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Epitaxial growth of ultrathin vanadyl-naphthalocyanine films on RbI, KI and KBr

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Abstract. Ultrathin films of vanadyl-naphthalocyanine (VONc) have been prepared on the (001) faces of RbI, KI, and KBr by molecular beam epitaxy. Molecular arrangements were determined by reflection high-energy electron diffraction. VONc molecules form square lattices ($\sqrt{10} \times \sqrt{10} - R \pm 18.4^\circ$) on these substrates. The lattices are commensurate to the substrates and the intermolecular distance varies from 1.64 nm on RbI to 1.48 nm on KBr, in keeping with the lattice constant of the substrates. The position of the molecules is primarily determined by electrostatic interaction between molecules and the substrates. VONc molecules stay on the surface via electrostatic interaction and steric hindrance between projecting naphthalene rings is avoided by minimizing the van der Waals interaction between molecules.

1. Introduction

Epitaxial growth of metal phthalocyanines (MPcs) and their related compounds has long been examined on various substrates [1–21], since they are expected to show interesting optical and electrical properties. Epitaxial features of rather thick MPc films on cleaved faces of muscovite [1–4], alkali halides (AHs) [5–7], and graphite [8] have been investigated by Uyeda, Ashida, Kobayashi and their co-workers by means of transmission electron microscopy (TEM) and transmission electron diffraction (TED). Buchholz and Somorjai analysed the surface structures of monolayer MPc films on clean metal surfaces via low-energy electron diffraction (LEED) [9]. These pioneering works show that epitaxial features are strongly influenced by the lattice constants and the symmetry of the substrate surface, as well as growth conditions.

More recently, highly ordered MPc films are found to be obtained by molecular beam epitaxy (MBE) [10–19]. Structures of rather thick MBE-grown films were investigated by TEM and TED [16–19], and those of ultrathin films were studied by reflection high-energy electron diffraction (RHEED) [10–15]. RHEED is one of the most powerful methods used to analyse the surface structure of ultrathin MBE-grown films, from the very initial stage of growth [10–15, 20]. We made a systematic investigation of ultrathin MPc films grown on some AHs by RHEED and found that the molecular arrangements were affected by the lattice constants of the AHs [12–14]. The results are summarized in table 1 and figure 1. The molecules form three types of commensurate square lattices (3×3 , $\sqrt{10} \times \sqrt{10} - R \pm 18.4^\circ$, and $\sqrt{13} \times \sqrt{13} - R \pm 33.7^\circ$) on AHs, where Wood's notation is given using surface unit vectors, indicated by the arrows in figure 1(a). We call these lattices types A, B, and C

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in the following. The MPc molecules in table 1 have pyramidal molecular structures, in common where the centre metal atoms deviate from the molecular planes (see figure 2) [21–24]. Thin films of planar MPc molecules such as CuPc and NiPc gave spotty RHEED patterns, indicating the island growth of α -type crystals [25]. Similar lattice models are proposed for rather thick films (several tens of nanometers) of VOPc [17], AlPcCl [17], lanthanide-Pc2 [18, 19, 26, 27], F-bridged- and Cl-bridged-Al-Pc polymers (AlPcF) $_n$ [16] and (AlPcCl) $_n$ [28] from the results of TEM and TED observations. Some of these lattices are incommensurate to the substrates. The films are so thick that the molecular arrangements are hardly affected by atomic arrangements of the substrates. The molecules pack together as close as possible via the van der Waals force.

