

Molecular Morphology and Electrical Conduction of Evaporated Vanadyl Phthalocyanine Thin Films

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The epitaxial thin films of vanadyle phthalocyanine (VOPc) on various substrates were prepared by the MBE and normal vacuum deposition techniques. The molecular stacking of these films are largely affected by the substrate materials and their temperature. In the case of fused quartz and glass, the molecular plane of VOPc is oriented perpendicular to the substrate plane. However, parallel orientation of the molecular plane are observed in the VOPc films deposited onto the KBr (001) and spin-coated PVDF film. The lateral electrical conductivity and their activation energy are dependent on the molecular orientation.

TEXT

A vanadyl phthalocyanine (VOPc) molecule has a dipole moment due to its shuttlecock structure.[1] Large THG properties have been obtained in a VOPc and TiOPc thin film comparing to CuPc and CoPc with a plane structure. It is well known that the molecular arrangement is controlled by substrate materials temperature (T_s) and heat pre-treatment of the substrate.

Thin films of VOPc were prepared by the molecular beam epitaxy (MBE) at the pressure of 10^{-7} Pa and common vacuum evaporation (VE) techniques at 10^{-4} Pa. VOPc was obtained from Eastman Kodak Co. This material was used without further purification. Evaporating conditions were as follows; in the case of the MBE, the temperature of deposition (T_d) was 300°C , substrate's temperature was changed from room temperature to 200°C , in the case of the VE, T_d and T_s were 390 and $60\sim 130^\circ\text{C}$. Ultraviolet and visible absorption spectra were measured for thin films of VOPc prepared by the equilibrium (MBE) and nonequilibrium (VE) vapor phases deposition onto quartz slides. Both films showed similar spectra. Three absorption peaks were observed in the visible region. The peaks at 640 , 730 nm belong to the phase I and main peak at 840 nm originates from the phase II crystalline part.[2] Then the VOPc films obtained were suggested to be a mixture of both crystalline phases. The typical visible absorption spectra of the films with

different thickness on a fused quartz are shown in Fig.1

The molecular arrangement was evaluated by a thin film X-ray diffractometry and SEM. The periodicity of 1.21 nm ($2\theta=7.3$ degree) was observed in the specimen prepared onto a fused quartz and glass slides. This has been known as the diffraction from the (002) surface suggesting that the VOPc molecular plane is stacked perpendicularly to the substrate. In this case stacked molecules form columns which b axis orients parallel to the substrate. The molecules deposited onto a white mica formed microcrystals arranging somewhat at random at low substrate temperature (60°C). However, epitaxial growth of crystals was observed at elevated temperature T_s . With increasing substrate temperature the grain size of the crystals became larger. Figure 2 shows a SEM photograph of the VOPc film deposited onto a mica substrate ($T_s=200^\circ\text{C}$) by the MBE technique. Many crystals with various sizes and shapes were observed. In the case of the cleaved KBr and KCl, diffraction peak at 27.4 degree was only observed. These molecules deposited onto the cleaved KBr, KCl and spincoated polyvinylidenefluoride are judged to orient parallel to the substrate. The interplanar spacing of VOPc molecules was estimated as 0.33 nm.

H. Tada suggested that the thin films deposited by MBE technique onto alkali halides crystallize epitaxially with the modified lattice constants by the influence of substrates.[3]

Figure 3 shows the X-ray diffraction spectra

measured at the incident angle of 1 degree for the VOPc thin films on various substrates.

Anisotropic electrical conduction originating from the molecular morphology is observed in phthalocyanines.[4] Electron clouds along the molecular stacking direction becomes maximum resulting in higher conductivity along the molecular column. Therefore the evaluation of the lateral conductivity gives a macroscopic measure of the molecular orientation in a sense.

A pair of comb type Au electrodes with 150 gap were deposited onto the VOPc films. Figure 4 shows the I-V characteristics of the lateral conduction for the films prepared on-to various substrates. The conductivities changed about five orders in magnitude ($10^{-7} \sim 10^{12}$ S/cm) depending on the substrate material. We can put the conductivities in order; fused quartz = glass slide > white mica > spin-coated PVDF > KBr. This order well agreed with the sequence of the molecular orientation (perpendicular to the substrate). The molecular orientation and electrical conduction depended on the substrate temperature (T_s) strongly. The lateral conductivity and diffraction intensity at $2\theta=7.3$ degree were plotted against T_s for the VOPc films deposited onto fused quartz and white mica by the VE technique in Fig's 5 and 6. The conductivity and diffraction intensity of the VOPc films on fused quartz increased lineally with increasing substrate temperature.

