

Spin Polarization in Molecular Orbitals of Copper–Phthalocyanine Deposited on a Magnetized Fe(100) Substrate

Taku Suzuki,* Mitsunori Kurahashi, and Yasushi Yamauchi

National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Received: February 20, 2002; In Final Form: May 17, 2002

From a structural analysis using low-energy ion scattering spectroscopy, it is shown that Cu–phthalocyanine (CuPc) molecules adsorb on the Fe(100) surface with their planes parallel to the surface when the film thickness is one monolayer, while the structure of the film becomes disordered with an increase in the thickness. This thickness dependence of the CuPc film structure agrees with that determined from the metastable deexcitation spectroscopy (MDS) spectra, and the origins of the CuPc peaks in the MDS spectra are determined. The spin polarization in the molecular orbitals of CuPc on Fe is detected by spin-polarized MDS (SPMDS). The polarity of the spin polarization in the CuPc molecular orbitals is the same as that of the Fe surface. The adsorption of oxygen on Fe prior to the CuPc deposition is found to induce a remarkable difference in the spin polarization of the CuPc orbitals.

1. Introduction

The magnetic properties of surfaces, interfaces, and ultrathin films are part of a rapidly developing field of research. The magnetism of such systems is generally expected to be remarkably different from the bulk because of the low dimensionality.¹ In such low-dimensional systems, the detection of the magnetism of adsorbed atoms on surfaces has been attempted.^{2,3} Although numbers of experiments have investigated the influence of adsorbates on surface magnetism, the observation of magnetism of the adatom itself has been rare. This is difficult because extreme surface sensitivity is required to separate the magnetic properties of the adsorbates from the underlayers.

In the present experiment, spin polarization in molecular orbitals of Cu–phthalocyanine (CuPc) deposited on an Fe(100) surface is observed using spin-polarized metastable deexcitation spectroscopy (SPMDS). Metal–Pc (MPc) is of great interest for technological applications, such as dyes, catalysis, optoelectronic devices, and solar cells.^{4,5} MPc is also used as the model of biological molecules such as porphyrins, hemoglobin, and chlorophyll because of the similarity in structure. In these applications of MPc, the interaction between MPc and the supporting substrates, including the magnetic interaction, sometimes plays an important role. In this context, the nature of the MPc–support surface interaction is of major interest in recent research.⁶

The surface sensitivity of SPMDS is extreme, and the spin-resolved electronic structure on the outermost surface layer can be selectively analyzed.^{7,8} Spin polarization in the molecular orbitals of CuPc induced by magnetization of the supporting Fe surface was clearly observed in the present experiment. To our knowledge, this is the first study in which the spin polarization of adsorbates has been detected in organic molecular adsorption systems by SPMDS.

For a discussion of the interaction between the adsorbate and the substrate surface, the structure of the adsorbed layer must be determined. In the present experiment, low-energy ion

scattering (LEIS) is utilized for the structural analysis of the CuPc films. It has been suggested that LEIS is not well suited for the structural analysis of organic films because of the small scattering cross-section of the constituents. Structural analysis of organic films using LEIS has not been reported to date, although it has been utilized for compositional analysis. The present experiment, however, shows the capability of LEIS for the structural analysis of organic molecular adsorption systems.

2. Experiment

The experiments were performed in an ultrahigh-vacuum (UHV) chamber (base pressure 5×10^{-11} Torr) which was equipped with a sample transfer system, a rotatable electrostatic hemispherical sector analyzer (Omicron, SHA50), a beam line for metastable helium (He^*) atoms, a Stern-Gerlach analyzer, RHEED, and an ion beam line for coaxial impact collision ion scattering spectroscopy (CAICISS). CAICISS is a specialized LEIS whose scattering angle is almost 180° .⁹ Time-of-flight (TOF) spectra were taken during the CAICISS measurements using 3 keV Ne^+ ions, where the path length of scattered particles from a sample to a microchannel plate was 36 cm. The Ne^+ ion beam was generated using an electron impact ion source and was chopped by electrostatic deflection plates. In the measurement using MDS, TOF techniques were employed in combination with a pulsed discharge in the He^* source to separate the contributions to the ejected electron spectra from He I photons and He^* metastables. The 2^1S atoms produced in the source were deexcited using a quench lamp which was positioned between the source and the sample,¹⁰ and the ratio of the $\text{He}^* 2^3\text{S}$ to $\text{He}^* 2^1\text{S}$ atoms impinging on the sample measured using a Stern-Gerlach analyzer was 8:1. Circularly polarized 1083 nm radiation from a laser diode (SDL 6702) was utilized to optically pump and thus spin polarize the $\text{He}^* 2^3\text{S}$ beam.¹⁰ The incidence angle of He^* and the emission angle of electrons were 45° and 0° , respectively, with respect to the surface normal in the (SP)MDS experiment. The sample was pulse-magnetized in the plane transverse to the He^* beam prior to the SPMDS measurement, that is, along the Fe[100] easy axis of bcc-Fe, and the spectra were obtained in the remanent

* To whom correspondence should be addressed. Fax: +81-298-59-2801. E-mail: suzuki.taku@nims.go.jp.

