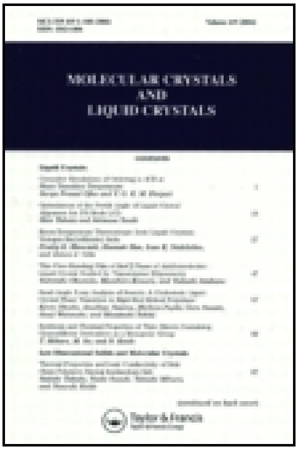

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Selective On-top Crystal Nucleation in Organic Multilayer Formation

Kaname Yoshida [a], Masahiko Tsujimoto [a], Seiji Isoda [a], Takashi Kobayashi [a], Toshihide Kamata [b] & Masaru Matsuoka [c]

[a] Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611, Japan

[b] National Institute of Materials and Chemical Research, Tsukuba, Ibaraki, 305, Japan

[c] Department of Materials Science, Kyoto Women's University, Higasiyama, Kyoto, 605, Japan

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Selective On-top Crystal Nucleation in Organic Multilayer Formation

KANAME YOSHIDA[a], MASAHIKO TSUJIMOTO[a], SEIJI ISODA[a], TAKASHI KOBAYASHI[a], TOSHIHIDE KAMATA[b] and MASARU MATSUOKA[c]
[a]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan
[b]National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan
[c]Department of Materials Science, Kyoto Women's University, Higasiyama, Kyoto 605, Japan

Structure and epitaxy of double-layered heterostructure of organic materials formed on four kinds of alkali halides were investigated. These films were fabricated by vacuum deposition. Crystallographic orientation and mutual registration of organic double layers were examined by transmission electron microscopy(TEM) and atomic force microscopy(AFM). As concluded from these observations, we found three kinds of growth modes as for the second layers depending on the combination of materials. Selective on-top growth, one of the growth modes, is important phenomenon for fabrication of organic-superlattice. Such selectivity originates not only in lattice matching between the two layers, but also in surface topography of the layers.

Key Words: Organic Multilayers; Epitaxy; Selective Nucleation

INTRODUCTION

In the case of multilayer formation, like device fabrication, it is important to construct every layer being overgrown exactly on an intended area.This kind of crystallization can be achieved by selective on-top nucleation, which means that a layer grows selectively on a designed area. Suzuki *et al.* reported recently that some organic layer can be formed selectively on an inorganic substrate [1]. Such selective on-top growth, shown schematically in FIGURE 1-c, is important phenomenon for fabrication of organic superlattice.

In the present paper, we report some examples of selective growth of organic crystal on organic substrate and discuss the mechanism of these growth modes in doubly-deposited films from the view point of surface structure and morphology.

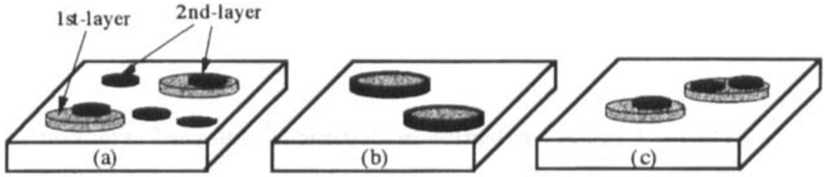

FIGURE 1 Growth modes of doubly deposited thin film on substrate; (a) random growth, (b) selective side growth, (c) selective on-top growth.

EXPERIMENTAL

In this study, we used six organic materials for organic doubly-deposited thin films, molecular structures of which are shown in FIGURE 2. By vacuum-deposition, singly- or doubly-deposited thin films were formed on a (001) cleaved surfaces of alkali-halide single crystalline substrate (KCl, KBr and NaCl) under the following conditions: deposition was carried out at room temperature with a deposition rate of about 1nm/min. Crystallographic orientation and mutual registration were examined by atomic force microscopy (AFM) and transmission electron microscopy (TEM).

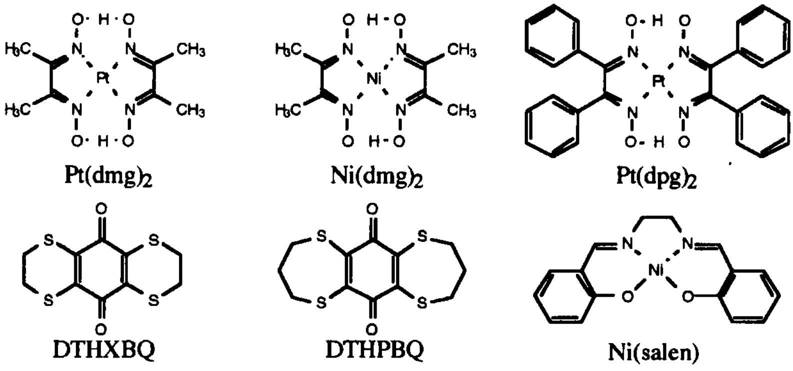

FIGURE 2 Structural formula of organic materials used in this study

These molecules have plane plate-like shape, and tend to form columnar structure in their crystals owing to their *d*-electronic or π -electronic intermolecular interaction, whose direction is parallel to their c-axes in crystals. This feature is interesting to form multi-layer with a special interfacial interaction. The crystallographic data of these crystals are shown in TABLE 1, from which one recognizes that they have orthorhombic unit cell.

