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Epitaxial Growth and Its Growth Mechanism in Physical Vapor Deposited Films of Alkyl Octadecanoates

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Esters of octadecanoic acid and three primary alcohols such as methanol, ethanol, and propanol were deposited on substrates of potassium chloride (KCl), mica and amorphous carbon film under vacuum. The surface morphology of their films was observed by transmission electron microscope. They grew epitaxially to form the rectangular crystals with lateral molecular orientations on KCl substrate. On the other hand, ester molecules tend to arrange normal to the surface of mica and amorphous carbon film and construct the molecular layers like to Langmuir-Blodgett films. The crystal axis relationship between esters and KCl(001) surface was followed; c-axis$_{\mathrm{ester}}$ is parallel to $\langle 110\rangle_{\mathrm{KCl}}$ direction and $\langle 110\rangle_{\mathrm{ester}}$ direction inclines with an angle of about ±16° corresponding to $\langle 110\rangle_{\mathrm{KCl}}$. These molecules had resemble crystal structures with trans configuration in the ester moiety. The optimum temperatures of substrates in the former epitaxial growth exist and the temperature decreases in proportion to the chain length of alcohol group with the discrepancy of about 10 to 30 °C.

Organic thin-solid-film was studied for the new devices for electronic, magnetic and optical thin films[1]. The thin-solid-films of octadecanoic acid (stearic acid; $C_{17}H_{35}$ COOH) have been used as the lubricated films,[2] photo-resist and insulators.[3] The preparing of such organic films was carried out by the Langmuir-Blodgett (LB) methods, which were used the air–water interface.[4] Their films, however, had only molecular arrangements normal to the surface and the molecular packing in the first monolayer was not perfect from the results of transmission electron microscopic observation.[5] On the other hand, physical-vapor-deposition (PVD) method could give the alternative molecular orientations.[6] The molecules in the films laid along or stood normal to the surface. The crystal morphology on the substrate had the own habits and molecular orientations in the crystal could be identified by the granularity of the germanium decoration.[6] If the deposition conditions of PVD were controlled, the alternativity in the molecular orientations revealed. Therefore, uniform and well-defined crystal films could be obtained. Furthermore, the lengths of linear chain molecules such as fatty acids of hexadecanoic (palmitic), octadecanoic (stearic), eicosanoic (arachidic) and docosanoic (behenic) acids became clear to relate with the molecular orientations in given deposition conditions of PVD.[7] The longer molecules gave the tendency of normal orientations at same deposition condition than shorter ones.

Fatty acids such as octadecanoic acid form esters with primary alcohols. T. Malkin[8] firstly studied the crystal structures of them by powder X-ray diffractometry. Then single crystal X-ray analysis was carried out for methyl octadecanoate (18-1) by S. Aleby and E. von Sydow[9] and for ethyl octadecanoate (18-2) by S. Aleby[10,11] and A. McL. Mathieson and H. K. Welsh.[12] These crystals belong to monoclinic. The cell dimensions of 18-1[9] are a=5.61, b=7.33, c=106.6 Å, β=116.78° with space group of $A2/a$. Those of 18-2, however, are a=5.59, b=7.40, c=57.1 Å, β=118° with Aa[10] and a=5.59, b=7.40, c=55.0 Å, β=113.5° with Ia[11]. The difference between two cell parameters of 18-2 exists in the configuration of ester group (C_1–O_1–C_{01}–C_{02}). The former has trans configuration, while the latter has cis form as same as that of 18-1 (C_1–O_1–C_{01}). The molecules in the crystal arrange to construct the layer normal to the c-axis. From these cell dimensions the angle of c-axis with ⟨110⟩ direction in the crystal is 105.9° for 18-1 and 106.4° and 103.9° for 18-2, respectively. The crystal structure of 18-3, however, was not revealed yet.

The ester molecules were not good at forming the LB films in order that their ester groups had low hydrophilic properties.[13] The PVD of methyl triacontanoate (30-1; $C_{29}H_{59}COOCH_3$) was carried out by Y. Ueda.[14] He evaporated it on KCl in vacuo. The crystal structure and the growth mechanism were studied by using electron microscope and electron diffraction. The film was composed of V-shape crystals. The 30-1 molecules grew epitaxially with the defined axial relations. The c-axis which is alkyl chain direction of molecule had the angles of ±16° with ⟨110⟩ direction on KCl (001) plane.