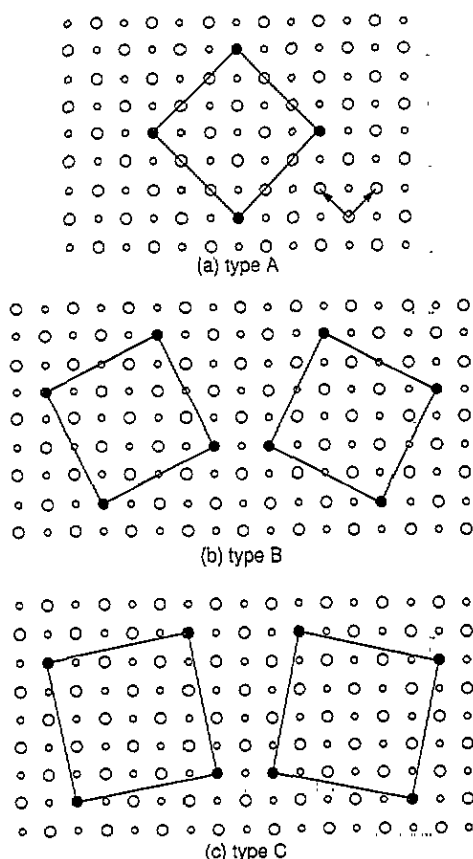


Figure 1. Three types of surface unit meshes of ultrathin MPc films grown on AH(001) surfaces: A, 3×3 ; B, $\sqrt{10} \times \sqrt{10} - R \pm 18.4^\circ$; and C, $\sqrt{13} \times \sqrt{13} - R \pm 33.7^\circ$. The small and large open circles represent the alkali cations and halogen anions, respectively. Wood's notation is given using the surface unit vectors indicated by the arrows in figure 1(a).

It should be noted that molecular arrangements in some MPc films on AHs are classified into three types of square lattices, while various structures are reported in bulk specimens. This indicates that the position of MPc molecules in the initial layer is primarily governed by electrostatic interactions between molecules and AH substrates. Each molecule is placed on the AH surfaces via the electrostatic interaction, with an appropriate intermolecular distance to minimize the van der Waals potential between neighbouring molecules.

It is thus interesting to examine the epitaxy of the MPc based compounds of larger molecular diameter, and to investigate the size effect on molecular arrangements. Metal-2,3-naphthalocyanine (MNC, NC=C₄₈N₈H₁₆) is one of the most hopeful compounds for this

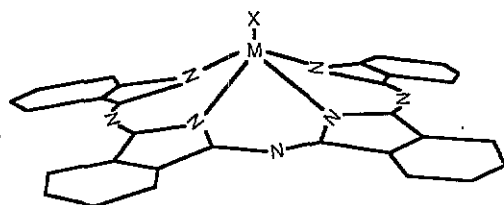


Figure 2. A schematic view of a metal phthalocyanine molecule having a pyramidal molecular structure. $M-X: Pb, V=O, Al-Cl$, and so on.

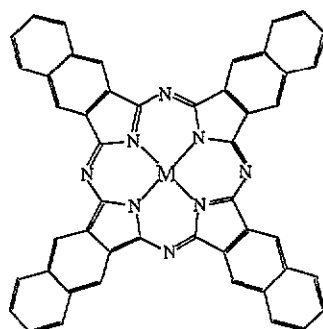


Figure 3. The molecular structure of metal-2,3-naphthalocyanine.

Table 1. Molecular arrangements of metal phthalocyanines on various alkali halide substrates. A, B and C represent the types of lattices which these MPc molecules form on the AH substrates (see figure 1). The values in the table show the lattice constants for the alkali halides and the intermolecular distances between the neighbouring molecules in MPc films.

	PbPc ^a	VOPc ^b	AlPcCl ^c
KI	d	d	A
0.71 nm			1.50 nm
KBr	A	A	B
0.66 nm	1.40 nm	1.40 nm	1.48 nm
KCl	B	B	B
0.63 nm	1.41 nm	1.41 nm	1.41 nm
NaCl	B	B	C
0.56 nm	1.26 nm	1.26 nm	1.43 nm

^a [13].

^b [12].

^c [14].

^d Unsettled.

purpose since it has four additional benzene rings to MPc (figure 3). In the present paper, we show the epitaxial growth of ultrathin VO-naphthalocyanine (VONc) films on AHS. The VONc molecule is thought to have a pyramidal molecular structure, like VOPc, although no structural data for VONc have been reported. Molecular arrangements in a VONc film with a thickness of 50 nm, grown on KCl, have been investigated by Yanagi *et al* [29]. According to their results for high-resolution electron microscopy (HREM), VONc molecules form incommensurate type-C lattices on KCl with their molecular planes almost parallel to the surface. We examined epitaxial growth of VONc on several AHS having larger lattice constants, and investigated the effect of the variation in the lattice constant of the substrates on molecular arrangements. Since single crystals of KI and RbI could not be obtained easily, we prepared epitaxial films of these AHS on KBr substrates by the MBE method [30].

