Interface electronic structure and dynamics of tris-(8-hydroxyquinoline) aluminum on Cu(100)

Chang-Ki Min¹, Youhong Lee¹, Yongsup Park²,³ and Jeong Won Kim¹,³

¹ Korea Research Institute of Standards and Science, Daejon 305-340, Korea
² Department of Physics and Research Institute for Basic Sciences, Kyung Hee University, 1 Hoegi-dong, Dongdaemun, Seoul 130-701, Korea
E-mail: parky@khu.ac.kr and jeongwonkriss.re.kr

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Abstract. We have investigated the evolution of occupied and unoccupied electronic states of tris-(8-hydroxyquinoline) aluminum (Alq₃) molecules adsorbed on Cu(100) using ultraviolet photoelectron spectroscopy and interferometric time-resolved two-photon photoemission (ITR-2PPE). The adsorption of Alq₃ lowers the work function of the surface, which allows an unambiguous observation of Cu(100) surface resonance coupled with d-band state and molecular interband transition in our ITR-2PPE setup. No evidence of an anion state, which used to be formed by dynamic charge transfer from metal to a molecular unoccupied state, is identified. Analysis of relaxation dynamics of the transiently occupied electronic states shows that the lifetimes for those excited states at this surface are independent of the Alq₃ thickness. These results indicate that the Alq₃–Cu(100) interface is described as a weak van der Waals interaction.

³ Author to whom any correspondence should be addressed.
1. Introduction

Occupied and unoccupied electronic states and their alignment at interfaces have been an issue of fundamental importance in various electronic devices and associated physical systems. Development of easy-to-use and reliable femtosecond (fs) pulse lasers and related techniques made it possible to follow the ultrafast behavior of electrons in a time domain, opening a flourishing new field of ultrafast surface electron dynamics. Using pump–probe techniques, time-resolved two-photon photoemission (2PPE) is a powerful tool for studying a variety of ultrafast charge carrier dynamics at solid surfaces and interfaces [1, 2]. The 2PPE has proven to be an excellent tool for probing unoccupied molecular orbitals, crystal band structure, electronic coupling, energy stabilization, etc.

The electron transport across the interfaces in organic semiconductor devices is an important issue in performance evaluation of electronic devices such as organic light-emitting diodes (OLEDs). Tris-(8-hydroxyquinoline) aluminum (Alq₃) is a prototypical light-emitting and electron-transporting material used in OLEDs. Recently, Ino et al reported the formation of an anion state at the interfaces of Alq₃/Cu(111) and Alq₃/Au(111) and measured their lifetimes [3]. The anion state is created by the excitation of electrons from the metal substrate to an unoccupied state of the Alq₃ molecule. Since the electron emission from the surface state for the clean Cu(111) or Au(111) is suppressed as a result of Alq₃ adsorption, the hybridization of the metallic surface state and a molecular orbital at the specific interface seems to play an important role in the formation of the anion state. This is evidenced by the increase of the anion state lifetime with increasing molecule coverage, where the interface metallic electron scattering is important for the relaxation mechanism [3]. However, such a strong and localized interaction has usually been observed only on a highly electronegative molecular system such as C₆F₆ on Cu(111) [4, 5]. Therefore the strength of electronic coupling between the Alq₃ and a metallic surface such as Cu(100) with no occupied surface state is an important issue.

We used ultraviolet photoelectron spectroscopy (UPS) and interferometric time-resolved two-photon photoemission (ITR-2PPE) to study the interface electronic structure and dynamical behavior on Alq₃/Cu(100). The energy-level alignment and the excited state electron dynamics at the molecule/metal interface were analyzed. We found no evidence of anion state formation while the lowered work function upon Alq₃ adsorption on Cu(100) allowed clear observation of a surface resonance state coupled with bulk d-band. Such a weak molecule–metal interaction was also confirmed in energy-dependent lifetimes of excited states, which is not affected by the adsorption of Alq₃ molecules.
2. Experimental

