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The Effect of the Substrate on the Epitaxial Growth of the Hexatriacontane Crystal

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The epitaxial crystallization of hexatriacontane vacuum-evaporated onto a gold-covered KCl (001) surface was investigated as a function of the gold coverage. The hexatriacontane film on the KCl surface was composed of rod-like crystals taking the orientation of $(110)_{\mathrm{H}}//(001)_{\mathrm{KCl}}$ and $[001]_{\mathrm{H}}//[110]_{\mathrm{KCl}}$. The film on evaporated gold film was composed of lamellar crystals taking the orientation of $(001)_{\mathrm{H}}$ parallel to the substrate and a random orientation in the azimuthal direction. The hexatriacontane film evaporated on the substrate which was partly covered with gold particles was composed of both rod-like and lamellar crystals. When the coverage ratio of the gold particles was low, the lamellar crystals in the hexatriacontane film took the orientation of $(001)_{\mathrm{H}}//(001)_{\mathrm{KCl}}$ and $[110]_{\mathrm{H}}//[110]_{\mathrm{KCl}}$. The numbers of lamellar crystals increased, and their orientation in the azimuth became more random, with and increase in the gold coverage.

In recent years thin films of organic compounds have attracted a good deal of attention because of their electronic and photoelectronic properties as semiconductors. The properties of ultrathin films are probably controlled by the molecular arrangement in the films. The main methods of preparing oriented thin films are the Langmuir–Blodgett (L-B) method and the vacuum-evaporation method. The former has been developed for preparing oriented organic thin films by mean of a wet process, and the properties of L-B films have been reported by many investigators.[1] In the case of vacuum-evaporation as a dry process, on the contrary, although there have been a number of reports on the structures of metals and inorganic compounds, there have been few reports on those of organic compounds.[2–5] We have investigated the orientation of vacuum-deposited films of organic compounds which consist of planar molecules, such as polycyclic aromatic compounds[6] and phthalocyanines.[7] The organic crystals composed of linear molecules, such as normal paraffins,[8] polyethylene[9] and polypropylene,[10] were also found to grow epitaxially in two modes on alkali halide, depending on the substrate temperature. When the substrate was preheated at 150 °C and kept at about 25 °C, the film was composed of rod-like crystals in which the linear molecules lay parallel to the substrate surface. On the substrate kept at temperatures in the vicinity of the respective melting points, the film was composed of disk-like crystals in which the molecules were oriented perpendicularly to the substrate. These two types of epitaxial crystallization have been reported for many polymers crystallizing on the surfaces of alkali halides and mica from organic solutions.[11–16] It has also been observed by X-ray diffraction that hexatriacontane film vacuum-evaporated on a copper block at room temperature is composed of crystals growing in such a way that the chain axes are oriented perpendicularly to the metal surface.[17] Those findings suggest that the orientation of vacuum-evaporated organic films depends on the substrate temperature and the substrate material. The interaction between the substrate surface and the linear molecules probably gives the nucleation of these two types of oriented crystals.

In the present work, in order to change the strength of the substrate-molecule interaction, a cleavage surface of a KCl single crystal was covered partly with either oriented gold particles or random ones and was then used as the substrate for vacuum-evaporated hexatriacontane film. The effect of the gold coverage and the substrate structure on the orientation of hexatriacontane crystal was investigated by using electron microscopy and electron diffraction.

Experimental

Gold was evaporated onto a cleavage surface of a KCl single crystal which had been maintained at room temperature (25 °C) or 400 °C in a vacuum of 10^{-5} Torr†. The amount of evaporated gold was controlled with a quartz-crystal microbalance. The coverage of gold particles on the KCl surface and the particle size were measured by means of electron micrographs by using a Laxer 450-particle analyzer. A clean KCl (001) surface and a gold-covered KCl surface were used as the substrates for preparing hexatriacontane films. The substrates were preheated at 150 °C for 1 h and were then kept at room temperature in a vacuum of 10^{-5} Torr, as has been described in a previous paper.[8] Hexatriacontane obtained from the Tokyo Chemical Industry Co., Ltd., was evaporated onto the substrate from a quartz crucible source heated with a tungsten coil. The deposition rate was about 2 nm min^{-1}. The thickness of the deposited films was controlled at about 100 nm by using a quartz-crystal microbalance. The specimens used for electron microscopy were prepared by dissolving the KCl crystal in water after the film had been backed with evaporated carbon film.

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† 1 Torr=133.322 Pa.

The films were examined by means of a HU-11A Electron Microscope.