2. Experimental

The apparatus consists of two ultrahigh vacuum chambers with base pressures of about 2×10^{-7} Pa. One is used for epitaxial growth and the other for electron spectroscopic

analysis of the specimen with a double-pass cylindrical mirror analyser (CMA, PHI 15-255G). The specimen can be transferred *in vacuo* between two chambers through a gate valve. The (001) surface of KBr was obtained by cleavage of a single crystal block (Horiba Seisakusho) in the air just before loading into the chamber. KI and RbI substrates were prepared by heteroepitaxial growth on KBr (001) surfaces. KI or RbI powder was heated in a Knudsen cell at about 350 °C, and it sublimed into molecular forms. The surface structure was observed by RHEED with a 20 keV incident electron beam. Single-crystalline films were grown epitaxially on KBr at a substrate temperature of 150 °C. The specimen surfaces were checked to be free from contamination by Auger electron spectroscopy (AES).

VONc was synthesized by heating a mixture of 2,3-dicyanonaphthalene and V_2O_5 according to the established method [31]. It was purified by repeated vacuum sublimation and identified by infrared and visible absorption spectroscopy. The purified powder was placed in a Knudsen cell and heated up to 400 °C. The substrates were kept at room temperature during the growth of VONc. The growth rate was controlled at about 0.5 MLE min^{-1} with a quartz oscillator located near the substrate. The thickness was calibrated by the optical density in the visible absorption spectra of the films grown on AHS. Here the amount of 1 MLE (monolayer equivalence) means the number of molecules needed to just cover the surface with an arrangement to be discussed below. Molecular arrangements were determined by RHEED patterns observed for several directions of the 20 keV incident electron beam. No noticeable change due to film damage caused by an electron beam was noticed during the observation.

3. Results and discussion

3.1. Preparation and characterization of the substrates

Figures 4(a)–(c) show the RHEED patterns of a KBr(001) surface for three different azimuths. The incident beam is parallel to the [100](a), [210](b) and [110](c) axes of the substrate. The positions of the streaks are shown above each photograph by short lines with indices corresponding to the two-dimensional reciprocal lattice rods. The spacing between the (00) and ($\bar{1}1$) rods in the pattern for the [100] azimuth corresponds to the reciprocal of the half the lattice constant, that is $(2/0.660) \text{ nm}^{-1}$. In the pattern for the [110] azimuth, we observe the intensity alternation between streaks originating from the extinction rules for the electron diffraction of rock-salt-type AHS. The intensity of the (01) and ($0\bar{1}$) rods is weaker than that of the (00), (02) and ($0\bar{2}$) rods.

Figures 4(d)–(f) show the RHEED patterns of a KI film heteroepitaxially grown on KBr. Film thickness is estimated to be 10 nm. The spacing between streaks in figures 4(d)–(f) is narrower by about 6% than that in figures 4(a)–(c), which corresponds to the difference in the lattice constants between KI (0.707 nm) and KBr (0.660 nm). This shows that a single-crystalline KI film having its own lattice constant grows heteroepitaxially on a KBr substrate with their crystallographic axes parallel to each other. RbI substrates were prepared in a similar way.

Figure 5 shows Auger electron spectra of an as-cleaved KBr (001) surface (a), and the KI film grown on it (b), which were taken with CMA. The primary electron beam was of energy 3 keV. There are no Auger signals from contamination of carbon at an energy of 270 eV in both spectra. A small peak around 270 eV is a satellite of the Auger signals of potassium. The Auger signals for oxygen at 510 eV are not seen in spectrum (a), while the signals for iodine appear at the same energy in spectrum (b). In addition, no Auger signal for bromine is observed in spectrum (b). This indicates that the underlying KBr substrate

