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Vibration spectroscopic study of the interaction of tris-(8-hydroxyquinoline) aluminum (Alq_3) with potassium

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Abstract

The interaction between Alq_3 and potassium was studied by using Raman and infrared spectroscopies. Infrared reflection absorption spectroscopy (IRRAS) spectra of Alq_3 films show significant changes after potassium deposition, such as the appearance of new bands and changes in relative intensity. Surface-enhanced Raman scattering (SERS) spectra obtained using the 413.1 nm line of a Kr^+ laser reveal similar changes. Changes are even more obvious when the 530.9 nm line was used for excitation. Changes in the SERS for excitation with the 413.1 nm line are less obvious due to a strong photoluminescence. The vibrational pattern of potassium-doped Alq_3 cannot be explained by the formation of radical anion by simple charge transfer, indicating the excess electron is not delocalized over the molecule. The observed spectral change suggests that the potassium atom interacts with both nitrogen and oxygen atoms of Alq_3 molecule.

Keywords: Tris-(8-hydroxyquinoline) aluminum (Alq_3); Potassium; Raman spectroscopy; Infrared reflection absorption spectroscopy

1. Introduction

Tris-(8-hydroxyquinoline) aluminum (Alq_3) is most widely used as the electron transport/light emitting layer in organic light emitting diodes (OLEDs) [1]. The chemical structure of Alq_3 is shown in Fig. 1. A typical OLED consists of indium tin oxide (ITO) as the anode, organic thin films, and low work function metals as the cathode. Since the properties of the metal/organic interface affect the performance of such devices, the understanding of the interaction between metals and organic molecules is important. The interfaces between Alq_3 and low work function metals such as Al, Mg, Ca, Li and K have been investigated experimentally and theoretically [2–5]. Johansson et al. [3] studied the electronic structure of Alq_3 upon doping with potassium and lithium based on a combination of X-ray and ultraviolet photoelectron spectroscopies with quantum-chemical calculations at the density functional theory level. They concluded that each electron transferred from an alkali metal atom is stored on one of the three ligands of the Alq_3 molecule, resulting in a new spectral feature in the valence band.

Vibration spectroscopy is a powerful technique for the analysis of chemical structure. In this work, we studied the interaction between Alq_3 and potassium using surface-enhanced Raman scattering (SERS) and infrared reflection absorption spectroscopy (IRRAS). SERS, with the enormous enhancement of Raman

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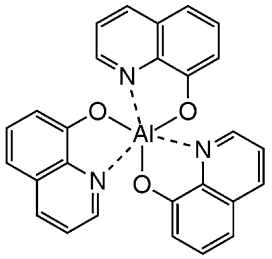

Fig. 1. The chemical structure of Alq_3.

scattering induced by silver clusters, and IRRAS possess high sensitivity and resolution and are powerful probes for structure and chemistry of surface and interface. In addition, Raman spectroscopy and IR spectroscopy are complementary to each other. Moreover, spectra in the low frequency region, where metal/organic vibrations are located, which are difficult to measure by IR spectroscopy, can be obtained by Raman spectroscopy.

2. Experimental

Alq_3 films were prepared by vacuum evaporation from a Knudsen cell onto a silver film deposited in advance on hydrogenated Si(1 1 1) substrate kept at room temperature in ultrahigh vacuum (UHV) chambers (base pressure $< 4 \times 10^{-8}$ Pa). The thickness of Alq_3 films was monitored by a quartz microbalance and kept at 3 nm for all samples investigated. Potassium was deposited on the Alq_3 films from SAES getter sources. Raman spectra were measured at TU Chemnitz using a triple monochromator (Dilor XY) with a charge-coupled device detector that was optically aligned to an UHV chamber. The 530.9 and 413.1 nm lines of a Kr^+ laser were used for excitation. The laser beam ($P < 30$ mW) was focused to a spot of about 300 μm in diameter on the sample surface. The spectral resolution was 2.5 cm^{-1}. To obtain strong Raman signals by surface enhancement, silver of 1 nm thickness was deposited on the Alq_3 films after K-deposition. IRRAS spectra were measured at Nagoya University using an IRRAS system consisting of an FT-IR spectrometer (Mattson R/S-1), a mercury cadmium telluride (MCT) detector, and an UHV chamber. The spectra were obtained in single reflection mode with p-polarized light at an angle of incidence of 80° relative to the surface normal. The reflected light was detected with an MCT detector with a resolution of 4 cm^{-1}.

3. Results and discussion

Fig. 2 shows the changes in the IRRAS spectra of the Alq_3 film as a function of potassium deposition time. The spectrum for the clean Alq_3 film is similar to that of powder Alq_3. After deposition of potassium, significant changes occurred in the IRRAS spectra. The vibrational bands at 1606, 1500 and 1388 cm^{-1} assigned to ring stretching vibrations [6] significantly decreased in intensity. New bands appeared at 1552, 1296, 1273, 1083 cm^{-1} and a shoulder at the low frequency side of the 1468 cm^{-1} band. These bands are in the region of ring stretching and CH bending modes.

