Proceedings of the 2nd International Conference
on the Structure of Surfaces (ICSOS II),
Amsterdam, The Netherlands, June 22–25, 1987

High Sensitivity Detection of a Few Atomic Layers of Adsorbate by RHEED-TRAXS (Total Reflection Angle X-Ray Spectroscopy)

S. Ino, S. Hasegawa, H. Matsumoto, and H. Daimon

Department of Physics, Faculty of Science, University of Tokyo,
Bunkyo-ku, Tokyo 113, Japan

1. Introduction

In detecting X-rays excited in RHEED (reflection high energy electron diffraction) experiments [1,2], when the X-ray take off angle is set to be the critical angle for total reflection of the characteristic X-ray emitted from deposited atoms on a surface, the detection efficiency for the deposit was found to become drastically higher owing to the refraction and absorption effects of the X-ray [3]. We called this method RHEED-TRAXS (total reflection angle X-ray spectroscopy).

2. Take off angle dependence of X-ray spectra obtained from Si(111)-Au surface

Figure 1 shows four X-ray spectra measured by applying RHEED-TRAXS method, changing the take off angles of emitted X-rays obtained from a clean Si(111) surface on which one monolayer (1.2 Å) of Au is evaporated. When the take off angle of the emitted X-rays changed to a, b, c, and d, the peakheight of the characteristic X-rays and the form of the white X-rays changed as shown in Fig. 1 in which the spectra are normalized to SiK_α line from the substrate.

Figure 2 shows a detailed take off angle dependence of the peakheight of SiK_α, AuM, AuL_α and AuL_β. With the increase of the take off angle θ_t, the intensity of SiK_α line from the substrate increases slowly at first, rapidly subsequently, and then slowly, making a shoulder like form at about 1.0° of θ_t. This θ_t dependence accords perfectly with that obtained from Si(111) surface evaporated one monolayer of Ag atoms [3]. On the contrary, the intensity of AuM from evaporated Au atoms increases and forms one peak at about 0.8°, then decreases and becomes nearly constant at the higher take off angles. AuL_α and AuL_β change similarly, but make each peak at different take off angles and different constant values at the higher take off angles.

To see the change of a relative value of AuM, AuL_α and AuL_β against SiK_α, the value of AuM/SiK_α, AuL_α/SiK_α and AuL_β/SiK_α are plotted against the change of θ_t as shown in Fig. 3. These curves correspond to the take off angle depen-

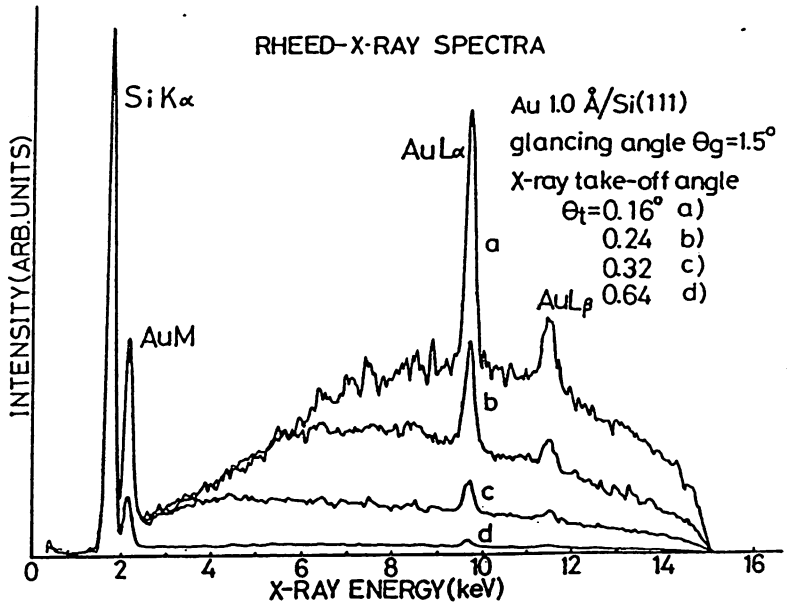

Fig.1. X-ray spectra of RHEED-TRAXS detected at different take-off angles a,b,c and d measured from the Si(111) surface evaporated 1.0 ML of Au. The spectra are normalized to SiK_α line from the substrate.

