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Surface-enhanced Raman scattering study of silver deposition on thin Alq_3 layers

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Abstract

Surface-enhanced Raman scattering (SERS) spectroscopy is applied to study in situ the interface formation of silver on thin Alq_3 films. The changes in the frequencies of Alq_3 vibrational modes are moderate and their line-shape is preserved upon Ag deposition. Moreover, a good correspondence appears between the SERS and powder spectra and frequencies predicted by density functional calculations for the meridianal isomer. The behaviour of Raman spectra indicates that no chemical interaction occurs between the Ag atoms and Alq_3 molecules. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Tris-(8-hydroxyquinoline) aluminum (Alq_3) is a semiconducting organic material frequently used as electron transporting layer in organic devices. For organic light emitting diodes (OLEDs) with Alq_3 active layer, Mg/Ag is one of the most commonly used top metal contact [1]. In spite of the importance of metal contacts to organic layers for the device performance, they are still far from being well understood.

Up to date the chemistry and the electronic properties of metal/organic semiconductor interfaces were mainly investigated by means of electron spectroscopies. Ultraviolet photoemission spectroscopy (UPS) studies showed that Mg [1] and Ca [2] interact strongly when deposited onto Alq_3 films. The reactivity of noble metals (Ag and Au) with Alq_3 molecules is low when Alq_3 is deposited onto these substrates [3,4], and the same holds for Au when deposited onto Alq_3 [5]. To our knowledge, no investigation has yet been performed concerning the Ag deposition onto Alq_3.

Vibrational spectroscopies are scarcely applied in this field in spite of their non-destructive surface-sensitive character. Only few works were dedicated to Ag boundaries with perylene derivatives [6,7].

This paper reports in situ Raman studies on the interface formation of silver on thin Alq_3 films. The particular advantage of this technique lies in the enormous enhancement of Raman scattering by molecular vibrations when silver is deposited. Enhancement factors observed in similar systems (metallic Ag

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clusters embedded in organic films, e.g. PTCDA [6] or Me-PTCDI [8]) are in the range of two orders of magnitude. Surface enhanced Raman scattering (SERS) predominantly probes organic molecules in the vicinity of Ag clusters, i.e. it is an ideal tool to investigate the interface region. It is now commonly accepted that two types of mechanisms can be responsible for SERS [9]. The first mechanism of chemical nature can involve either the formation of a chemical complex between the molecules and metal atoms and/or a charge transfer (CT) among them. The second can be related to a huge amplification of the electromagnetic field in the presence of Ag clusters (via localised and/or coupled surface plasmons). The small amount of experimentally observed frequency shifts for Ag/Alq_3 suggests the electromagnetic mechanism to be predominantly responsible for SERS. Here it is demonstrated that SERS spectra provide valuable information about the interface structure.

2. Experimental

p-Type Si(1 1 1) wafer pieces (3×10^{15}–5×10^{15} cm^{-3}) were used as substrates for the fabrication of Ag(1 1 1) films. The silicon pieces were wet chemically cleaned under atmospheric conditions as follows: they were first degreased of organic contaminants by successively dipping into acetone, ethanol and de-ionised water in an ultrasonic bath, for 5 min each; then the surface oxide was removed by etching in concentrated HF (40%) for 2 min. The latter has the advantage to hydrogen-passivate the substrate [10]. Immediately after etching, the substrates were installed in a transfer chamber that reached the pressure (10^{-6} Pa) necessary for transfer into an ultra-high vacuum (UHV) deposition and analysis chamber (2×10^{-8} Pa) in about 30 min. The amount of C and O containing contaminants left on the surface was determined by means of Auger electron spectroscopy to be less than 0.7 ML. Low energy electron diffraction (LEED) pattern showed a 1×1 reconstructed surface. Onto the Si(1 1 1) substrates Ag was thermally evaporated for 60 min from a Knudsen cell kept at 1200 K resulting in a deposition rate of approximately 1.6 nm min^{-1}. The obtained film showed a sharp LEED pattern corresponding to the Ag(1 1 1) surface. The Alq_3 source material (purchased from Aldrich) was evaporated with a rate of 0.1 nm min^{-1} from a Knudsen cell operating at 470 K. The calibration for the evaporation rates was performed by means of atomic force microscopy. For the investigation of interface formation between Ag and the thin Alq_3 film (3 nm), the Ag deposition was performed under the conditions described above.

