14. Effect of Cleavage Steps of Muscovite on the Epitaxial Growth of Copper Phthalocyanine

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Introduction. When condensed polycyclic aromatic compounds are deposited *in vacuo* onto freshly cleaved face of muscovite through sublimation, many of the resulting thin films take well-defined orientation over-growth as previously reported by some of the present authors.¹⁾ The orientation of a total film relative to that of the substrate muscovite is another significant property to be elucidated with regard to the epitaxial growth of these organic films.

Recently, the optical and electron microscopy revealed that the surface structure of the muscovite, being associated with its three dimensional lattice configuration, had a certain effect on the relative orientation of these thin films on the substrate face. The results were reasonably interpreted in terms of the stacking vector of mica subcell which was proposed by Smith and Yoder.²⁾ The details will be discussed with respect to the epitaxial growth of copper phthalocyanine films which have the single-directional orientation.

Experimental. A small piece of muscovite was cleaved in air and placed in a vacuum-evaporating chamber, the inside pressure of which was kept at about 10^{-5} Torr. The copper phthalocyanine powder, purified in an ordinary way,³⁾ was sublimated from a crucible of fused silica with a resistance furnace and vertically deposited onto the cleaved face of muscovite which had been kept at a constant temperature ranging from 150–170°C.

The direction of the crystal axis in the substrate muscovite was determined with a polarizing microscope. For the further confirmation, the cleaved face of the substrate crystal was etched with fluoric acid, insomuch as an etching figure on muscovite face is well known to assume a mono-symmetric pattern.⁴⁾ As the etchant did not destroy the deposited thin film, this method was also applied to the substrate muscovite with the copper phthalocyanine films on it to determine the lattice orientation of the latter relative to that of the substrate crystal under an electron microscope by the application of the methylcellulose-carbon replica method.

Results. The total area of the cleaved face of muscovite covered

with the copper phthalocyanine film of α form was thoroughly examined with a polarizing microscope which facilitated to detect the orientation of copper-phthalocyanine raft. The crystal strips of the evaporated films which run parallel in their b-axis cover. Local domains of the muscovite face defined by conspicuous boundary lines as shown in Fig. 1a. The direction of the fibre axis in individual domains changes from one to the other. For instance, in the area A in Fig. 1a, the fibre axis makes an angle of $+60^\circ$ with the a-axis of the substrate muscovite as designated in the photograph. On the other hand, in the neighbouring area B, this angle is found to be -60° . The boundary line in this case coincides with a visible step line of the muscovite face which appears as a dark line in the photomicrograph.

Fig. 1. Optical photomicrographs of domain structure of copper-phthalocyanine film vacuum-deposited onto mutually cleaved face of muscovite.

Similar coincidences of the domain boundary and the step line are rather frequently observed. On the other hand, it was also observed that the direction of the fibre axis of the phthalocyanine raft was not altered even at a clearly visible step line of the muscovite face was shown at C in Fig. 1a. It also took place like at D in very seldome occasions that there were no visible step lines to coincide with the conspicuous boundary lines though the raft orientation was altered to make the angle of 120° .

The electron micrograph in Fig. 2a shows an example of the replica of the etch figures. The diamond-shaped etch pit defines the direction of the crystal axis of muscovite as shown in the figure. The striped pattern with small dark fragments on it is due to the copper phthalocyanine strips which run parallel in the diagonal direction of the figure, making an angle of 60° with the a-axis of muscovite. Fig. 2b is a reproduction of the optical micrographs of the etch

Fig. 2. (a) Electron micrograph of etch figure on muscovite face with copper phthalocyanine raft on it. (b) Optical photomicrograph of domain boundary of raft structure and etch figures.

figures on the muscovite face also with the copper phthalocyanine film on it. The direction of the rafts was changed by 60° at the boundary line which coincides with a step line of muscovite face. Since the etch figures (E) with a similar diamond-like shape appeared with the same orientation on both sides of the step line, the general lattice orientation of the muscovite was not different in these two domains regardless of the alteration in the orientation of the copper phthalocyanine raft. As for the two other cases, the etch figures always oriented themselves in the same way as above showing that whether or not the orientation of the raft was altered at the boundary did not have any relation to the total orientation of the substrate crystal.

A sheet of muscovite was cleaved into two pieces and both freshly formed faces were used as the substrates on which copper phthalocyanine was simultaneously evaporated in the same way as above. These two faces are considered to be completely complementary to each other as far as the general surface configuration is concerned. As a matter of fact, the two photographs in Fig. 1, a and b, are the example of these pairs. As the directions of the a-axis of muscovite in both photographs were assimilated in a vertical line as designated in the figure, the patterns defined by the step lines and domain boundaries in these two photographs are actually in the relation of a mirror symmetry. The extra lines designated as P or Q are due to some cracks instead of the step lines. However, the orientation of the copper phthalocyanine raft in corresponding domains shows no mirror symmetry but runs parallel to each other. Thus, the direction of the fibre axes will cross each other at an angle of 120° when the two cleaved faces of mica are put together as it used to be.

Discussion. The crystal structure of muscovite is composed of a regular stacking of the layered mica subcell of about 10 Å in thickness with a hexagonal network of potassium ions on top of it.⁵⁾ The main body of the subcell is, as schematically shown in Fig. 4a, a pair of networks of oxygen tetrahedron with silicon or aluminum atom in it. Regardless of that all elementary networks assume trigonal⁷⁾ or hexagonal symmetries, the complication arises where the two opposite tetrahedron networks are linked together with corresponding vertex oxygen atoms across the central aluminum layer with a staggering in either of the $[110]$ or $[\bar{1}\bar{1}0]$ axis of the total crystal. Smith and Yoder²⁾ have introduced the idea of the stacking vector K which determines the direction of this staggering or, in other words, the horizontal displacement between two tetrahedron sheets. In muscovite, the displacement occurs alternatively so that

Fig. 3. The schematic demonstration of the staggering of tetrahedron sheets (a, b) and the mutual orientation of stacking vectors of top subcells of muscovite at the mutually cleaved faces (c).

the stacking vectors form a sequence of zig-zag lines as a whole. The crystal of muscovite is known to be cleaved at the layer of potassium ions.⁵⁾ The subcell of the subsequent cleavage face has a displacement in either of the above mentioned two directions as shown in Fig. 3 a and b with arrows K and K'. The mutual orientation of the stacking vectors in the top subcells of two neighbouring domains bounded by a step line depends upon the step height or the number (n) of the subcell which form the step. If n is odd, these two staggering directions will meet at an angle of 120° making the a-axis the bisector of this angle, whereas they will be parallel when n is even. According to the results of the multiple beam interferometric topography of muscovite face reported by Tolansky,⁶⁾ the possibility of the appearance of such odd numbered step height was not fully ruled out, although even number seemed to be more favoured. Furthermore, the property of muscovite used would vary depending upon the source. When the two mutually cleaved faces are placed as in the case of Fig. 1 a and b, the directions of the two stacking

vectors of the top subcells evidently become parallel with respect to the individual pairs of corresponding domains as schematically illustrated in Fig. 3c. All these properties of the stacking vectors in the top subcell seemingly have a close similarity to that of the copper phthalocyanine rafts as far as the orientation is concerned, although it has to be uncovered whether both directions perfectly coincide or not. However, it is not unreasonable to deduce that the relative orientation is more or less strongly influenced rather by the three dimensional configuration of the mica subcell at the cleavage face than by the two dimensional configuration of the surface layer.

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