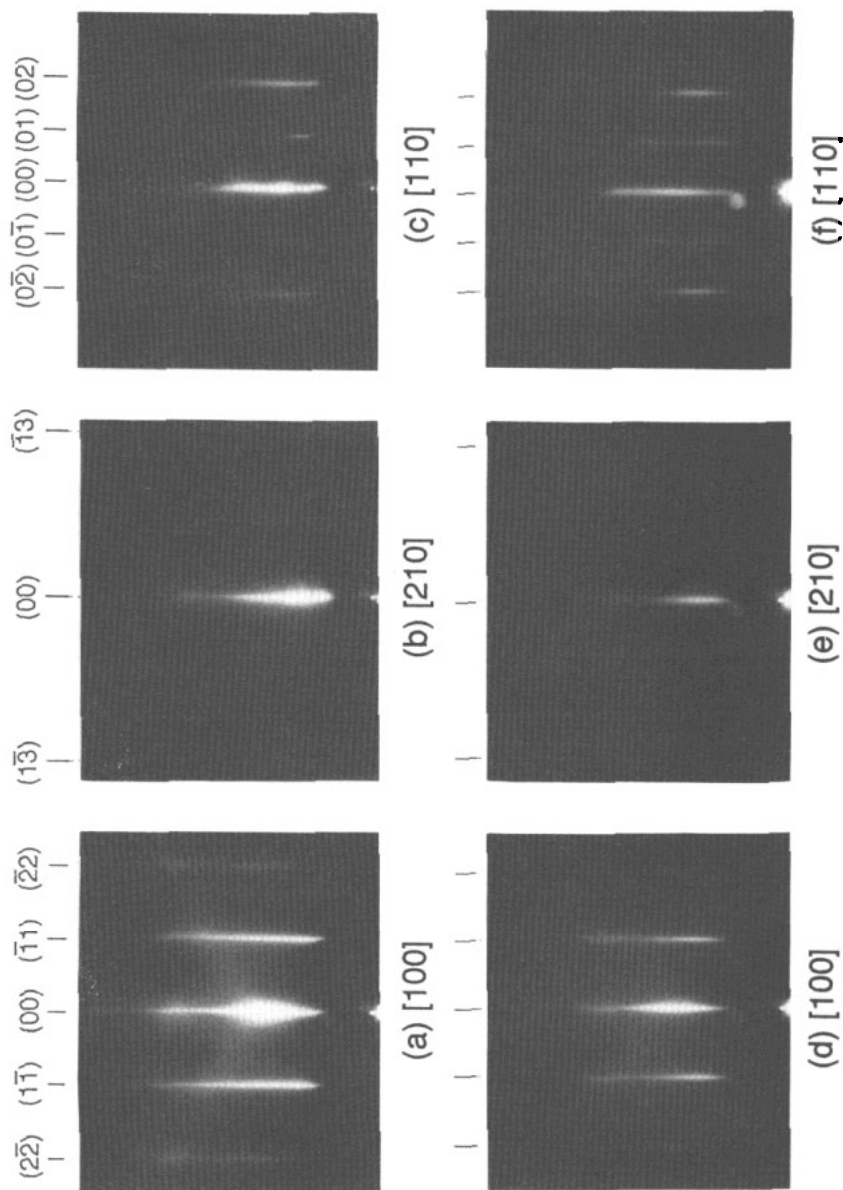


Figure 4. RHEED patterns of an as-cleaved KBr(001) face (a)–(c) and a KBr film grown on it (a)–(f). The incident electron beam is parallel to the $[100]$, $[010]$, and $[110]$ crystallographic axes of the KBr substrate. The short lines above each photograph indicate the positions of the streaks and the indices correspond to the two-dimensional reciprocal lattice rods of the substrate.

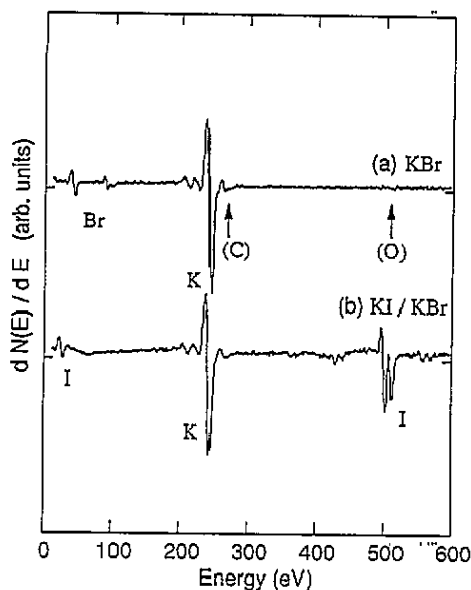


Figure 5. Auger electron spectra of a KBr(001) face (a), and a KI film grown on it (b), taken with an incident electron energy of 3 keV.

is completely covered by the epitaxially grown KI film. Formation of single-crystalline KI films was also confirmed by a low-energy electron energy loss spectrum shown in figure 6. The kinetic energy of the incident electron was 150 eV. Adoption of a pulse counting method reduces the probing electron current down to 1 nA, which achieves the reduction of surface damage [30,32]. A clear band gap appears in both the spectra for KBr(a) and KI(b), and no defect peaks are seen in the band gap region.

