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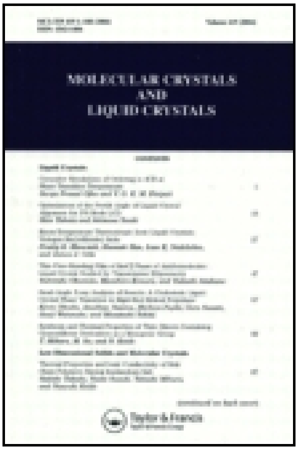

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VUV Induced Doping of Cu-Phthalocyanine Thin Films: A Possibility of n-Type Doping

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The new type doping method, VUV-induced doping, has been applied to copper phthalocyanine (CuPc) thin film. The highest occupied molecular orbital (HOMO) peak in the ultraviolet photoelectron spectrum of CuPc film was gradually shifted toward high binding energy side upon the irradiation of He Iα radiation. Furthermore, the radiation induced gap states were observed up to the Fermi level. The shift of the HOMO peak in the low-dose region depends in a semi-logarithmic fashion on the irradiation time, indicating that the intentional n-type doping of CuPc film can be realized by VUV irradiation.

Keywords: copper phthalocyanine; n-type doping; organic semiconductor; photoelectron spectroscopy

INTRODUCTION

Intentional doping of organic semiconductor films, i.e., control of the Fermi level (E_F) position in the band gap, is crucially important in realizing high performance organic devices. It enables one to locate the valence- or conduction-band edge at a desired energy position relative to E_F. The doping of organic films has been usually performed by co-evaporation of dopant and host molecules [1–3] or sequential

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deposition [4–6] of dopant onto a host film. Although these methods have been widely used, it is difficult to obtain a homogeneously doped film, particularly in the case of molecular doping, because the solid solution of the organic molecules is rarely formed with a few exceptions such as the mixed crystal of 2,3-dimethylnaphthalene with anthracene [7]. As a result the guest molecules can easily aggregate, which make an inhomogeneously doped film.

We have been studying a new doping method for organic films using photochemical reaction with high-energy photons. Organic molecules easily decompose or polymerize by irradiation of high-energy photons such as VUV light and x-ray. The irradiation products can introduce doping effects into the host film by two mechanisms, chemical and physical effects. In the former case, the photodecomposed or photopolymerized molecules directly act as dopants, if their energy levels locate at appropriate positions in the band gap of the film. On the other hand, in the latter case a local change in the film structure, such as change in the environment of pristine host molecules around the reaction product molecule, induces shift of energy levels of the host molecules due to change in the polarization energy, which can also play as dopants. In both cases the concentration of dopants can accurately be controlled only by dose level. Furthermore, a uniformly doped film can be easily fabricated if the radiation penetrates deep into the film. In this work, we adopted the VUV-induced doping method to thin films of copper phthalocyanine (CuPc) that generally show *p*-type character. The change in the electronic structure by VUV irradiation was observed by ultraviolet photoelectron spectroscopy (UPS). The results demonstrate that (i) *n*-type doping can be realized for CuPc by the VUV doping method and (ii) the irradiation creates new electronic density-of-states in the band gap which distribute up to the Fermi level.

EXPERIMENTAL

A newly constructed high-resolution UPS system was used in the present experiments. It consists of a 200-mm-radius energy analyzer (A-1, MBS-Toyama), a microwave discharge He lamp (L-1, MBS) and a troidal monochromator (M-1, MBS-Toyama). A monochromatic He Iα radiation was used as the source. It can reduce the background due to photoelectrons excited by higher-energy emission lines such as He Iβ and He II. Therefore, very low density-of-states in the gap region, which is not detected with nonmonochromatic He I radiation, can be measured. Total energy resolution of the present measurement was $\sim$20 meV. CuPc purified by three-cycle sublimation in an Ar

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stream of 13 Pa was *in-situ* deposited onto a clean Au/H-Si(111) substrate under the ultrahigh vacuum of 3×10^{-8} Pa. The film thickness, 5.3 nm, and deposition rate, 0.09 nm/min., were measured by a quartz thickness monitor. Sample temperature was 296 K for all measurements. The photoelectron current from the sample was typically $\sim$2 nA.

RESULTS AND DISCUSSION

Figure 1 shows the He Iα UPS spectra of the CuPc thin film in the region of highest occupied molecular orbital (HOMO) band as a function of the irradiation time; the ordinates are spectral intensities in (a) linear and (b) logarithmic scales. The binding energy (E_B) refers to the E_F of the substrate. With increasing the He Iα irradiation time, it is clearly seen that (i) the HOMO band shifts gradually toward the

