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Parabolic dispersion and effective mass of hot electrons in oriented thin films of copper phthalocyanine determined by means of low-energy-electron transmission

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Low-energy-electron transmission (LEET) spectra were measured for thin films of copper phthalocyanine (CuPc) with different crystalline order using electron energies below 15 eV. The LEET features were highly dependent on the crystalline order, indicating that they do not originate from the electronic states localized in the individual molecules, but from those which reflect the crystal structure. For oriented polycrystalline films of α-form CuPc with the crystal *bc* plane parallel to the surface, the energy positions of the LEET minima were found to be in excellent agreement with those of the band gaps obtained by assuming a parabolic conduction band in the direction perpendicular to the crystal *bc* plane. Further, we estimated the effective mass of hot electron m^* to be $2.2_2 m_0$, where m_0 is the free-electron mass, and the inner potential V_0 to be -1.3_3 eV in the direction perpendicular to the *bc* plane of α-form CuPc. The results show that the specular reflection of the incident electron at the band gap is a main factor for the LEET features and the hot-electron state can be well described by the parabolic dispersion even near the vacuum level.

I. INTRODUCTION

Low-energy-electron transmission (LEET) spectroscopy has become powerful in studying transport of hot electrons and their behavior at interfaces in thin dielectric films. In general, structures observable in LEET spectra of condensed films may be broadly divided into the following two categories: those which result from electron-energy-loss processes and the others which are produced by electron elastic interactions.[1-4] In the case of organic molecular solids, the main LEET features derived by the energy-loss processes correlate with molecular excitons localized at the individual molecules and they generally do not depend on the crystalline order of the sample film.[1-5] By contrast, the LEET features resulting from the elastic processes are very sensitive to the crystalline order[2,3,6-9] and/or to film thickness[10-12] due to quantum-size effects. They reflect the structure of crystal conduction bands.[9-14]

On the other hand, it is known from low-energy electron diffraction (LEED) experiments that the electron-reflection coefficient on a perfect single crystal is strongly dependent on the conduction-band structure.[15] The specular reflection of the incident electron at normal incidence shows maxima for incident electron direction and energies coincident with those of forbidden gaps in the crystal conduction band.[15] The reason is simply understood as electrons cannot be injected into a band gap.

Bader *et al.*[14] performed LEET experiments on polycrystalline films of Ar, Kr, Xe, N_2, CO, and O_2 condensed on cooled Pt substrates, and they proposed a quasi-free-electron model to describe the LEET features which originate in the electron elastic processes. Their model assumes a parabolic state for the injected hot electron, and it is basically similar with that used in analyzing the energy dependence of the intensity of the (0,0) beam in LEED experiments on single crystals.[15] In this case, the band gaps exist at the Brillouin-zone boundaries where the Bragg condition is satisfied.[16] They found fairly good agreement between the energy positions of the LEET minima and those of the band gaps calculated with the lattice constants of the film, although the LEET features may not necessarily be explained by invoking the (0,0) beam intensities in LEED experiments. Such an agreement yields a possibility that the LEET features, which are sensitive to the crystalline order, are dominated by the energy dependence of the (0,0) beam intensity. If this is the case, LEET spectroscopy can give the effective mass m^* and the inner potential V_0 of hot electrons when we know the lattice parameters of the film,[14-16] and it will become more important in investigating the conduction-band structure in very-low-energy regions where the LEED experiment is difficult to perform. One of our purposes of the present work is to examine such a possibility using oriented thin films of copper phthalocyanine (CuPc) where only azimuthal disorder is present.

The phthalocyanine class of materials have been the subject of a vast amount of the study, both experimental and theoretical, since they are typical organic semiconductors, and are very stable both thermally and chemically.[17] Among these, CuPc has been actually used as a photoreceptor. Although the valence bands of CuPc were studied extensively for both gaseous[18] and crystalline[19-23] states, we have little information on the conduction band where the hot electron propagates. The hot-electron states are important for a quantitative understanding of the transport of photoexcited and photoinjected electrons before their thermalization. Further, the effective mass m^* and the inner potential V_0 are key parameters in discussing the transport properties of hot electrons in ultrathin films.