The detailed setup of our homemade cavity-dumped Ti:sapphire laser system is described elsewhere [6]. The laser system produces 15 fs, 40 nJ pulses at a repetition rate of 1 MHz at a wavelength of around 800 nm. A 75 µm-thick BBO crystal was used to obtain a wide phase-matching second-harmonic spectrum, and mirrors with a 100 mm radius of curvature were used for focusing and collimating beams at both sides of the beta barium borate (BBO) crystal. The frequency-doubled beam was passed through a Mach–Zehnder interferometer that generated a pair of identical pulses with precisely controlled time delays. Final group velocity dispersion (GVD) and third-order dispersion (TOD) optimizations were carried out using a fused-silica prism pair and a negative GVD mirror pair for the frequency-doubled pulses. The width-optimized pulses were delivered into a ultrahigh vacuum (UHV) chamber through a fused silica window. The focused laser beam was incident 50° to the sample surface normal in colinear geometry.

The optical spectrum of the laser pulse was centered at 405 nm (3.06 eV) with a bandwidth of 16 nm (140 meV). The width of this pulse was 19 fs as estimated by a time-resolved photoemission measurement of a clean Cu(100) surface at the Fermi edge using a conventional hemispherical electron energy analyzer (VG ESCALAB 200i), and a deconvolution of a phase-averaged pump–probe correlation signal. Careful design of the Mach–Zehnder interferometer allowed us to achieve a repeatability of scanner position less than 10 nm over the time period of 10 min without additional feedback, which translates into a pump–probe delay time repeatability of less than 0.067 fs. In the interferometer, we used a piezoelectric linear translation stage with a built-in closed loop control with capacitive position sensor. The whole system was enclosed in a small box to reduce fluctuations due to air flow and temperature change. The scanned time delay range was 650 fs, over which many scans were averaged at a rate of 0.2 Hz to reduce environmental noise and low frequency drift. A digital function generator sent a sawtooth wave voltage signal to the piezoelectric scanner driver, while a multichannel scaler triggered by the function generator collected the electron signal at the detectors of electron energy analyzer. The signal was typically averaged over 200 scans.

The UHV chamber (base pressure = 1.0 × 10^{-10} Torr) was equipped with a hemispherical electrostatic electron energy analyzer, an x-ray source, and a He discharge lamp. The Cu(100) crystal surface was cleaned by repeated cycles of Ar+ sputtering and annealing at 750 K. Commercially available Alq3 powder (Ludís, purity > 99%) was used without further purification. The Alq3 molecules were thermally evaporated in a separate preparation chamber on the sample surface kept at 300 K. The typical growth rate was 0.01 monolayer (ML) s⁻¹. These steps of sample preparation are very similar to the previous cases on Cu(111) and Au(111) surfaces [3]. The Alq3 coverage was estimated by comparing the measured work functions with the reported values [3]. The thickness of 1 ML of Alq3 is estimated to be about 8 Å. The data were recorded at the sample temperature of 300 K, along the surface normal direction with an acceptance angle of 8° with p-polarization geometry. On the sample, pump and probe pulses were focused to 50 µm beam size. The pulse energy was equally 200 pJ in the experiment with a clean Cu surface and was reduced less than that to avoid the saturation of the electron detector. In these power ranges, any signal nonlinearity with laser power or sample damage by the excitation laser pulses was not observed. The energies of 2PPE spectra were referenced to the Fermi energy ($E_F$).
3. Results and discussion

3.1. Steady state spectra at the Alq₃/Cu(100) interface

Figure 1 shows valence band spectra of Alq₃/Cu(100) interface as a function of Alq₃ coverage. On the clean Cu(100) surface at the bottom spectrum, several peaks appear at 2.8 ± 1.0 eV, which are well known as Cu 3d bulk bands. Since the normal emission geometry is used, no surface state is observed except for the Fermi edge distribution. As the Alq₃ coverage increases, the Cu 3d band emission as well as electron population at Fermi edge is attenuated while new molecular orbital features of Alq₃ grow. The series of the molecular orbital states agrees well with the data reported previously for Alq₃ film [7]. At the thickness of 20 Å, the onset of the highest occupied molecular orbital (HOMO) level becomes clearly visible at 2.37 eV.

