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PSEUDOMORPHIC STRUCTURE OF VACUUM-DEPOSITED FLUORINATED VANADYLPHTHALOCYANINE (VOPcFx) AND ITS OPTICAL ABSORPTION SPECTRA

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Abstract Pseudomorphic structure of fluorinated vanadylphthalocyanine was formed on alkali halides and was analyzed by electron diffraction method using imaging plate and high resolution molecular imaging. The body-centered-tetragonal structure analyzed exhibits peak shifts in optical transmittance depending on the sort of alkali halides used as substrates.

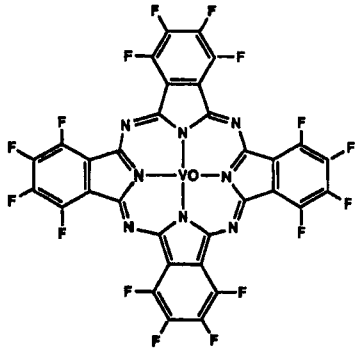
INTRODUCTION

Recently many pseudomorphic structures of organic materials have been made by vacuum-deposition or molecular beam epitaxy on inorganic substrates[1,2] and also on organic substrates[3]. In order to analyze such pseudomorphic structures, STM, X-ray, RHEED and LEED are generally used at present. In this paper, we present a new method for analyzing structures of such thin and small crystallites by electron diffraction intensities measured with imaging plate[4], which is a highly reliable two-dimensional detector for electron beam[5]. Pseudomorph of fluorinated vanadylphthalocyanine (VOPcFx) was analyzed with the imaging plate and the result was discussed in relation to the epitaxy and the optical property. High resolution images by electron microscopy were also employed and supported the result obtained by electron diffraction analysis.

EXPERIMENTAL

VOPcFx was kindly supplied by Mr.O.Kaieda, Nippon Shokubai Co. Ltd. The degree of fluorination of the sample was estimated from conventional elemental analysis. The weight fractions of

H-, C-, N- and F-atoms were 0.09, 43.78, 13.46, 33.09%, respectively, and then the numbers of respective atoms in one VOPcFx molecule are H=0.74, C=30.36, N=8 and F=14.49, which means that about 14.5 atoms in 16 peripheral hydrogens are substituted with fluorines on an average; x=14.5 in VOPcFx.



Using this material, thin film of VOPcFx was formed by vacuum-deposition on an air-cleaved (001) surface of KBr, KCl or NaCl single crystal under a vacuum of 10^{-5} Pa. The thickness of VOPcFx film was controlled by monitoring with quartz microbalance. The deposition rate was usually 1.0nm/min and the substrate temperature was kept at a temperature between 170 and 200°C. Electron diffraction patterns and high resolution molecular images were taken with JEM-200CX operated at 200kV. Imaging plate used for measuring diffraction intensities under 200kV electron beam was the type DL-UR_{III} commercially supplied by Fuji Photo Films Co. The thickness of a photo-excitable phosphor layer of the plate is about 140μm. Micro-elemenal-analysis for the deposited film was performed with a parallel electron energy-loss spectrometer (Gatan 666-PEELS) equipped to JEM-2000FX electron microscope.

Fig.1 shows X-ray powder diffraction pattern of VOPcFx taken with CuKα-radiation, where the diffraction peaks can be indexed with a monoclinic structure having the unit cell dimensions of a=1.39nm, b=1.32nm, c=1.45nm and β=102.8°. This monoclinic structure is similar in size with that of titanylphthalocyanine (TiOPc)[6].

The deposited film was investigated by electron energy-loss spectroscopy (EELS) at -110°C, in order to confirm that no thermal decomposition of VOPcFx molecule occurred during