In this paper we describe the results of LEET experiments for thin films of CuPc with different crystalline order. The LEET spectra depended highly on the crystalline order and the LEET minima observed for the oriented thin film of α-form CuPc with the crystal *bc* plane parallel to the surface could be clearly explained by the specular reflection of incident electrons at the Brillouin-zone boundary under the assumption of the quasi-free-electron model. The results demonstrate for the α-form CuPc that the hot-electron state is well expressed by a parabolic conduction band in the direction perpendicular to the crystal *bc* plane.

II. EXPERIMENTAL

In the LEET measurements a monoenergetic electron beam impinges on a thin film deposited on a metal substrate, and the electron current transmitted through the film (I_t) is measured at the substrate as a function of the incident-electron energy (E_i). The LEET spectrometer was described in Refs. 5, 8, and 9. The incident electron beam was normal to the film surface, and the incident-beam current (I_i) was kept at 1×10^{-11} ($\pm3\times10^{-13}$) A. The number density of the incident electron at the sample surface was estimated to be $(3-5)\times10^{-8}$ Å^{-2}s^{-1} by measuring the beam diameter with the method described in the literature.[9] Under these beam conditions, no change of the LEET spectra of CuPc films due to radiation damages was observed even after repeated measurements. All LEET spectra were recorded at a vacuum condition of $10^{-9}-10^{-10}$ Torr. Commercially obtained CuPc was purified by a sublimation in a current of argon gas ($\sim$0.15 Torr), followed by three-times sublimation in a high vacuum of 10^{-5} Torr.

The crystalline thin films of various thickness (30–400 Å) were obtained by vacuum evaporation of the purified CuPc onto well-polished polycrystalline copper substrates at room temperature as a function of the deposition rate ($R_D=2-14$ Å/min) and the vacuum condition ($P=10^{-5}-10^{-9}$ Torr). These films showed similar LEET features and their energy positions did not depend on the film thickness, although their sharpness was better for the films prepared in higher vacuum and at lower deposition rate. The x-ray diffraction measurements for thicker films yielded that the films consisted of oriented polycrystals of α-form crystal structure[24,25] with the crystal *bc* plane parallel to the substrate surface. Further we confirmed with the x-ray diffraction[26] that the α-form films were changed to β-form[25,27] films by the heat treatment[23] of about 3 h at 250 °C. Amorphous thin films were also prepared by vacuum evaporation onto similar copper substrates cooled at -117 °C under a base pressure below 2×10^{-9} Torr ($<2\times10^{-8}$ Torr during evaporation).

The film thickness was measured with a quartz thickness monitor assuming the film density of 1.62 (Ref. 24) for both crystalline and amorphous films.

III. RESULTS AND DISCUSSION

Figure 1 shows the effects of *in situ* heat treatment of the oriented α-form film of 397-Å thick ($R_D=13.2$ Å/min, $P=5\times10^{-5}$ Torr) on the LEET spectra [$I_t(E_i)$ and $dI_t(E_i)/dE_i$ curves]. The LEET features become sharp by the heat treatment and 8 LEET minima ($A-H$) are observed for $E_i<15$ eV. The spectra change drastically after heating at 250 °C for 3 h which can produce the $\alpha\rightarrow\beta$ change as is observed by x-ray diffraction measurements.[23,28] The spectral features and their changes are seen more clearly in $dI_t(E_i)/dE_i$ curves.

In Fig. 2 the LEET spectra of the amorphous film of 148 Å thick ($R_D=2.9$ Å/min) are shown together with those of α- and β-form films. Here, the results of α-form film of 107 Å thick prepared at conditions ($R_D=3.6$ Å/min and $P\simeq10^{-9}$ Torr) different from those for the α-form film in Fig. 1 are shown. The energy positions of the LEET minima of α-form films are insensitive to the film thickness and the deposition conditions. The insensitiveness of the energy positions to the film thickness indicates that these features do not originate in the interference of the electron waves[10-12] between the film-substrate and film-vacuum interfaces probably due to small electron mean free path in comparison with the film thickness (30–400 Å). A clear difference can be seen between the LEET spectra depending on the crystalline order. These results lead to a conclusion that the LEET features observed for the crystalline films originate in the elastic phenomena which are very sensitive to the crystalline order of the film, and not in the inelastic processes of the incident electrons, namely, not in the excitations of molecular excitons.[4] In fact, we found no meaningful correlation between the energies of the LEET features and molecular excitons[29,30] even if we took into account the unoccupied states localized at the individual molecules observed by inverse photoemission spectroscopy (IPES).[31] Consequently, we expect a possibility of the specular reflection of the incident electron to have a maximum when the incident electron energy is coincident with that of a band gap.

