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Vibrational structure of ultrathin 8-hydroxyquinoline aluminum films studied by high-resolution electron-energy-loss spectroscopy

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High-resolution electron-energy-loss spectra have been measured from submonolayer- and monolayer-thick 8-hydroxyquinoline aluminum (Alq) layers vacuum-deposited on metal substrates. Vibrational structures are different in the two cases. But no significant difference is found between the energy-loss spectrum of monolayer-thick Alq and the Fourier-transform infrared spectrum of bulk Alq. This seems to indicate that although there exists some weak bonding between the discretely adsorbed Alq molecules and the substrate, van der Waals interaction predominates upon the formation of a continuous Alq film. The structures in the loss spectrum are tentatively assigned. [S0163-1829(99)02440-6]

Organic light emitting diodes (OLED's) have recently attracted much attention due to their potential applications in multicolor flat-panel displays. Both small molecules and polymers are extensively used in these devices. A small-molecule-based OLED consists typically of a couple of thin organic films sandwiched between two electrodes, and 8-hydroxyquinoline aluminum (Alq), a complex of aluminum cation Al^{3+} coordinated by three 8-quinolinolate anions, is the key electroluminescent material currently used in the device.¹ The chemical structure of the molecule is shown in Fig. 1. So far, quite a number of studies have been done on the electronic structure of Alq, by using surface-sensitive photoemission techniques as the major tools.² However, relatively little work has been done on the vibrational structures of the material.

In this paper, we present an application of high-resolution electron-energy-loss spectroscopy (HREELS) to the observation of vibrational spectra of ultrathin Alq films deposited on metal substrates. The results obtained are excellently consistent with the bulk vibrational spectrum acquired using Fourier-transform infrared (FTIR) spectroscopy, indicating that for OLED-related surface and interface studies, HREELS is as powerful as previously confirmed for other organic/inorganic systems.³⁻⁸

The experiments were performed in an ultrahigh-vacuum (UHV) surface analysis system equipped with an LK Technologies Model 3000 HREEL spectrometer. Alq deposition was carried out in a multisource deposition chamber UHV-connected to the main chamber. The substrates used were polished molybdenum plates, covered with an *in situ* deposited silver layer. The cleanliness of the metal substrates was doubly checked by Auger electron spectroscopy (AES) and HREELS. Only those with no C and O traces in the Auger spectra and no vibrational loss structures in the HREEL spectra would be used as the substrates for further deposition of Alq. During deposition, the substrate was kept at room

temperature and the thickness of the organic layer was monitored by a quartz crystal oscillator. The HREEL spectrometer was operated with a primary electron energy of 3 eV and all the spectra were collected in the specular direction with the electron beam directed 60° from the surface normal. The full width at half maximum (FWHM) of the elastic peak measured from the bare Ag surfaces was less than 25 cm^{-1} , and became enlarged to around 30 cm^{-1} upon the deposition of Alq.

Figure 2 shows the HREEL spectra taken from the Alq-covered Ag surfaces. The thicknesses of the overlayers range from 0.1 to 1.5 nm. They are equivalent to the coverages from less than 0.1 monolayer (ML) to around 1 ML, assuming that the diameter of the Alq molecule is slightly larger than 1 nm.⁹ As is immediately evident from the figure, all spectra corresponding to submonolayer coverages (up to 0.9 nm) possess a similar overall structure: a broad doublet at the loss energy of around 3000 cm^{-1} , a wide band from 700 to 1600 cm^{-1} , and a separate peak at around 420 cm^{-1} . As the Alq thickness is increased from 0.9 to 1.5 nm, however, significant changes occur in the loss structure. Most of the peaks in the spectrum become relatively sharp and well resolved. In particular, the intense peak centered at 3085 cm^{-1} dominates in the loss structures over there. No additional

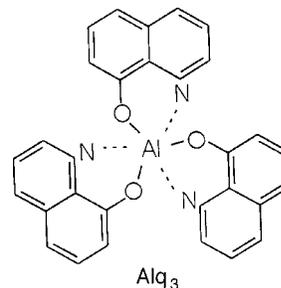


FIG. 1. Chemical structure of Alq.

