DEVELOPMENT OF TOTAL REFLECTION X-RAY DIFFRACTOMETER FOR STRUCTURAL ANALYSIS OF ULTRA-THIN FILMS BY LAUE METHOD

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A new evaluation method for molecular structure and orientations in ultra thin films has been developed. The principle of the measurements and the system construction utilizing the Laue diffraction method connected with total X-ray reflection are explained. Successful applications to the "In-situ" observation studies on phase transition and epitaxial growth mechanism in evaporated organic thin films are also described.

1. Introduction

Recently, organic electronic materials, which have been used mainly as a passive material such as insulating parts, have been recognized as one of the most important promising electronic materials and attracting many researcher's interests based on the concept of the molecular devices. Moreover, it has been considered that the principal limitations exist for future electronic devices in the present inorganic electronic materials composed mainly of silicon, germanium and compound semiconductors, and also pointed out the possibilities of the evolutionary development will be made by utilizing superior functionalities of organic molecules.

In order to fabricate the functional organic thin films and to create new organic devices such as quantum electronic molecular devices, it has been indispensable to develop the methods of controlling the molecular structure and orientations at atomic and/or molecular levels. As the techniques of structural and/or orientational control, the following methods have been utilized; a wet process such as Langmuir-Blodgett technique, a dry process such as vacuum deposition, sputtering, chemical vapor deposition (CVD) and molecular beam epitaxy (MBE), etc.

To form exactly thin films as one designs and wishes, it is also essential to evaluate the molecular structure as well as orientations in the fabricated films. Especially the "In-situ" observation during the thin film formation process has been considered to be the most useful evaluation technique for thin films, which can throw the light to elucidate the mechanisms of the molecular orientation and epitaxial growth.

Although the electron diffraction methods such as a reflection high energy electron diffraction (RHEED) and a low energy electron diffraction (LEED) have been widely used for the "In-situ" observation in the structural evaluation of thin films and the surfaces and has made remarkable achievements, there exist some difficulties in the structural analysis due to the electron multiple reflections in the dynamical diffraction effect and the electron beam damages especially for the organic materials. Moreover, these methods can not be applied when the structural evaluation is attempted for the molecules growing under electric and/or magnetic fields, or at a plasma state. Therefore, some alternative methods, that is, X-ray diffraction methods should be employed to elucidate the transient structures of growing organic crystals without any damage.

By the way, one of the present authors (T.H.) proposed and demonstrated first in 1971 the applicability of the total reflection phenomenon to the micro-chemical fluorescent analysis [1]. Since then, the total reflection X-ray fluorescent analysis (TXRF) method has been recognized to be one of the most sensitive evaluation methods and in these years is extensively introduced in the production line of semiconductor wafers, as an epoch-making nondestructive inspection method of impurities, and further its application area is now spreading over various research fields.

As further extension, one may get the idea to apply the TXRF analysis method to the diffraction studies. This sort of studies were already reported concerning with the observation of the
interfacial lattice matching in epitaxially grown compound materials [2] and the "In-situ" observation utilizing synchrotron X-ray radiation [3]. While, the present authors also have developed the energy dispersive-type total reflection X-ray diffractometer (TRXD) [4] and applied to the observation of molecular structure and orientations in ultra thin organic films [5-7]. Since the microchemical analysis (TRXF) and (TRXD) studies utilizing the total reflection X-ray phenomena were reviewed in a previous volume [8], the readers are suggested to refer it for further details.

In this review, a new proposal is presented that the full information on molecular structure and orientations in ultra thin films can be obtained by combining the color Laue X-ray method with the total reflection phenomena, including its diffraction condition and the constitutions of the apparatus.

Furthermore, some applications are described concerning the "In-situ" observations of the phase transition and orientations with temperature variation, and the epitaxial growth in the evaporated organic thin films.