The band gaps in momentum space are located at the electron wave vectors (**k**) which undergo optimal Bragg scattering. For the specular reflection at normal incidence, we can write

$$\mathbf{k}=\tfrac{1}{2}G\ , \tag{1}$$

where G is a reciprocal-lattice vector.[16] If we assume that the hot-electron state in the film can be expressed with a parabolic conduction band, it is described by the effective mass m^* and the energy V_0 for the bottom of the parabolic conduction band (inner potential) as

$$E=\hbar^2k^2/(2m^*)+V_0\ , \tag{2}$$

where E is the energy of the electron with respect to the vacuum level.[14,16] This type of relationship is, in general, used in the LEED experiments.[15] Although such a sim-

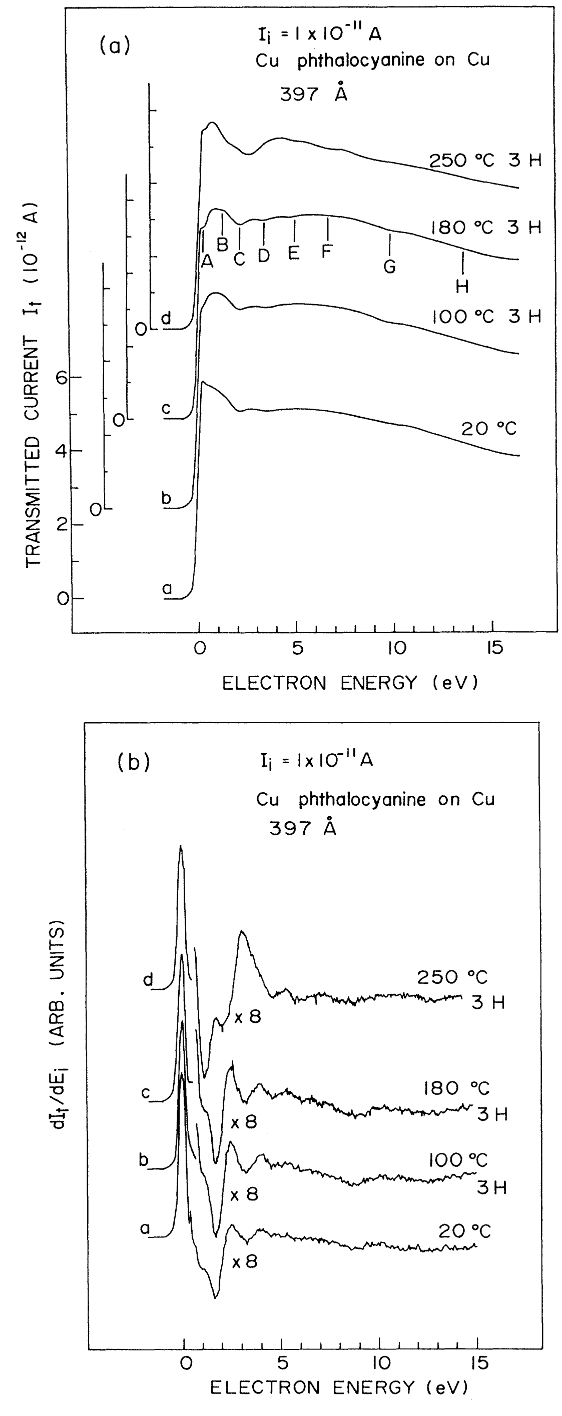

FIG. 1. Effects of heat treatment of the oriented polycrystalline film (397 Å thick) of copper phthalocyanine on low-energy electron transmission spectra. (a) $I_t(E_i)$ curves; (b) $dI_t(E_i)/dE_i$ curves. *a*, measured at 20 °C for α-form copper phthalocyanine without heat treatment. The crystal *bc* plane is parallel to the surface. *b*, measured at 23 °C for α-form copper phthalocyanine after heat treatment at 100 °C for 3 h. The crystal *bc* plane is parallel to the surface. *c*, measured at 22 °C for α-form copper phthalocyanine after heat treatment at 180 °C for 3 h. The crystal *bc* plane is parallel to the surface. *d*, measured at 23 °C for β-form copper phthalocyanine after $\alpha \rightarrow \beta$ crystal change by heat treatment at 250 °C for 3 h (Ref. 23).