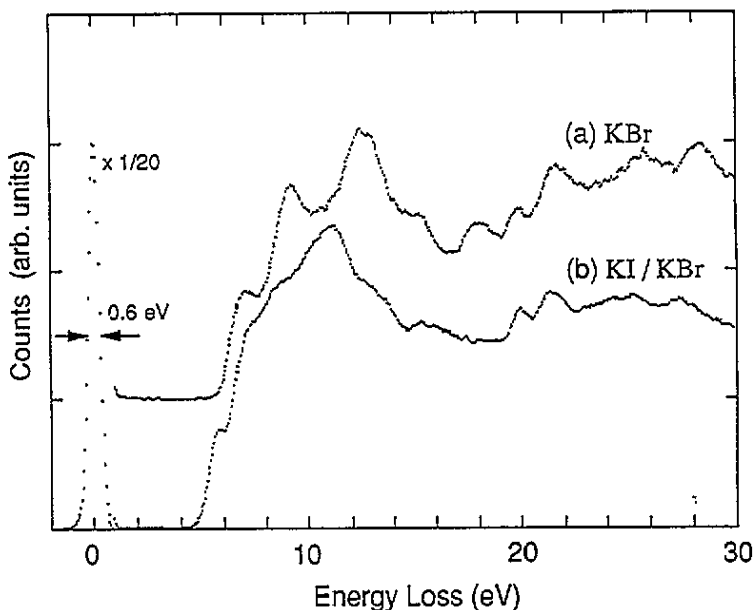


Figure 6. Low-energy electron energy loss spectra of a KBr(001) face (a), and a KI film grown on it (b). The kinetic energy of the primary electron beam is 150 eV.

3.2. Epitaxial growth of ultrathin VONc films

A remarkable change was observed in the RHEED patterns when the VONc films began to grow on the substrates. Among the VONc films grown on three substrates, the films grown on KI gave the sharpest RHEED patterns. Streak patterns could be observed in the film with a thickness of more than 5 MLE. The RHEED patterns of the films grown on KBr were the weakest ones. They became diffuse with increasing film thickness and vanished at about 3 MLE.

Figures 7(a)–7(c) show the RHEED patterns for an ultrathin VONc film grown on a KI substrate for three different azimuths. The film thickness was about 2 MLE. When the incident beam is parallel to the [100] azimuth of the substrate, new streaks appear at the centre between the substrate streaks (figure 7(a)). In the pattern for the [210] azimuth, streaks with the narrowest spacing can be seen (figure 7(b)). The spacing between the VONc streaks is one tenth of that between the (00) and ($\bar{1}$ 3) reciprocal lattice rods. In the pattern for the [110] azimuth, there are no new streaks between substrate ones on the zeroth Laue zone (figure 7(c)). The intensity alternation observed between streaks in figure 4(f) disappears in figure 7(c). Short streaks are observed at both sides of the (00) rod on the first Laue zone.

Since these features are the same as those observed for the VOPc and PbPc films grown on KCl and NaCl, and AlPcCl films on KBr and KCl [12–14], it is expected that VONc molecules form type-B lattices on a KI substrate.

Figure 8 shows the two-dimensional reciprocal lattice of the type-B lattices in figure 1(b). Full circles represent the reciprocal lattice of the left-hand side square lattice in figure 1(b). The reciprocal lattice of the right-hand side one is shown by small open circles, which are mirror images of the full ones. Hatched circles stand for the overlapping of both reciprocal lattices. Large open circles with indices are the reciprocal lattices of the substrates. Full lines represent the intersections of the Ewald spheres for three different azimuths. The RHEED patterns expected from this reciprocal lattice are drawn schematically in figure 8. The observed RHEED patterns agree well with the predicted ones. Since the type-B lattice gives streaks which overlap with the substrate streaks in the pattern for the [110] azimuth, there are no new streaks between substrate streaks on the zeroth Laue zone. It is concluded from these analyses that VONc molecules form a type-B lattice on a KI(001) surface at room temperature.

Figures 9(a) and 9(b) show the RHEED patterns for the [100] azimuth of 1 MLE VONc films grown on RbI and KBr, respectively. The VONc streaks appear at the centre between the substrate streaks, indicating the formation of type-B lattices. The RHEED patterns for other azimuths also showed that VONc molecules formed type-B lattices on RbI and KBr substrates.

