Crystal Growth and Molecular Orientation of Vanadyinaphthalocyanine in Thin Films

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Vanadyl-2,3-naphthalocyanine (VONc) was vacuum-evaporated onto a KCl (001) surface. The crystal structure and molecular arrangement were determined by high-resolution electron microscopy (HREM) and electron diffraction. The crystal growth depended on the substrate temperature. The thin film deposited on KCl kept at 30 °C was composed of amorphous and microcrystalline structure. At the substrate temperature range of 100-200 °C the deposited VONc formed tentacle-like crystals, the column axes of which lay on the substrate surface. The epitaxial film grew on KCl kept at temperatures higher than 300 °C. The high-resolution structure image elucidated that the planar VONc molecules tilt and stack in parallel along the b axis which stood perpendicular to the substrate surface. The origin of the molecular stacking was attributed to the V-O bonds which stick out of the molecular plane. The epitaxial nucleation was explained in terms of interaction between the electronegative oxygen atoms in the VONc molecule and the positive potassium ions in the KCl surface. The relative orientation between the deposit and the substrate cyrstals originated in the close lattice match of both crystals. Absorption and reflection spectra showed that the optical properties were significantly changed according to the differences in the orientation growth. Deposition of VONc at 300 °C results in an intensive absorption at 872 nm.

Introduction

In a rapidly advancing information-orientated industry, extensive studies have focused on high-density optical data recording (ODR) media. Organic dyes such as phthalocyanines (Pc)¹ become candidates for ODR applications in place of metallic materials owing to their chemical stability and facility for synthetic modification. An important property required for ODR materials is long-wavelength absorption in the writing process by semiconductor lasers. Some Pc compounds are known to exhibit absorption at a laser light range (780-890 nm), for example, the solvent-treated magnesium Pc (MgPc)² and the annealed vanadyl Pc (VOPc).^{3,4} The requirement for laser-addressed recording systems has led to molecular design and synthesis of other phthalocyanine derivatives.⁵ 2,3-Naphthalocyanines (Nc's, tetranaphtho[2,3-b:2',3'-g:2",3"-l:2"',3"'-q]porphyrazine) have strong absorption bands in the near-infrared region at longer wavelengths than those for Pc's because of their larger π -electron conjugated systems with the additional benzoannulation.⁶⁻⁹ The spectral properties and structural features of Nc's have been investigated in thin films prepared by a vacuum sublimation technique.⁹ The absorption maxima of their solid-state spectra were found to shift to longer wavelengths than those of the solution spectra. The X-ray diffraction study of the thin films suggested the disordered and microcrystalline structures. An expected phase transition in the crystalline film of Nc's has attracted much interest for application to ODR materials. However, the crystal structure of Nc's in solid films has not been determined in detail so far.

For constructing practical ODR devices, crystal growth should be controlled to obtain the most effective molecular arrangement in thin films. As is well-known, vacuum-evaporated Pc compounds grow epitaxially on a cleavage surface of alkali-metal halides.¹⁰ Copper Pc (CuPc) deposited on a KCl (001) plane takes a standing b-axis orientation in which planar Pc molecules come into parallel contact with the KCl surface.¹¹ The molecular arrangement of chlorinated CuPc in a thin film was directly observed by highresolution electron microscopy (HREM).¹² HREM is very convincing to investigate the local structure and molecular orientation in thin crystals which cannot be analyzed by the X-ray diffraction method.

In the present study, a thin film of vanadyl Nc (VONc, Figure 1) was prepared by vacuum evaporation onto a KCl (001) surface.



Figure 1. Molecular structure of vanadyl-2,3-naphthalocyanine.

The condition for growth of crystalline films was examined at various substrate temperatures. The crystal structure was determined by electron diffraction and molecular arrangement in the thin film was directly observed by HREM. The VONc thin film had intensive absorption and reflection bands in the long wavelength spectra (700-900 nm).