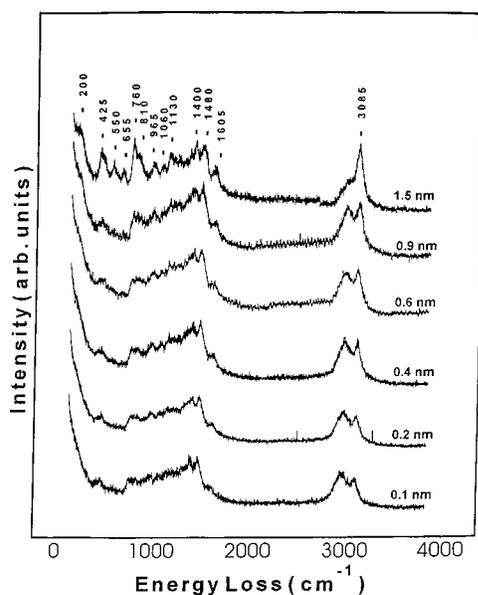


FIG. 2. HREEL spectra measured from Alq-covered Ag surfaces. The thicknesses of the Alq films range from 0.1 to 1.5 nm.

variation can be observed if the Alq thickness is further increased beyond 1.5 nm (not shown in the figure).

The variation of the loss structure with thickness clearly indicates that a continuous Alq film is formed during the coverage transition from submonolayer to monolayer. In other words, uptake of the Alq molecules on the Ag substrate is uniform in the submonolayer stage. This is also confirmed by separate atomic force microscopy (AFM) observations. In such observations, we have found that, in the Alq coverage range concerned, roughness of the surfaces is always smaller than 2.0 nm, consistent with the mode of layer-by-layer uptake. Actually, if three-dimensional islands were formed in the submonolayer stage, no significant change in the vibrational structure would have occurred during the nominal submonolayer-monolayer transition process. Evolution of the loss structures at around 3000 cm^{-1} is thus understandable. It is well known that vibrational peaks in the region from 2700 to 3100 cm^{-1} are associated with various C-H stretch modes and that, roughly speaking, the peaks below and above 3000 cm^{-1} can be ascribed to the vibrations in aliphatic and aromatic compounds, respectively.¹⁰ That means only the

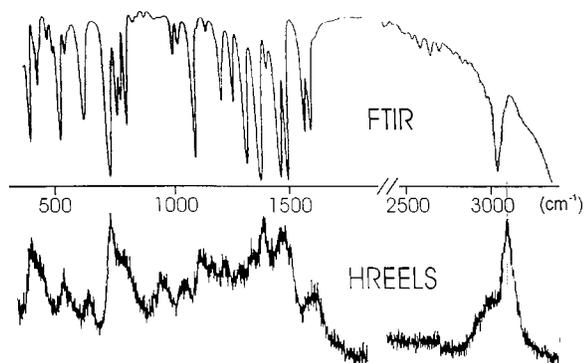


FIG. 3. Comparison of two sorts of vibrational spectra. Above: FTIR spectrum of bulk Alq. Bottom: HREEL spectrum of monolayer-thick Alq film.

TABLE I. HREELS peak assignments for the 1.5-nm-thick Alq film deposited on Ag.

| Peak position (cm^{-1}) | Assignment |
|------------------------------------|------------------------|
| 200 | ring pucker |
| 425 | out-of-plane ring bend |
| 550 | in-plane ring bend |
| 655 | in-plane ring bend |
| 760 | out-of-plane C-H bend |
| 810 | out-of-plane C-H bend |
| 965 | ring breath |
| 1060 | in-plane C-H bend |
| 1130 | in-plane C-H bend |
| 1400 | ring stretch |
| 1480 | ring stretch |
| 1605 | ring stretch |
| 3085 | C-H stretch |

higher-loss-energy component in the doublet is intrinsic to Alq and the lower-loss-energy component may originate from some other effect. It is unlikely that the latter component is due to surface contamination as we cannot find its trace in the spectrum measured from the bare Ag surface. Thus, we suspect it is the weak bonding between part of the carbon atoms in the 8-quinolinolate anions and the surface metal atoms that downward shifts the C-H vibration frequency and gives rise to the lower-loss-energy component. While the number of the carbon atoms involved in bonding to the substrate is relatively large in the submonolayer stage, lateral molecule-molecule interaction may play a more important role when a continuous film is formed so that a more bulklike feature can then dominate in the loss spectrum. Coverage-dependent, two-component C-H stretching structures were also observed from other aromatic/metal systems, and were ascribed to the coexistence of symmetric and asymmetric stretching modes previously.^{7,8}

In order to check if the vibrational structure in the spectrum of the 1.5-nm-thick film is representative of bulk Alq, we have performed transmissive FTIR measurements using a separately prepared self-sustaining Alq film as the specimen. The spectrum obtained is shown in Fig. 3 together with the HREEL spectrum of the 1.5-nm-thick Alq. The agreement of the two spectra is excellent. This is consistent with our speculation that only van der Waals interaction may exist between the organic overlayer and the metal substrate so that the vibrational spectrum of the layer will not be significantly affected by its adhering to the substrate. Therefore, it should be possible to assign all the peaks in the HREEL spectrum based on bulklike consideration.