TABLE 1 Crystallographic data of organic materials used.

Sample	Crystal System	Space Group	a/nm	b/nm	c/nm
$Pt(dmg)_2$[2]	Orthorhombic	*Ibam*	1.682	1.056	0.6513
$Ni(dmg)_2$[3]	Orthorhombic	*Ibam*	1.668	1.044	0.649
$Pt(dpg)_2$ [4]	Orthorhombic	*Iba2*	2.273	1.54	0.699
[5]	Tetragonal	*P4 /ncc*	2.0	2.0	0.66
DTHXBQ[6]	Orthorhombic	*Iba2*	0.9444	1.659	0.7196
DTHPBQ[7]	Orthorhombic	*Pccn*	0.9779	1.688	0.8007
Ni(salen)[8]	Orthorhombic	*Pbca*	1.383	2.616	0.7482

RESULTS AND DISCUSSION

SINGLY-DEPOSITED THIN FILM

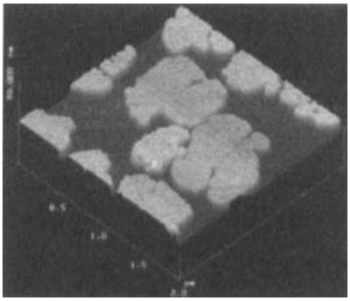

FIGURE 3 AFM image of $Pt(dmg)_2$ fabricated on KCl

In order to find the preferable organic substrate (first layer in double layer), singly-deposited film of each molecule by vacuum deposition was examined. As a result of AFM and TEM observations, in almost all cases the c-axis (column axis) orients epitaxially perpendicular to KCl and KBr surface, except for the cases of Ni(salen) or $Pt(dpg)_2$. On NaCl, however, the columnar axis is likely to orient parallel to the substrate surface, while the crystals show epitaxial growth. For example, $Pt(dmg)_2$ and $Ni(dmg)_2$ formed on KCl or KBr take definite orientation with respect to the alkali-halide by epitaxy and comparatively flat top surface (FIGURE 3). Therefore these are advantageous as the first layer in organic double-layer. As the high resolution electron diffraction obtained from $Pt(dmg)_2$ or $Ni(dmg)_2$ epitaxial films reveals, its c-axis (stacking axis of the molecules) is perpendicular to the surface of KBr or KCl, and its [110]-directions align along the [110]-direction of KCl and KBr.

DOUBLY-DEPOSITED THIN FILM

Hetero-multi-structures were formed by double-deposition of various combinations of molecules. For instance, $Pt(dmg)_2$ layer was formed on KBr or KCl with a mean thickness of about 8nm. Successively another material was deposited on $Pt(dmg)_2$ substrate with a thinner mean thickness of about 2nm. As shown from the AFM image shows in FIGURE 4-a, DTHXBQ molecule was found surprisingly to grow only on the islands of $Pt(dmg)_2$ as well as DTHPBQ. Then the DTHXBQ and DTHPBQ molecule nucleate selectively on the top surface of $Pt(dmg)_2$, not directly on alkali-halide single crystal. This kind of growth is named "On-top selective growth", which leads to double-layer formation. On the other hand, $Pt(dpg)_2$ or Ni(salen) molecule was found to grow either on $Pt(dmg)_2$ or on alkali-halides (FIGURE 4-b), which can be called as random growth.

This selective on-top growth was observed in the case of DTHXBQ or DTHPBQ / $Pt(dmg)_2$ or $Ni(dmg)_2$, where one of the a- and b-axis dimensions are similar each other. Selected area electron diffraction (SAED) of the double-layered films showing the selective on-top growth was taken to determine correlation of crystal orientation in these films. SAED pattern indicates an epitaxial relation of second layer with the first layer of $Pt(dmg)_2$. The epitaxial relation can be expressed; a_{DTHXBQ} // $b_{Pt(dmg)2 \text{ or } Ni(dmg)2}$, a_{DTHPBQ} // $b_{Pt(dmg)2 \text{ or } Ni(dmg)2}$. The orientation correlation is also confirmed from high resolution TEM image, in which the double-layer displays parallel Moire fringes caused from the small discrepancy in the size between the shorter axes of each layer. The parallel Moire fringe extended over a wide area of the interface. The regular Moire may leads us to a conclusion that lattice matching would be considered to originate the selectivity of on-top growth, because the selective on-top growth was only observed in the cases of the similarity in lattice dimensions between the layers. In order to examine whether the selectivity in second layer growth originates from such high matching of lattice, double deposition with reverse order was investigated. As a result of the AFM observation, the second layer of $Pt(dmg)_2$ was found to be selective side-growth in the both first layers of DTHXBQ and DTHPBQ (FIGURE 4-c). Accordingly the similarity of lattice dimensions is an important factor to realize the selective on-top growth, whereas there may be more essential reason for selectivity. In order to consider the origin of such