ple relation seems a bit naive for electrons of very low energy, it may be reasonable for CuPc, since LEED patterns were observed for epitaxial CuPc films with low-energy electron beams of 14–25 eV.[32,33] Thus we may write as an approximate relation giving the energies E_G at which the band gaps exist and we expect the electron reflection to occur[14–16]

$$E_G = \hbar^2(\tfrac{1}{2}G)^2/(2m^*) + V_0 \ . \tag{3}$$

Our task is to examine the applicability of Eq. (3) to the LEET spectra of the oriented CuPc film.

Since the present LEET spectra show strong current at $E_i \cong 0$ eV, we can conclude for the crystalline CuPc films as $V_0 < 0$ eV.[4,8,9,34] From the low-energy-electron-loss spectroscopy (LEELS) (Refs. 29 and 30) and the optical-absorption spectroscopy,[35] on the other hand, the electronic excitation to the continuous conduction band is expected to take place at least for energies greater than ~ 3.2 eV, since this energy gives the onset of the strong second exciton band overlapped by various spectral features including the feature due to the electron transition to the continuous conduction band. Further, the ionization threshold was determined to be 4.8_8 eV (Ref. 23) for α-form CuPc. Thus V_0 is expected to -1.6_8 eV $\lesssim V_0 < 0$ eV.

For various m^* and -1.6_8 eV $\lesssim V_0 < 0$ eV, we tried to fit the energies of the minima in the $I_t(E_i)$ curves for the α-form CuPc to Eq. (3) using the G values calculated with

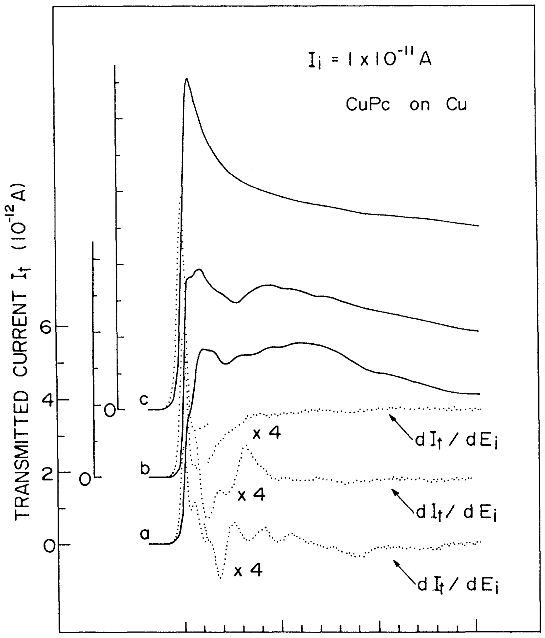

FIG. 2. Comparison of low-energy electron transmission spectra for thin films of amorphous, α-form, and β-form copper phthalocyanine. *a*, measured at 20 °C for oriented α- form film of 107 Å thick with the crystal *bc* plane parallel to the surface. *b*, measured at 23 °C for β-form film (same as in Fig. 1). *c*, measured at -117 °C for the amorphous film of 148 Å thick.