Results and Discussion

Figure 1 shows the stage of the growth of the gold evaporated onto a cleavage surface of KCl maintained at 400 °C. At the initial stage of deposition, fine particles were dispersed uniformly over the substrate surface, as is shown in Fig. 1(a), these gold particles grew larger (b, c), until they eventually joined to form isolated islands(d) and finally formed a continuous film, with an increase in the amount of the deposit. The electron-diffraction pattern from these films displayed the same single-crystal pattern as is shown in Fig. 2, indicating that the individual fine particles were single crystals with the same orientation of $(001)_{\mathrm{Au}}//(001)_{\mathrm{KCl}}$ and $[100]_{\mathrm{Au}}//[100]_{\mathrm{KCl}}$. The characteristics of the evaporated gold films shown in Fig. 1 are given in Table 1. In the case of gold evaporated on a cleavage surface of KCl at room temperature, gold particles were dispersed randomly over the surface in the initial stage and then accumulated to form a continuous film when the deposit increased. All films formed at room temperature gave a polycrystalline diffraction pattern, in contrast to the case at 400 °C.

As has been described in the previous paper,[8] hexatriacontane film on a cleavage surface of KCl without heat treatment was composed of small granules giving a ring-diffraction pattern. Epitaxial growth of hexatriacontane occurred on the cleavage surface of KCl which had been preheated at 150 °C for 1 h and then kept at about 25 °C. Therefore, the same heat treatment was carried out for all the substrates before the evaporation. The hexatriacontane film evaporated on a clean surface of KCl was composed of raft-like crystals crossing each other orthogonally, as is shown in Fig. 3(a). The electron-diffraction pattern from the film gave a superposition of two identical fiber diagrams rotated at 90° with respect to each other, as is shown in Fig. 3(b). The hexatriacontane crystal has an orthorhombic subcell with dimensions of a=7.42 Å, b=4.954 Å, and c=2.546 Å. It was found from the electron-diffraction pattern that the hexatriacontane crystal had its (110) plane parallel to the KCl (001) surface and its c-axis along the [110] direction of the KCl crystal; that is, the crystal took the parallel c-axis orientation.[8] When hexatriacontane was evaporated on the KCl surface 11% covered with gold particles, the film was composed of rod-rike crystals crossing each other

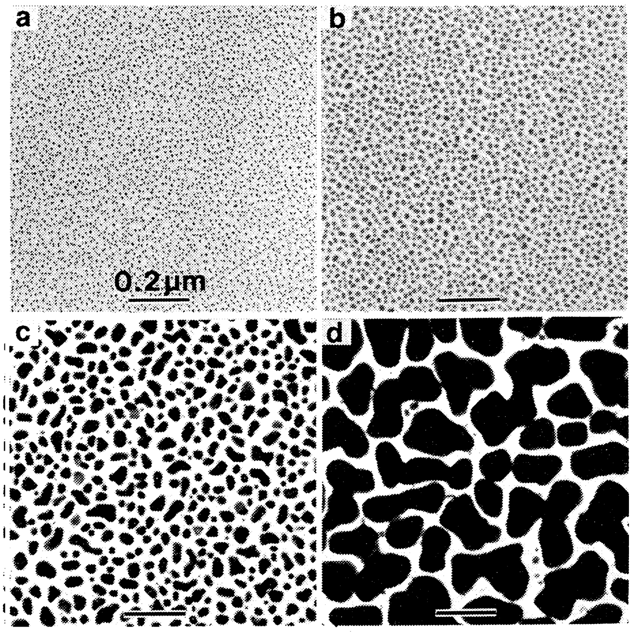

Fig. 1. A sequence of electron micrographs showing various stages of growth of gold films formed at 400 °C on KCl. The coverage of gold are (a) 11%, (b) 24%, (c) 54%, and (d) 74%.

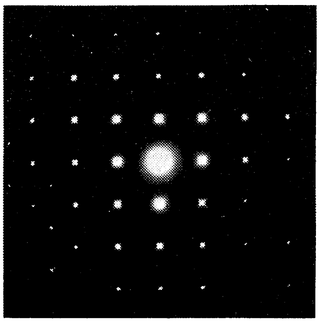

Fig. 2. Electron diffraction pattern of the gold films shown in Fig. 1.