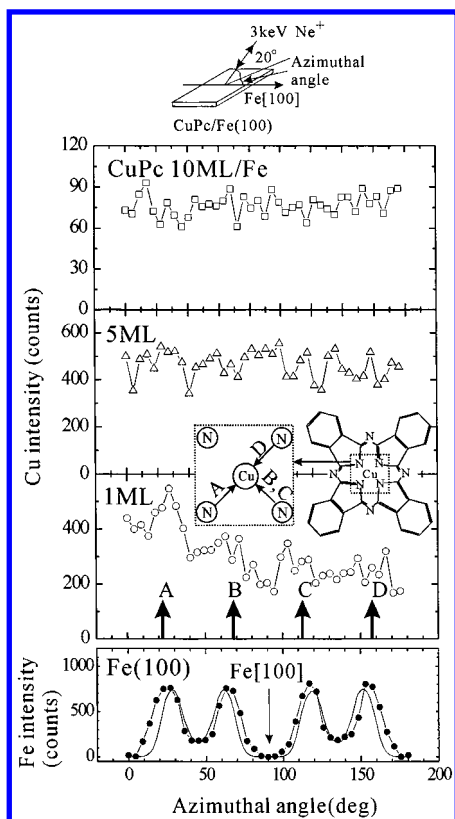


Figure 1. Intensity variation of Fe of the clean Fe(100) surface and Cu of CuPc on Fe(100) in the CAICISS azimuthal angle scan measurements, where the polar angle of the incidence He^+ was fixed at 20° . The solid line shown together with the Fe intensity variation indicates the computer simulation for the ideal Fe(100) surface. The inset shows the molecular structure of CuPc as well as the atomic pairs in the focusing effect causing the peaks A–D.

state. The MDS spectra were obtained in the constant pass energy mode at 4 eV, while the SPMDS spectra were obtained in this mode at 40 eV.

Fe(100) films were grown on MgO(100) substrates by the vapor deposition of Fe (purity 99.99%) using an electron beam evaporator (Omicron EFM3T). The epitaxial growth of Fe was confirmed by RHEED and CAICISS. Commercial CuPc powder (Aldrich) was purified three times by vacuum sublimation prior to the deposition that was performed at room temperature. The organic elemental analysis for C, H, and N of the purified CuPc was in agreement with the calculated values in the range of $\pm 0.2\%$. The deposition rate of CuPc was monitored using quartz crystals and was controlled at 0.3 monolayer (ML)/min, where 1 ML corresponds to the molecular plane spacing in the β form of the CuPc crystal.

3. Results and Discussion

Figure 1 shows the intensity variation of the CAICISS signals of scattering from Fe and Cu as a function of the azimuthal angle for a fixed polar angle of 20° . The Fe data obtained on the Fe(100) clean surface exhibit a 4-fold symmetry which reflects the symmetry of the bcc-Fe(100) surface. The intensity variation agrees well with the computer simulations for the ideal Fe(100) surface, and epitaxial growth of the Fe(100) film on MgO(100) is indicated. The simulation was carried out using a method for the 180° backscattering events developed by Williams et al.¹¹ The data for scattering from Cu in the CuPc 1 ML film also exhibit 4-fold symmetry. The peaks labeled A–D are located on both sides of Fe(100), where the angle between

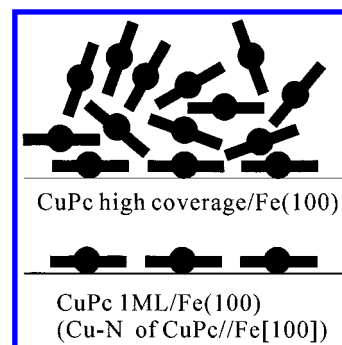


Figure 2. Schematic of the adsorption structure of CuPc on Fe(100).