2. Total Reflection Effect and Difractons of X-rays

When the incident characteristic X-rays with the wavelength of $\lambda$ go through at the very small glancing angle ($\phi$) from the vacuum/air to the films on the substrate as shown in Fig. 1, the critical angle ($\phi_c$) in the total reflection is expressed by Eq. (2.1)

$$\phi_c = \frac{\omega n_o}{\pi mc^2}$$

where $m$, $e$, $c$ and $n_o$ are respectively the mass, electric charge of an electron, the light velocity in vacuum and the number density of electrons in thin films.

On the other hand, when the white X-rays are used as an incidence, we obtain as an energy dispersive type diffraction condition the next equation (2.2) for the critical energy ($E_{c,vo}$) in the total reflection at the given glancing angle ($\phi$),

$$E_{c,vo} = \frac{hc}{\phi} \sqrt{\frac{\omega^2 n_o}{\pi mc^2}}$$

where $h$ is the Planck’s constant. Similarly, at the boundary between the thin films and the substrate, the critical energy ($E_{c,os}$) is given as follows,

$$E_{c,os} = \frac{hc}{\phi} \sqrt{\frac{\omega^2 (n_s - n_o)}{\pi mc^2}}$$

where $n_s$ is the number density of electrons in the substrate materials. In general, the number density of electrons in organic materials is much lower than that in substrate material such as metals, crystals, glasses and so on, so that $E_{c,os}$ becomes larger than $E_{c,vo}$. For this reason, if the energy of the incident X-rays, $E$, is in the range of $E_{c,vo} < E < E_{c,os}$ the X-rays can pass through the organic thin films and then be totally reflected at the boundary between the interface of thin films and the substrate. While, X-rays with the energies larger than the $E_{c,os}$ are refracted into the substrate, and generate the obstructive noisy scattering X-rays, therefore the high energy parts in the incident X-rays should be cut effectively by some proper tools such as a lowpass filter method using an optical flat.

The energies, $E_{hkl}$, of the diffracted white X-rays in the thin films are precisely analyzed by a solid state X-ray detector (SSD) and converted into the lattice spacings, $d_{hkl}$, of crystallite in thin films using the next Eq. (2.4),

$$E_{hkl} = \frac{nch}{2d_{hkl} \sin \theta}$$

![Fig. 1 Schematic picture of the principle under total reflection diffraction condition on the boundary of thin films and substrate. Symbols are in the text.](image-url)
where \( n \) and \( \theta \) are the order of reflection and the Bragg angle, respectively.

Figure 2 shows a schematic picture of the apparatus which has been utilized in the early stage of this study (4) and to observe the stacking layer structures. This type of system is called a normal type diffraction apparatus, because the reciprocal lattice vectors are normal to the substrate. It is important to note here that in this apparatus all the X-ray components of an X-ray tube, Soller slits, and SSD can be fixed without any rotational movement, therefore this measuring system can be easily applied even to the measurements under the special environments such as high pressure, high vacuum, high and low temperatures and so on. This might be also an another advantage of this type measuring system over the conventional \( \theta/2\theta \) method. However, there exist some limitations in this type diffraction method, namely although the only molecular structures and orientations whose reciprocal lattice vectors are in a part of the scattering plane normal to the substrate surface are analyzed, the X-rays diffracted from the molecular crystals with other directional lattice vectors can not be detected in principle. To overcome this problem, we are developing further a new-type total reflection X-ray diffractometer based on a color Laue method, which make it possible to observe the whole space of the reciprocal lattice vectors in the thin films. Further consideration for the color Laue method is described next section.

3. Energy Dispersive Laue Method

Photo 1 shows the color Laue photograph of a silicon and a diamond single crystals. The difference between a common Laue method and a color one exists whether the energy of the diffracted X-rays in Laue spots can be analyzed with colors or not. This situation is very similar to the visible light spectra analysis (rainbow spectra), where the color discrimination is conducted by corresponding the high energy (short wavelength) diffraction and the low (long) one to violet and red, respectively. As demonstrated in Photo 1, the two kind of single crystals belonging to the same space group of the crystal structure, diamond structure (Fd3m), can be easily distinguished from the difference in the colors of Laue spots. This fact suggests that one can get the very useful information on the crystal structure from the energy analysis of the Laue spots, which is lost in the common Laue method. The details on this color Laue method was already described in our previous paper [9].

