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Surface Science 593 (2005) 38–42
SURFACE SCIENCE
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Laser-based photoemission micro-spectroscopy for occupied and unoccupied states of inhomogeneous surfaces

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Available online 18 July 2005

Abstract

Performance of our micro-spot photoemission spectrometer based on fs-laser radiation has been applied to observe (a) surface images due to an unoccupied electronic state and (b) inhomogeneous electronic structure of a thin organic film. Two-photon photoemission spectroscopy was performed with lateral resolution of 0.6 μm for a polycrystalline copper plate. We have observed lateral distribution of the unoccupied image-potential state of Cu(1 1 1) surface. In addition to μm-scale information from the surface image, the high-energy resolution spectroscopy provides insight on the step size of nm-scale. By employment of focused VUV light of 8.86 eV, one-photon photoemission spectroscopy was performed for a copper phthalocyanine film grown on the polycrystalline copper plate with a lateral resolution of 0.3 μm and an energy resolution of 30 meV. The photoemission band due to the highest occupied molecular orbital peaked at the binding energy of either 1.6 or 1.2 eV depending on the sample positions. Polarization dependence of the band showed that molecules are poorly oriented even on the (1 1 1) surface. The results demonstrate that a large inhomogeneity exists in the interface electronic structure.

Keywords: Electron microscopy; Laser methods; Photoelectron spectroscopy; Interface states; Photoelectron emission; Surface electronic phenomena; Polycrystalline surfaces; Semiconducting films

1. Introduction

The electron and hole transportations at the interface between metal surface and adsorbed molecules are the most fundamental issue for understanding the functionalities of organic semiconductors [1–3]. It is typically assumed that the hole (electron) injection barrier at an organic–metal

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doi:10.1016/j.susc.2005.06.043

interface is determined by the energy difference between the Fermi level (E_F) of the metallic electrode and the highest occupied (lowest unoccupied) molecular orbital (HOMO (LUMO)) of the organic film. For elucidation of the origin of the barrier, the energy level alignment at organic/metal interfaces has been extensively studied [1,2]. One of the difficulties of these studies is the impact of spatial inhomogeneity on the interface electronic structure. Organic devices are usually prepared on polycrystalline substrates. As the interaction between the substrate and the organic film depends on the crystalline orientation, facet size, and morphology of the substrate, the electronic structures of organic films on polycrystalline surfaces should be highly inhomogeneous. Furthermore, thin films are frequently composed of fine grains even on single crystalline substrates. Another difficulty on interface electronic structures arises from experimental methods to probe the unoccupied states. In spite of many methods such as the inverse photoemission, X-ray absorption, electron energy loss, and optical spectroscopy, information on LUMO is little when compared with HOMO which can be measured with photoemission spectroscopy [1,2].

We intend to overcome these difficulties by employment of fs-laser radiation as light sources of photoemission spectroscopy. By focusing coherent VUV radiation at a wavelength of 140 nm (8.86 eV photon energy), our micro-spot ultraviolet photoemission spectroscopy (micro-UPS) achieved 0.3 μm-lateral resolution and 30 meV-energy resolution [4–7]. We apply micro-UPS to a thin film of copper phthalocyanine (CuPc) deposited on a polycrystalline copper substrate, demonstrating the high lateral/energy resolutions can successfully reveal inhomogeneous electronic structures [8]. A promising method to probe the unoccupied states, but not frequently applied to organic films, is the two-photon photoemission (2PPE) spectroscopy in which the first photon excites an electron to a normally unoccupied state, and the second photon stimulates photoemission from the unoccupied intermediate state [3,9,10]. By simply changing the VUV light to a wavelength tunable UV light, micro-2PPE can probe unoccupied states at sub-μm surface area. We have measured the first image potential state of Cu(1 1 1) surface formed on a polycrystalline copper sample [6]. Surface images and the micro-2PPE spectra measured at different sample positions are compared in detail.

2. Experiment

The micro-spot photoemission spectrometer has been reported previously [4,5]. The linearly polarized VUV light at a wavelength of 140 nm (8.86 eV photon energy) was generated by frequency tripling the second-harmonic output of a regeneratively amplified titanium sapphire (Ti:Sa) laser operated at a repetition rate of 250 kHz and a pulse width of 100 fs. The frequency tripling was performed through a four-wave mixing process in Xe gas. The polarization of the light is the same as the second harmonic light. The VUV light was focused onto a sample surface by a Schwarzschild objective of 0.29 numerical aperture. The incidence angle of the light was 55° from the surface normal. The beam size at the surface was 0.3 μm × 0.5 μm. Photoelectrons emitted to the surface normal were detected with a hemispherical energy analyzer (VG 100AX) of 20 meV-energy resolution. The energy resolution including the analyzer and the spectral width of the VUV light was about 30 meV [7]. The sample was scanned with 0.1 μm-resolution. 2PPE experiment was performed with UV light at a wavelength of 280 nm (4.43 eV photon energy) which is resonant to the transition between the Shockley state and the first image-potential state of Cu(1 1 1) surface. The light source is the third-harmonic output of a Ti:Sa laser operated at a repetition rate of 76 MHz. The lateral resolution with the 280 nm-wavelength light is about 0.6 μm.

A conventional polycrystalline copper plate was polished with diamond paste and cleaned by repeated cycles of Ar-ion sputtering and annealing at 650 K, and was used as the sample.

3. Results and discussion

3.1. Microscopy with the image-potential state

A series of 2PPE spectra measured with 1 μm steps is shown in Fig. 1. The horizontal axis is