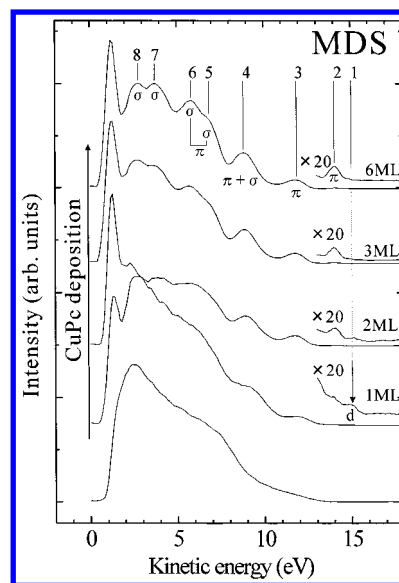


Figure 3. MDS spectra obtained on the CuPc film deposited on the Fe(100) substrate, together with the spectrum of the clean Fe(100) surface.

the peak and Fe(100) is 23° . These peaks are attributed to the focusing effect from neighboring N atoms to Cu, judging from universal shadow cones calculated using the Thomas–Fermi–Moliere potential.¹² This situation is illustrated in the inset of the CuPc molecular structure. The appearance of peaks originating from this focusing effect indicates that the CuPc molecule adsorbs on the Fe surface with its molecular plane parallel to the surface. The direction of the Cu–N bond is parallel to Fe(100), as determined from the azimuthal angle of the focusing peak. It is noted that the focusing peaks are missing in the azimuthal angle scan measurements when the coverage of CuPc increases. This indicates that the structure of the CuPc film becomes disordered with increasing coverage. The result of the structural analysis is schematically displayed in Figure 2.

Figure 3 shows the MDS spectra of the CuPc/Fe surface together with that of the Fe clean surface (bottom curve). The MDS spectrum for Fe is almost structureless, and this is typical of the MDS spectra from clean metal surfaces.⁷ The hump at 7 eV is due to the slight contamination of the surface by oxygen. In contrast, the spectrum for the CuPc/Fe surface exhibits peaks, numbered 1–8. The assignment of these peaks is determined using the adsorption structure of CuPc analyzed by CAICISS as follows. Peak 1 depends on the CuPc film thickness and is clearly observable in the spectrum of CuPc (1 ML), but not in the spectra at high coverage. The CuPc molecule, being a perfectly square planar environment, belongs to the point group of D_{4h} .¹³ Taking the molecular plane to be parallel to an xy plane, Cu d_{xz} , d_{yz} , and d_{z^2} orbitals interact with the incident He^+

atom if the molecule adsorbs with its plane parallel to the surface. However, if the CuPc film has a disordered structure as shown in Figure 2, the molecular orbital of the Pc ring shields the wave function of Cu 3d, and thus, the d component is hardly detected by He*, which interacts only with the outermost surface.¹⁴ In this context, peak 1 is indicated to be due to Cu 3d. A recent calculation of the electronic structure around the Fermi level of an isolated CuPc molecule by Liao and Scheiner also indicates that the occupied orbital that has the lowest binding energy corresponds to the Cu 3d component.¹⁵ Peaks 2 and 3 have no dependence on the thickness. By considering the spatial distribution of the molecular orbitals, the π component of the Pc ring interacts with He* for both the planar adsorption and random structure. In contrast, the σ component interacts with He* only when CuPc adsorbs with its plane perpendicular to the surface. Therefore, the MDS peak of the σ component shows a thickness dependence, while the π peak has no dependence on the thickness. This indicates that peaks 2 and 3 basically reflect the π component. The calculation by Liao and Scheiner also indicates that the second and third bands in the occupied levels correspond to the π component of the Pc ring although they indicate a slight contribution from Cu 3d to the third band.¹⁵ Peak 4 is detected in the spectrum of 1 ML, while the peak intensity increases with thickness. Thus, both σ and π components are thought to exist at the energy position of peak 4. The hump at 6.2 eV in the 1 ML spectrum is attributed to the π component judging from the planar adsorption structure of CuPc. With increasing coverage, two peaks, numbered 5 and 6, grow. From this thickness dependence, these two peaks are attributed to the σ orbitals. Thus, it is indicated that the overlapping of the contributions from the π and σ components occur for peaks 5 and 6. Peaks 7 and 8 are detected only for the high-coverage sample, and thus, these peaks are attributed to the σ orbitals.

