth of X-rays is of the order of 1 μm, for XMA it has long been considered impossible to analyze the chemical composition of the last several atomic layers.

Recently Sewell et al.[2-6] and Ino et al.[7] showed that it is possible to detect an adsorbate of less than one monolayer by measuring the characteristic X-rays excited by the primary electron beam of RHEED (reflection high energy electron diffraction) during RHEED observations. This technique is far more sensitive to surfaces than usual XMA because the glancing angle of the primary electron beam with respect to the surface is so small ($<5°$) that the beam does not penetrate into the crystal so deeply. Therefore, the region of X-ray emission is restricted to within several hundred angstroms below the surface.

The information obtained by this X-ray spectroscopy is quite affected by the experimental conditions, such as the energy E_0, the glancing angle θ_g and azimuthal angle ϕ of the incident electron beam with respect to the crystal orientation of the substrate, and the take-off angle θ_t of the emitted X-rays with respect to the surface (Fig. 1). In this paper we report some experimental results on the θ_t-dependence of the X-ray spectra because they were most drastically affected by the change of θ_t. It has been learned that the surface sensitivity of this X-ray spectroscopy becomes more than several score times as high as that of the one by Ino et al.[7] when the X-ray take-off angle θ_t is set very small and closely corresponding to the critical angle for total reflection of the marked characteristic X-

ray. Then the surface sensitivity of this X-ray spectroscopy, called "total-reflection-angle X-ray spectroscopy in RHEED experiments (RHEED-TRAXS)", becomes comparable to that of AES in general, and superior to it for the detection of heavier elements on surfaces. This enhancement of surface sensitivity around the total reflection angle in the RHEED-TRAXS can be largely explained by the refraction effect of the emitted X-rays at the surface.

Figure 1 is a schematic illustration of the usual RHEED apparatus combined with a Si (Li) solid-state X-ray detector. The X-rays excited by the primary electron beam of RHEED pass successively through two beryllium windows and reach the Si (Li) detector. The first beryllium window with a 10 mm diameter and 25 μm thick is used to seal the ultrahigh vacuum of the chamber and the second, 5 mm in diameter and 14 μm thick, to seal the vacuum of the detector tube in which the Si (Li) crystal is placed. A narrow slit is put in front of the second beryllium window to obtain the resolution of 0.08° on θ_t. The angle between the direction of the incident electron beam and that of the Si (Li) detector is fixed at 90° in this experiment. The X-ray take-off angle θ_t is varied
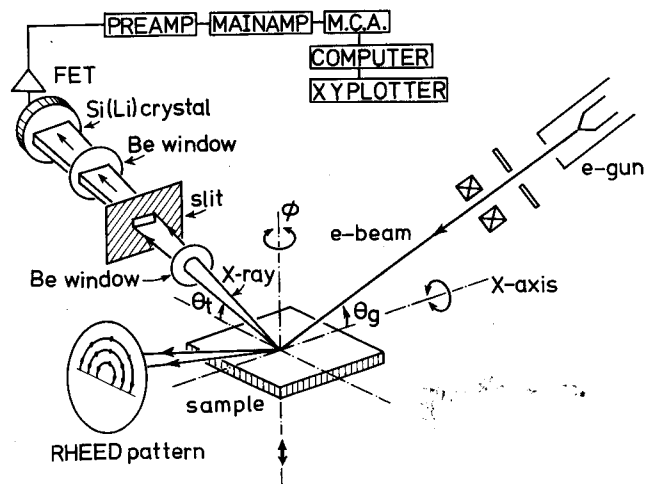

Fig. 1. Schematic illustration of the apparatus used for total-reflection-angle X-ray spectroscopy in RHEED experiments (RHEED-TRAXS).

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by rotating the sample around the X-axis (see Fig. 1).

A mirror polished Si(111) wafer was used as a substrate and was carefully cleaned by electron bombardment annealing to obtain a distortion-free surface. When a silicon wafer is heated to 1200°C in a vacuum of the order of 10^{-10} Torr, a clean and flat surface is usually obtained and a clear RHEED pattern of the 7×7 structure appears at room temperature.[8,9] Ag was deposited onto this surface from W-filaments. The deposited film thickness was monitored by a quartz oscillator.