Fig. 3 shows Raman spectra obtained using the 530.9 nm excitation line for clean and potassium exposed Alq_3 film with additional 1 nm of silver. The deposition of silver on Alq_3 films led to a pronounced increase in the intensity of Raman scattering. This intensity enhancement is attributed to SERS. The frequencies and the relative intensities of the Alq_3 vibrational modes were not changed upon Ag deposition, indicating that no chemical reaction accompanied by a charge transfer occurs [7].

The situation is different for the evaporation of potassium on Alq_3 films. Raman spectra of Alq_3 obtained

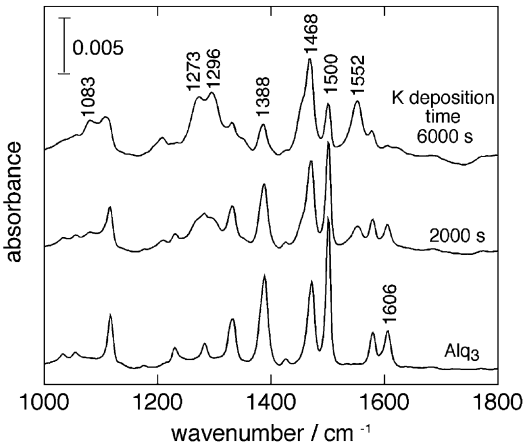

Fig. 2. The changes of IRRAS spectra of the Alq_3 film as a function of potassium deposition time.

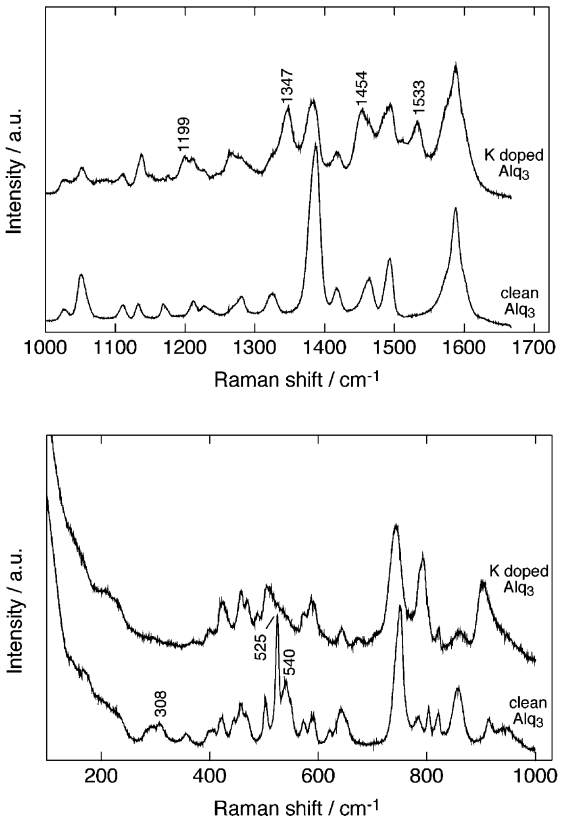

Fig. 3. Raman spectra of clean and potassium exposed Alq_3 films obtained by 530.9 nm excitation line.

using the 413.1 nm line show changes in relative intensities and the appearance of new bands. Change is even more obvious when the 530.9 nm line is used for excitation. The less obvious changes in the SERS for 413.1 nm line is ascribed to the strong photoluminescence background. In the region from 1000 to 1700 cm^{-1}, which is the region of ring stretching and CH bending modes, new bands at 1533, 1454, 1347 and 1199 cm^{-1} appeared after potassium deposition. The relative intensities of bands also significantly change and the frequencies of some bands are shifted. In the region below 1000 cm^{-1} the bands assigned to Al–O and Al–N stretching modes at 540, 525 and 308 cm^{-1} decrease in intensity. The modes related to quinoline such as ring deformation, CH wagging and ring torsion also change in relative intensity.

In the case of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), calculated vibrational modes shift up to $\sim$80 cm^{-1} due to the formation of anion by charge transfer and the vibrational pattern of the molecule is completely changed [8]. In contrast, the modes in IRRAS and Raman spectra of potassium doped Alq_3 do not show large shifts and the original bands partly remain. This suggests that the perturbation by K atom is not so significant as to completely rearrange the chemical bonds. Our recent study of near edge X-ray absorption fine structure (NEXAFS) also agree with this conclusion [9]. This result is consistent with the theoretical study of Li doped Alq_3 by Curioni and Andreoni [2]. They concluded that the charge distribution of the excess electron is localized on the pyridyl side of ligands, as in the case for an isolated radical anion, but a strong polarization is induced on the oxygen lone pairs by the positive ion. The latter conclusion is also consistent with our results that the most dominant changes with respect to intensity and lineshape are observed for vibrational modes, which have a contribution of Al–O or Al–N vibrations. Therefore, we conclude that potassium atoms mainly affect the O and N atoms at the quinoline groups.

4. Summary

The interaction between Alq_3 and potassium was studied using IRRAS and SERS. The changes of vibrational pattern could not be explained by simple anion formation. Since the most dominant changes with respect to intensity and lineshape are observed for vibrational modes, which have a contribution of Al–O or Al–N vibrations, we conclude that the perturbation by potassium atoms are localized around the O and N atoms of the quinoline groups. Calculations of vibrational modes of potassium doped Alq_3 molecule are currently being performed.

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