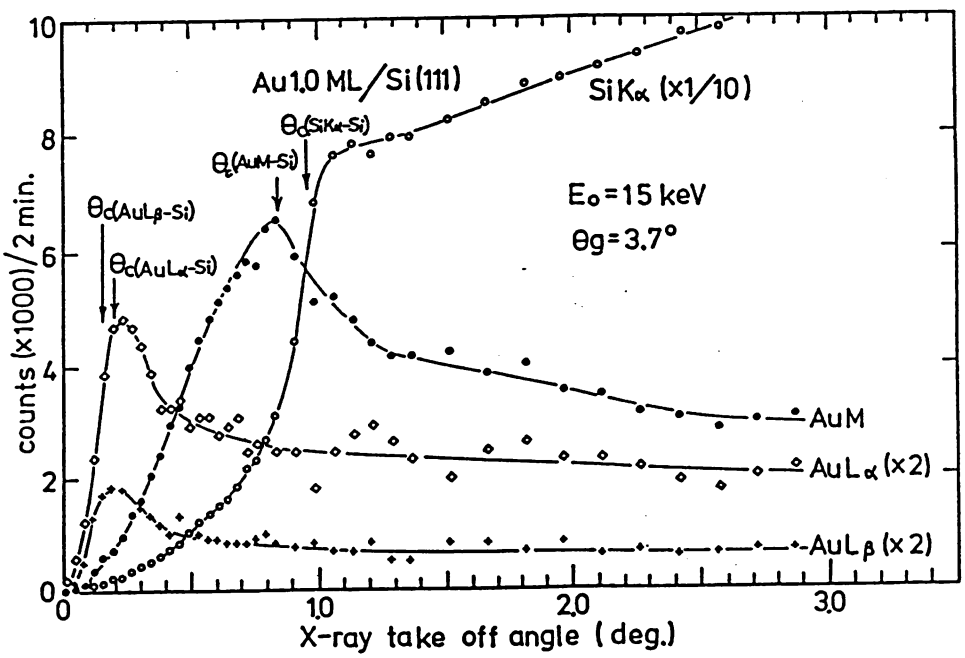

Fig.2. Take-off angle dependences of the absolute intensities of characteristic X-rays SiK_α, AuM, AuL_α and AuL_β. The spectra were measured from the same samples as Fig. 1. Arrows show the critical angles for total reflection of each characteristic X-rays by Si.