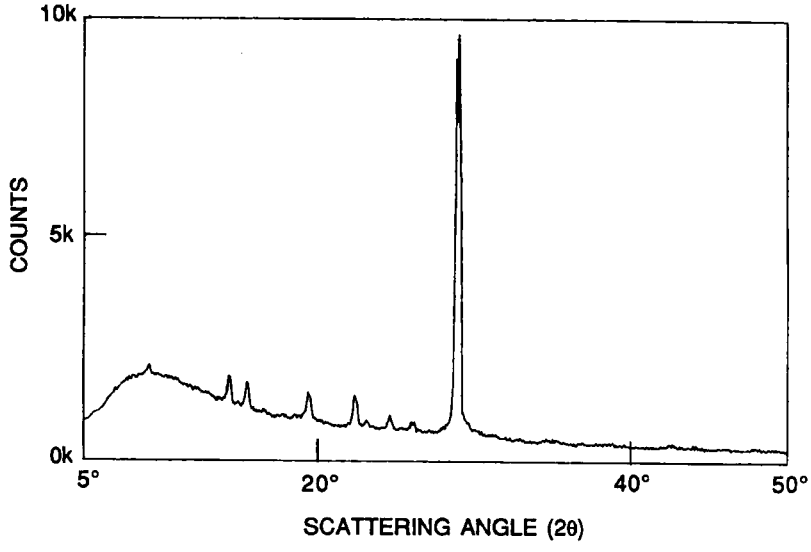


FIGURE 1 X-ray diffraction pattern of original VOPcFx taken with CuKα-radiation.

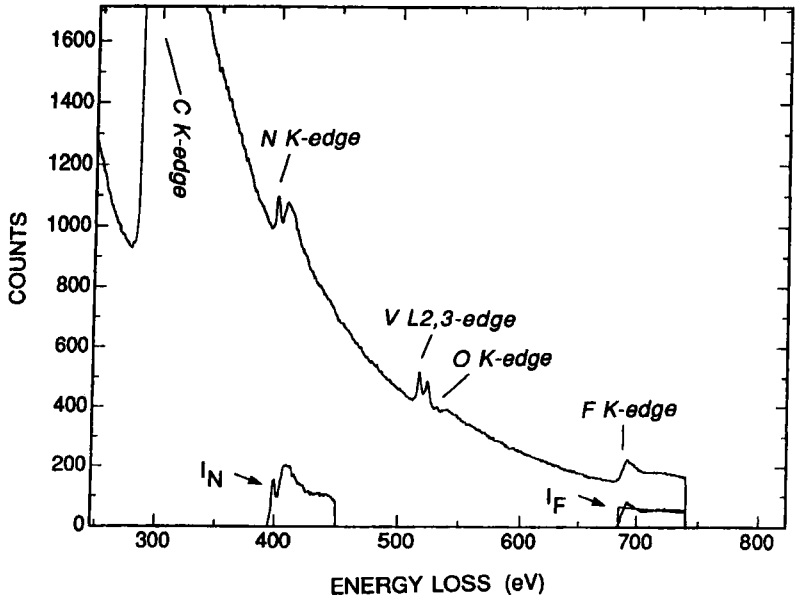


FIGURE 2 EELS spectrum of vacuum-deposited VOPcFx film. Atomic ratio of F to N was estimated from the absorption peak intensities, I_F and I_N.

the vacuum-deposition. EELS can provide us the atomic ratio of nitrogen to fluorine atoms for the present specimens. A small single crystalline area in the film, in the order of about 100nm in diameter, was selected and studied by analyzing the energy-loss of transmitted electrons due to excitation of the inner-shell electrons. Fig.2 shows a typical EELS spectrum from the vacuum-deposited VOPcFx film, in which one can observe several peaks caused by K-shell excitations of C, N, O and F in addition to L-shell excitation of V. After background subtraction, EELS absorption intensities of N and F atoms, I_N and I_F, were evaluated. As the result, the number of F atoms was found between 12.7 and 14.3 for one molecule. This indicates that thermal decomposition did not happen so seriously in the present vacuum-deposition condition.