Here, we would like to explain briefly the color Laue method, the outline of which is illustrated schematically in Fig. 3. The white X-rays, which are generated by the scanning electrons synchronizing to CRT display at the thin film target irradiate the crystal at the various angles. Diffracted X-rays from the crystal area limited with the pinhole collimator are detected with SSD, the detected X-rays are analyzed with a multi-channel pulse height analyzer, and then converted correspondingly to three different colors of red, green and blue with the aid of a computer. Finally, the color Laue pattern is displayed on a CRT. The optical system employed here is similar to that of usual Laue method except the inverse optical path of X-rays and the position of SSD.

In general, the structural analysis for the highly oriented ultra-thin films is extremely difficult, because such films are similar to the single crystal in Laue method, but the \( \chi \omega \) operation using in single crystal structure determination can not be conducted under the total reflection condition. Therefore, the application of this color Laue method to the TRXD/TRXF makes first possible to obtain simultaneously the infor-
mation of the crystal structure and its orientation in any reciprocal lattice space, which cannot be obtained in principle by other methods. On the basis of this concept, we are now developing the new system which can measure whole reciprocal lattice space vectors in the epitaxially grown organic films.

4. Total Reflection X-ray Diffractometer for Whole Reciprocal Lattice Space in Thin Films

Figure 4 shows the optical system to measure the structure and orientations in thin films by utilizing the color Laue method. Incident white X-rays, which are collimated and their higher energy side is cut by the optical system consisted of an optical flat and a Soller slit, are injected into the thin films on a substrate at a very small glancing angle under the total reflection condition. The diffracted X-rays, namely Laue spots, are detected and analyzed in the energies by the optical system composed of a Soller slit and a SSD, the relations between scattering angle ($2\theta_g$), a horizontal angle ($2\theta_h$) and the vertical ($2\theta_v$) is given by the equation in Fig. 4. If the surface of substrate is defined here the horizontal
plane, the reciprocal lattice vectors in the arbitrary scattering plane with an angle of \( \xi \), denoted azimuthal angle, to the horizontal plane can be obtained by the vector analysis in the horizontal and vertical goniometers. Thus, we will be able to get the parameters for the computer operation by the vectorial calculation of the spherical solid angle as equations listed in the figure. In addition, it is necessary to control the resolution vector (\( \vec{R} \)) of the Soller slit so as to be parallel to the scattering plane in the case of a scattering plane being vertical, that is \( \xi = \pi/2 \), for the observation of stacking structure, or perpendicular in the case of \( \xi = 0 \) for the "In-plane" observation. Furthermore, considering a crystal symmetry, we can observe the whole reciprocal lattice space in the range of \( 0 \leq \xi \leq \pi/2 \) by rotating the substrate around its normal. This has never been possible by any other methods.

5. The Applications of the Total Reflection X-ray Diffractometer to "In-situ" Observation for Ultra-thin Films

The "In-situ" observation system for the organic thin films during an evaporation process in high vacuum is schematically illustrated in Fig. 5. Details in this system are described in a previous paper [10]. The optical system is constituted of two Soller slits for the incidence and diffracted X-rays and SSD, and please refer the previous section for the details. In actual experiments, all parameters, such as a degree of vacuum, an evaporation and a substrate temperatures, an evaporation rate and a thickness of film, are recorded by a multi-pen recorder, providing the useful information for the "In-situ" observation in the thin film forming process. Furthermore, in order to observe the epitaxial growth, the precise rotation mechanism of the substrate is installed.
5.1 The "In-situ" Observation in the Organic Evaporated Thin Films by the in-plane Diffractometer

Figure 6 shows the Ewald's construction with an in-plane X-ray diffraction geometry, namely, the scattering plane is in organic thin films on a substrate, in which the linear molecules orient their molecular axis to laterally or normally to the substrate. Therefore, only the reciprocal lattice vectors \((\mathbf{q}_{\text{hk}0})\) of the molecular crystallites existing in this scattering plane are naturally detected.