The spin polarization of the molecular orbitals of CuPc on a magnetized Fe substrate is shown in Figure 4. The bottom curve indicates the spin asymmetry for SPMDS on Fe(100). The spin asymmetry is defined as $(I_p - I_a)/(I_p + I_a)$, where I_p and I_a denote the intensities obtained using He* ²³S atoms polarized parallel and antiparallel to the majority spin direction in the Fe substrate, respectively. The positive spin asymmetry observed at the Fermi level (16 eV) agrees with previous reports.^{8,16,17}

The spin asymmetry $(I_p - I_a)/(I_p + I_a)$ provides a measure of the surface spin polarization. However, the background of secondary electrons, whose intensity strongly depends on kinetic energy, influences the value of the asymmetry. For example, the absolute value of the asymmetry becomes smaller (larger) with a larger (smaller) background of secondary electrons. Most earlier SPMDS experiments have been performed on surfaces where He* deexcites via the Auger neutralization (AN) process. It is difficult to subtract the secondary electron background from such MDS spectra, which generally have a broad structure. Furthermore, only the asymmetry at the Fermi level directly reflects the spin polarization at the surface.⁸ Thus, the spin asymmetry at the Fermi level obtained from the raw experimental data has generally been utilized for the discussion of the spin polarization. In contrast, the MDS spectra in the present system CuPc/Fe originate from the Auger deexcitation (AD) process, and the surface electronic structure is reflected in the spectra as in photoemission spectra.⁷ This fact allows discussion of the spin polarization for each CuPc molecular orbital which spans a broad energy range. The spin polarization at different positions in a spectrum is discussed in terms of $I_p - I_a$ together with the spin asymmetry in the present paper.

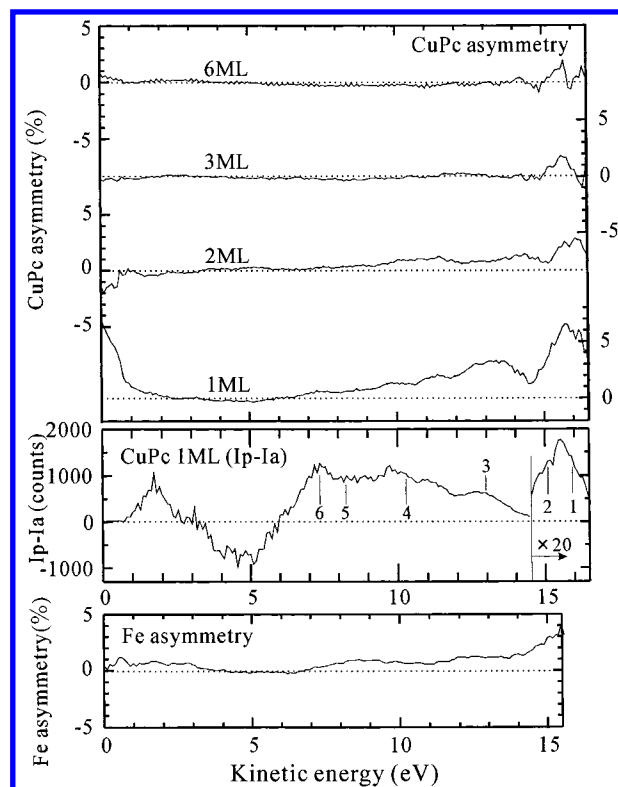


Figure 4. SPMDS asymmetry observed on the Fe(100) clean surface (bottom), $I_p - I_a$ curve in SPMDS on the 1 ML CuPc films deposited on the Fe(100) substrate (middle), and spin asymmetry in SPMDS for various amounts of coverage of the CuPc film on Fe.

The intensity variation $I_p - I_a$ for CuPc (1 ML) is presented in Figure 4. The spin polarization is clearly observable at each molecular orbital position. In the case of MDS spectra of the AD process, the value of the spin asymmetry corresponds to the spin polarization at the point of the He* deexcitation on the surface. Using an estimate of the secondary electron background, the spin polarizations in the molecular orbitals at the positions of peaks 1, 3, 4, and 6 are about 6%, 6%, 13%, 40%, respectively. The polarity of the spin polarization in the CuPc molecular orbitals is the same as that in Fe at the Fermi level. The spin polarizations in the molecular orbitals of CuPc decrease with an increase in the film thickness, as shown in the asymmetry curves of CuPc for various coverages.