RESULT AND DISCUSSION

Figure 3 (a) shows an electron micrograph of a thick VOPcFx film (about 20 nm in thickness) grown epitaxially on KBr at 172°C. The corresponding selected area electron diffraction pattern is shown in Fig.3 (b), where the incident direction of the electron beam is perpendicular to the film. The diffraction pattern shows that the VOPcFx has a new crystalline form, because the diffraction spots cannot be indexed with the monoclinic structure described above. Since this new crystalline form is only observed in thin film on substrate, it is considered to be a pseudomorph as in the case of vanadylphthalocyanine (VOPc) [2]. The electron diffraction pattern can be interpreted with two tetragonal patterns with a=1.47nm superimposed on each other as indicated in Fig.3 (b). This unit cell dimension of the pseudomorph is slightly longer than that of VOPc, a=1.40nm [2,7], which might be caused with the larger size of fluorine atom than that of hydrogen. Only the diffraction spots with h+k=even are allowed. The two-dimensional symmetry group is considered to be p4 instead of p4gm for VOPc, and accordingly a probable three-dimensional lattice is body-centered-tetragonal, whose c-axis is perpendicular to the film surface. The a-axis of the tetragonal VOPcFx orients along the [210] and [120] directions

of KBr substrate, and on the other substrates, KCl and NaCl, the same epitaxial orientation was also observed in the present deposition condition. In the case of VOPc, the tetragonal pseudomorph is also formed and its a-axis orients also along the [210] and [120] directions of NaCl and KCl substrates, while on KBr the a-axis is along the [110] direction of the substrate because of the lattice matching[2]. In the present case, the larger unit cell of VOPcFx realizes good lattice matching of the a-axis of VOPcFx with a repeat distance along the [210] of KBr substrate as described later.

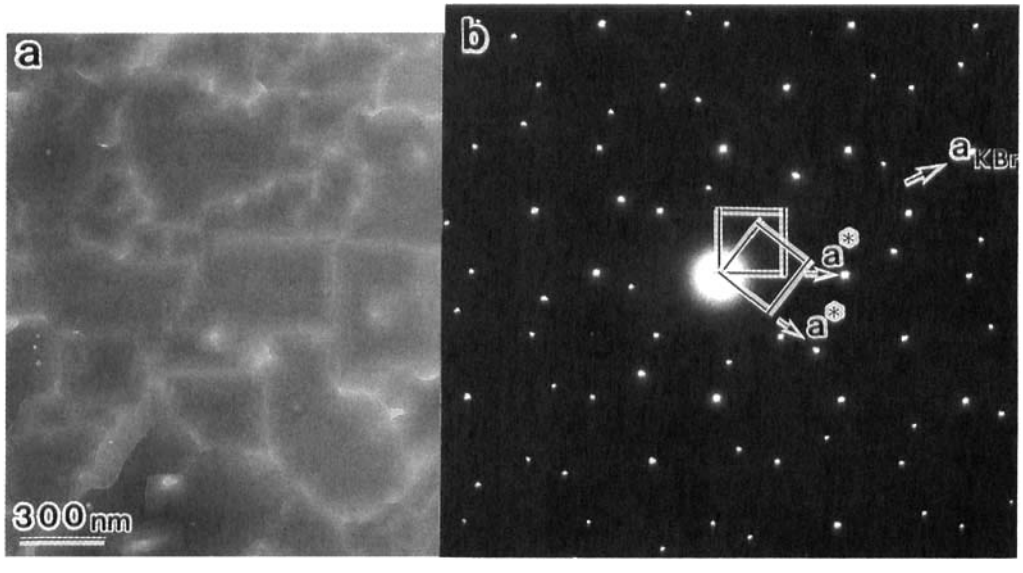


FIGURE 3 (a) VOPcFx film deposited on KBr.
(b) The corresponding electron diffraction pattern.

In order to know epitaxial correlation at the interface, the molecular packing in the unit cell of the pseudomorph was analyzed by imaging plate method and high resolution electron microscopy. The imaging plate is a detection system for electron beam as well as for X-ray. The characteristics of the imaging plate are followings: high sensitivity, good linear response and wide dynamic range[5] as shown in Fig.4. These points assure us that the imaging plate is suitable for a quantitative measurement of electron diffraction intensities of organic

materials[8], which often crystallize as microscopic small crystallites and are hard to be analyzed by X-ray method.