Figures 7(a) and (b) show the in-plane X-ray diffraction profiles of an as-evaporated, as well as an annealed thin film of linear molecules \((n\text{-C}_{33}\text{H}_{68})\) on the SiO\(_2\) glass substrate. There exist the four peaks denoted the 110 and 200 reflections in an orthorombic crystal of \(n\text{-C}_{33}\text{H}_{68}\) and the characteristic X-rays of MoK\(_\alpha\), K\(\beta\) from Mo target used as a white X-ray source.

Our attention is paid on the ratio of the integrated intensities of the 110 and 200 reflection peaks, \(I_{110}/I_{200}\). This value is notably different between the value of the as-evaporated, 2.33 and the annealed one 3.11, that is, showing an increase of the ratio with an annealing process. Also, the value of \(I_{110}/I_{200}\) for the annealed sample is almost same as that of the powder sample with random molecular orientation, providing some information on the molecular orientation in the evaporated films, as described below.
amorphous SiO₂ glass substrate surface. For further details, please refer our previous paper [10].

Figure 9 shows the changes in in-plane X-ray diffraction profiles of the n-C₃₃H₆₈ evaporated films with different film thickness observed during an evaporation process. Besides the two reflections, 110 and 200, of the molecular crystallites, the characteristic X-rays, MoKα and Kβ, denoted above, are observed which are due to the elastic Rayleigh scattering from mainly molecules in thin films and the substrate scattering are eliminated under the total reflection condition. Therefore, the intensity data showing an increase with the thickness of the thin films will become good and reliable indicator of the film thickness as those of a quartz oscillation monitor.

The film thickness dependencies in the integrated intensities of these peaks, Rayleigh scattering, and 110 and 200 reflections are shown in Figs. 10(a), (b) and (c), respectively. In contrast to monotonous increase in the intensities of 200 reflection with the film thickness, the one of 110 reflection obviously changes the thickness dependency from a low to a high rate at about 50 nm in thickness. Hence, it is suggested that the alteration in molecular orientation might
occur when the film thickness reaches around this value, probably because of the weak interaction between the $n$-C$_{33}$H$_{68}$ molecules and the SiO$_2$ substrate surface.

5.2 "In-situ" Observation of Epitaxial Growth

It has been extensively known that an epitaxial growth of the molecules in the evaporated organic thin films onto cleaved ionic single crystals is observed by an electron microscope and/or diffraction, and so on. Utilizing an electron microscope and diffraction, it was reported that the molecules in the evaporated n-paraffin thin films onto the KCl single crystal orient their molecular axes (c axis) to the (110) direction of KCl crystal as shown in Fig. 11(a) and adsorb their (110) plane facing to the (100) plane, namely, surface of KCl [11] as illustrated in Fig. 11(b). However, in these electron diffraction methods, it is difficult to conduct the "In-situ" observation because of some problems in sample preparations such as the specimen isolation from substrate on water, and so on.

In order to control the molecular arrangement and/or orientation in vacuum evaporated organic films, the epitaxial growth has been strongly expected as one of the hopeful and useful controlling methods. Moreover, the elucidation of the growth mechanism is very important and indispensable to construct the molecularly ordered films.

On this point of view, it is essential to develop the method of "In-situ" observation, so that we applied our TRXD method to the "In-situ" observation of the epitaxial growth mechanism, then could obtain the results similar to those obtained by the electron microscopy, in addition some new information which have been never gotten by any other methods. Details of those results are described in our paper [12].