This paper describes the preparing of well-defined thin solid films of three esters of fatty acids such as methyl octadecanoate (18-1; $C_{17}H_{35}COOCH_3$), ethyl octadecanoate (18-2; $C_{17}H_{35}COOC_2H_5$) and propyl octadecanoate (18-3; $C_{17}H_{35}COOC_3H_7$) and the film morphology of them.

Experimental

Methyl octadecanoate (18-1), ethyl octadecanoate (18-2), and propyl octadecanoate (18-3) were provided from Sigma Co. Ltd. with the purity of about 99%. These materials have melting points (mp) at the inversely proportional to the alkyl chain lengths of ester groups, as shown in Fig. 1.

The sample was set in the vacuum system and deposited on three substrates. These substrates were three types; air-cleaved KCl and mica, amorphous carbon film (amorphous film) forming on mica before. The vacuum was kept at 6.7×10^{-4} Pa (5×10^{-6} Torr). After the substrates were baked at the temperature of greater than 100 °C for 1 h, the substrates were cooled down to 30 °C or less temperatures by using a cold trap and then the sample was evaporated. The temperature dependence of substrate with molecular orientations was found from the thin crystal morphology.

As the sample has low mp, it is difficult to evaporate in vacuo. So that the indirectional heating system was performed. The heater of tungsten wire and the sample holder of quartz plate were separated to differ from each other at the distances corresponding with specimen. When the temperature around the heater was kept at 500 to 800 °C, the specimen melted to sublimate.

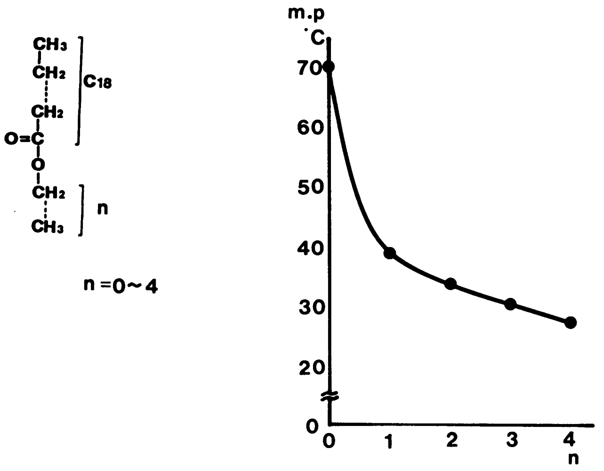

Fig. 1. Molecular shape and its melting point of alkyl octadecanoates (18-*n*; *n*=0, 1, 2, 3, and 4).

After the specimen was deposited on the substrates with the thickness of about 10 nm, germanium and carbon were successively evaporated in same vacuum system. The deposited germanium is surface decoration of organic crystals. When the surface was methyl-end like to (001) plane of octadecanoic acid, germanium grew discrete grains with star-like shapes. While, on the other plane it revealed the continuous layers. So that germanium decoration becomes indirect method for the determination of molecular orientation in thin-solid-films[6].

The three layers of sample, germanium and carbon were stripped off from the substrates on the surface of distilled water. Electron microscope used here was Hitachi HU-11DS with the accelerating voltage of 75 kV. The direct magnification was 5000 and 16000.

Results and Discussion

The typical electron micrographs are represented in Fig. 2(a), (b), and (c). These are thin-solid-films of 18-2 formed at substrate temperature of 10 °C on KCl, 0 °C on mica and −10 °C on amorphous film, respectively. On KCl, 18-2 molecules laid on the substrate surface. The molecular orientation was determined by the appearance of germanium decoration. The axis relation between thin crystal and substrate surface was decided by the shadowing direction of germanium along ⟨110⟩ direction of KCl (001) surface. Molecules formed the rectangular crystals and revealed the epitaxy. The bisectional direction of twinned crystals