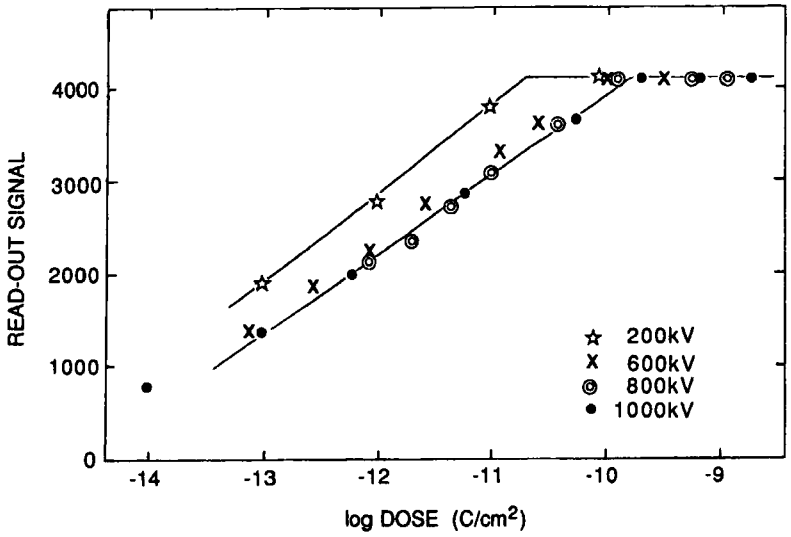


FIGURE 4 Response of imaging plate for fast electron beam.

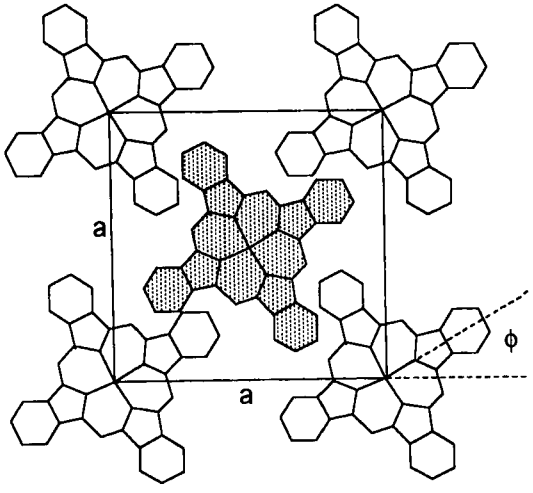


FIGURE 5 A model of molecular packing in the tetragonal unit cell.

Scattering intensities of electron diffraction collected with imaging plate can be quantitatively compared with scattering intensities calculated for a model molecular packing in the unit cell shown in Fig.5, where the central

molecule with a creen-tone shifts (1/2)c along the c-axis. In calculation of scattering intensities from the model, atomic coordinates in VOPcFx were assumed to be the same with those of VOPc[9], and one parameter to be determined was an orientation angle, ϕ, of isoindole ring from the a-axis.

The R-factor is plotted as a function of ϕ in Fig.6, where $R=\Sigma\{||Fobs|-|Fcal||\}/\Sigma|Fobs|$, Fobs and Fcal are the observed and the calculated structure factors obtained from the diffraction intensities and the model. From Fig.6, the minimum R-value, that is, most reliable molecular packing, is obtained at $\phi=28°$ for thin film of about 3nm thick. Such molecular packing may be energetically favored for side-by-side packing of VOPcFx molecules. Moreover, the molecular orientation in the unit cell seems favorable with respect to the atomic arrangement on the alkali halide substrates.