Figure 2 shows 2PPE spectra of Alq₃/Cu(100) interface as a function of Alq₃ coverage in the same sequence as in figure 1. The final state energy (horizontal axis) is the sum of the work function of the surface and the kinetic energy of the electron, which is the electron energy relative to the Fermi level. The sample was biased to −5 V for enhanced low energy photoemission and secondary cutoff, from which the work function changes were measured. The work function of the clean surface is 4.60 eV, which decreases to 3.14 eV when 20 Å of Alq₃ is deposited, as seen on the top spectrum. The 2PPE spectrum for the clean Cu(100) surface is relatively featureless dominated only by the secondary electron tail at about 4.5 eV.
Figure 2. Normalized 2PPE spectra of Alq₃/Cu(100) interface as a function of Alq₃ coverage in the same sequence as in figure 1. The inset schematically shows the 2PPE process and the effects of work function lowering, where VL1 and VL2 are vacuum levels for clean and Alq₃-covered Cu(100) surfaces, respectively. The positions of the SR and its final excitation are also indicated.

and the Fermi edge emission at about 6 eV. The deposition of Alq₃ decreases the work function as clearly seen in the increased width of the observable spectrum, which also reveals a new peak at 3.88 eV. The intensity of 2PPE spectral features depends strongly on the laser power and the surface conditions. Therefore, the spectra in figure 2 were normalized so that the intensities of $E_F$ emission above background are identical for all spectra. After the normalization, the intensity and position of the new peak at 3.88 eV remains unchanged regardless of the Alq₃ coverage. Compared with the anion state ($E - E_F = 5.9$ eV) reported for Alq₃/Cu(111) surface [3], the energy of 3.88 eV peak is much lower and insensitive to the Alq₃ coverage. Another peak at around 3.2 eV becomes dominant at higher Alq₃ thickness, albeit obscured by a secondary electron tail.

The peak at 3.88 eV in figure 2 corresponds to $E_i = 0.82$ eV above $E_F (E = E_i + \hbar \omega)$ and its normalized intensity is constant with no dependence on Alq₃ coverage. We initially
thought this peak was due to the unoccupied surface resonance state originating from the clean Cu(100) surface because the position of this peak is in good agreement with the previous inverse photoemission measurement [8]. It was made visible by the decreased work function of the surface after the Alq$_3$ adsorption. However, the transient occupation of the resonance state must first come from an occupied ground state, which is the d-band state as discussed below. The binding energy of the d-band electrons that can transiently occupy this surface resonance is 2.24 eV below $E_F$, which is accessible with the 3.06 eV photons we used. In the established band structure of the Cu(100) surface, there are several unoccupied states that could be probed by 2PPE including the image potential states that are located higher than 4 eV above $E_F$. The image state has been extensively studied using 2PPE and inverse photoemission techniques and various relaxation dynamics for the electrons excited into the image states have been well elucidated [8]–[12]. These image states are not accessible in our experiment because we used a single-photon energy of 3.06 eV. However, the surface resonance state can be readily accessible with this photon energy provided the work function of the surface is appropriate. Mention of the surface resonance in the context of 2PPE can be found in the literature [13, 14], but no detailed investigation has been made.

To find further evidence for the origin of the 3.88 eV peak, a similar experiment was performed for a Cu(100) surface intentionally made rough. The rough surface was created by sputtering the Cu(100) crystal surface with Ar$^+$ ion beam at 3.0 kV for 20 min without subsequent annealing. Figure 3 shows the comparison of 2PPE spectra before and after the Alq$_3$ adsorption on the rough and ordered Cu(100) surfaces, respectively. Before the Alq$_3$ adsorption, the two 2PPE spectra are not very different, probably because there is no surface state on the Cu(100) surface. However, at the coverage of 6 Å, the peak intensity at 3.88 eV for the ordered
Cu(100) surface is higher than that for the rough surface, while the rough surface shows a huge secondary electron tail. This result is evidence that the peak at 3.88 eV is indeed due to the unoccupied surface resonance that would be strongly populated on the well-ordered Cu(100) surface. However, the fact that the 3.88 eV feature did not completely disappear on the rough surface is evidence that it is partly due to the occupied d-band feature [14].