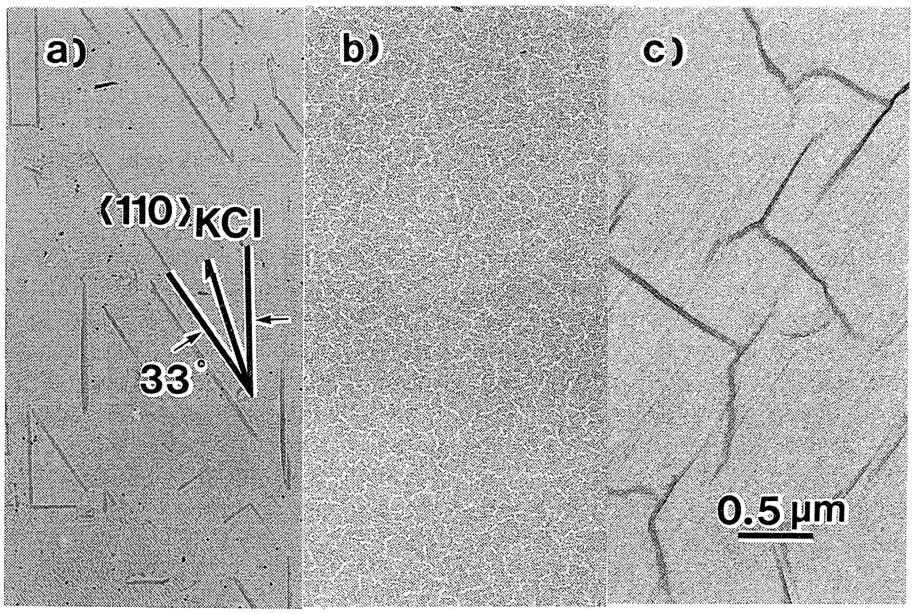

Fig. 2. Electron micrographs of deposited ethyl octadecanoate (18-2) on KCl at sustrate temperature of 10 °C (a), on mica at 0 °C (b) and on amorphous carbon film at −10 °C (c). On KCl (001) surface, 18-2 molecules grew epitaxially along two directions. Each direction indinate an angle of ±16.5° corresponding to KCl ⟨110⟩ direction.

was ⟨110⟩ direction of KCl (001) plane. The longitudinal direction of rectangular crystals crosses with an angle of 33°(±16.5°). This value can be led by the angle relationship between c-axis and ⟨110⟩ direction which is 106.4° (90°+16.4°). The fact shows that deposited films take the cell dimensions of reference [10] and the ester group of 18-2 would have trans configuration. The latitudinal direction is corresponding to c-axis. This result coincides with that for 30-1 by Ueda.[14] On the other hand, the regions covered with granular germanium on mica revealed, as shown in Fig. 2(b). Molecules in the film stood normal to the substrate surface and had no crystal habit. The same result was obtained in the deposition film formed on amorphous carbon film, as shown in Fig. 2(c).

The temperature dependency of substrate with molecular orientations was carried out at −20, −10, 0, and 10 °C for 18-1 and 18-2; from −60 to 10 °C with a step of 10 °C for 18-3 on KCl, mica and amorphous

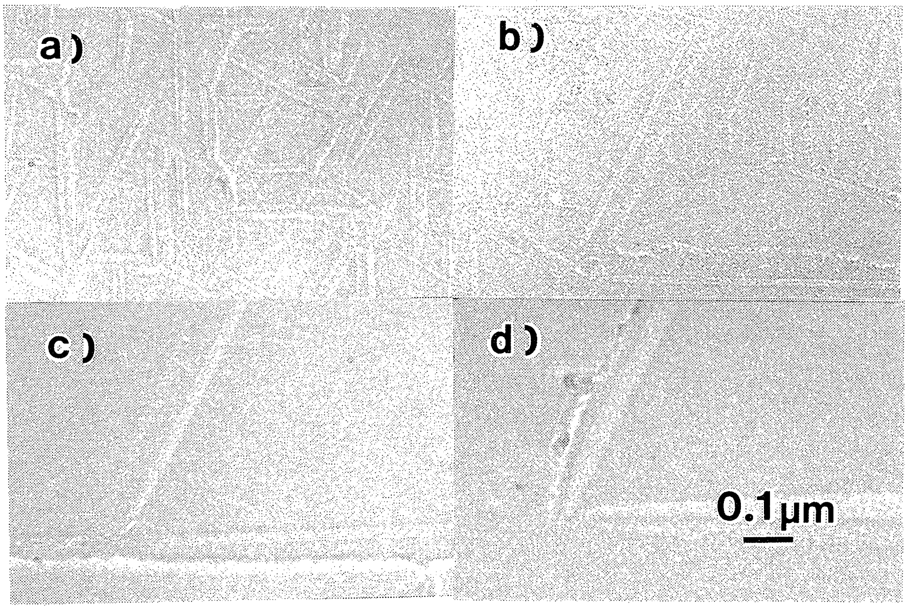

Fig. 3. Thin films of methyl octadecanoate (18-1) formed on KCl at −20 °C (a), −10 °C (b), 0 °C (c), and 10 °C (d).