The UHV chamber is optically aligned with a Dilor XY spectrometer equipped with triple monochromator and Peltier cooled CCD detector. This setup offers the possibility to monitor in situ deposition processes in a backscattering geometry. In the macro-Raman configuration used the Kr^+ laser beam (2.34 eV, 530.9 nm) having a power of 20 mW was focused onto the sample under an incidence angle of $\sim 30^\circ$ onto a spot with diameter of ~ 300 μm. Raman spectra of Alq_3 powder were collected using a micro-Raman configuration with an incident power of 1 mW. The low power density prevented any damage of the Alq_3 samples in both cases. The spectra were recorded with similar resolution (~ 2.5 cm^{-1}).

The excitation line used has an energy lower than the absorption onset of Alq_3 (2.6 eV, 480 nm) [11], hence the recorded signal has a low intensity even for powder. The use of higher energy laser lines (e.g. 2.7 or 3 eV), however, has the disadvantage that a very strong photoluminescence background screens the Raman vibrational lines. Additionally, the advantage of the green line lies in providing an appropriate energy for SERS.

3. Results and discussion

The Alq_3 molecule exhibits 150 modes of internal vibrations. Two chiral isomers [12] with different symmetry, facial (C_3) and meridianal (C_1, depicted in Fig. 1), have been reported to coexist in powder and thin films. The isomer with lower symmetry was found to be more stable [12]. Both isomers lack a centre of inversion, therefore most of the vibrations are Raman as well as infrared active. The large number of vibrational modes together with the coexistence of the two isomers complicates the interpretation of experimental spectra. However, our ab initio density functional theory (DFT) calculations (performed with B3LYP: 3-21 G, Gaussian '98) for the *mer*-isomer agree with those performed using a Hartree–Fock Hamiltonian

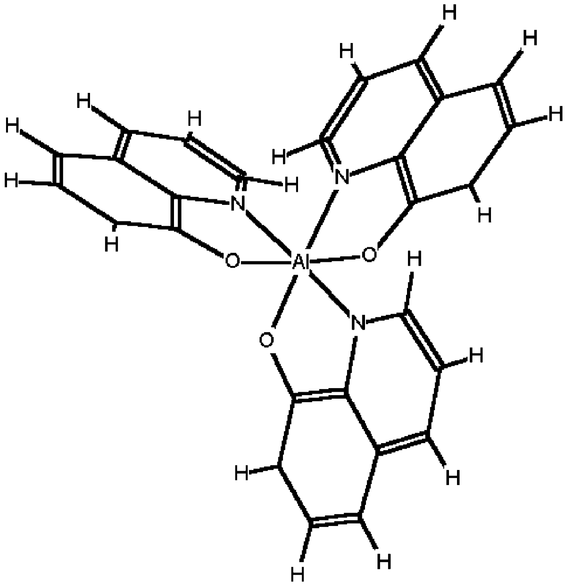

Fig. 1. Chemical structure of the meridianal isomer of Alq_3.

approach [13] in describing the modes below $1000\ cm^{-1}$ as having dominant metal–ligand character. The quinolinato chelatil-agent vibrations are concentrated in the spectral region between 1300 and $1600\ cm^{-1}$.

For the 2.34 eV excitation line no Raman signal was observed from the 3 nm Alq_3 films as deposited. The Alq_3 internal modes appear as soon as 0.3 nm Ag (nominal thickness) is deposited, and that is a clear indication of the SERS effect. Their relative intensities do not change upon further Ag deposition (Fig. 2), while the absolute intensity increases by a factor of approximately 18 for a Ag coverage of about 1 nm compared to that at 0.3 nm (see Fig. 3a). When comparing the present results with previous ones obtained for the deposition of Ag onto PTCDA thin films [6], where spectral changes were found to develop gradually upon Ag coverage, it may be reasonable to assume that changes of vibrational modes are negligible for Ag coverages below 0.3 nm on Alq_3.

In the first stages of deposition (0.3 nm Ag), the frequencies of metal–ligand modes (▼, ★) and ring stretch modes (●) deviate by less than $1\ cm^{-1}$ from those observed in Alq_3 powder (Fig. 3b). Upon further Ag deposition, they exhibit a similar behaviour: they first shift towards lower frequencies up to a Ag cover-

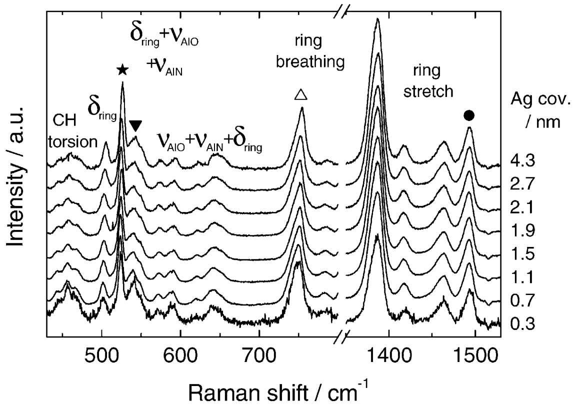

Fig. 2. SER spectra of a thin Alq_3 film (3 nm) recorded for different Ag coverages. Spectra were normalised with respect to the strongest mode corresponding to the ring stretching at $1385\ cm^{-1}$ for a better comparison of the line-shape.