On the other hand, the VOPc film on mica showed maximum value at $T_s = 100^\circ\text{C}$ on both the conductivity and diffraction intensity. It was clarified by X-ray studies that the parallel oriented molecules increased and the perpendicular molecules decreased at higher substrate temperatures ($T_s = 130^\circ\text{C}$) to the contrary.

The temperature dependence of the conductivities were measured. these activation energies were estimated as 0.66 and 0.92 eV for specimens prepared onto a fused quartz and spin-coated PVDF film as shown in Fig.7. This results support that the conduction along the molecular column need a small activation energy because of the maximum overlapping of the electron cloud.

The band gap was estimated at 1.32 eV for the VOPc film deposited onto a fused quartz. This corresponds to the absorption edge of 940 nm.

X-ray photoelectron spectroscopic (XPS) study was employed to clarify the chemical composition of the deposited thin films of VOPc. The XPS spectra of C1s, N1s and V2p_{3/2} showed sharp peaks, respectively. However, a

broad O1s peak was observed in both the as-received powder and evaporated films. The O1s peak can be divided into three components; the binding energy were 530.9, 532.5 and 534.3 eV respectively. The first peak is supposed due to V=O bond. The second and third peaks may originate from the adsorbed water, -OH bond. This results suggest VOPc molecules to be hydrophilic. Further investigation by using FTIR will be continued on this point.

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FIGURES

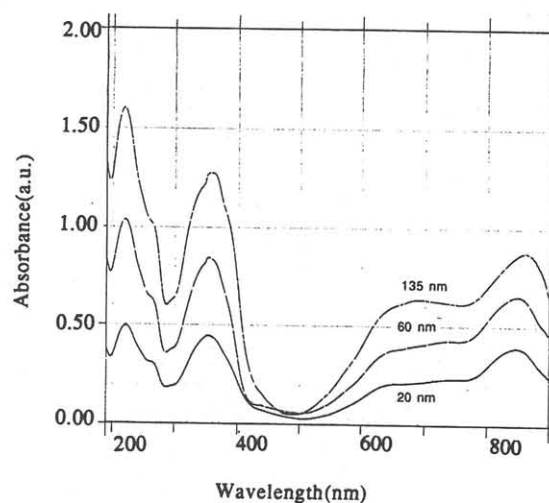


Fig.1. Absorption spectra of VOPc films deposited on fused quartz by VE.

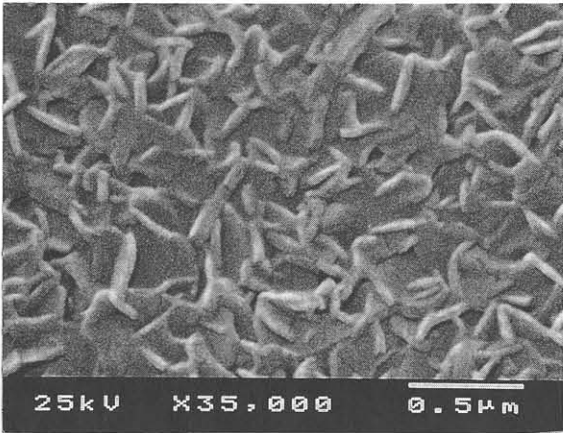


Fig.2. Electron micrograph of VOPc film deposited on mica by MBE.

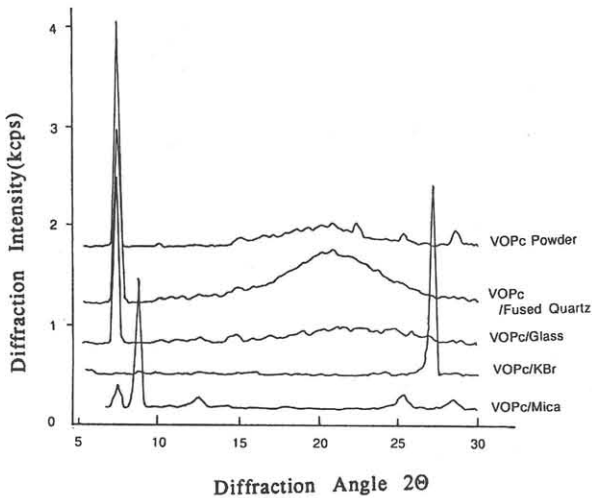


Fig.3 X-ray diffraction spectra of VOPc films deposited on various substrates by VE.