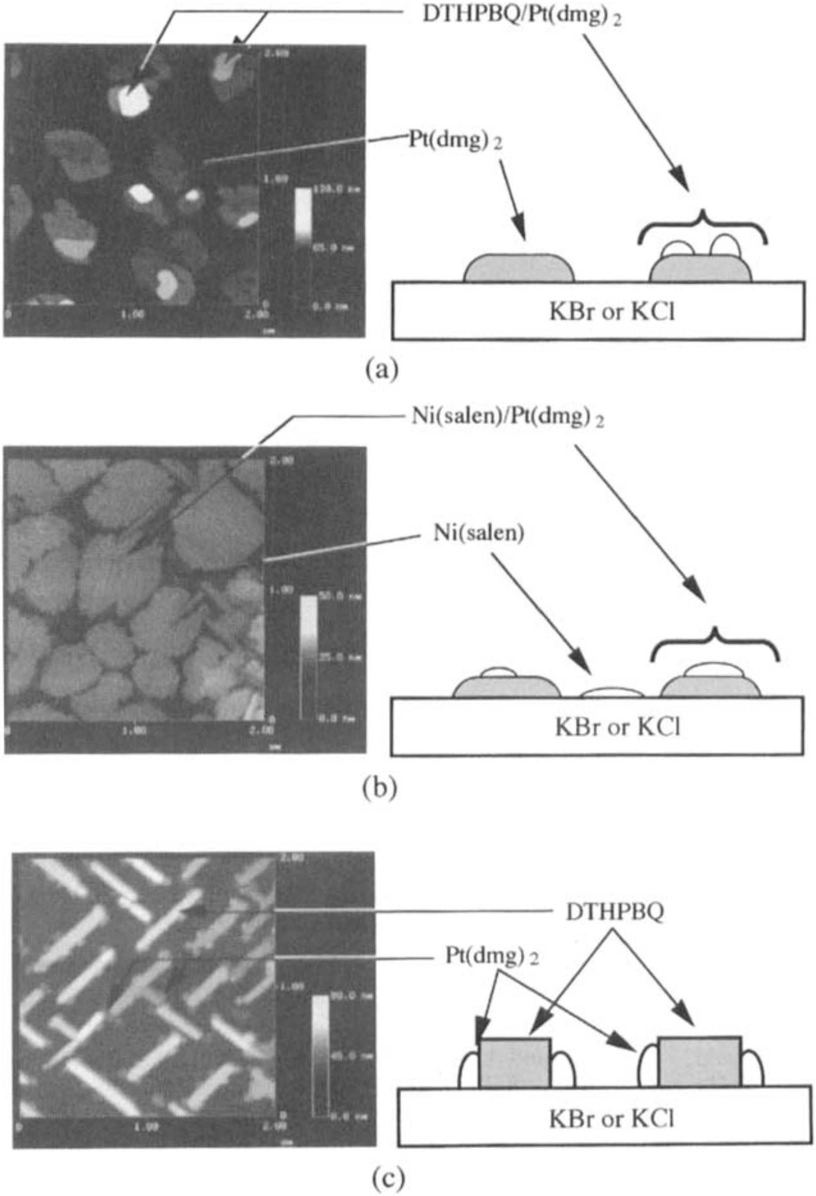

FIGURE 4 AFM images and cross-section models of DTHPBQ / Pt(dmg)$_2$ (a), Ni(salen) / Pt(dmg)$_2$ (b) and Pt(dmg)$_2$ / DTHPBQ (c)

selectivity, surface of the substrate layer was examined in detail by AFM. As shown in FIGURE 5, the surface of Pt(dmg)$_2$ exhibits some roughness of the order of several nm, probably owing to the columnar growth of the crystal. It might be, therefore, plausible to consider pits of the molecular order would exist over such rough surface. Consequently the overdeposited DTHXBQ or DTHPBQ molecules tends to be adsorbed in the pit, so that nucleation follows there. Since Pt(dpg)$_2$ or Ni(salen) molecule whose size is bigger than such pit of Pt(dmg)$_2$, does not be expected to be stabilized in the pit, nucleation takes place at any positions.

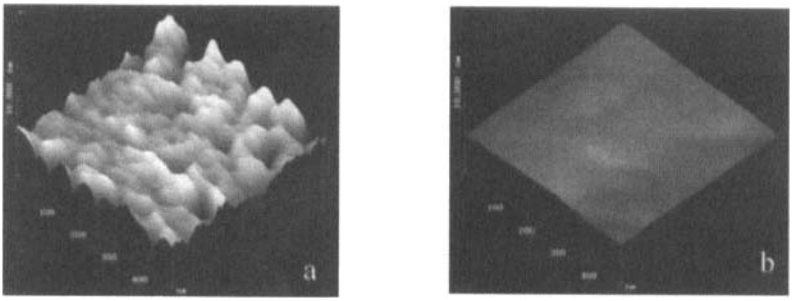

FIGURE 5 AFM images of the surfaces of Pt(dmg)$_2$ (a) and DTHPBQ (b).

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