The appearance of spin polarization in the CuPc molecular orbitals is the result of the charge transfer between the CuPc adsorbates and the Fe substrate. There is no net spin polarization in the isolated CuPc molecule. When the molecule adsorbs on the magnetized substrate, charge transfer occurs as a result of the overlapping of the wave functions of the adsorbate and substrate surface. In this charge transfer, there may be a difference in the number of transferred electrons between the up and down spins. In this simple picture, the observed spin asymmetry at a certain energy would be related to the ratio of the number of transferred electrons to the total number of electrons at that energy. The decrease in the asymmetry with increasing CuPc thickness is attributed to a decreased net charge transfer between the Fe surface and the top layer of the CuPc thick film.

On the basis of this mechanism, it is expected that if the bonding state of CuPc with the underlying surface is changed, the spin polarization of CuPc may be modified. This situation is observed in Figure 5. Figure 5 shows the spin asymmetry and $I_p - I_a$ for a surface deposited with CuPc (1 ML), where

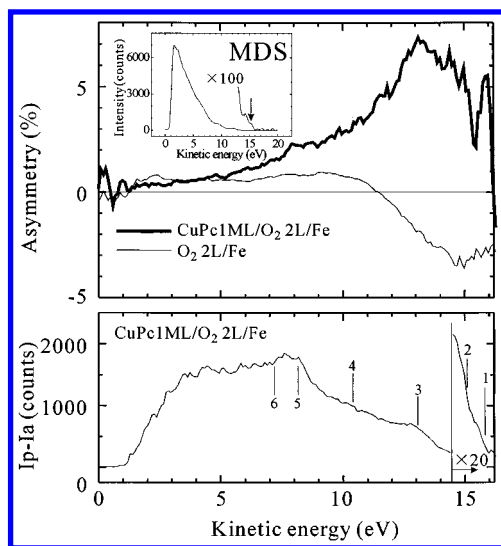


Figure 5. Spin asymmetry and $I_p - I_a$ observed on the 1 ML CuPc film deposited on the Fe(100) substrate exposed to 2 langmuir of O_2 together with the Fe(100) surface exposed to 2 langmuir of O_2 . The inset shows the MDS spectrum obtained on the CuPc (1 ML)/ O_2 (2 langmuir)/Fe(100) surface.

the Fe substrate surface was exposed to 2 langmuir of oxygen (1 langmuir = 10^{-6} Torr·s)). The asymmetry curve observed on the O_2 (2 langmuir)/Fe surface is also presented. The Cu 3d peak is observable in the MDS spectra as indicated by the arrow in the inset, and thus, the planar adsorption structure of CuPc on the O/Fe surface is indicated. The relative intensity ratio of $I_p - I_a$ at the peak positions of 2, 3, and 4 is almost the same between CuPc/Fe and CuPc/O/Fe, and therefore, the $I_p - I_a$ curves for CuPc/Fe and CuPc/O/Fe are compared by referring to $I_p - I_a$ at these peak positions. In this comparison, the $I_p - I_a$ curve for CuPc/O/Fe is different from that of CuPc/Fe in the following three aspects. First, $I_p - I_a$ at the position of peak 1 decreases. Second, the intensity at the positions of peaks 5 and 6 is enhanced. Last, the sign of the asymmetry at around 5 eV is reversed.

Prior oxygen adsorption on the Fe(100) surface introduces two features to the surface density-of-states.¹⁷ One is a decrease in the density-of-states at the Fermi level, and the other is an increase in the density-of-states at about 8 eV below the Fermi level, originating from the O $2p_z$ component. It is reasonable to expect that the O $2p_z$ component significantly contributes to the bonding with the CuPc adsorbates. In this case, the spin polarization at the energy position of O $2p$, which is observable on the asymmetry curve of O/Fe in Figure 5, is well transported to the CuPc adsorbates compared with the Fe surface. This change in the bond formation between CuPc and the surface by oxygen adsorption may cause the decrease and enhancement of $I_p - I_a$ at the Fermi level and low kinetic energy region, respectively.

The origin of the opposite spin polarity at around 5 eV on CuPc/Fe and CuPc/O/Fe is not clear. However, this opposite spin polarity may simply reflect the spin polarity at the Fe and O/Fe surfaces. The signs of the spin asymmetries at 5 eV on Fe and O/Fe are positive and negative, respectively, and these are in agreement with those of CuPc/Fe and CuPc/O/Fe. The 1 ML CuPc film has no state interacting with He^* , judging from the MDS spectra, at the corresponding energy position, and hence, it is interpreted that there is no spin asymmetry originating from CuPc at this energy region. The opposite spin

polarity on the underlying surface may be observed by the presence of the bare surface on which CuPc does not adsorb.