Possible models for molecular arrangements of VONc on RbI, KI and KBr in real space are shown in figures 10(a), (b) and (c), respectively. Broken lines in each figure represent the surface unit meshes of the type-B lattice, determined by the RHEED patterns. The mirror images of these square lattices are omitted in these figures. The VONc lattices are commensurate to the substrate and thus the distance between the neighbouring molecules is $\sqrt{5}$ times as long as the lattice constant of the substrate, that is 1.64 nm on RbI, 1.58 nm on KI, and 1.48 nm on KBr. In figures 10(a)–(c), VONc molecules are drawn on the assumption that their molecular planes are parallel to the surface, although the actual molecular orientation can hardly be determined by electron diffraction alone. In the case of the growth of VONc on KBr, the intermolecular distance of 1.48 nm is rather small for a VONc molecule to lie in parallel on the surface without strain, as can be seen from figure

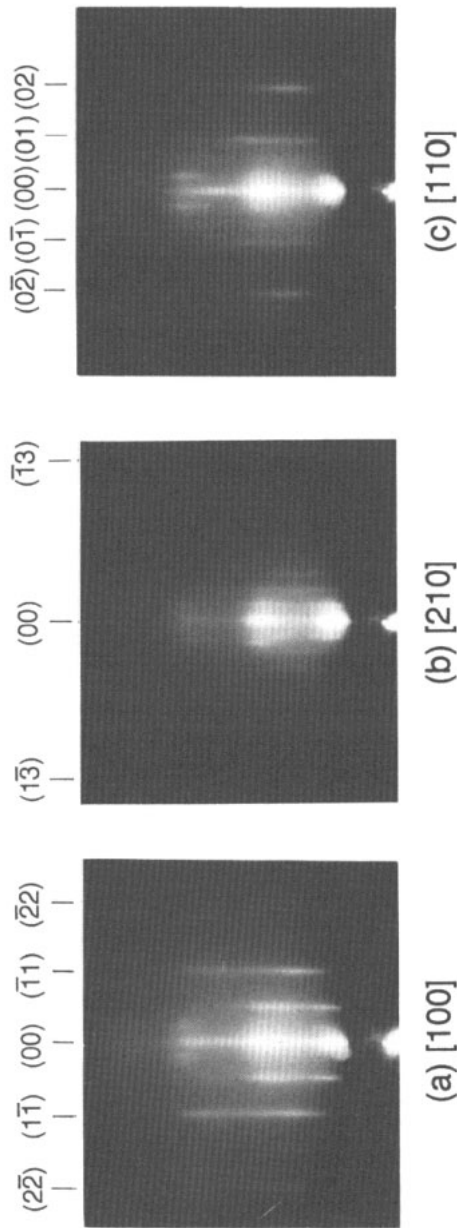


Figure 7. RHEED patterns of an ultrathin VOx film grown on a KI substrate. The film thickness is estimated to be 2 MLE. The incident electron beam is parallel to the $[100]$ (a) $[210]$ (b), and $[110]$ (c) axes of the substrate. The short lines with indices indicate the positions of the substrate streaks.

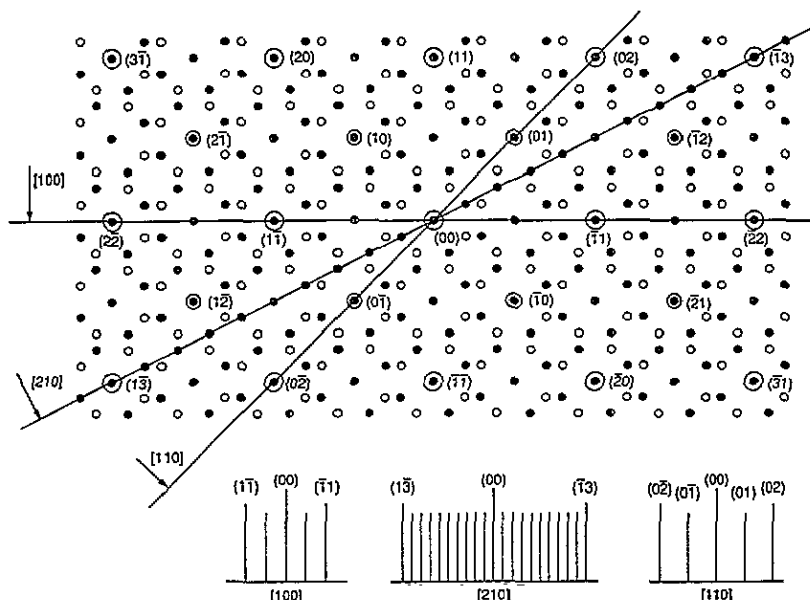


Figure 8. A two dimensional reciprocal lattice of the type-B lattice and the expected RHEED patterns. The full and small open circles represent the reciprocal lattice of the left-hand side and the right-hand side square lattices in figure 1(b), respectively. Hatched circles stand for the overlapping of both reciprocal lattices. Large open circles with indices are the reciprocal lattice of the substrate. Full lines represent the intersections of the Ewald spheres for three different azimuths.