Table 1. Character of Gold Deposits on (001) Surface of KCl

Substrate	Weight of Au mg/cm^2	Particle number of Au µm^{-2}	Mean diameter of Au Å	Coverage of KCl surface %
a	$1.0\times10^{-2}>$	1322	51.7	11.1
b	1.4×10^{-2}	1264	78.4	24.4
c	3.4×10^{-2}	563	218.1	54.3
d	5.2×10^{-2}	film	film	73.7

orthogonally and lamellar crystals filling in the space among the former, as is shown in Fig. 4(a). The electron-diffraction pattern in Fig. 4(b) shows the net pattern overlapping with arc spots, which indicates that the film contains two kinds of crystals with different orientations. The reflection spots are indexed as is shown in Fig. 5. The net-reflection spots with strong intensity coincide with the diffraction pattern observed from the film in Fig. 3(a). The arc-reflection spots on the ring pattern have the indices of *hk*0 and show a C_{4v} symmetry, whose mirror planes correspond to the (110) planes of KCl. These reflection spots suggest that the crystals take their *c*-axes perpendicularly to the substrate surface. Therefore, the arc pattern is composed of four sets of a net pattern, one of which is given by open circles, with C_{4v} symmetry. It is noted that the series of 110 and its higher-order reflection spots in the ring pattern coincide with the [110] direction of KCl and that this oriented direction agrees with that of the *c*-axes of the crystals illustrated in Fig. 3(b). On the basis of these diffraction patterns, the relative orientation between deposited gold particles and

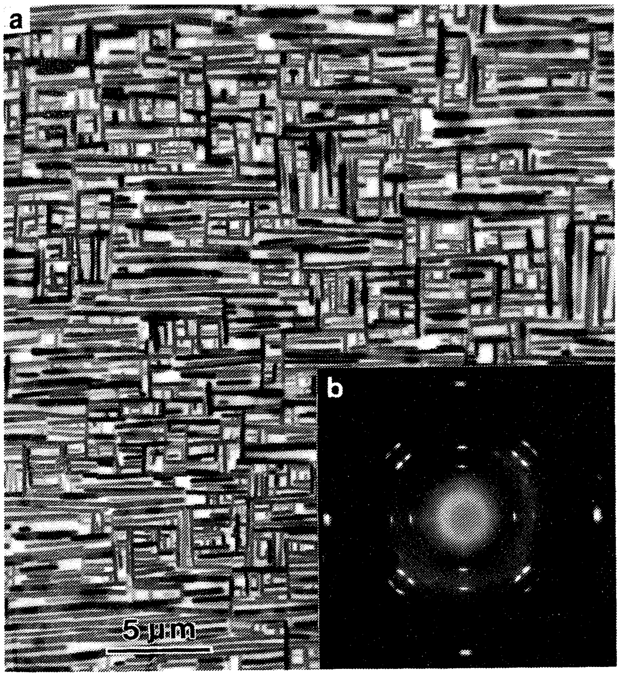

Fig. 3. Electron micrograph (a) and electron diffraction pattern (b) of hexatriacontane film evaporated on a clean cleavage surface of KCl.

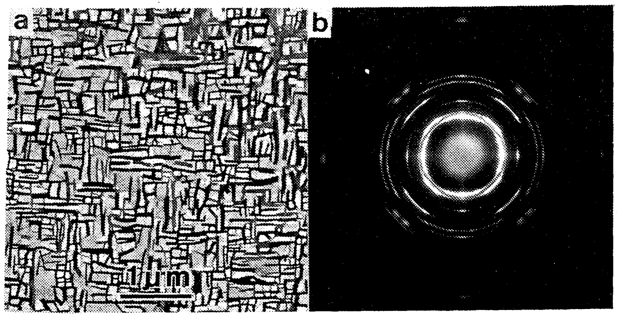

Fig. 4. Electron micrograph (a) and electron diffraction pattern (b) of hexatriacontane film evaporated on KCl surface covered with gold partices by 11%.

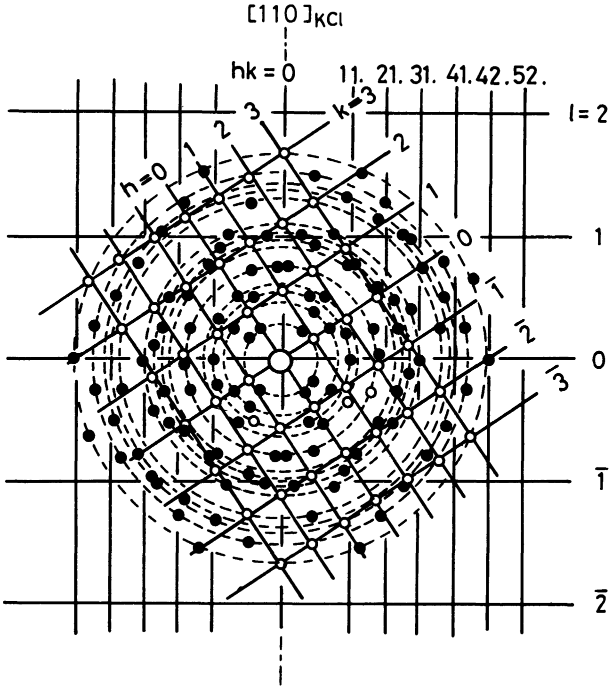

Fig. 5. The interpretation of the diffraction pattern shown in Fig. 4(b). Open circles are reperesentation of the basic single crystal pattern.