Figure 2 shows the θ_t-dependence of the X-ray spectra taken from a Si (111) surface onto which a 1.0 monolayer of Ag was deposited at room temperature. The energy of the primary electron beam was 15 keV and the glancing angle, 3.7°. The counting time was 120 sec for each measurement. When θ_t is set to be 2.6°, the intensity of the SiK_α line (1.74 keV), which comes from the Si substrate, is very strong compared with that of AgL_α (2.99 keV) and AgL_β (3.15 keV) lines which are emitted from the deposited Ag atoms. At $\theta_t = 0.6$°, however, the

AgL_α line stands out from the fluctuation of the background continuous X-ray so clearly that the peak to background ratio increases about seven times more than that at $\theta_t = 2.6$°. Hence, one can detect an extremely small quantity of Ag on the surface with much higher sensitivity at this take-off angle than at $\theta_t = 2.6$°. When θ_t is less than 0.6°, the intensity of AgL_α line is comparable to that of SiK_α line and the shape of the continuous X-ray spectra varies markedly with θ_t.

In Fig. 3 the θ_t-dependences of the absolute intensities (peak heights) of AgL_α and SiK_α lines are shown. With the increase of θ_t, the intensity of the AgL_α line increases rapidly and takes a maximum value at $\theta_t = 0.6$°, and then decreases to a smaller constant value. In contrast, the intensity curve of the SiK_α line bends sharply at $\theta_t = 1.0$° and then gradually increases as θ_t becomes larger than 1.0°. The critical angles for total reflection of AgL_α ($\theta_{c,Ag}$) and SiK_α ($\theta_{c,Si}$) lines by silicon are calculated on the basis of a free electron model and are indicated by arrows in Fig. 3. The AgL_α line intensity shows a strong peak, but the SiK_α line intensity a shoulder at each critical angle for total reflection.

The θ_t-dependence of the relative intensity (peak height ratio) of AgL_α line to SiK_α line is shown in Fig. 4. The relative intensity AgL_α/SiK_α takes a maximum value around $\theta_t = 0.3$° and decreases rapidly when θ_t becomes larger than 0.6°. The value of AgL_α/SiK_α at $\theta_t = 0.3$° is approximately 25 times as large as that at $\theta_t = 3.0$°, which nearly corresponds to the experimental condition of the previous report by Ino et al.[7] The relative intensity of the AgL_α line to the SiK_α line, which indicates the intensity ratio of the signal from the topmost layer of the surface to that from the substrate Si crystal below the Ag film, is an index of the surface sensitivity of this detection method. So it can be said that the surface sensitivity varies with θ_t as shown in Fig. 4 and is highest around $\theta_t = 0.3$°.

The reason the intensities of the characteristic X-rays emitted from the deposited film and the substrate vary with the X-ray take-off angle θ_t in this way can be explained as follows. Since the refractive index of materials for X-rays is slightly less than unity, the X-ray emitted from the inner bulk refracts at the surface as shown in Fig. 5
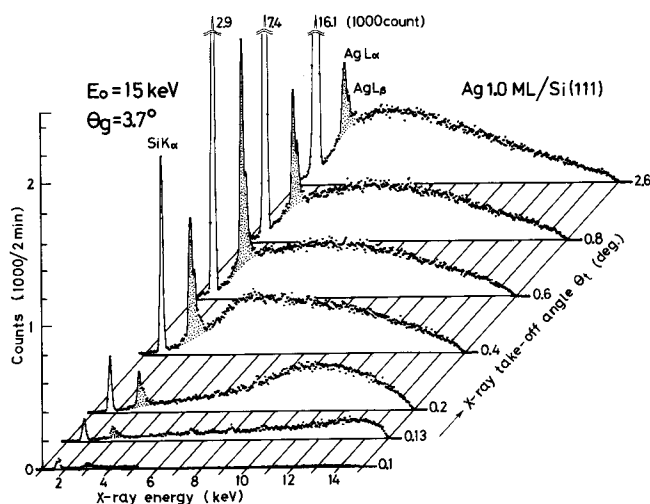