In this review, only the outlines of the measuring principle and the construction in the TRXD apparatus and experimental results are explained. A KCl single crystal substrate with a precisely made rotational mechanism is incorporated by way of a vacuum feed through into the vacuum chamber as illustrated in Fig. 5, as already presented in the previous section. Figure 12(a) shows the "In-plane" diffraction geometry with the substrate rotation mechanism, where the scattering plane including not only the vectors of diffraction and incidence X-rays but also the reciprocal lattice vectors of the molecule and KCl crystals are parallel to the

![Fig. 11](image1.png)

**Fig. 11** Schematic drawing of $n$-C$_{33}$H$_{68}$ epitaxially grown thin films on a cleaved (001) surface of KCl single crystal; (a) molecular axis (c-axis) oriented to KCl (110) direction, (b) lateral oriented (110) molecular packing observed by an "in-plane" TRXD system.

![Fig. 12](image2.png)

**Fig. 12** Schematic diagram of the "In-plane" TRXD geometry for epitaxial growth observation; (a) The relations between a single crystal substrate rotated about its normal axis and diffraction geometry. (b) The Ewald's construction for energy dispersive "In-plane" TXRD. Symbols are in the text.
substrate surface. By rotating the substrate, both reciprocal lattice vectors rotate and satisfy the Bragg diffraction condition at a given rotating angle (ω), called here the "azimuthal angle". Therefore, we can know the mutual direction of both vectors, in other word, the orientational relation ship between the epitaxial grown thin film and the substrate crystals.

Further detailed illustration is shown in Fig. 12(b), using Ewald's construction with the spheres of reflection, whose radii are proportional to the incident white X-ray energies, where $E_{c,\nu}$, $E_{c,\cos}$ and $E_{hkl}$ were denoted in the previous section. The reciprocal lattice vectors of $OH_0$ and $OH_s$ are of the molecular and substrate crystals, respectively. When these vectors in the reciprocal lattice space ($hk0$), namely in-plane, are coupled to the reflection spheres, diffracted X-rays can be detected at the same direction ($2\theta$) at the same time.

Figure 13(a) shows a series of X-ray diffraction profiles of $n$-C$_{33}H_{68}$ as-evaporated films on a KCl single crystal observed at different azimuthal angle (ω). At ω=0 (where the intensity of KCl 220 reflection is the maximum), the intensities of 110 and 200 reflections of molecules also show the maxima. This fact suggests that the molecular axis (c axis) crystallizes epitaxially parallel to the (110) direction of a KCl single crystal. Our X-ray results are basically coincident with the findings of Ashida et al. [11], by means of electron microscopy and electron diffraction.

Moreover, to examine the time relaxation in the molecular crystallite, we carried out in-situ measurements for the sample kept for 2 days under a high-vacuum condition after an evaporation. As shown in Fig. 13(b), it is clearly found that subpeaks in the intensity distribution appeared at azimuthal angles (ω) of about ±5°, suggesting that some orientational relaxation in the crystal arrangement takes place during the keeping time. The relative integrated X-ray intensities of this relaxed and the as-evaporated thin film samples with the azimuthal angle (ω) are shown in Fig. 14. Since this kind of phenomenon has never been observed for the case of bulk samples, it might be suggested that the interactions between the $n$-C$_{33}H_{68}$ molecules in thin films and the surface atoms of KCl single
crystal mainly gives rise to this phenomena and the stress induced by the lattice mismatching may be relaxed by inclining the molecular axis.

Figure 15 shows the lattice spacings in 110 diffraction with the azimuthal angle (ω), comparing with that of bulk samples. These data reveal that when the azimuthal angle is small, the molecules are extended in length, that is, under a tensile stress, while large angle, under a compressional stress. It is expected that the detailed information obtained by these X-ray diffraction in experiments might be greatly useful for to elucidate the mechanism of the epitaxial growth.

6. Summary
We described the fundamental principle for the energy dispersive total reflection X-ray thin film diffractometer. Especially, it was stressed that the introducing the color Laue method to the total reflection X-ray diffraction should be indispensable for evaluating the molecular structure and orientations in ultra-thin films. Moreover, by constructing practically such the system, it was proved that the measurement of the whole reciprocal lattice space in thin films becomes possible even under the total reflection condition. Then, some applicable measurements utilizing the total reflection in-plane X-ray diffractometer equipped with the vacuum evaporation chamber were presented, proving to be useful.

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