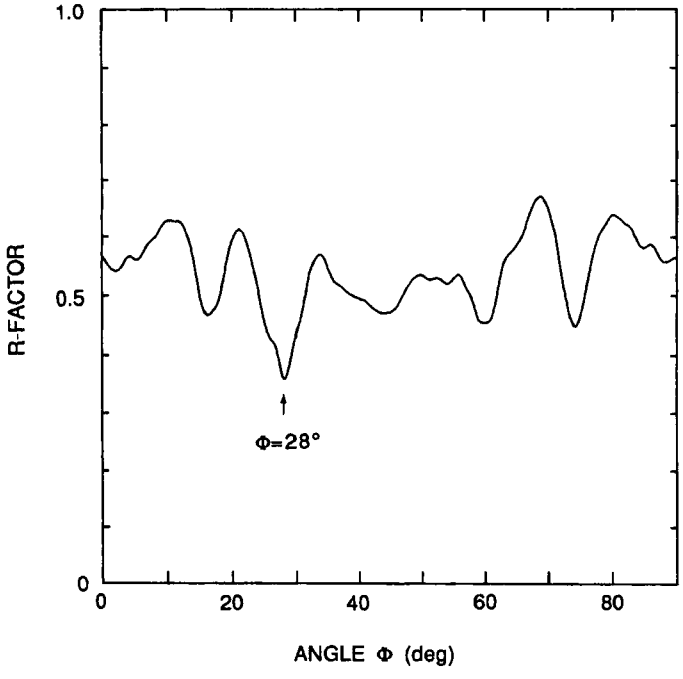


FIGURE 6 The minimum R-factor is observed at $\phi=28°$.

The molecular orientation with $\phi=28°$ is shown schematically in Fig.7 on an alkali halide substrate, KBr. Considering axial orientation of VOPcFx to the alkali halide,

isoindole ring in VOPcFx orients approximately along the [100] of substrate, which is an energetically plausible orientation on substrate as in the case of VOPc[7].

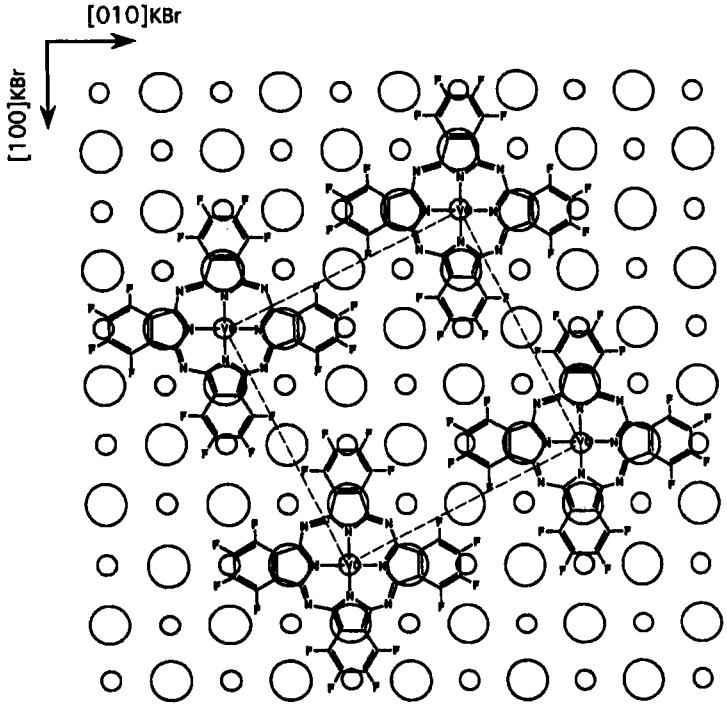


FIGURE 7 Expected deposition site of VOPcFx on KBr from the structure analysis.

Such molecular packing was directly imaged with a high resolution electron microscope having a theoretical point-to-point resolution of 0.2nm. High resolution image can confirm the result obtained from the imaging plate method. One typical image is shown in Fig.8, which corresponds well to the computer-simulated image shown in Fig.9 calculated on the basis of the structure obtained from the imaging plate method, where the specimen thickness was assumed to be 3.5nm. This proves that the analyzed structure is a reliable one.

Recently Yamashita *et al.* have observed peak shift in UV-VIS absorption spectra of VOPc and TiOPc deposited at different substrate temperatures on sapphire[10]. They have concluded that the peak shift is resulted from difference in crystal structure. In the present case, we also observed small

peak shift in UV-VIS spectra of the deposited films depending on the substrates as shown in Fig.10. However, the crystal

