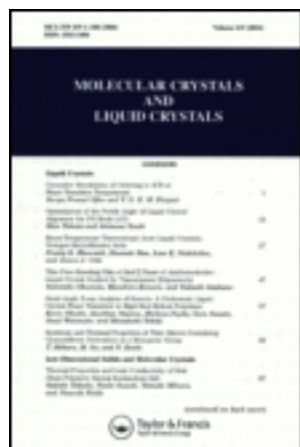


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Kenji Ishida^a, Toshihisa Horiuchi^a & Kazumi Matsushige^a

^a Department of Electronics Science and Engineering, Faculty
of Engineering, Kyoto University, Yoshidahonmachi, Sakyo-ku,
Kyoto, 606-01, Japan

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HETEROEPITAXIAL GROWTH OF FLUORINATED LONG CHAIN MOLECULE ON $\text{CaF}_2(111)$ AND GOLD COATED $\text{KCl}(001)$

KENJI ISHIDA, TOSHIHISA HORIUCHI and KAZUMI MATSUSHIGE

Department of Electronics Science and Engineering,

Faculty of Engineering, Kyoto University,

Yoshidahonmachi, Sakyo-ku, Kyoto 606-01, Japan

Abstract Heteroepitaxial growth of fluorinated long chain molecules ($n\text{-C}_{20}\text{F}_{42}$) on two different substrates was evaluated by an energy dispersive grazing incidence x-ray diffractometer. It was found that the $n\text{-C}_{20}\text{F}_{42}$ molecules grow normally and epitaxially on the $\text{CaF}_2(111)$, aligning their $\langle 100_{\text{hex}} \rangle$ in the $\text{CaF}_2\langle 110 \rangle$ with the inclination of about 12° , through slight interactions between the terminal CF_3 and CaF_2 surface. While, the molecules evaporated on the Au coated $\text{KCl}(001)$ was revealed to form polycrystalline structures in in-plane direction, due to the surface roughness and difference in the grain sizes between $n\text{-C}_{20}\text{F}_{42}$ and Au films.

1. INTRODUCTION

Recently, there are considerable interests in developing the effective methods for the control of molecular organization, because the highly oriented organic molecules have the potential for novel optical and electronic applications. Heteroepitaxial growth in a vacuum evaporation process is capable of controlling the molecular orientation without any contaminations¹. However, since the epitaxial structure is affected by the various factors, such as the kind of crystal substrates, their temperature, the evaporation rate and so on, it is difficult to predict their behavior exactly. Therefore, the characterizations of the epitaxially grown molecular films are indispensable in clarifying its mechanism and in developing a molecular arrangement technique.

We previously reported that perfluoro- n -alkane molecules ($n\text{-C}_{20}\text{F}_{42}$) evaporated on a $\text{KCl}(001)$ crystallize epitaxially, aligning the molecular chain axes in the thin films normal to the substrate, and their $\langle 100_{\text{hex}} \rangle$ parallel to the $\text{KCl}\langle 110 \rangle$ ^{2,3}. In this study, the epitaxial

growth of the $n\text{-C}_{20}\text{F}_{42}$ molecules, evaporated on $\text{CaF}_2(111)$ crystal as well as Au coated on $\text{KCl}(001)$, were investigated by an energy dispersive grazing incidence x-ray diffraction (ED-GIXD) method in order to clarify the influence of substrate materials. The epitaxial behavior of long chain molecules was discussed, based on the variations in the in-plane diffraction peaks at different azimuthal angles(ω) of the substrate.

2. EXPERIMENTAL

The sample used in this study was $n\text{-C}_{20}\text{F}_{42}$ (perfluoro- n -eicosane) of 97% purity and no further purification was carried out. Air-cleaved faces of $\text{CaF}_2(111)$ and Au thin films of 60nm thickness, evaporated on $\text{KCl}(001)$ at 400°C in a vacuum of 10^{-4} Pa, were used as the substrate. The $n\text{-C}_{20}\text{F}_{42}$ thin films were fabricated by vacuum evaporation method. The substrate was preheated at 300°C for 6h in order to obtain a clean surface and kept at -30°C under a vacuum of 10^{-4} Pa. The samples were sublimated vertically from a quartz crucible source. The growth rate and average thickness was controlled to be about 0.5nm/min and 10nm, respectively, by using a quartz crystal oscillator.

