

論文の内容の要旨

論文題目

Formation of Phthalocyanine Ultrathin Layers on Inorganic Solids via Wet Processes (湿式プロセスによる無機固体上へのフタロシアニン超薄層の形成)

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I. Introduction

Organic-inorganic interface has attracted much attention because the interface plays important roles in recent functional organic semiconductor devices. So far, simple oxides such as ZnO and TiO₂ have often been adopted to investigate the nature of the interface [1]. On the other hand, multiple oxides such as perovskite type ones possess various fascinating functionalities such as high temperature superconductivity and half metallicity, which are expected to be utilized in future organic semiconductor devices [2].

A simple method for fabricating organic semiconductor/perovskite oxide junctions is deposition of organic molecules onto the oxide surface. Here, how the initial molecular layer is formed on the oxide as a consequence of molecule-oxide interaction is of significant importance, because it often determine the structure and orientation of the organic layer as a whole which finally governs the performance of devices. Vapor deposition techniques such as vacuum deposition and molecular beam epitaxy have been used to study the organic ultrathin layers deposited on oxide substrates, however, they have difficulty in observing the weak interaction at the interface due to the kinetic deposition process.

In my research, ultrathin organic layers were formed by two types of wet processes: Langmuir-Blodgett (LB) method and so-called immersion method. In the former method, two metallophthalocyanines with flexible substituents and different central metals were compared in order to understand the molecular orientation and Langmuir monolayer formation on hydrophilic substrates. In the latter method, ultrathin layers of phthalocyanine were prepared on single crystals of perovskite oxides, LaAlO₃(100) and SrTiO₃(100) that have different surface termination, LaO and TiO₂ layers, respectively.

II. Experimental

In LB method, octaoctyloxy metallophthalocyanines (*MOOPc*, $M = \text{Cu, Zn}$) were dissolved in chloroform and spread onto water subphase. The substrate was glass plate, whose surface was made hydrophilic by immersion in CH₃OH:HCl aq and then in conc. H₂SO₄ aq, and rinsed by ultrapure water,. After the evaporation of the solvent, the floating layer on water subphase was compressed by two barriers. Surface pressure was kept at 3 or 20 mN/m for 15 min. Subsequently, LB monolayer was deposited by withdrawing the glass substrate. .

In immersion method, LaAlO₃ (LAO) and SrTiO₃ (STO) substrates with (100) orientation were used after annealing in air at 1200 and 1050 °C, respectively, to obtain atomically flat surfaces. These substrates were immersed into a pyridine solution of iron phthalocyanine chloride (FePcCl). After immersion, the residual solution was removed by nitrogen gas blow and the substrates were dried in vacuum.

The surface morphology of the samples were measured by atomic force microscope (AFM) in tapping mode using cantilevers with spring constant of 28 N/m for LB method and 3.5 N/m for immersion method. For the latter, the oscillation amplitude of cantilever was restrained to prevent the molecular layer from the mechanical damage.

III. Results and Discussion

1. Langmuir-Blodgett method

Figure 1 shows π - A curves of MOOPc. The surface pressure gradually increased reflecting their flexible octyloxy chains. The limiting areas were 1.04 nm² and 1.33 nm² for CuOOPc and ZnOOPc, respectively. These molecules indicated different isotherms at lower pressure due to different orientation of the monolayers, in spite of almost the same molecular structure. Such difference in isotherms resulted in different surface morphology, as follows.

Figure 2 shows surface morphology images of MOOPcs deposited at a surface pressure of 3 mN/m. The observed difference in the surface morphology originated from different molecular orientation, because the areal densities of molecules at a surface pressure of 3 mN/m were significantly different (Figure 1). The ZnOOPc film showed an assembly of islands with partial coverage. The height of the ZnOOPc islands was about 1.6 nm, which is much smaller than the lateral size of ZnOOPc molecule with long octyloxy chains. Hence, the islands were the assembly of the monolayers whose molecular plane is inclined towards the surface, due to hydrophilic nature of the central metal Zn. CuOOPc monolayer showed a flat and homogeneous surface, and its molecular plane was expected to be less inclined due to smaller area per molecule.

The effect of different central metal was also observed for films deposited at a higher surface pressure. From the time evolution measurements of water trough area after the application of surface pressure (Figure 3), it was found that ZnOOPc only showed rapid decrease in trough area at 20 mN/m. This result indicates that the high surface pressure induced further compression to maintain the surface pressure. Accordingly, ZnOOPc became densely packed at the high surface pressure probably because of intermolecular attractive interaction dominating over the hydrophilic interaction as described above. Figure 4 shows UV-vis absorption spectra, indicating that ZnOOPc exhibits larger absorption than CuOOPc at the surface pressure of 20 mN/m due to the further compression. Moreover, almost the same absorption intensities at several points within a sample suggested more effective transfer of ZnOOPc Langmuir monolayers than those of CuOOPc. X-ray reflection (XRR) measurements smaller thickness of ZnOOPc monolayer transferred at 3 mN/m, supporting the molecular orientation in LB monolayers proposed above.

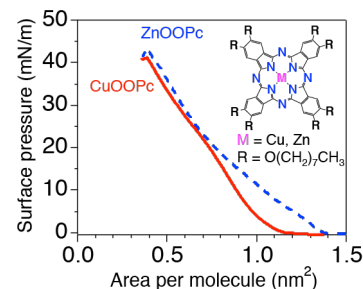


Fig. 1. Surface pressure-area isotherms for MOOPc ($M = \text{Cu}$ and Zn) monolayers.