Fig. 2. X-ray spectra of RHEED-TRAXS taken at different take-off angles of the emitted X-ray from the Si(111) surface after Ag deposition of 1.0 monolayer. The energy E_0 and the glancing angle θ_g of the primary electron beam were 15 keV and 3.7°, respectively.
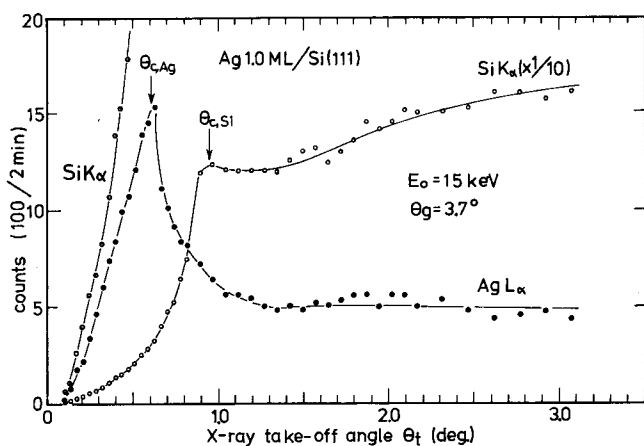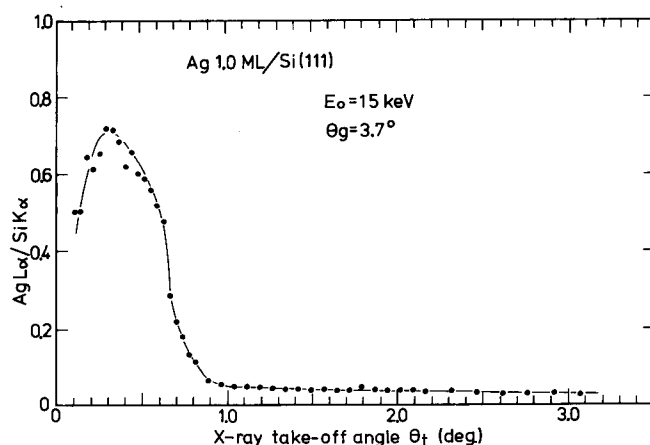

Fig. 3. Depedences of the absolute intensities (peak heights) of the characteristic X-rays on the X-ray take-off angle θ_t. The spectra were taken from the clean Si(111) surface after Ag deposition of 1.0 monolayer. Arrows show the critical angles for total reflection of each characteristic X-ray by silicon.

Fig. 4. Relative intensities of the characteristic X-ray (AgL_α line) from the deposit with respect to that (SiK_α line) from the substrate versus the X-ray take-off angle θ_t.
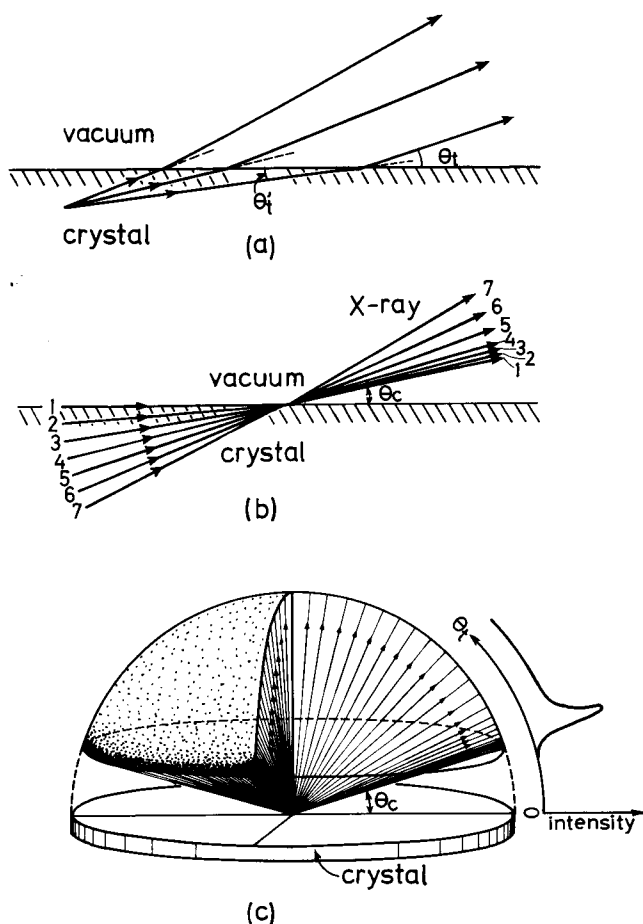
Fig. 5. Refraction effect of the emitted X-rays from the atom in the surface region. (a) Refraction of X-rays at the surface emitted from a point in the crystal. (b) The propagative directions of X-rays in the vacuum side change with the glancing angle θ_t' in the crystal. Although the X-ray emitted with a large θ_t' does not greatly change the propagative direction, the X-ray propagating with a small θ_t' changes its course remarkably. θ_c is the critical angle for total reflection. (c) The flux and the intensity distribution of X-rays emitted from an atom in the topmost layer.