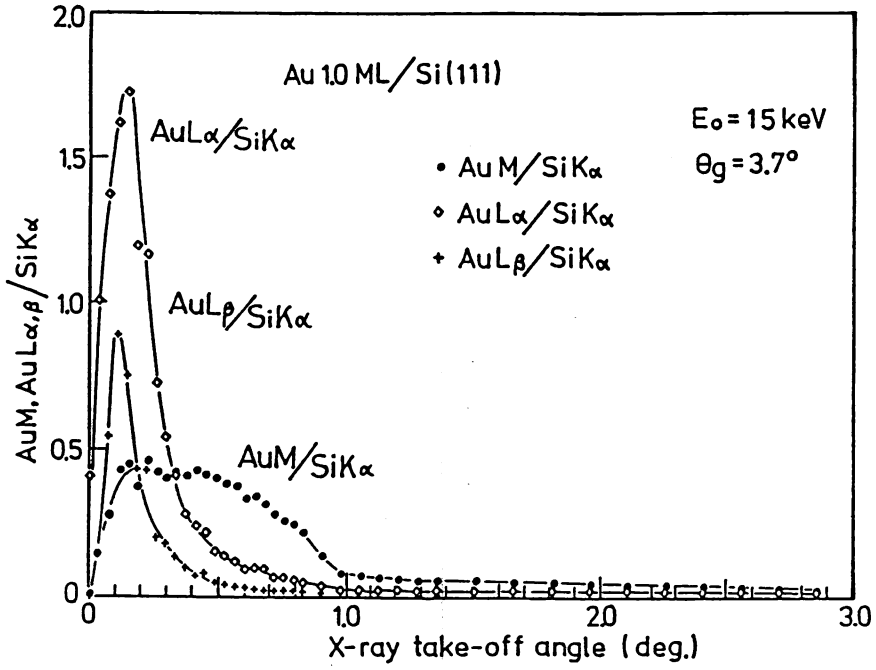

Fig.3. Take-off angle dependences of AuM/SiKα, AuLα/SiKα and AuLβ/SiKα.

dence of the detection sensitivity at surface. For $\theta_t > 1.0°$, the detection sensitivities of one monolayer Au atoms at the surface are not high (this condition corresponds to the previous experiment [2]) but for $\theta_t < 1.0°$, they become very high, although depending on the X-ray energies. At the highest detecting condition, the intensity of the characteristic X-rays of only one monolayer of Au atoms becomes comparable to that of SiKα from the substrate. Especially, for AuLα, extremely high detection sensitivity is obtained, which is also seen in Fig. 1.

3. An Explanation of Principle for RHEED-TRAXS

Figure 4 illustrates the phenomenon of total reflection of X-rays, for small glancing incidence angles. When the glancing angle θ of the X-rays is smaller than the critical angle θ_c of the total reflection, $\theta < \theta_c$, the incident X-rays reflect at the surface O and proceed along BOB'. For $\theta > \theta_c$, the incident X-rays refract and proceed along AOA". If AO approaches to CO, OA" approaches also to OC". X-rays incident with the total reflection angle θ_c reflect almost along COC', but proceed partly to OC" direction within a small distance from O if absorption effect is not neglegible.

Taking into consideration the above phenomena, it is easy to explain how the X-rays excited by electron beam proceed at the surface. In the case of the X-rays which were emitted at S_0 excited by the electron beam proceed parallel to the