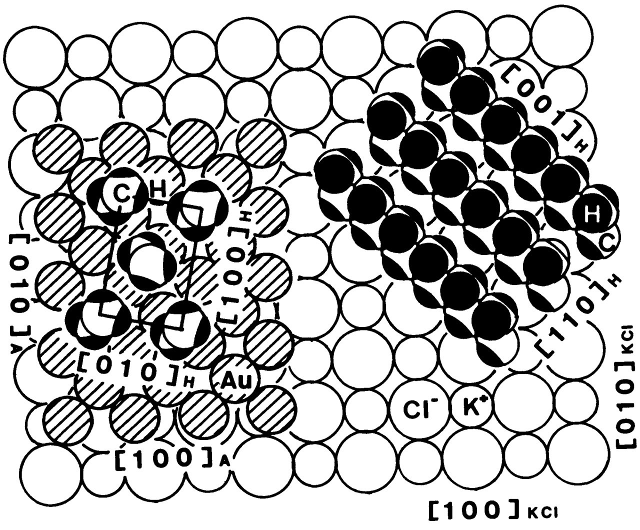

Fig. 6. Schematic diagram of the relative orientation of hexatriacontane crystals, gold and KCl (001) surface shown in Fig.4.

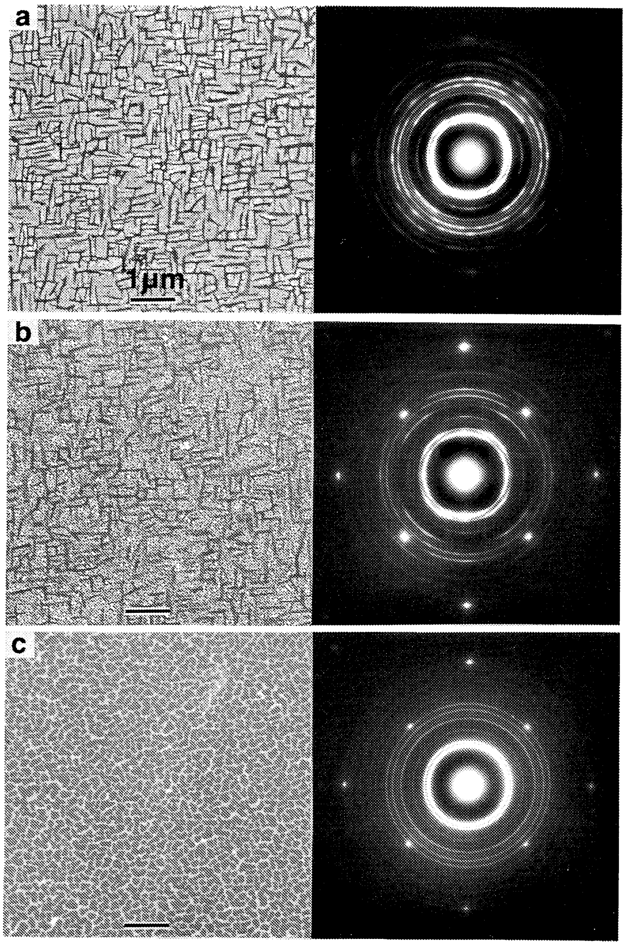

Fig. 7. Electron micrographs and electron diffraction patterns of hexatriacontane films evaporated on KCl surfaces covered with gold particles by(a) 24, (b) 54, and (c) 74%, respectively.

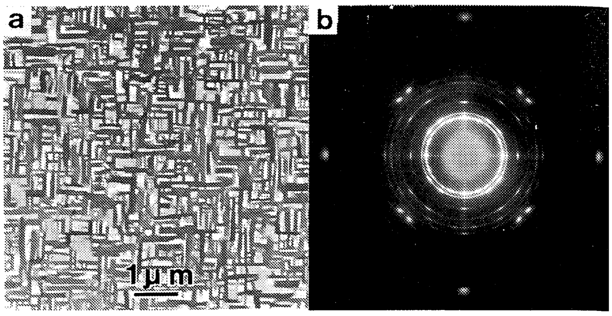

Fig. 8. Electron micrograph (a) and electron diffraction pattern (b) of hexatriacntane film evaporated on KCl surface covered by 12% with randomly-oriented gold particles.

