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Lateral inhomogeneity of unoccupied states for PbPc films

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ABSTRACT

Micro-spot two-photon photoemission (micro-2PPE) spectroscopy is used to probe unoccupied electronic levels at sub-monolayer (ML) films of lead phthalocyanine (PbPc) on graphite (HOPG). The high-energy resolution (30 meV) 2PPE spectra with high-lateral resolution (0.4 µm) show well-resolved features due to molecule-derived occupied/unoccupied levels and the image potential state (IPS). The surface images based on photoemission from the highest occupied molecular orbital (HOMO) become laterally uniform after an annealing procedure. By contrast, the images based on the peak due to the lowest unoccupied molecular orbital (LUMO) and the next LUMO (LUMO + 1) are laterally inhomogeneous even after the annealing. The IPS peak is broadened to higher energy by 0.3 eV for sub-ML films and becomes sharp when a 1 ML film is formed. The broadening indicates that the electron in the IPS is scattered by molecules within the mean free path in the range from 1 to 10 nm. PbPc molecules are randomly distributed including nm-clusters. The LUMO and LUMO + 1 levels are stabilized as the cluster size increases. The inhomogeneity of the surface image due to the LUMO + 1 peak arises from the size distribution of the nm-clusters. The present results demonstrate that the unoccupied levels are more sensitive to the environment than the occupied levels.

1. Introduction

The electronic structures at interfaces between inorganic substrates and functional organic films have attracted wide interest both in surface science and materials science [1–5]. One of the problems in the field of the interface electronic structure is the lateral inhomogeneity of organic films. Owing to complicated substrate-molecule and intermolecular interactions, the growth of organic films is typically inhomogeneous, and the lateral inhomogeneity complicates the electronic structures and carrier transportation. In order to probe the inhomogeneity of the electronic structure, we have developed micro-spot two-photon photoemission (micro-2PPE) spectroscopy in which fs-laser light is focused to a spot of sub-µm diameter [6–8]. In 2PPE spectroscopy, a first photon excites an electron to an unoccupied level. The electron in the normally unoccupied level is probed by photoemission with the second photon. The two-step process competes with the coherent 2PPE process from occupied levels. As the photon energy is increased by $\Delta h\nu$, the photoelectron energy from the two-step process increases by $1\Delta h\nu$ and that from the coherent 2PPE process, by $2\Delta h\nu$. Thus we can measure the occupied and unoccupied levels at the same time [9].

We have reported previously that highly-resolved and well-reproducible 2PPE spectroscopy for lead phthalocyanine (PbPc) films became feasible by the micro-2PPE method [9]. We have assigned molecule-derived occupied and unoccupied levels in the vicinity of the Fermi level (E_F) for a well-ordered one-monolayer (1 ML) film formed on a highly oriented pyrolytic graphite (HOPG) substrate. Also detected were the unoccupied image potential states (IPS) on the HOPG surface and on the 1 ML film. Photoexcitation processes between occupied and unoccupied levels were discussed in detail [10,11]. The well analyzed system is very suitable for characterizing the effect of lateral inhomogeneity on the electronic structure. The environment of molecules in the sub-ML films is less uniform than in the well-ordered 1 ML film. The fluctuation of the environment modulates the interface electronic structure. In particular, unoccupied levels are considered to be more sensitive to the environment than occupied levels. Because of the antibonding character, the unoccupied molecular orbital extends outside the molecule, resulting in enhanced interaction with neighboring molecules. In this paper, we investigate the environment-induced modulation of occupied and unoccupied levels through micro-2PPE spectroscopy and surface imaging. We show changes in the unoccupied levels of PbPc films by the lateral distribution of molecules. It is found that the unoccupied levels are sensitive to surface morphology at the nm-scale.

