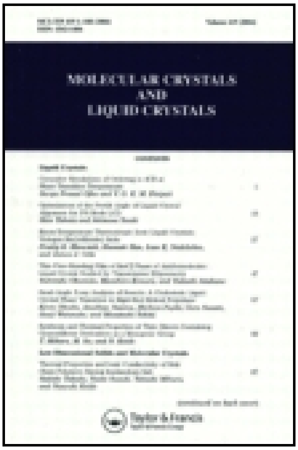

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Local Electrical Properties of Vanadyl Phthalocyanine Multilayers Studied by Atomic Force Microscopy

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Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 1999, Vol. 337, pp. 505-509
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Atomic force microscopy (AFM) was used to study the growth and electrical properties of vacuum evaporated vanadyl phthalocyanine (VOPc) thin films at the initial growth stage.

Keywords: phthalocyanine film; atomic force microscopy; electrical properties

INTRODUCTION

Metal phthalocyanines are interesting organic materials of great technological importance [1]. With the development of nanotechnology, their possible applications in nano-electronic devices are extremely attracting. For the possible applications in nano-electronic devices, it is necessary to understand their growth on an interface and the corresponding electrical properties on a nanometer scale. In this respect, suitable method to prepare monolayer or grains of only a few layers with a thickness on a scale of only a few nanometers is desirable. Tada and Mashiko found layer-by-layer epitaxial growth of VOPc thin film prepared on molybdenum disulfide (MoS_2) substrate at ultrahigh vacuum (UHV) condition [2]. More recently, Yanagi et al. studied molecular stacking structures in epitaxial crystals of titanyl phthalocyanine (TiOPc) and VOPc prepared by physical vapor deposition (PVD) and molecular beam epitaxy (MBE), on the (001) face of a KBr substrate [3]. As to author's knowledge, no reports on the electrical properties of VOPc monolayer or grains of only a few layers have been found so far.

EXPERIMENTAL DETAILS

Thin film preparation was carried out with a pressure of 4.0×10^{-5} Pa at room temperature (~20℃). The substrate was molybdenum disulfide (MoS_2) which was cleaved in air and immediately transferred into the vacuum chamber after cleavage. The deposition rate was about 0.1 nm/min. The thickness of the film was monitored by a quartz oscillator.

Non-contact mode AFM was adopted in the topography observation and contact mode AFM was used in the current-voltage characteristic measurement. The current-voltage characteristics were obtained by applying DC voltage to the sample surface through the conductive cantilever while the sample was connected electrically to a metal sample stage by a conductive paste.

RESULTS AND DISCUSSION

Figure 1 shows the non-contact mode AFM image and height profile of VOPc monolayer on MoS_2. In this image, separated, flat monolayer of VOPc can be found on MoS_2 surface. The size of these grains varies between 1 and 2 μm and the thickness of the monolayer is about 0.35 μm. Topography and height profile of VOPc multilayers on MoS_2 can be found in Fig. 2 in which flat grains of various sizes have been formed and piled up demonstrating that the VOPc molecules grow in layer-by-layer fashion. Several higher order layers can be identified and ascribed to the second, third, fourth, and fifth layers according to the appearance of plateau in the height profile along the line indicated in Fig. 2(a). It is noticeable that the height difference between the neighboring layers is nearly identical, about 0.7 nm. In other regions of the image, tiny grains can also be found at the top of some layers where subsequent layers are to be formed. It is known that VOPc molecules form square lattice in respect to the hexagonal lattice of MoS_2 with a lattice constant of 0.316 nm. The lattice constant of the VOPc molecules is 1.37 ± 0.02nm as obtained from RHEED measurement [2]. In the first layer, VOPc molecules array themselves in the square lattice which contact parallel to the surface of the substrate MoS_2. For the non-planar structure of VOPc molecule in which oxygen and vanadium atoms protrude from the plane of phthalocyanine ring, all of the axial oxygen atoms face up as known from the previous energy calculation [4]. The second layer is piled on the body-centered position of the first layer with a ring-ring separation of about 0.35nm with the oxygen atoms facing downward. The molecules of the third layer with the oxygen atoms facing up come to contact with the molecules of the second layer, forming face-to-face configuration. The molecules of the fourth monolayer with the oxygen atoms facing downward form head-to-head configuration. The dimer row which resulted from the face-to-face configuration between the third and second layer has a thickness of about 0.7 nm. Similar dimer rows with nearly the same thickness may form for higher order monolayers.