10(c). Because of this strain, ordered domains on KBr are thought to be smaller than those on RbI and KI, which explains the observed weak RHEED patterns.

The intermolecular distance in the type-B lattice varies within the range of 10% in keeping with the lattice constant for the substrates in a manner similar to the case of MPc films [12–14, 16, 17, 19]. This indicates that the molecular arrangements are determined primarily by the electrostatic interaction between molecules and the substrates. Two possible models are proposed for the position of the molecule on AHS. Yanagi *et al* [29] have assumed the negatively charged oxygen atom of VONc to be put on an alkali cation, on the basis of the HREM image of rather thick VONc films grown on KCl. We proposed a metal-anion contact model where the positively charged centre metal atom is put on a halogen anion, as shown in figures 10(a)–(c). This model is supported by the experimental results that epitaxial films of PbPc molecules give the same RHEED patterns [13], while PbPc has neither additional halogen nor oxygen atoms to the centre Pb atom. Moreover electron-rich bridge nitrogen atoms can be close to alkali cations, when the centre metal atom is put on halogen anions. This was suggested by Ashida as the most probable molecular orientation of copper-Pc on KCl [5].

This orientation also seems favourable for molecular packing of VONc in the type-B lattice, to minimize the van der Waals potential between neighbouring molecules. When each VONc molecule is put on the substrate with such molecular orientation in the type-B lattice, projecting naphthalene rings of a VONc molecule can get into the hollows of the neighbouring molecules, as shown in figures 10(a)–(c). In most organic crystals, molecules are closely packed together with minimum voids, where the projections of one molecule

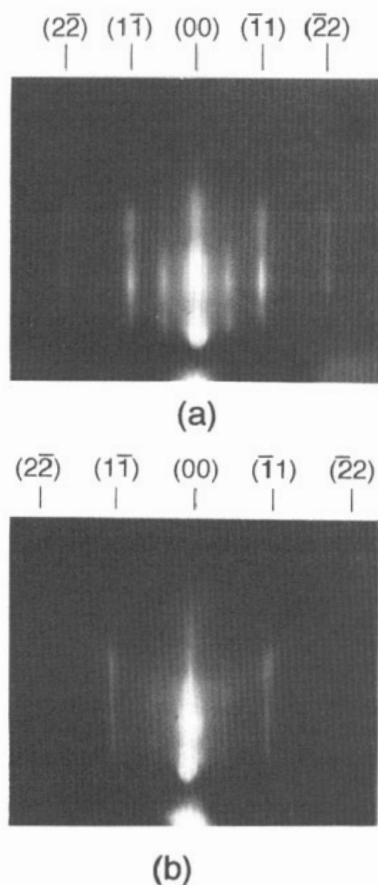


Figure 9. RHEED patterns for 1 MLE VONc films grown on RbI(a) and KBr(b) substrates. The incident electron beam is parallel to the $[100]$ azimuth of the substrates.