hexatriacontane crystals on the KCl surface can be explained in terms of a real lattice, as is shown schematically in Fig. 6. When the rod-like crystals take the orientation of $(110)_{\mathrm{H}}//(001)_{\mathrm{KCl}}$ and $[001]_{\mathrm{H}}//[110]_{\mathrm{KCl}}$, a closed-packing layer of the linear molecules lies adjacent to the KCl surface, with their long axes along the substrate [110] direction. On the other hand, it seems that the lamellar crystals nucleate on gold particles and grow over the surrounding KCl surface. The linear molecules in the lamellar crystal stand perpendicular to the substrate surface, and their closed-packing layers are arranged along the substrate [110] direction. Figures 7(a), (b), and (c) show electron micrographs and electron-diffraction patterns of the films deposited on the substrates covered about 24, 54, and 74% respectively with gold particles. The number of rod-like crystals decreased and the lamellar region increased with an increase in the coverage of the gold. Corresponding to these morphological variations, the more the substrate was covered with a gold deposit, the more predominancy of the ring pattern was observed in the electron-diffraction patterns. On the substrate with a gold coverage above 74%, the lamellar crystals covered the substrate uniformly, and the electron-diffraction pattern from the film showed a complete ring of (*hk*0) reflections of hexatriacontane crystals and net spots of gold crystals. These findings indicate that the film consists of polycrystals with their c-axes perpendicular to the substrate surface and with a random azimuthal orientation when the substrate surface is covered largely with a gold deposit. Figure 8 shows an electron micrograph and electron diffraction pattern of the hexatriacontane film evaporated on a substrate which is about 12% covered with gold particles taking a random orientation. The film was composed of rod-like and lamellar crystals as well as the film evaporated on the oriented gold. The ratio of the lamellar crystals to the rod-like crystals increased with an increase in the amount of gold deposited. This tendency was similar to the result for the films growing on the substrate surface covered with oriented gold. Consequently, it may be concluded that the orientation of hexatriacontane is dependent on the coverage of gold particles, but is independent of their orientation.

Alkali halide crystals have lines of unicharge ionic species which are aligned in the [110] direction of the (001) face, and the species exert a long-range dipole force which influences the orientation of long-chain molecules.[18] When hexatriacontane molecules are deposited on a clean surface of KCl, their long chains are arranged parallel to the [110] direction of KCl in the most closely packed way by means of an interaction between the KCl surface and the molecules, which causes the crystal to take the orientation of $(110)_{\mathrm{H}}//(001)_{\mathrm{KCl}}$ and $[001]_{\mathrm{H}}//[110]_{\mathrm{KCl}}$. On the other hand, the molecules deposited on gold particles yielded a nucleus of the oriented crystallite having $(001)_{\mathrm{H}}//(001)_{\mathrm{Au}}$. In the case of solution-grown polymers, two ways have been proposed for the nucleation of the crystals with their chain axes perpendicular to the substrate surface; that is, nucleation in the solution[13] and nucleation at the side of the crystals already grown with their chain axes parallel to the substrate surface.[16] It has been concluded that a prerequisite condition for the formation of such oriented crystals is the presence of a weak interaction between the substrate surface and the polymer molecules.[15] It is well known that hexatriacontane crystals grow in lamellae, in which the long chains are arranged perpendicular to the flat face, from organic solutions.[19] This fact suggests that this crystal habit for hexatriacontane is the most stable form thermodynamically. Therefore, if there is little interaction between deposited molecules and a substrate, hexatriacontane molecules deposited on the substrate surface probably grow to a lamellar crystal on the surface. It seems that hexatriacontane molecules deposited on the gold surface form a nucleus of lamellar crystal, independently of the orientation of the deposited gold.

On the substrate surface covered partly with gold particles, some molecules deposited on the KCl surface grow to rod-like crystals, taking the parallel c-axis orientation, while the other molecules deposited on gold particles nucleate in lamellar crystals. Once nucleation and partial growth has occurred on fine gold particles, the reorientation of these "precrystals" to align with a preferential epitaxial growth direction on the KCl substrate would account for the regular crystalline orientation observed for epitaxy on KCl. Finally, the growth of these crystals directed by the epitaxial interaction with the KCl substrate may produce the unique azimuthal orientation of $[110]_{\mathrm{H}}//[110]_{\mathrm{KCl}}$. Alternatively, crystals growing on large gold particles and the gold substrate cannot experience these epitaxial interactions; thus, the hexatriacontane film may be composed of lamellar crystals with a random azimuthal orientation.

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