The fabricated films were investigated by the ED-GIXD at room temperature under an atmospheric pressure. The ED-GIXD can effectively analyze the crystal structure as well as its orientation, including the epitaxial growth in thin films, without any obstructive scattering noise from the substrate. The details of our ED-GIXD system have been described elsewhere⁴⁻⁶

3. RESULTS AND DISCUSSIONS

A. $n\text{-C}_{20}\text{F}_{42}$ on $\text{CaF}_2(111)$

Figure 1 shows the in-plane diffraction profile of the $n\text{-C}_{20}\text{F}_{42}$ thin films evaporated on $\text{CaF}_2(111)$ substrate, observed at $2\theta=11.31^\circ$. The three peaks were detected at $E=12.93$, 17.47 and 33.28 keV,

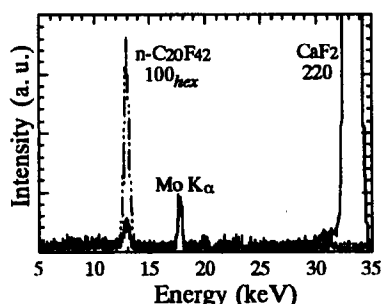


FIGURE 1 The X-ray diffraction profile of $n\text{-C}_{20}\text{F}_{42}$ thin films on $\text{CaF}_2(111)$ substrate, observed at $\omega=0^\circ$ (solid line) and $\omega=12^\circ$ (broken line).

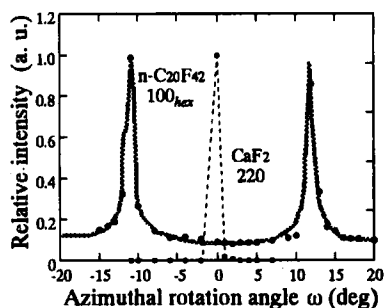


FIGURE 2 Angular variation in the relative intensities of the 100_{hex} reflection of $n\text{-C}_{20}\text{F}_{42}$ thin films evaporated on $\text{CaF}_2(111)$, and that of the 220 reflection of CaF_2 substrate.

which correspond to 100_{hex} reflection of the $n\text{-C}_{20}\text{F}_{42}$ films, the Mo characteristic x-ray ($K\alpha$), and the 220 reflection of the CaF_2 single crystal substrate, respectively. The appearance of the CaF_2 220 reflection, which refers to the surface diffractions on the $\text{CaF}_2(111)$, prove that our diffraction experiments were conducted under the in-plane geometry.

Similar x-ray diffraction profiles were examined at different azimuthal rotation angles by rotating the substrate. Figure 2 shows the angular dependence of the relative intensities of $n\text{-C}_{20}\text{F}_{42}$ 100_{hex} reflection and CaF_2 220 reflection. Here, the zero degree of the azimuthal rotation angle ($\omega=0^\circ$) is defined as the angle where the intensity of the CaF_2 220 reflection becomes the maximum. The relative intensity of the CaF_2 220 reflection sharply decreased with increasing ω , while that of the $n\text{-C}_{20}\text{F}_{42}$ 100_{hex} reached its maximum value at $\omega=\pm 12^\circ$, followed by a symmetrical decrease. This result suggested, surprisingly, that the normally oriented $n\text{-C}_{20}\text{F}_{42}$ molecules grow epitaxially on the $\text{CaF}_2(111)$ surface, aligning the $n\text{-C}_{20}\text{F}_{42} \langle 100_{\text{hex}} \rangle$ in the $\text{CaF}_2 \langle 110 \rangle$ with an inclination of about 12° , through the slight interactions between the terminal CF_3 groups and substrate crystals. The epitaxial growth of $n\text{-C}_{20}\text{F}_{42}$ on the $\text{CaF}_2(111)$ is represented schematically in Fig. 3. This is different from that of $n\text{-C}_{20}\text{F}_{42}$ evaporated on the $\text{KCl}(001)^{2,3}$, where the molecules align their $\langle 100_{\text{hex}} \rangle$ parallel to the $\text{KCl} \langle 110 \rangle$. Thus, it become evident that the nucleation and growth in epitaxially-grown $n\text{-C}_{20}\text{F}_{42}$ crystals are greatly depended on the substance used as the substrate.