2. Experimental

The micro-2PPE apparatus has been reported previously [6–8]. The third harmonic output of a titanium sapphire laser was focused onto the sample surface with a Schwarzschild objective of 0.29 numerical aperture. The incident angle was 55° from the surface normal. The

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lateral resolution was 400 nm, a factor of √2 smaller than the diffraction limited diameter of the laser spot [7]. Photoelectrons emitted along the surface normal were detected with a hemispherical energy analyzer (VG100AX). The energy resolution including the band width of the light was 30 meV. Surface images were measured by scanning the sample with the energy analyzer fixed at the energy of interest.

The sample was prepared similarly to previous studies [9–12]. The HOPG substrate was cleaved in air and heated in UHV at 670 K for 60 h. Purified PbPc was deposited by sublimation on HOPG in a preparation chamber. The amount and rate (0.04 nm/min) of deposition were measured by a quartz microbalance. The deposited films were annealed at 370 K for 1 h. In the annealed sub-ML film, the phthalocyanine ring lies flat on the substrate directing Pb atom to the vacuum [13]. The work function for the sub-ML film decreases almost linearly with increasing coverage [12,13]. The decrease in the work function is due to the uniform dipole layer at the interface. The work function change is comparable, but opposite in direction, to the case of a titanyl phthalocyanine (OTiPc) film for which the electric dipole moment perpendicular to the Pc ring was estimated using the Topping model [14]. As the coverage exceeds 1 ML, the work function increases, approaching that of the substrate at 2 ML coverage [12]. The increase of the work function is due to the cancelation of the dipole layer by the second layer molecule which directs Pb atom toward the substrate [13]. We define the coverage of 1 ML as that at the work function minimum. The work function of the 1 ML film is 4.27 eV, which is 0.18 eV lower than that of HOPG (4.45 eV). All experiments were performed at room temperature.

3. Results

3.1. Typical coverage-dependence of 2PPE spectra

The 2PPE spectra for sub-ML films are position-dependent even after the annealing. To demonstrate the typical coverage dependence, the most frequently observed 2PPE spectra measured at a photon energy of 4.33 eV are shown in Fig. 1. The vacuum level (VL) determined from the low-energy cutoff reproduces the work function change [12,13]. The first (n = 1) image potential state (IPS) on bare HOPG appears at a final energy of 7.93 eV (IPS1, closed triangle). The binding energy from VL is 0.85 eV [9,11]. The width of the IPS1 peak is 140 meV. The deposition of PbPc causes the IPS feature to broaden toward the higher final energy side by 0.3 eV, as shown in Fig. 1 by the upside down closed triangle. We note that the broadening of the IPS feature occurs only toward the higher energy side, indicating that it is not due to a homogeneous effect such as lifetime broadening. At coverage values above 0.4 ML, a new component, IPS2, indicated in Fig. 1 by an open triangle, appears at an energy slightly below the IPS1 peak. As the coverage increases, the IPS2 component intensifies and shifts to lower final energy. The IPS2 component becomes a sharp peak at 7.85 eV for the 1 ML film. The IPS2 peak for the 1 ML film reproduces the IPS on the well-ordered 1 ML films [9,11]. The peak is stronger than the IPS1 peak for bare HOPG by mixing with a molecule-derived unoccupied level [11]. The broadened feature labeled by the upside down closed triangle disappears when the 1 ML film is formed.

In addition to the IPS feature, four peaks labeled L0, L1, H-1, and H0 are observed. The peaks were assigned based on the photon energy dependence [9,11]. The energy of the unoccupied level is given by (final energy) − hν, where hν is the photon energy. The initial energy of the occupied level is given by (final energy) − 2hν. The L0 and L1 peaks are due to the unoccupied levels derived from the lowest unoccupied molecular orbital (LUMO) and the next LUMO (LUMO + 1). LUMO and LUMO + 1 are degenerate in a free molecule. The degeneracy is lifted upon adsorption and the split levels appear as the two peaks [9,11]. The levels are populated by transitions from the occupied levels deeper than the next HOMO (HOMO-1) [11]. The peak denoted by H-1 is due to the coherent 2PPE from the HOMO-1 derived level. Optical transition between the HOMO and LUMO + 2 levels is forbidden for a free molecule, but adsorption-induced symmetry degradation allows the transition and generates the peak labeled H0 [11]. The energy of the H0 peak is determined by the initial energy of the HOMO derived level: the peak due to the LUMO + 2 derived level appears at higher photon energies [9,11].