In addition to the aforementioned C-H stretches, condensed ring aromatic compounds are usually characterized by sharp bands in the ring stretch region. For quinolines, the ring stretch modes should appear in the region of 1300 – 1600 cm^{-1} .¹⁰ So we can assign the sharp peaks at 1400 , 1480 , and 1605 cm^{-1} to ring stretches with confidence. Vibrational spectra of aromatics are also featured by their out-of-plane C-H bending (adjacent hydrogen wagging) modes in the region of 700 – 900 cm^{-1} . Two peaks (760 and 810 cm^{-1}) are in the region and can thus be assigned to the wag modes. Similarly, we can assign the 1060 - and 1130-cm^{-1} peaks to

in-plane C-H bending. One may notice that the 1130-cm^{-1} peak has a broad shoulder towards higher loss energies. This is probably due to overlapping of the peak with the C-O stretch peak in the vicinity. The peaks at 425 , 550 , and 655 cm^{-1} can be assigned to the ring-bending modes, out-of-plane for the first one, which is somewhat broad, and in-plane for the other two. We are not quite sure about the origin of the peak at 200 cm^{-1} . But the possibility of its originating from a substrate-molecule mode can be ruled out, as it emerges only when the coverage approaches 1 ML. For the consideration of bulk excitation modes, a peak with such a loss energy may result either from the ring puckering¹⁰ or from the Al-O stretch as the loss energy is in the range of what appears when oxygen associatively adsorbs on a metal surface.¹¹ Finally, it is not clear why the peak at 965 cm^{-1} , which can probably be assigned to ring breathing, does not appear in the FTIR spectrum. All of our assignments are summarized in Table I.

As is well known, HREELS is a surface-sensitive technique. It can be applied not only to clean organic surfaces, but also to gas- and/or metal-covered surfaces, and hence

will be very useful in solving OLED-related surface and interface problems. So far, only optical techniques such as infrared spectroscopy have been employed in investigating variation in vibrational structures induced by chemical changes at the interfaces involved, but the information was acquired *ex situ* in air.¹² By preparing the interfaces concerned via gas introduction and/or metal deposition *in situ* in UHV, detailed and precision information about the variation in bonding configuration at the clean, controlled surface can be obtained by subsequent HREELS measurements. Related studies are currently in progress.

In summary, HREELS has been applied to vacuum-deposited, ultrathin Alq films. All the loss peaks observed are tentatively assigned. Film-thickness-dependent variation of the vibrational structure is observed, which is indicative of a uniform uptake of the Alq molecules on the metal substrate and of a relatively weak interaction between the film and the substrate.

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¹C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).

²For a recent reference, see H. Ishii, K. Sugiyama, D. Yoshimura, E. Ito, Y. Ouchi, and K. Seki, *IEEE Trans. STQE* **4**, 24 (1998).

³J. J. Pireaux, P. A. Thiry, R. Caudano, and P. Pfluger, *J. Chem. Phys.* **84**, 6452 (1986).

⁴B. G. Frederick, M. R. Ashton, and N. V. Richardson, *Surf. Sci.* **292**, 33 (1993).

⁵T. Bitzer, T. Alkumshalie, and N. V. Richardson, *Surf. Sci.* **368**, 202 (1996).

⁶R. V. Plank, N. J. DiNardo, and J. M. Vohs, *Surf. Sci.* **340**, L971 (1995).

⁷R. V. Plank, N. J. DiNardo, and J. M. Vohs, *Phys. Rev. B* **55**,

R10 241 (1997).

⁸K. K. Lee, J. M. Vohs, and N. J. DiNardo, *Surf. Sci.* **420**, L115 (1999).

⁹I. Fujii, N. Hirayama, J. Ohtani, and K. Kodama, *Anal. Sci.* **12**, 153 (1996).

¹⁰N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy* (Academic, Boston, 1990).

¹¹See, for example, H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982).

¹²H. Aziz, Z. Popovic, C. P. Tripp, N.-X. Hu, A.-M. Hor, and G. Xu, *Appl. Phys. Lett.* **72**, 2642 (1998).