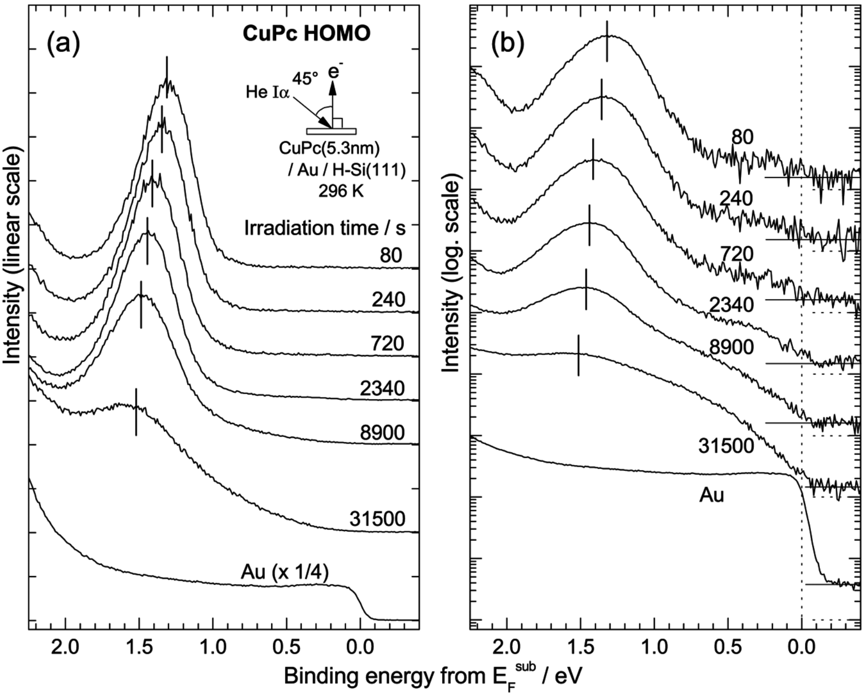

FIGURE 1 The He Iα UPS spectra of a CuPc film as a function of irradiation time; ordinates are photoelectron intensies in linear scale (a) and logarithm scale (b). All spectra were measured under similar discharge condition of He light source.

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high E_B side, (ii) the HOMO band becomes broadened slightly and (iii) a large tailing of the HOMO into the band gap region appears as shown in Figure 1(b). The peak shift can be attributed to the change of the Fermi level position in the gap of the CuPc film as described later. It is of note that the mid-gap states produced by the irradiation reach the E_F in the heavily irradiated film [see Fig. 1(b)]. Furthermore, the low-E_B tailing of the HOMO is observed even after 80-second irradiation.

The shift of other main peaks in the valence band region was also observed without remarkable changes in the shape of the UPS spectra (not shown). Hence it is difficult to consider that the shift of the peaks in the valence band region originates from the simple overlap of the UPS spectra of photoproduct molecules.

The observed irradiation-time dependence of the HOMO band positions is shown as a semi-logarithmic plot in Figure 2. It clearly shows a linear relationship between the peak position and the logarithm of the irradiation time at $<1\times10^3$ s.

In the case of donor doping, the position of E_F in the film moves to the conduction band and thus the valence band shifts to the high E_B side depending on the donor concentration (N_d). The shifts of E_F and the valence band are proportional to logarithm of donor concentration (N_d) in the low temperature approximation and on the assumption of

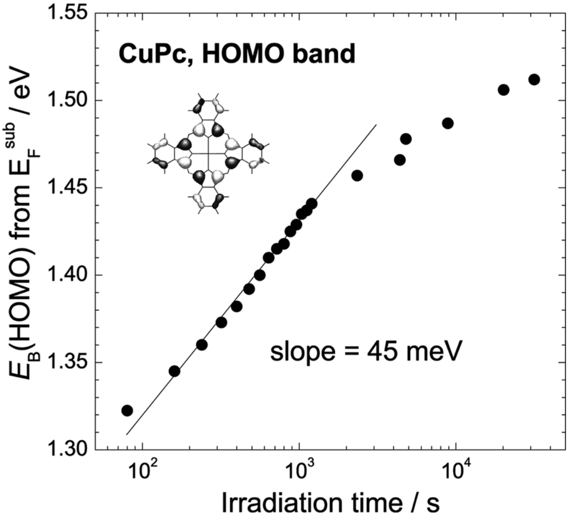

FIGURE 2 Relation of the binding energy of the HOMO band against irradiation time.

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one donor level in the band gap with N_d [8]. As N_d is considered to be proportional to the irradiation time at the early stage, the HOMO-band shift is ascribed to that of E_F in the CuPc film by n-type doping. The linear relationship was also observed with an opposite energy-level shift for PTFE thin film by VUV and soft x-ray irradiation, reflecting p-type doping [9]. Gao and Yan reported similar phenomena observed for the Cs doped CuPc film with photoelectron spectroscopy, where the HOMO, C1s, N1s and Cu2p bands move to the high E_B side in the similar fashion to the present result, i.e., a linear relationship reflecting n-type doping at low Cs concentration [4].

The above-described simple doping model [8,9] leads to qualitative explanation of the experimental results, especially the linear relationship in the semi-logarithmic plot. However, the slope of the plot in Figure 2 ($\sim$45 meV) is about 4 times larger than the expected slope of $k_\mathrm{B}T/2 \sim 12.5$ meV in the model. In other organic systems the slopes were $\sim$100 meV for Cs doped CuPc [4], $\sim$280 meV for Cs doped Alq$_3$ [5] and $\sim$600 meV for PTFE doped by VUV irradiation [9]. One possible origin of the discrepancy is enhanced concentration of dopants which should be proportional to the qth power of the incident photon number or density of the introduced impurity (D), $N_\mathrm{d} = aD^q$, with a being constant. This gives an enhanced slope of $qk_\mathrm{B}T/2$ [9]. Two mechanisms that derive the exponent q are considered: (1) the photochemical reaction order of q for the final products [9], and (2) enhancement of the dopant concentration due to the physical effect. A local change in the film structure induced by photoproducts can be a possible origin of the enhancement in the mechanism (2). Another possibility of the discrepancy originates form the shape of the energetic distribution of the density-of-states. If the energy dependence of the density-of-states is described by a broad Lorentzian with $\Gamma > k_\mathrm{B}T$, the slope in the semi-logarithmic plot is given as $\sim\Gamma$ [4]. In the present case, however, the UPS band shape of the HOMO is not expressed by Lorentzian but by Gaussian. Thus the discrepancy may originate from the enhancement factor q.

Although the mechanism of the present effect is not clear at present, the result suggests occurrence of n-type doping of CuPc film by VUV irradation. The present results also demonstrate that the mid-gap states induced by VUV irradiation distribute up to the Fermi level.

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