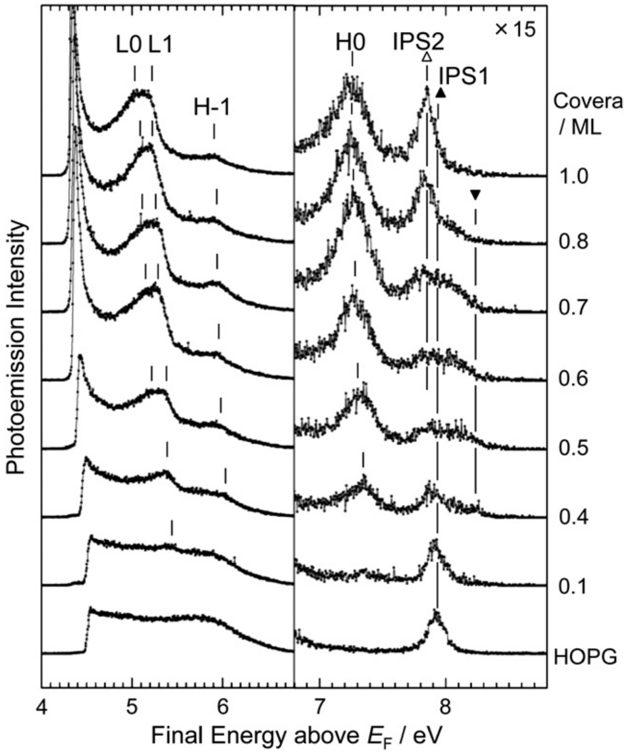

Fig. 1. Micro-2PPE results for different coverage of PbPc on HOPG measured with p-polarized light at a photon energy of 4.33 eV. Coverage is indicated on the right. The horizontal axis is the final energy of photoelectrons with respect to the Fermi level (E_F). The traces in the right panel are expanded by a factor of 15 relative to those in the left panel. The peaks labeled L0 and L1 are due to split features derived from originally degenerate LUMO and LUMO + 1 levels, respectively. The shoulder labeled H-1 arises from the HOMO-1 derived level, and the peak labeled H0, from the HOMO derived level. The IPS feature on the clean HOPG (IPS1) is indicated by a closed triangle and that on the well-ordered 1 ML film (IPS2), by an open triangle. The IPS features on sub-ML films are 0.3 eV wide, as indicated by the upside down closed triangle.

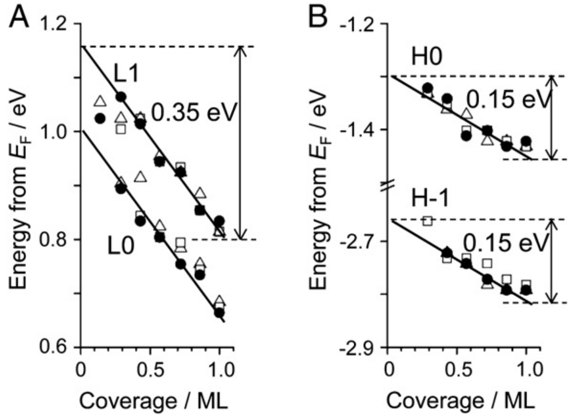

Fig. 2. The peak positions in Fig. 1 are plotted as a function of coverage. The different marks show data points for different experimental runs. The energy shifts of 0.35 eV for the L0 and L1 peaks shown in (A) are larger by 0.2 eV than that (0.15 eV/ML) for the H-1 and H0 peaks shown in (B). The shifts for the HOMO and HOMO-1 levels are comparable to the VL shift of 0.18 eV/ML.