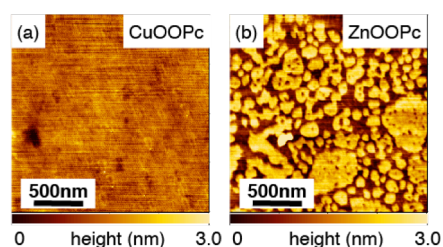


Fig. 2. AFM images of (a) CuOOPc and (b) ZnOOPc LB monolayers deposited at 3 mN/m surface pressures.

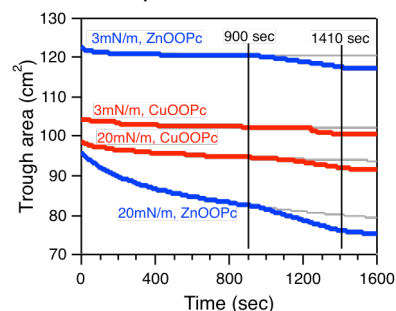


Fig. 3. Time evolution of the trough area after reaching 3 or 20 mN/m surface pressure for CuOOPc and ZnOOPc monolayers. Thin lines denote fitting curves.

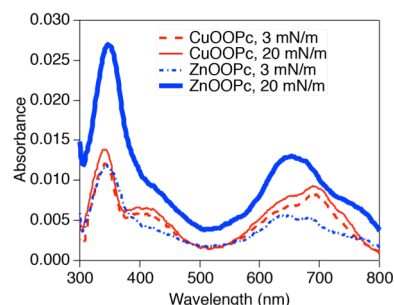


Fig. 4. Absorption spectra of LB monolayers deposited at different surface pressures.

2. Immersion method

Figure 5 shows AFM images of FePcCl ultrathin layers on LAO and STO substrates after drying. The surface coverage was significantly different between LAO and STO substrates, indicating the preferential molecular adsorption on LAO. Such difference in adsorption amount was also confirmed by X-ray photoemission spectroscopy (XPS). FePcCl contains eight nitrogen atoms per molecule, so that peak intensity of N 1s should reflect the adsorption amount of phthalocyanine on surface. The N 1s peak from FePcCl on LAO(100) exhibited stronger intensity than that from FePcCl on STO(100), being consistent with the results of AFM observation. The surface termination of each substrate is known to be TiO₂ for STO(100) and LaO for LAO(100) [3,4]. Thus, it is possible that the surface termination affected the molecular adsorption. Density functional theory (DFT) calculation was performed to evaluate and compute adsorption energy of the molecule on each substrate. As a result, the adsorption energy on LaO of LAO(100) was found to be larger than that on TiO₂ of STO(100) by about 3 eV, being consistent with the experimental observations. These results indicate that surface termination of perovskite oxide influences the adsorption behavior of the phthalocyanine molecules.

From the surface morphology seen in the AFM images, it was difficult to determine the detail molecular orientation. Alternatively, linear dichroic (LD) ratio, which reflects the orientation of transition dipole moment [5], was measured to deduce the average angle of phthalocyanine plane normal with respect to substrate normal. From visible absorption spectroscopy for FePcCl on STO(100) using polarized light, the LD ratio as a function of incident light angle was evaluated. Figure 6 shows the observed LD ratio vs. incident light angle (solid diamond). By comparing the experimental spectra with theoretical curves at different orientation angles θ in Fig. 6 (solid curve) [6], the orientation angle was deduced to be 39°. This indicates that the molecular plane was not in perfectly horizontal geometry, but was inclined towards the surface. Moreover, crystal truncation rod (CTR) measurements, being a surface analysis method to observe scattered X-ray, was also conducted. By analyzing the experimental scattering intensity spectra assuming surface models, the orientation of adsorbed molecules on LAO substrate was estimated, suggesting close planar geometry with respect to the substrate surface.

IV. Conclusion

In summary, phthalocyanine ultrathin layers were formed on inorganic solids by wet processes. It was revealed that interaction between the molecules and the scaffold, which was herein water subphase or perovskite oxide substrate, can be a key factor for formation of the ultrathin layers by wet process. This study would also contribute to controllable formation of ultrathin organic layers on oxides such as perovskite materials and to exploration of functionalities such as inorganic surface-molecule magnetic interaction by using wet process.

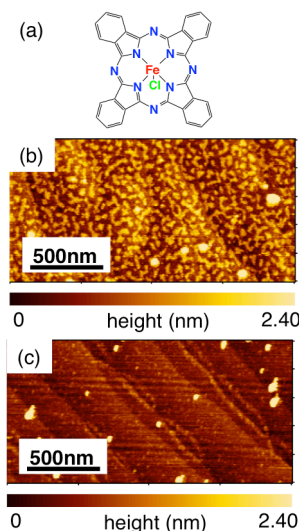


Fig. 5. (a) Molecular structure of FePcCl and AFM images of FePcCl ultrathin layers on (a) LAO and (b) STO substrates.

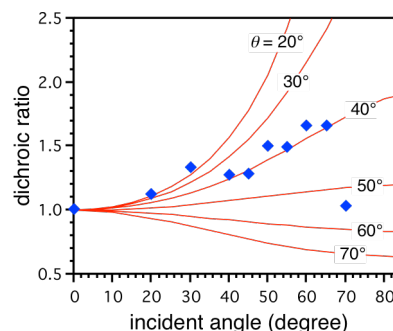


Fig. 6. LD ratio as a function of incident angle for several θ . Experimental data (diamond) and theoretically simulated curve (solid curve).

References

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