B. $n\text{-C}_{20}\text{F}_{42}$ on Au coated KCl(001)

In order to examine the crystal growth on metal surface, we performed the in-plane diffraction measurements of the $n\text{-C}_{20}\text{F}_{42}$ thin films evaporated on an Au coated KCl(001). Depending on the $n\text{-C}_{20}\text{F}_{42}$ thin film, Au film and KCl single crystal, some diffraction and characteristic x-ray peaks were observed in Fig. 4. In this case, the azimuthal rotation angle $\omega=0^\circ$ is defined as the angle where the intensity of the KCl220 reflection becomes the maximum. Figure 5 shows that the relative

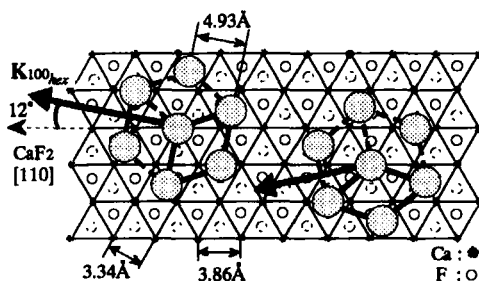


FIGURE 3 Schematic diagram of the relative orientation between the $n\text{-C}_{20}\text{F}_{42}$ crystal in evaporated films and $\text{CaF}_2(111)$ substrate. $n\text{-C}_{20}\text{F}_{42}$ molecules are represented by the shaded circles.

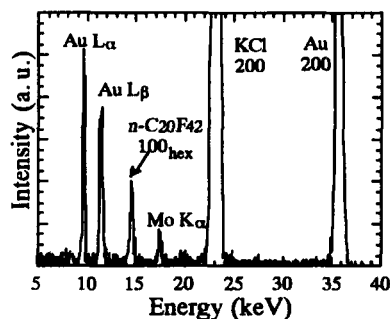


FIGURE 4 The x-ray diffraction profile of $n\text{-C}_{20}\text{F}_{42}$ thin films on Au films, observed at $\omega=45^\circ$.

intensity of Au 200 reflection exhibit a very sharp angular distribution around $\omega=45^\circ$. Thus, the Au thin films grow epitaxially on the KCl(001), aligning their $\langle 100 \rangle$ in the KCl $\langle 100 \rangle$. On the other hand, the relative intensity of $n\text{-C}_{20}\text{F}_{42}$ 100_{hex} reflection stays approximately constant for ω variations. This result indicates that the normally oriented $n\text{-C}_{20}\text{F}_{42}$ molecules, evaporated on the epitaxially grown Au films, form a polycrystalline structure in in-plane direction, so-called fiber structure.

Next, in order to obtain information about the surface morphology, we conducted an atomic force microscope (AFM) observation for the thin films. The epitaxially grown Au films and the $n\text{-C}_{20}\text{F}_{42}$ thin films evaporated on KCl(001) showed the different grain structures of sub-micron and micron order, respectively. Therefore, the possible reasons why the $n\text{-C}_{20}\text{F}_{42}$ thin films did not grow epitaxially on the well-ordered Au thin films may be these surface roughness and difference of grain size between $n\text{-C}_{20}\text{F}_{42}$ and Au thin films. Judging from the above, the preparation of ultraflat metal surface as substrate will be a key technique to fabricate the highly oriented organic thin films on metal films.

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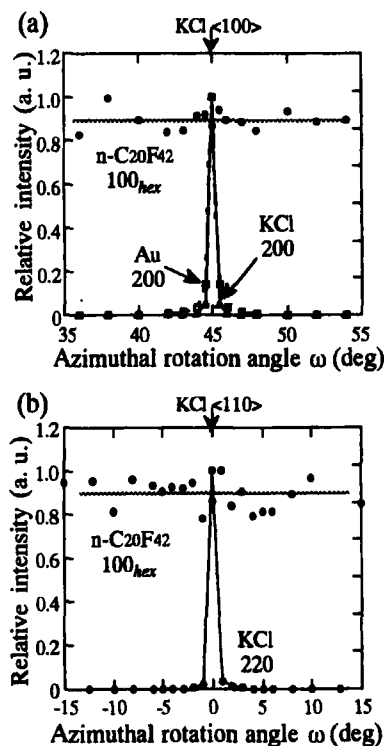


FIGURE 5 Angular variation in the relative intensities of the 100_{hex} reflection of $n\text{-C}_{20}\text{F}_{42}$ thin films evaporated on Au films, that of 200 reflection of Au film and that of the 200, 220 reflection of KCl crystal around (a) $\omega=45^\circ$ and (b) $\omega=0^\circ$.