At the Alq₃ thickness of 20 Å, the maximum point of the HOMO peak is located at 3.20 eV as seen in figure 1, which is quite different from the onset at 2.37 eV. The work function on this surface is 3.14 eV. Therefore, the ionization potential, the energy difference between the HOMO maximum and vacuum levels is 6.34 eV, which is within the range of the ionization potentials observed before [3, 15]. The HOMO maximum position of the Alq₃ on the rough Cu(100) surface is observed at 3.12 eV (not shown here), which differs only by 0.08 eV from the value on the ordered surface. This indicates that the HOMO position is not much dependent on the crystalline order of the Cu(100) surface. However, the HOMO maximum position of Alq₃ on Cu(111) is reported to be 2.63 eV, which is about 0.5 eV higher than the value for Cu(100) surface. A similar energy shift is observed in the work functions of the Alq₃ on Cu(111) and on Cu(100), leading to an equivalent ionization potential. The difference in the energy-level alignment of the Alq₃ molecules at two different crystal faces is possibly due to the existence of an occupied surface state on the Cu(111) that can hybridize with Alq₃ molecular orbital. Since there is no surface state in the occupied band of the Cu(100) surface, the HOMO position seems to be insensitive to the initial surface conditions. In any case, it is clear that the hybridization between the Cu(100) surface and the adsorbed Alq₃ molecule is minimal.

The strong emission at 3.2 eV in figure 2 can be related to the Alq₃ molecule itself, since its appearance does not depend on the initial surface condition. Because the work function of this surface is 3.14 eV, the prominent emission might be mixed with single-photon photoemission at our photon energy of $\hbar\omega = 3.06$ eV. However, in a previous report on the Alq₃/Cu(111), it was argued that a molecular singlet state can be observed at 0.5 eV above $E_F$ [3]. By the rigid shift of the energy-level alignment difference (about 0.5 eV) between the two surfaces, there should be a similar molecular singlet state transition near the threshold of the photoemission at the Alq₃/Cu(100) for $\hbar\omega = 3.06$ eV [16]. Further evidence for this molecular transition-related feature will be discussed below.

### 3.2. Time-resolved 2PPE

The dephasing and population dynamics of hot electrons at the interface can be probed through ITR-2PPE measurements, which yields interferometric two-pulse correlation (I2PC) traces for photoemitted electrons. We measured the I2PC traces for various energy positions and Alq₃ coverages to obtain detailed information on the excited electron relaxation dynamics at the Alq₃/Cu(100) interface. The I2PC data analysis procedure detailed in the literature was used [17].

Figure 4 shows an example of an I2PC measurement results and peak fitting procedure for the extraction of relevant time constants. The I2PC data can be modeled as a three-level system with dynamic processes for population and phase relaxation. According to the optical Bloch equation, the $0\omega$ component in I2PC contains information on both population relaxation and dephasing of an intermediate state. In addition, the $1\omega$ and $2\omega$ components contain information

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4 The background of I2PC signals for 3.28 eV was increased due to the single photoemission whose contribution was estimated about 50% of the total intensity.
Figure 4. Schematic of the fitting procedure of an ITR-2PP spectrum using three different envelope functions. The definition of involved time constants is shown in the upper left corner. This spectrum is obtained from a clean Cu(100) surface at the final state energy of 6.1 eV corresponding to the Fermi edge. Three envelope functions shown here are used as instrumental response functions for time-resolved analysis for various other final state energies.

on an intermediate state and a final state dephasing, respectively. Each component was fitted by a model function convoluted with an instrument response function after phase average. The instrumental response function was obtained from an I2PC scan near the Fermi edge of the clean Cu(100) surface in figure 4. The pump laser pulse incident on the sample excites electrons from the initial state $|0\rangle$ to the intermediate state $|1\rangle$. While the excited electrons in $|1\rangle$ state start to decay, they interact with the probe pulse and may be excited into the final ionized state $|2\rangle$ and detected by the electron energy analyzer. The coherent interaction of the hot electrons in state $|1\rangle$ and the probe pulses gives linear or nonlinear polarization, which can be decomposed to the $1\omega$ or $2\omega$ envelope. The incoherent interaction gives a phase-independent $0\omega$ envelope, which is associated with intermediate state electron population relaxation.