(a). The take-off angle θ_t is slightly larger than the glancing angle θ_t' in the crystal. As θ_t' approaches zero, θ_t approaches a finite value θ_c, the critical angle for total reflection as shown in (b); hence, in the region of θ_t from 0 to θ_c, no x-rays would be emitted into the vacuum side. Therefore, if we ignore the self-absorption effect of X-rays, the intensity of the detectable X-rays emitted isotropically from an atom of the inner crystal is (1) zero for $0 < \theta_t < \theta_c$, (2) maximum at $\theta_t = \theta_c$ because the X-ray flux converges around $\theta_t = \theta_c$, and (3) a smaller constant for $\theta_t > \theta_c$. This intensity distribution along θ_t is similar to that of the AgL$_\alpha$ line shown in Fig. 3, except that the intensity of AgL$_\alpha$ remains for $0 < \theta_t < \theta_{c,Ag}$ (0.6°). This explanation of the intensity modulation by the refraction effect can thus also be applied qualitatively to the X-rays from the atoms in the topmost layer. The X-ray flux diverges into the vacuum from an emitting atom in the topmost layer as shown in (c). The discrepancy between theory and experiment in the intensity of AgL$_\alpha$ line for $0 < \theta_t < \theta_c$ may be attributed to the surface roughness, the absorption effect of X-rays, or the wave mechanical phenomenon including the distribution of refractive index at the surface. The features of the intensity curve of the AgL$_\alpha$ line versus θ_t shown in Fig. 3 can be understood in this way by the refraction effect of the X-ray. Since the SiK$_\alpha$ line is emitted from the region ranging from the surface to the inner bulk crystal, the features of the intensity curves of SiK$_\alpha$ line versus θ_t shown in Fig. 3 can be understood by integrating the X-ray intensity emitted at each depth layer, taking into account the absorption effect of both the primary electron beam and the emitted X-ray in the material, and the refraction at the surface.

The reason for the enhancement of the surface sensitivity shown in Fig. 4 is considered to be as follows. The X-rays, which are emitted from the atoms in the topmost layer in the direction parallel to the surface, are considered to propagate through a pass line "1" as shown in Fig. 5(b). Then, if the X-ray detector is set along the pass line "1" in Fig. (b), at the critical angle θ_c for total reflection, we can detect the X-rays emitted only from the atoms near the surface. This preferential detection of only the surface atoms may be furthered when θ_t is set between 0 and θ_c because of the absorption effect of X-rays. In this condition, furthermore, when the θ_c of the characteristic X-ray from the substrate is larger than that of the deposit X-ray as in the case of SiK$_\alpha$ and AgL$_\alpha$, the substrate X-ray scarcely reaches the detector. And, since θ_c is usually very small, the continuous background X-rays of the same energy as the marked characteristic line from the deposit, which come from the deeper bulk, are weak because of the absorption effect in the sample. Under these conditions, the S/N ratio (or peak to background ratio) of the detection of the surface composition increases about ten times as high as that of the previous experiment by Ino et al.[7] where θ_t was about 3°, far larger than the critical angle for total reflection (0.6°). Consequently, the detection sensitivity of Ag atoms on the Si (111) surface becomes comparable to or higher than that of AES.

The θ_t-dependences of the X-ray spectra can be summarized from two viewpoints, variation of the absolute intensity of the X-ray from the surface, and variation of the surface sensitivity (the detection efficiency of the surface composition) as follows. When the X-ray take-off angle θ_t is set to be the critical angle θ_c, for total reflection of AgL$_\alpha$ line from the deposited Ag atoms, its absolute intensity becomes two or three times as strong as that at $\theta_t > \theta_c$, and the detection efficiency for Ag atoms of 1.0 monolayer becomes 25 times as high as that at $\theta_t > \theta_c$. This phenomemon was observed also in the case of the Au/Si(111) system and hence these results can be generalized.

This X-ray spectroscopy is effective not only for chemical analysis of the topmost atoms, but also for chemical analysis of the deeper region from the surface. That is, if θ_t is set to be larger than θ_c, the X-ray from the inner bulk becomes detectable and the deeper region of the sample comes into view by means of X-ray. Thus, by changing θ_t, the depth profile of the element distribution can be determined non-destructively.

Moreover, in this RHEED-TRAXS the chemical composition and the periodicity of the atomic arrangement of the same surface area can be simultaneously examined. The X-ray spectra can be easily measured during the

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deposition onto the surface or during the desorption from the surface without interrupting RHEED observation. These features remarkably contrast this method with LEED-AES (Low Energy Electron Diffraction-Auger Electron Spectroscopy). RHEED-TRAXS will thus be an effective tool for the chemical analysis of solid surfaces, and especially favorable for MBE (molecular beam epitaxy) and the analytical electron microscope.

Acknowledgement

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