The sign of the asymmetry of CuPc at the Fermi level is positive on both the CuPc/Fe and CuPc/O/Fe surfaces, whose sign is positive (Fe) and negative (O/Fe) at the Fermi level, respectively. Generally, the ionization of He^* occurs more than 2 Å away from the top surface. Therefore, SPMDS measures the spin polarization in the surface-vacuum region. On the other hand, the hybridization of the orbitals of the adsorbates and the substrate surface occurs at their interface. The calculation by Wu and Freeman indicates the dependence of the spin polarization and its sign on the distance from the surface in the surface-vacuum region on the Fe and O/Fe surfaces.¹ The positive asymmetry of CuPc in SPMDS on both surfaces of positive and negative asymmetry may be due to the difference in the distance from the surface to the point where the bonding formation occurs and the point of deexcitation of He^* .

4. Conclusion

CuPc on Fe(100) has been investigated using CAICISS and (SP)MDS. The structural analysis of the 1 ML film by CAICISS indicates that the CuPc molecules are adsorbed with their molecular plane parallel to the Fe surface, while the structure becomes disordered with an increase in thickness. This structural analysis enabled the assignment of the peaks in the MDS spectra. By the combination of MDS with the spin polarization analysis, the spin polarization of the molecular orbitals of CuPc, which is about 40% maximum, induced by the magnetization of the underlying Fe surface was detected. To our knowledge, this is the first measurement in which the spin polarization of an organic adsorbate was observed by SPMDS. The spin asymmetry of a CuPc monolayer on the Fe and O/Fe surfaces was compared, and the spin polarization of CuPc was qualitatively discussed in terms of the charge-transfer mechanism between CuPc and the substrate surface.

Acknowledgment. We are grateful for valuable discussions with Prof. Ueno and Dr. Kera of Chiba University. The beneficial suggestions of Dr. Isago and the help of Dr. Kitazawa of National Institute for Materials Science are also greatly appreciated.

References and Notes

- (1) For example, Wu, Q.; Freeman, A. J. *Phys. Rev. Lett.* **1992**, *69*, 2867.
- (2) Getzlaff, M.; Bansmann, J.; Schonhense, G. *Phys. Rev. Lett.* **1993**, *71*, 793.
- (3) Johnson, P. D.; Clarke, A.; Brookes, N. B.; Hulbert, S. L.; Sinkovic, B.; Smith, N. V. *Phys. Rev. Lett.* **1988**, *61*, 2257.
- (4) Flynn, B. W.; Owen, A. E.; Mayor, J. J. *Phys. C* **1977**, *10*, 4051.
- (5) Ghosh, A. H.; Morel, D. L.; Feng, T.; Shaw, R. F.; Rowe, C. A. *J. Appl. Phys.* **1974**, *1*, 20.
- (6) Lu, X.; Hipps, K. W. *J. Phys. Chem. B* **1997**, *101*, 5391.
- (7) Harada, Y.; Masuda, S.; Ozaki, H. *Chem. Rev.* **1997**, *97*, 1897.
- (8) Onellion, M.; Hart, M. W.; Dunning, F. B.; Walters, G. K. *Phys. Rev. Lett.* **1984**, *52*, 380.
- (9) Aono, M.; Katayama, M.; Nomura, E. *Nucl. Instrum. Methods, B* **1992**, *64*, 29.
- (10) Riddle, T. W.; Onellion, M.; Dunning, F. B.; Walters, G. K. *Rev. Sci. Instrum.* **1981**, *52*, 797.
- (11) Williams, R. S.; Kato, M.; Daley, R. S.; Aono, M. *Surf. Sci.* **1990**, *225*, 355.
- (12) Oen, O. S. *Surf. Sci.* **1983**, *131*, L407.
- (13) Kahl, J. L.; Faulkner, L. R.; Dwarakanath, K.; Tachikawa, H. *J. Am. Chem. Soc.* **1986**, *108*, 5434.
- (14) Ozaki, H.; Harada, Y. *J. Am. Chem. Soc.* **1987**, *109*, 949.
- (15) Liao, M.; Scheiner, S. J. *Chem. Phys.* **2001**, *114*, 9780.
- (16) Getzlaff, M.; Egert, D.; Rappolt, P.; Whilhelm, M.; Steidl, H.; Baum, G.; Raith, W. *Surf. Sci.* **1995**, *331*, 1404.
- (17) Yamauchi, Y.; Kurahashi, M. *Appl. Surf. Sci.* **2001**, *169/170*, 235.