Figure 3(a) shows the contact mode AFM image of VOPc multilayers on MoS_2 obtained by using a gold-coated cantilever. It can be found that isolated grains have been formed on the substrates. Most of these grains are the first layers, however, the second and the third layers appear in some regions. Current-voltage characteristics can be measured at different locations in the image, as indicated in Fig. 3(b) where curve 1 stands for the current-voltage characteristic at bare MoS_2 substrate, curve 2 stands for that through the first layer, and curve 3 stands for that through the second layer. The current-voltage curve obtained at the bare substrate shows the formation of Schottky barrier of metal-semiconductor contact between gold and MoS_2. The currents at VOPc grains were lower than those at bare MoS_2 substrate at the same applied voltages. For the currents through the first layer and the second layer, lower currents were obtained through the second layer. The decrease of the current value was due to the increase of the resistance of the VOPc thin film which resulted from the increase of the thickness of VOPc thin film. The conductivity of VOPc layer can be estimated as about 0.21 S/cm at the bias of 3V on the monolayer. Effort is being made to elucidate the mechanism and quantity of the electrical conductivity of VOPc thin films at nanometer scale.

CONCLUSIONS

Growth and electrical properties of ultra-thin films of vanadyl phthalocyanine were studied by atomic force microscopy. It is found that VOPc molecules epitaxially grow in layer-by-layer fashion on MoS_2. The thickness of the first monolayer on MoS_2 is about 0.35 nm. Due to the possible formation of dimer row, the thickness of the subsequent layers is about 0.7 nm. Current-voltage characteristics obtained from the use of a conductive cantilever show Schottky behaviour. The currents decrease in regions covered by VOPc thin films as compared with those from the bare substrate at the same applied voltages. The current decreases further at VOPc multilayer than that at monolayer reflecting the resistance of thin films of VOPc as an organic semiconductor.

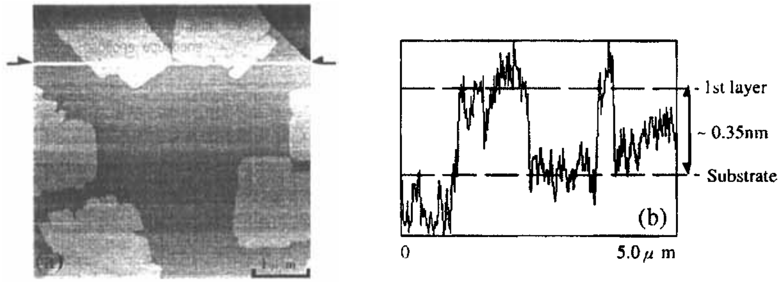

FIGURE 1 Non-contact mode AFM image and height profile of VOPc monolayer on MoS_2.

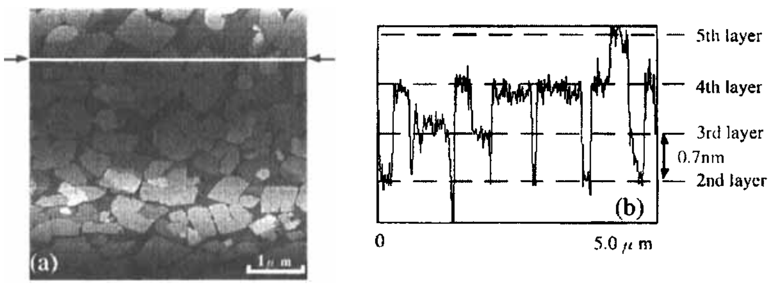

FIGURE 2 Non-contact mode AFM image and height profile of VOPc multilayers on MoS_2.

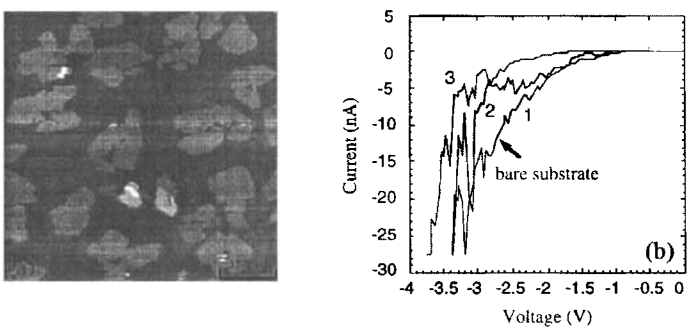

FIGURE 3 Current-voltage measurement of VOPc monlayer and multilayers on MoS_2 : (a) topography and (b) current-voltage characteristics.

See color plate XVII at the back of this issue.

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