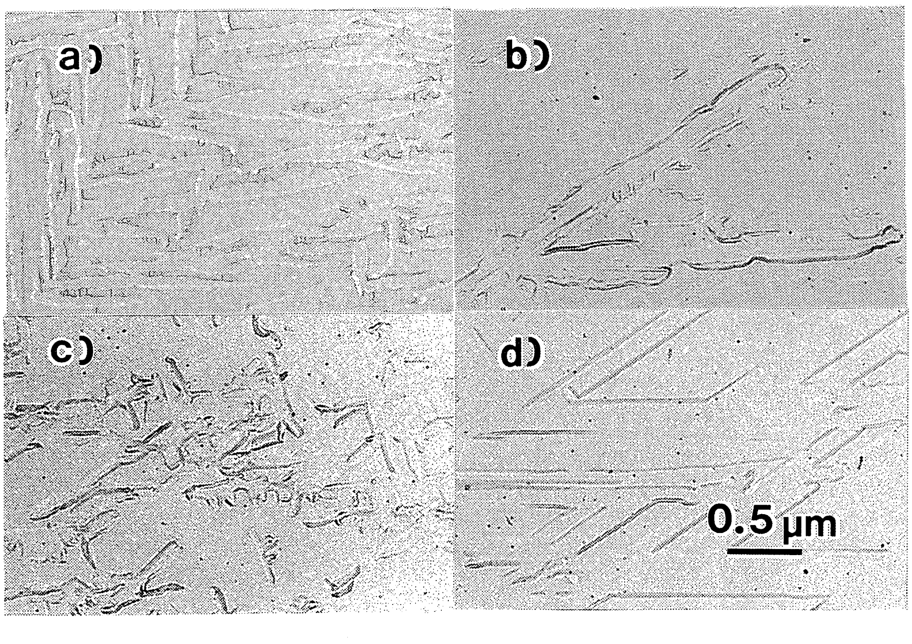

Fig. 4. Thin films of ethyl octadecanoate (18-2) formed on KCl at −20 °C (a), −10 °C (b), 0 °C (c), and 10 °C (d).

carbon film. These results only on KCl substrate are shown in Figs. 3, 4, and 5 for 18-1, 18-2, and 18-3, respectively.

There were the discrepancies of crystal morphology at each substrate temperature on KCl. On the other hand, molecules grew normal to the substrate surface on mica and amorphous carbon film without differency of substrates and substrate temperatures. When the substrate temperature of KCl increases, the thin crystals with parallel molecular orientations to the substrate surface grow greater and reveal more epitaxially. There are the optimum temperatures of substrates for epitaxial growth; 0 °C for 18-1, −10 °C for 18-2 and −40 °C for 18-3, as shown in Fig. 6. The cross angles of rectangular crystals were 58° for 18-1, 33° for 18-2 and 33° for 18-3, in which an angle of 58° is a supplement of 32°. The results represent as followed; three crystals were monoclinic, the angle

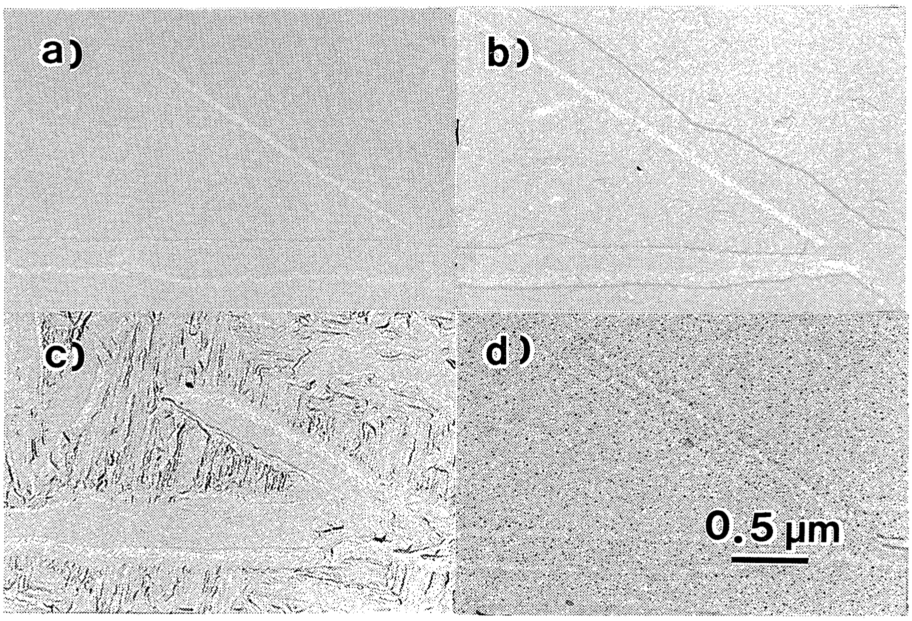

Fig. 5. Thin films of propyl octadecanoate (18-3) formed on KCl at −50 °C (a), −40 °C (b), −10 °C (c), and 0 °C (d).