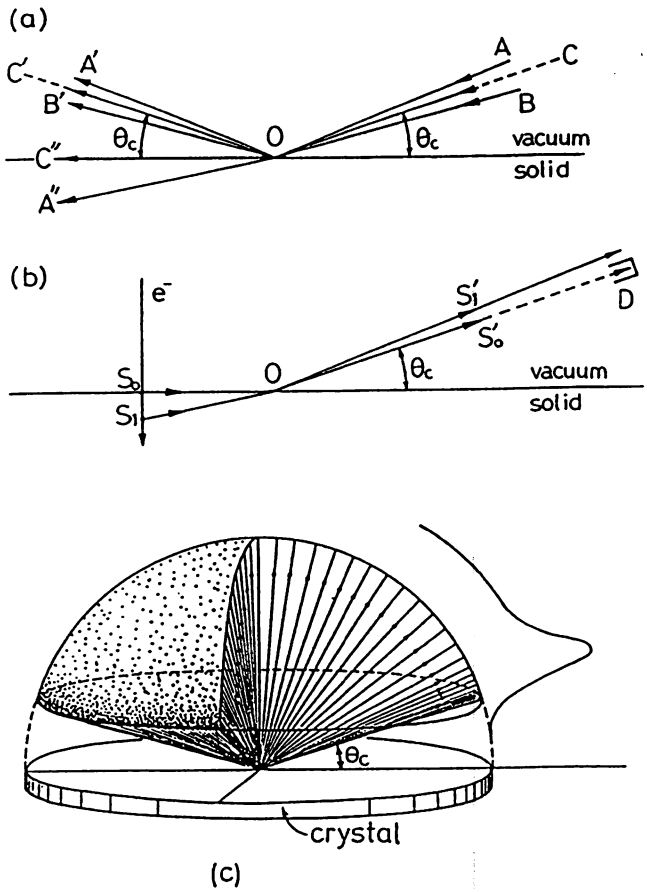

Fig.4. (a) An Explanation of the total reflection of X-rays. (b) Detector D put along θ_c direction catches only the X-rays which are emitted at the surface S_0 excited by the electron beam and proceed to the S_0O direction, because they should proceed along S_0OS_0' by the refraction effect at O. (c) An illustration of the change of X-ray flux produced with equal intensity to all direction at S_0. The figure at the right hand side shows a polar angle dependence of the detected X-ray intensity.

surface, they refract at the surface O and proceed along S_0OS_0'. Thus, if the X-ray detector D with fine slit is located at the position corresponding to the total reflection angle θ_c, the detector catches only the X-rays which were excited at the surface S_0 and proceed parallel to the surface along S_0OS_0'. Similarly, if the detector D is located at a take off angle little larger than θ_c, the X-rays emitted a little deeper point S_1 and proceed along S_1OS_1' should be detected. We cannot give more detailed explanations here, but this method has a very high sensitivity for the detection of a few layer adsorptions at the surface [3]. The X-ray flux produced from S_0 with equal intensity to all directions may be changed as shown in Fig. 4(c). The figure at the right hand side in (c) shows a polar angle dependence of detected X-ray intensity.

In the case of AES, there exists a very large background and small Auger peaks. On the other hand, RHEED-TRAXS shows very large characteristic X-ray peaks compared with the small background, giving higher sensitivity than AES. Besides, the Auger electron excited inside the crystal are emitted into the vacuum with a complicated process including multiple scattering and inelastic scattering, but the process of X-ray excitation and emittance into the vacuum is very simple, having an advantage for quantitative measurements.

4. Annealing Effects of Ge Films on Si(111) Surface

Figure 5 shows take off angle dependences of SiK_α and GeK_α peaks taken from the Si(111) surface which was evaporated one monolayer of Ge at room temperature. The curve of SiK_α is similar with that in Fig. 2. The take off angle dependence of GeK_α is also similar with that of AuM, AuL_α and AuL_β, except that the peak is sharp and high.

The sample on which 30 monolayers of Ge were evaporated shows take off angle dependences of SiK_α and GeK_α peaks as in Fig. 6. The peak position of GeK_α curve shifted a little to the larger side. This is explained in that the GeK_α X-rays now refract with the evaporated Ge film which have a higher electron density than the Si substrate. The fact that the width of the peak in GeK_α curve became wider is showing that Ge film is not perfectly flat. For $\theta_t < 0.75°$ the SiK_α from the substrate is hardly detected. For $\theta_t > 0.75°$ the SiK_α becomes detectable and increases linearly. The critical angle α_c, that for the smaller angle than α_c the characteristic X-ray from substrate cannot be detected, increases corresponding to the increase of the Ge film thickness. Thus the film thickness can be measured directly by observing the value of the critical angle α_c.

When the sample in Fig. 6 was heated at 400°C, the peak of GeK_α became sharper, indicating that the Ge film became uniform by the heating. Besides, the critical angle α_c in SiK_α curve shifted to the larger side, $\alpha_c \approx 0.90°$, indicating that Ge film became uniform and the boundary of Si and Ge became sharp. From the above facts, we can conclude that by