Experimental Section

The sample of VONc was prepared from 2,3-dicyanonaphthalene and V_2O_5 by modification of a known method.⁹ V_2O_5 ,

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Figure 2. Electron micrographs and electron diffraction patterns of the VONc thin films deposited on the KCl (001) surfaces kept at 30 (a), 150 (b), and 300 °C (c).

0.125 g (6.5 × 10⁻⁴ mol), and 2,3-dicyanonaphthalene, 0.86 g (4.8 × 10⁻³ mol), were mixed and sealed in an evacuated glass tube. After heating at 300 °C for 45 min, the crude product was stirred for 24 h in 1 N HCl in order to dissolve unreacted V₂O₅. Then followed an exhaustive Soxhlet extraction with ethanol, acetone, and *N*,*N*-dimethylformamide. The VONc was dried at 200 °C over P₄O₁₀ in vacuo and was identified by IR, UV/vis, and mass spectra.

A KCl (001) surface used as the substrate was cleaved in air and was immediately mounted on a heater in a vacuum chamber. The substrate was preheated at 150 °C for 1 h and was kept at temperatures between 30 and 350 °C in a vacuum of 1×10^{-4} Pa. VONc was evaporated onto the substrate from a quartz crucible source heated by a tungsten coil. The deposition rate was controlled at about 3 nm/min by using a quartz crystal microbalance. For electron microscopy the film was reinforced with an evaporated carbon film by the indirect evaporation method.¹³ After the KCl substrate was dissolved away by floating on water, the specimen film was transferred on a microgrid¹⁴ coated with a gold film. Electron micrographs and electron diffraction patterns were obtained by a JEM-200CX electron microscope. HREM observation was carried out using an objective pole piece with spherical aberration coefficient of 2.0 mm and a minimum dose system (MDS)¹⁵ at 100-kV acceleration. An accurate lattice spacing was calibrated from the electron diffraction patterns by comparison with the superposed diffraction ring of gold as references. High-resolution images were interpreted by comparing with the computer-simulated images. Image simulation was performed by the multislice program developed on NEC

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Figure 3. High-resolution electron micrograph of the epitaxial VONc thin film deposited on the KCl (001) surface kept at 350 °C.



Figure 4. Selected-area electron diffraction pattern of the epitaxial VONc crystal deposited on the KCl (001) surface kept at 350 °C.

PC-9801VM microcomputer.16

Electronic spectra were recorded on a Shimadzu UV-3100S. As described before, VONc was evaporated on KCl (001) surface and the spectra were measured in transmission and reflection.

Results and Discussion

The deposited films were identified as VONc from the intensive absorption spectra at a near-infrared region of 700–900 nm. Figure 2 shows electron micrographs and electron diffraction patterns of the films about 50 nm in thickness. The film deposited on KCl kept at 30 °C is composed of a continuous thin layer as shown in Figure 2a. The weak diffraction ring pattern of 0.7-nm spacing indicates that the film was composed of microcrystalline and amorphous structures. The crystallinity of films increases with elevation of the substrate temperature. The film deposited on KCl kept at 150 °C consists of small lamellar and tentacle-like crystals as seen in Figure 2b. The diffraction pattern shows superposition of several reflection series corresponding to each crystal which takes different orientation. At a substrate tem-





Figure 5. Selected-area electron diffraction pattern of the tentacle-like VONc crystal laid on the KCl (001) surface.



Figure 6. Schematic diagram of the presumed molecular arrangement in the ac (a) and ab plane (b) of the VONc crystal.



Figure 7. Enlarged structure image of the VONc crystal and the corresponding simulated image calculated at 90-nm underfocus.

perature higher than 300 °C, the deposited VONc forms an epitaxial film. Thin crystals orient in two definite directions which cross at an angle of 23° as shown in Figure 2c. The electron diffraction pattern is composed of two equivalent net patterns corresponding to the oriented crystals. The angular relation between the deposited and substrate crystals was determined from the [100] step on the KCl (001) surface. The crystal edges make angles of 11.5° clockwise or counterclockwise with the [100] and [010] direction of the KCl crystal. This relative orientation originates in anisotropic molecular adsorption and lattice matching between both crystals as described later.