Figure 5 represents two different $0\omega$ envelopes of I2PC traces at kinetic energies of (3.88 Alq₃: 6 Å) and 3.28 eV (Alq₃: 20 Å), respectively. These data were fitted nicely with convolution of two exponential functions with the instrumental response function, which is obtained from clean Cu(100) near the Fermi edge. Two exponential decays mean dephasing and population decay of the intermediate state, respectively, in the optical Bloch equations [1]. Initial fast decay is indistinguishable with instrumental response function due to the fast dephasing, and second decay shows the population relaxation of the intermediate state. While the 3.88 eV (Alq₃: 6 Å) trace exhibits a smooth decay process, and 3.28 eV (Alq₃: 20 Å) trace shows a residual
Figure 5. $0\omega$ envelopes of I2PC signals for two peak positions at 3.88 and 3.28 eV for the Alq$_3$ thickness of 6 and 20 Å, respectively. A weak periodic oscillation from coherent molecular vibrations can be seen for the 3.28 eV envelope.

feature extended to a long delay time. There are a few weak but clearly observable periodic oscillations that we tentatively attribute to the coherent molecular vibrations. A rough estimate of the oscillation period indicated in figure 5 is $63 \pm 4$ fs, which gives around 530 cm$^{-1}$. This is well matched with the Al–O stretching mode observed by IR/Raman spectra on Alq$_3$ film [18]. Such a beat structure supports that the 3.28 eV peak contains a component associated with a molecular vibration, further evidence that the 3.28 eV feature is due to HOMO–lowest occupied molecular orbital (LUMO) transition coupled with vibronic excitation of Alq$_3$ molecule.

Figure 6 exhibits the population relaxation time constants (lifetimes) of a few intermediate states as a function of the final state energy $E$. The energy of the intermediate state can be written as $E_i = E - \hbar \omega = E - 3.06$ eV. For most of the cases, the dephasing time constants were less than 6 fs. The population relaxation time constants, on the other hand, vary from 22 to 220 fs depending on the electron energy. This dependence is qualitatively consistent with the simple Fermi liquid theory prediction that the lifetime is inversely proportional to $(E_i - E_F)^2$. The lifetime of the resonant peak at 3.88 eV is 65 fs and the HOMO–LUMO transition state of Alq$_3$ at 3.28 eV is 220 fs. However, they are all nearly independent of the Alq$_3$ coverage on Cu(100). It is in contrast with the lifetime increase with molecular coverage in the case of Alq$_3$/Cu(111)
interface where an anion state was observed as well as at C₆F₆/Cu(111) interface, where a molecular resonance similar to the anion state was also observed [3]–[5]. The lack of an anion state in Alq₃/Cu(100) interface first indicates that the optical transition from metal to the molecule is either symmetry forbidden or the transition matrix element is very small. Also we can expect that the wave function overlap between the unoccupied state of Cu(100) and the molecular levels near LUMO of Alq₃ is small, otherwise the electrons first excited to a metallic unoccupied state could be transferred to molecular empty levels [19]. Therefore, considering the lack of new peaks in the UPS spectra of this interface and the absence of an anion state in 2PPE spectra, we are led to conclude that the main interaction between the Cu(001) surface and Alq₃ molecule is a weak van der Waals interaction. Such a weak interaction was also observed for various polyacene/Au(111) interfaces where the insensitivity of the image resonances to the size of polyacene molecules and the absence of electron transfer from the metal substrate to unoccupied molecular states both suggest that the molecular orbitals are not strongly coupled to delocalized metal states or image potential resonances [20].

4. Conclusions

The energy-level alignment and the electron dynamics on the Alq₃/Cu(100) interface have been investigated by the combination of UPS and time-resolved 2PPE. We found no evidence of an anion state at Alq₃/Cu(100) interface, which is in contrast with the Alq₃/Cu(111) interface. Instead, a surface resonance state that was coupled with d-band state could be clearly observed and evidence of a molecular interband transition was observed. This shows that the electronic interaction between Alq₃ and the Cu(100) surface is quite different from the cases for Alq₃/Cu(111) and Alq₃/Au(111). The analysis of I2PC traces obtained from ITR-2PPE experiment has been successfully performed and the relaxation time constants for intermediate state were extracted within the excitation-decay scheme of three-level optical Bolch equation model. The estimated population relaxation time constants were independent of the Alq₃
coverage, probably because of the absence of wave function mixing between the metal and the molecule at the interface.

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