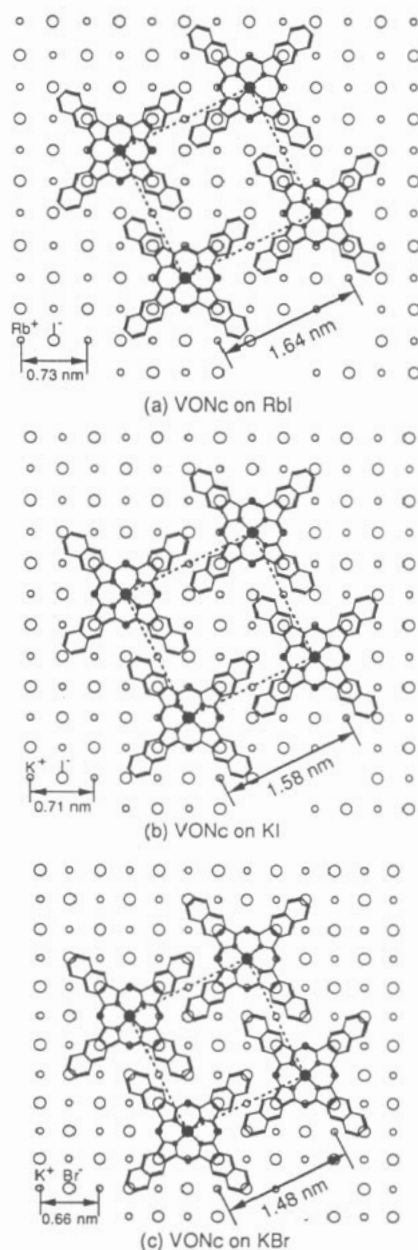


Figure 10. Possible molecular arrangements for VONc on RbI(a), KI(b) and KBr(c). VONc molecules form type-B lattices on these substrates. Broken lines represent the surface unit meshes determined by the RHEED patterns. The mirror images of these lattices are omitted in the figures.

get into the hollows of the neighbouring ones in order to minimize a Lennard-Jones-type potential [33]. This is called the dovetail principle. The dovetail principle seems also to be the case for the VONc films grown on AHS, as can be seen from figures 10(a)–(c). Each molecule stays parallel on the surface with an allowable intermolecular distance. The type-B lattice seems suitable to minimize both the van der Waals potential between molecules and the electrostatic potential between substrates and molecules.

In the case of MPc films, molecules change their arrangements from the type-B to the type-A lattice, in order to keep an appropriate intermolecular distance when the lattice constant of the substrate becomes larger. Since each molecule needs to rotate in a plane from the stable molecular orientation mentioned above, in order to avoid steric hindrance between benzene rings, negatively charged nitrogen atoms are not on alkali cations [13]. Table 2 shows the intermolecular distances for the three types of commensurate square lattices on several AHS. The values with underlines are experimental results. The best lattice matching seems to be realized in a film grown on KI, since it gives the sharpest RHEED patterns. The intermolecular distance in this film is 1.58 nm and this value agrees with the one observed by TED for rather thick films [29], where VONc molecules pack together with minimum voids via the van der Waals force.

Table 2. Intermolecular distances in VONc for the type-A, type-B and type-C lattices on various AH(001) surfaces. Values with underlines represent the experimental results in the present work.

	Lattice constant, a (nm)	Type A, $\frac{3\sqrt{2}}{2}a$ (nm)	Type B, $\sqrt{3}a$ (nm)	Type C, $\frac{\sqrt{26}}{2}a$ (nm)
RbI	0.734	1.557	<u>1.642</u>	1.872
KI	0.707	1.499	<u>1.580</u>	1.801
KBr	0.660	1.400	<u>1.476</u>	1.683
KCl	0.629	1.335	1.407	1.604

Although the distance of 1.557 nm for a type-A lattice on RbI seems an acceptable value, VONc molecules still form a type-B lattice with an intermolecular distance of 1.641 nm. A distance of 1.604 nm for the type-C lattice on KCl also seems suitable for epitaxial growth. We examined the film growth of VONc on KCl at room temperature, and actually observed some streaks indicating the formation of the type-C lattice, although the intensity of the streaks was very weak. These two results show that the electrostatic interaction between VONc molecules and the substrate is so strong that the molecules on the surface cannot reorient themselves easily at room temperature to realize a stable molecular packing.

4. Conclusion

Epitaxial growth of VONc films on RbI, KI, and KBr(001) surfaces has been studied by RHEED. VONc molecules are found to form two equivalent square lattices ($\sqrt{10} \times \sqrt{10} - R \pm 18.4^\circ$, type B) on these substrates. The VONc lattices are commensurate to the substrate surfaces and the distance between the neighbouring VONc molecules varies in a range of 10%, according to the lattice constants for the substrates. This indicates that the positions of the molecules are determined primarily by the electrostatic interaction between molecules and the substrates. Each molecule is thought to stay parallel on the surface with an allowable intermolecular distance. Type-B lattices are favourable for molecular packing of VONc,

since the molecules which stay on the stable sites via electrostatic interaction can avoid steric hindrance between projecting naphthalene rings, in order to minimize the van der Waals interaction between molecules. These features are the same as those obtained for MPe molecules, following the common rules in the epitaxial growth of MPe compounds having pyramidal molecular structures on the (001) surfaces of AlN substrates.

Acknowledgments

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