Figure 3 shows a high-resolution electron micrograph of the thin epitaxial crystal about 10 nm in thickness deposited on KCl kept at 350 °C. The lamellar crystallites of about 50-100 nm in length link each other to form a thin film. The orthogonal lattice image can be observed in the crystallites. All the crystallites take a single orientation in which the long axes of the lattices make an angle of 11.5° with the KCl [100] or [010] direction. The selected-area electron diffraction from the crystallite gave a single net pattern as shown in Figure 4. The orthogonal lattice spacings were precisely determined to be 1.57 and 1.58 nm. This diffraction pattern is equivalent to the single constituent of the superposed patterns shown in Figure 2c. The high-resolution image as marked with the arrowhead in Figure 3 reveals a fine structure in the crystal. The molecular arrangement can be analyzed from its enlarged micrograph. The X-shaped images arranged in the orthogonal array are considered to be the projection of VONc molecules because of coincidence with their size and shape of the molecule. The similar X-shaped image has been obtained from the metal phthalocyanine (MPc) crystal in which the MPc molecules are packed in an eclipsed stacking.¹⁷ It is considered from this finding that the VONc molecules are piled up in a column which stands perpendicular to the KCl substrate surface. The molecular stacking along the column was elucidated from

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Figure 8. Schematic diagrams of molecular stacking in the MPc (a) and VONc (b) crystals.

a selected-area electron diffraction pattern of the tentacle-like crystals which lie in parallel on the substrate surface, as shown in Figure 5. The reflection spots on the equator indicate a spacing of 1.57 nm which coincides with the interval between the longitudinal lattices shown in Figure 3. The fiber period of 0.38 nm corresponds to the interplanar spacing along the molecular column of the VONc crystal. This spacing is close to those of trivalent phthalocyanines such as GAPcF18 whose moelcular stacking is eclipsed and slightly slipped along the column.¹⁹ These trivalent phthalocyanines are classified into the same group of the crystal growth as VOPc, in which all the molecules stack in parallel and slipped orientation.^{3,4} The VONc crystal is also considered to consist of single columns with eclipsed and slipped molecular stacking. This single-column structure is confirmed from the unsymmetrical intensity distribution with respect to the meridian in the diffraction pattern in Figure 5.

On the basis of these findings, the molecular arrangement in the VONc crystal was presumed as shown schematically in Figure 6. The unit cell dimensions were determined as a = 1.57 nm, b = 0.38 nm, c = 1.58 nm. The molecular structure of VONc

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Figure 9. Schematic explanation of relative orientation between the VONc crystal and the KCl (001) surface.

was assumed to have a planar skeleton and the V-O bonding normal to the molecular plane by reference to those of VOPc.³ The position of vanadium atom was approximated to be at the center of the molecular plane. The molecules rotate clockwise around the b axis to make an angle of about 26° between the row of the benzoannulation and the *a* axis. The molecular planes were assumed to tilt about 10° around the axis drawn through the diagonal meso-bridging nitrogen atoms. The molecules are piled up in parallel to eclipse each other along the b axis. According to this presumed structure the atomic coordinates of the VONc molecule within the unit cell were calculated and the molecular arrangement in the epitaxial film was confirmed by comparison with the computer-stimulated images. The high-resolution structure image projected along the b axis was simulated by using various microscopic parameters and crystal thicknesses. Figure 7 shows the best match of the real image with the simulated one which was calculated at 90 nm underfocus with a crystal thickness of 11 nm. It can be clearly seen that the X-shaped image coincides with the molecular contour of VONc. Thus, the molecular arrangement in the VONc crystal was directly deduced from the high-resolution image. The packing of the VONc molecules is different from that of MPc compounds as schematically shown in Figure 8. As is well-known, the MPc crystal forms the herringbone structure, in which the molecular planes in the neighboring columns tilt at the opposite angles alternately.²⁰ In the epitaxial film of MPc vacuum-evaporated onto KCl the b axis of the crystal takes a tilting orientation, and the molecules in the alternative columns come into parallel contact with the KCl (001) cleavage surface.¹¹ Saito et al. have interpreted the epitaxial nucleation of MPc on KCl by means of energy calculations of the electrostatic and dispersion-repulsive potentials.²¹ They have pointed out that the total potential energy becomes minimum due to the dispersion-repulsive contribution as the MPc molecule lies in parallel to the KCl surface, and that the parallel-orientated crystals grow predominantly at higher substrate temperature. In the present case, all the VONc molecules are piled up making acute angles with the KCl surface, so that the dispersion-repulsive potential is estimated to be considerably low. Furthermore, the epitaxial nucleation of VONc can be attributed to electrostatic interaction between the KCl surface and the V-O bonds which stick out of the molecular planes. The electronegative oxygen atoms are assumed to take the most favorable positions on the