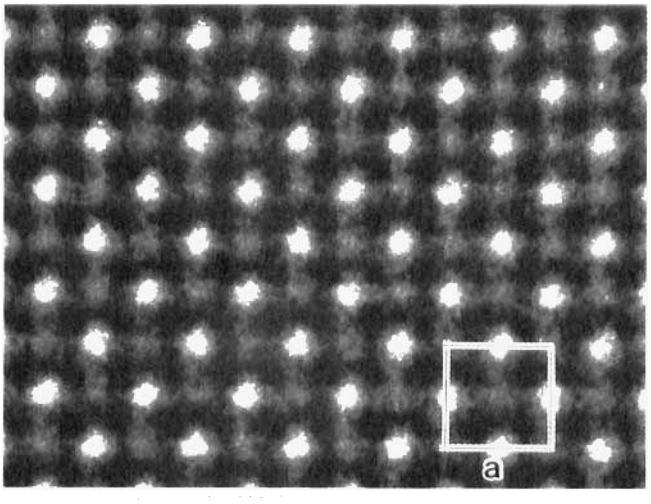


FIGURE 8 High resolution image of VOPcFx taken with JEM-200CX.

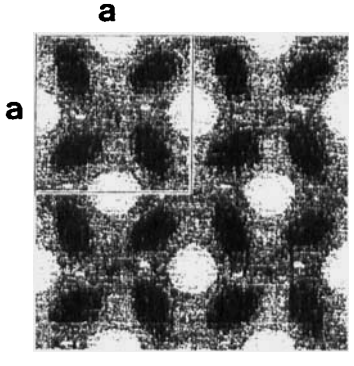


FIGURE 9 Computer-simulated image of VOPcFx at Scherzer focus assuming the thickness of 3.5nm.

structures of the deposited films on the different substrates exhibit the same unit cell and the same molecular packing. Therefore we cannot lay the responsibility on the structure itself. From the figure, the absorption peaks tend to shift toward longer wavelength with larger the lattice misfit. The lattice misfit values are listed in Table I. This means that one plausible origin of the peak shift may come from the strain of unit cell expected at the interface due to lattice

misfit. Since the structure analysis was carried out for the substrate-free films, such small strain may be relaxed already so that we could not detect any difference in the lattice dimensions on the different substrates.

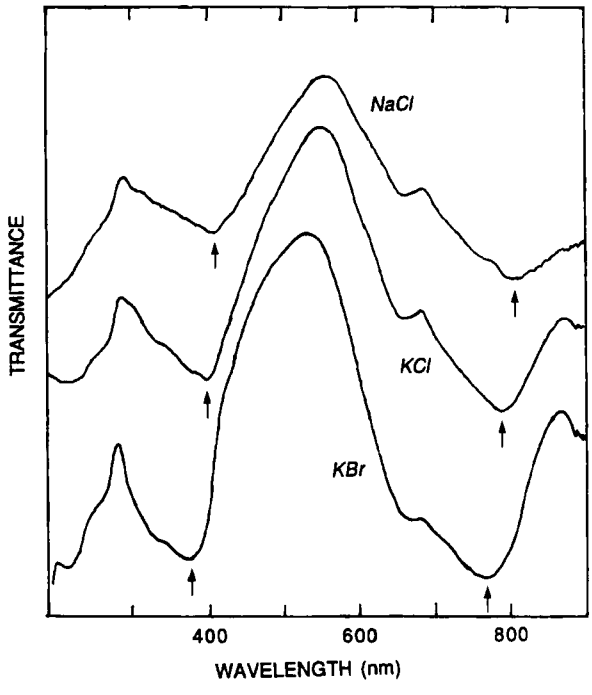


FIGURE 10 UV-VIS spectra of VOPcFx taken from a deposited film kept on the substrates. Arrows indicate absorption peaks.

TABLE I Lattice misfits for three substrates, here $d_{[210]}$ is a repeat distance along [210] direction of substrate.

substrate	$d_{[210]}$	misfit=$\{(a_{VOPcFx} - d_{[210]}) / d_{[210]}\} \times 100$
KBr	1.475 nm	-0.4 %
KCl	1.406 nm	4.6 %
NaCl	1.259 nm	16.8 %

CONCLUSION

The pseudomorph of VOPcFx epitaxially grown on alkali halides was analyzed using imaging plate to be body-centered-tetragonal crystal. The epitaxial orientation was different from that of VOPc, because of the larger a-axis dimension of VOPcFx. The UV-VIS absorption peaks were found to change depending on the substrates used and to shift correlating to the lattice misfits.

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