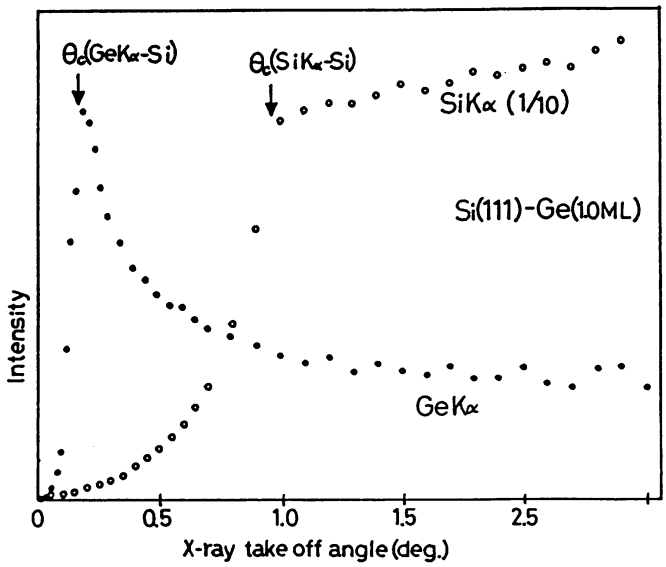

Fig.5. Take-off angle dependences of the absolute intensities of X-rays SiK_α and GeK_α measured from Si(111) surface with 1.0 ML of Ge. Arrows show the critical angles for total reflection of each X-rays by Si.

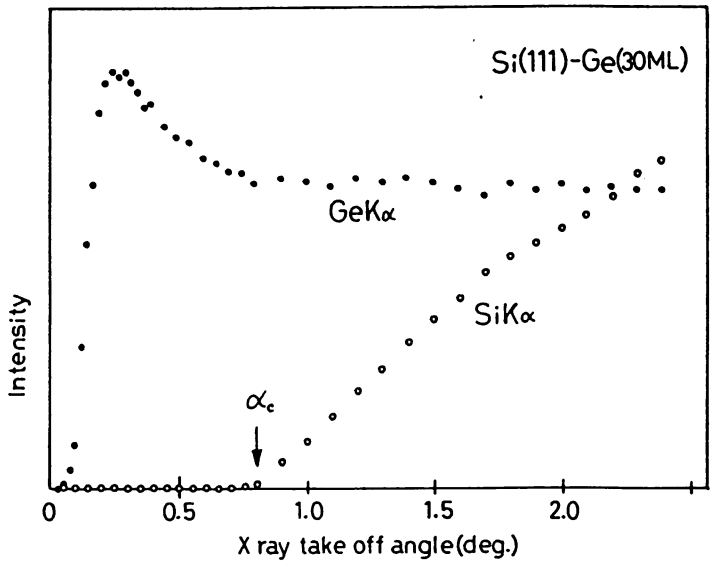

Fig.6. Take-off angle dependence of the absolute intensities of X-rays SiK_α and GeK_α measured from Si(111) surface evaporated 30 ML of Ge. SiK_α hardly detected for smaller take-off angle than α_c. We can know the film thickness directly from the value α_c.

the annealing at 400°C, Ge film became uniform, but the alloying of Ge and Si hardly happened. Next when the sample of Fig. 6 was heated at 600°C, the curve of GeK_α hardly changed from that of Fig. 6, but α_c shifted to the left side, $\alpha_c \approx 0.65°$. This effect is explained in that the boundary of Si and Ge became diffuse by the alloying effect. Thus, we can conclude that for the annealing at 400°C, the alloying of Si and Ge does not happen although the evaporated Ge film became a uniform structure. However, for the higher annealing temperature at 600°C, the alloying was actually starting to occur.

Thus, RHEED-TRAXS is very useful not only for the sensitive detection of a few atomic-layer adsorbate, but also for studies of thicker films and boundaries such as chemical analysis, growth process, structure changes and alloying effects.

Reference

[1] S. Ino: Japan J. Appl. Phys. 16, 891 (1977)
[2] S. Ino, T. Ichikawa ans S. Okada: Japan J. Appl. Phys. 19, 1451 (1980)
[3] S. Hasegawa, S. Ino, Y. Yamamoto and H. Daimon: Japan J. Appl. Phys. 24, L387 (1985)
[4] S. Hasegawa, H. Daimon and S. Ino: Surf. Sci. (1987) in press.