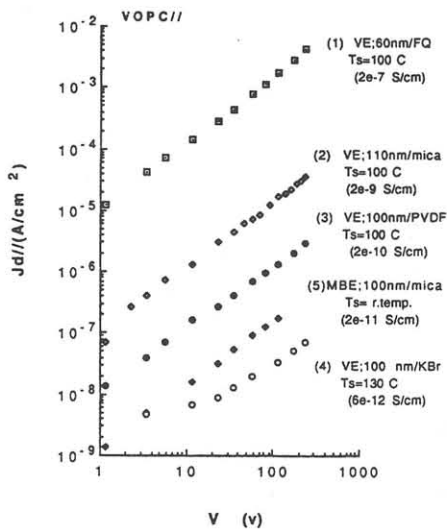


Fig.4. V-I characteristics of VOPc films on various substrates. VE; vacuum evaporation MBE; molecular beam epitaxy.

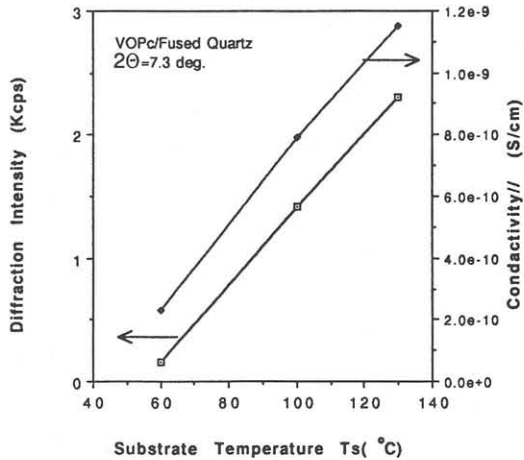


Fig.5. Diffraction intensity and conductivity vs Ts of VOPc film on fused quartz deposited by VE.

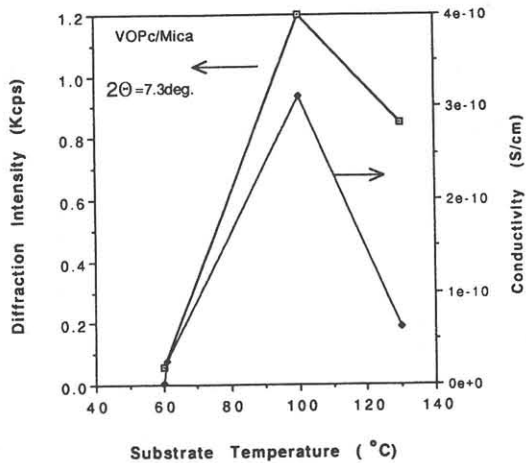


FIG.6. Diffraction intensity and conductivity vs Ts of VOPc film on mica deposited by VE.

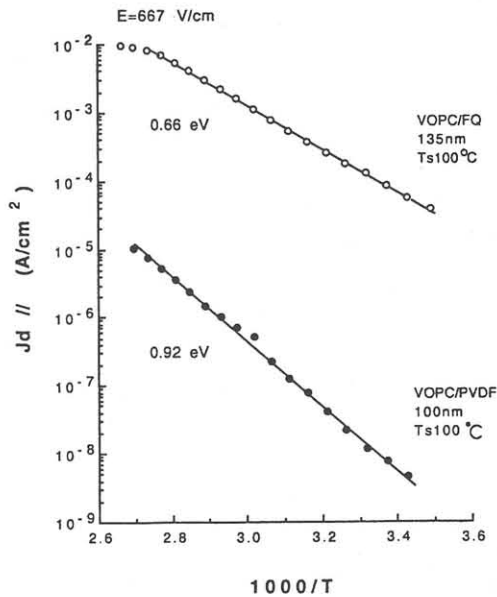


FIG7. Temperature dependences of conduction current of VOPc/fused quartz and VOPc/PVDF