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Figure 10. Electronic spectra of VONc films (thickness $0.4 \mu m$) on KCl (001) surface in transmission (a, KCl substrate kept at 30 °C; b, KCl substrate kept at 150 °C; c, KCl substrate at 300 °C).

positive potassium ions. The epitaxial orientation of the VONc crystal is found to originate from this anisotropic adsorption of molecules. The relative orientation of VONc and KCl crystals is schematically shown in Figure 9. The (010) planes of the VONc crystal are in contact with the KCl (001) surface. When the c axis of the VONc crystal makes an angle of $\pm 11.5^{\circ}$ or ± 11

Figures 10 and 11 show absorption and reflection spectra of the VONc films deposited on KCl kept at various temperatures. The position of the long-wavelength absorption in the absorption spectra (Figure 10) are 762, 838 nm (20 °C); 756, 856 nm (150 °C); 872 nm (300 °C). The absorption and reflection bands in the long-wavelength region (700-900 nm) are weak in the film deposited on KCl at 150 °C, while the epitaxial film deposited on KCl at 300 °C indicates the maximum absorption and reflection. These optical properties can be explained by the difference in the molecular orientation. In the lying tentacle-like crystals grown at 150 °C as shown in Figure 2b most of the planar molecular planes in the epitaxial film make an acute angle with the substrate surface as shown in Figure 8b. In the latter orientation the planar conjugated π -electron macrocycles are in

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Figure 11. Electronic spectra of VONc films (thickness $0.4 \mu m$) on KCl (001) surface in reflection (a, KCl substrate kept at 30 °C; b, KCl substrate kept at 150 °C; c, KCl substrate kept at 300 °C).

almost parallel configuration to the electron field of the incident beam. The spectra of the films deposited at 30 and 150 °C show two absorption peaks in the long-wavelength region. A shorter wavelength absorption around 760 nm also has been observed at 650 nm in the vacuum-deposited VOPc film by Griffiths et al.³ They have reported that this absorption can be attributed to a stacking disorder due to twinning, and the absorption intensity at 650 nm decreases by a thermal annealing. In addition, visible spectra of vacuum-deposited MPc films exhibit also two absorption peaks in the Q-band region.²² This Q-band splitting has been considered to be due to the herringbone structure, as shown in Figure 8a, in the solid state.²³ In the present case the shorter wavelength absorption around 750 nm of the epitaxial crystal deposited at 300 °C decreases to a shoulder, and the intensity of the absorption at 872 nm increases remarkably. Similar absorption spectra with a long-wavelength shift of the Q-band transition have been observed in thin films of AlPcCl, GaPcCl.²⁴ It has been considered that the Q band of these phthalocyanines are subjected to a red shift due to the single-column structure^{4,23} which is similar to the molecular stacking of the VONc crystal. These findings also confirms the single-column structure of VONc crystal as shown in Figure 8b. The spectral dependence of these molecular orientation envisages the ODR application of the VONc film using crystallization and phase transition by laser light.

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