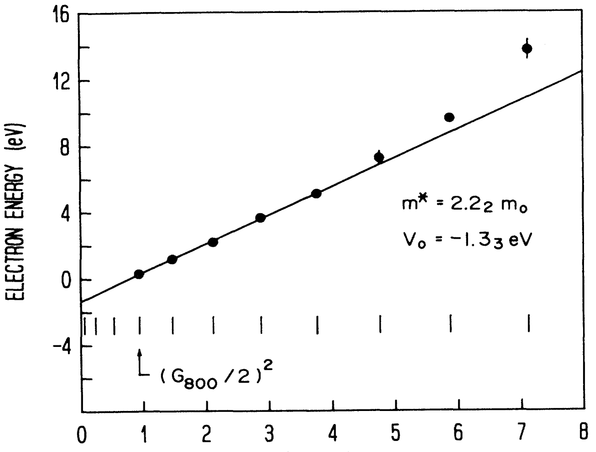

FIG. 3. The observed energies of the minima in the transmitted current $I_t(E_i)$ are plotted vs $(G/2)^2$ for the oriented α-form copper phthalocyanine with the crystal *bc* plane parallel to the surface. Positions of $(G_{h00}/2)^2$, where h is the even number, are shown by vertical bars. As an example, $(G_{800}/2)^2$ is indicated in the figure. The straight line was obtained with the method of a least-squares fit for data points of $E_i < 6$ eV. The effective mass m^* and the inner potential V_0 are shown in the figure.

the lattice constants of α-form CuPc ($a = 25.92$ Å, $b = 3.790$ Å, $c = 23.92$ Å, $\beta = 90.4°$).[24] We found that the energy positions of the LEET minima could be well expressed by Eq. (3) after the optimization for G, m^*, and V_0 with the method of least squares. The result is shown in Fig. 3, where E_i positions of the LEET minima for the oriented α-form CuPc film are shown as a function of $(\frac{1}{2}G)^2$. It is seen in Fig. 3 that only the G values corresponding to (h00) planes (G_{h00}), where h is an even number, are responsible. This is consistent with the x-ray diffraction patterns of the oriented film of α-form CuPc which showed the diffractions only from (h00) crystal planes where h is also an even number.[28] We wish to emphasize the excellence of the fit of the data points by the straight line of $m^* = 2.2_2 m_0$ and $V_0 = -1.3_3$ eV, where m_0 is the free-electron mass. The excellent agreement indicates that the hot-electron state can be well approximated by the parabolic conduction band, although there may be some contributions from the unoccupied molecular orbitals which were observed by IPES.[31] The poor fit at the higher energy region, namely the data points, located at upper region by the straight line, is reasonably understandable by considering that m^* is, in general, expected to reach m_0 by increasing in electron energy.

In the case of the oriented polycrystalline films of CuPc where only azimuthal disorder exists, we expect that the (0,0) beam intensity at normal incidence does not see any disorder and reflects the band gaps in the direction perpendicular to (h00) planes. Such an expectation is in excellent agreement with the present result.

As a matter of fact, the structure due to the specular reflection of the incident electron is a main factor for the LEET features of the CuPc films which do not show the quantum-size effects due to the interference of the electron waves, and the hot-electron state is expressed by the parabolic dispersion of $m^* = 2.2_2 m_0$ and $V_0 = -1.3_3$ eV in the direction perpendicular to the *bc* plane of α-form crystal.

IV. SUMMARY

LEET experiments were carried out for thin films of copper phthalocyanine (CuPc) with different crystalline order. We observed that the LEET features were highly dependent on crystalline order and there was no correlation between the LEET, the electron-energy-loss, and the inverse photoemission features. These results indicate that the LEET features do not originate in the energy losses of incident electrons by exciting molecular excitons, but in the elastic processes of the electrons which reflect the conduction-band structure determined by the crystal structure.

For oriented polycrystalline films of α-form CuPc with the crystal *bc* plane parallel to the surface, we found that the energy positions of the LEET minima are in excellent agreement with those of the band gaps which are obtained by assuming a parabolic conducton band. This indicates that the hot-electron state near the vacuum level can be well expressed by a quasi-free-electron state of parabolic dispersion. From these results, we estimated the effective mass of hot electron m^* to be $2.2_2 m_0$, where m_0 is the free-electron mass, and the inner potential V_0 to be -1.3_3 eV along the direction perpendicular to the *bc* plane of α-form CuPc.

The present analysis is limited to the films which do not show the quantum-size effects. For these films, however, the results demonstrate that the structure due to the specular reflection of the incident electron is a main factor for the LEET features and they reflect the band gaps in the conduction bands in the direction of the incident beam.

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