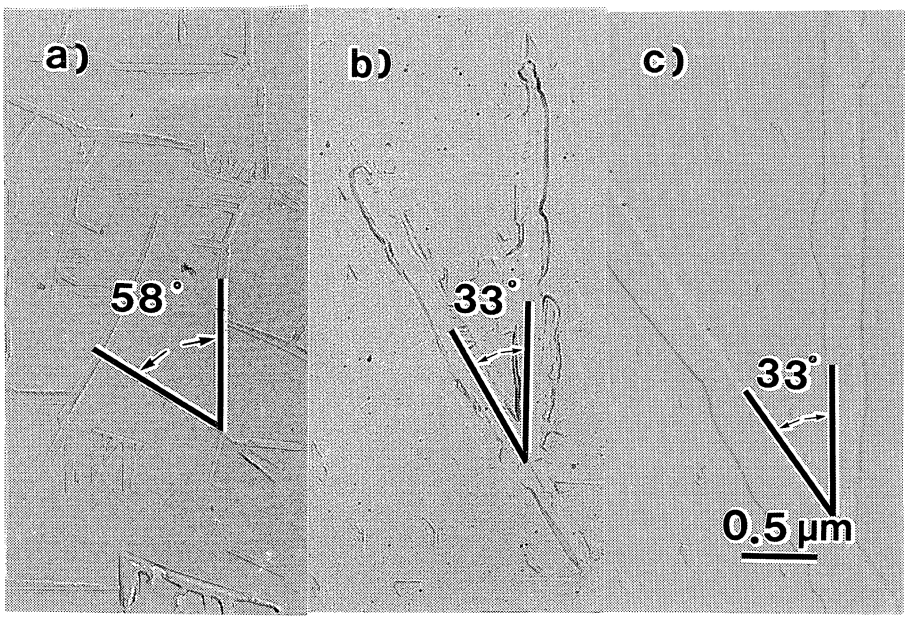

Fig. 6. Crystal morphology at optimum temperature of substrate on KCl. (a) 18-1 at 0 °C, (b) 18-2 at −10 °C, and (c) 18-3 at −40 °C. The angles between rectangular crystals were 58° for 18-1 (a), 33° for 18-2 (b), and 33° for 18-3 (c).

n Ts (℃)	1	2	3
10	L	L	L
0	L	L	L
-10	L/N	L	L
-20	L/N	L	L
-30			L
-40			L
-50			L/N
-60			L/N

Fig. 7. Dominant growth hillocks of alkyl octadecanoates at several temperatures of KCl substrate. The symbol of L or N represents the lateral and the normal orientations, respectively.

between the rectangular crystals could be led from the relation between c-axis with ⟨110⟩ direction, these esters had resemble cell shapes and one of crystal parameters for 18-3 which had not determined by other methods was an angle of 106°. Above the optimun temperature of substrate, molecules stood normal to the substrate as same as on mica or amorphous film.

The formation mechanism of thin-solid-films will be explained as followed. The alkyl chain of molecules tends to lay along the substrate surface with the good contact on cations or anions of KCl ⟨110⟩ direction, as described above. If the substrate temperature increased, molecules get the surface migration energy and crystallization energy from the substrate to let the crystal more epitaxial and larger. When the excess energy was supplied, molecules could not contact the substrate surface to stand normal to the surface. The normal crystal has the ability of surface migration and self-aggregation more than lateral one. The tendency revealed the thin crystals on mica and amorphous film. The surface of them had no tetragonal symmetry. The interaction between molecules and substrate surface was lower than ionic crystal surface of KCl. The long chain molecules did not lay on the surface but tended to stand normal to the substrate.

The morphology of deposited thin films on KCl was summarized in Fig. 7. The "L" and "N" are represented the dominant crystals of the film surface with lateral and normal orientations of molecules, respectively. The temperature effect is inversely proportional to the alkyl chain length. The facts are coincided with the resemble study,[7] which was performed on several fatty acids with different chain length.

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