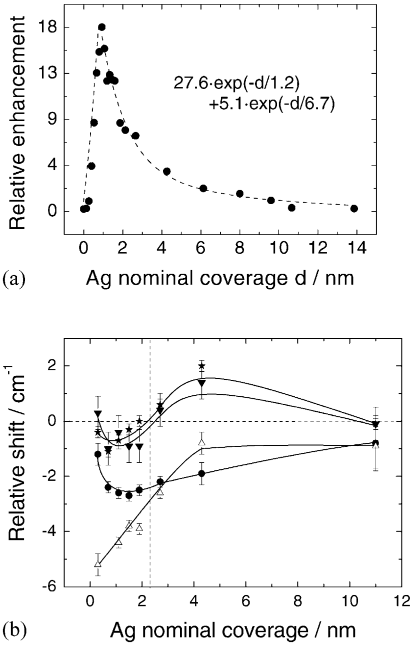

Fig. 3. (a) Effective enhancement factors of the Raman spectral intensity obtained during the Ag deposition for the 1150–$1690\ cm^{-1}$ spectral range. All factors were normalised relative to the integral intensity for 0.3 nm Ag coverage. The equation describes the exponential decay of the signal. (b) Changes in the frequency positions with Ag deposition calculated with respect to the mode frequencies of powder: ring stretch at $1494\ cm^{-1}$ (●); ring breathing at $748\ cm^{-1}$ (Δ); Al–O combined with Al–N and ring deformation at $540\ cm^{-1}$ (▼); ring deformation combined with Al–O stretch at $524\ cm^{-1}$ (★).

age of ~1 nm followed by an upward shift. Interestingly the coverage where maximum downward shift occurs coincides with maximum signal enhancement. A different behaviour is observed for the modes with dominant breathing character, e.g. the mode at ~748 cm^{-1} (Δ) revealing a shift of ~5 cm^{-1} towards lower frequencies at the beginning of deposition, the amount of this shift decreases with Ag coverage. For all modes, the powder frequencies are approached for a nominal Ag thickness of about 11 nm. For a detailed understanding of the frequency shifts, an in-depth theoretical treatment is in progress.

Ag deposition onto PTCDA has more dramatic effects on the Raman spectra: peaks observed in virgin films survive but suffer changes in the relative intensities while additional modes of lower symmetry appear. These changes are quite likely due to a charge redistribution over the molecule rather than a chemical interaction with Ag [6].

Theoretical calculations [14] and UPS studies have shown that highly reacting metal atoms (like Mg [1], Ca [2] and Al [4]) preferentially attack the phenoxil groups or the N shell, forming chemical complexes with the Alq_3 molecules. This should strongly affect the metal–ligand spectral region. Considering the small frequency shifts with respect to powder, in particular in the region of Al–O and Al–N vibrations, one can conclude that the chemical structure of the Alq_3 molecules is preserved upon Ag deposition. Moreover, the appearance of charge transfer from/towards the molecule towards/from Ag atoms is unlikely. The ionisation potential of Ag ($IP = 7.58\,eV$ [15]) is higher than that of the Alq_3 thin films ($IP = 5.7\,eV$ [3]). Therefore, one would expect that the Alq_3 molecule would be positively charged if any CT occurs. Curioni et al. have calculated that an extra hole on the Alq_3 cation should be confined on the phenoxide rings. The structural changes induced by the absence of an electron should be localised and similar for both isomers: the Al–O bond should increase and the Al–N distances should decrease, i.e. the frequencies of modes with Al–O (Al–N) contribution should decrease (increase). The amount and direction of shifts that we have observed for Al–O and Al–N vibrations together with the lack of changes in the relative intensities indicate that the transfer of a complete electron does not take place between Ag and Alq_3. Our conclusion concerning the non-reactive character of Ag/Alq_3 interface agrees with the experimental findings of Hill et al. [16] who have investigated the interface formation by means of UPS when Alq_3 was deposited onto Ag(1 1 1) substrates.

The signal enhancement with increasing Ag amount mainly arises from geometrical effects. Most probably, the Ag atoms arriving at the surface in the first deposition stages form clusters. These act as centres that locally amplify the incident and scattered electromagnetic field for the molecules in close vicinity resulting in the observed enhancement of Raman modes. The number and size of clusters increases with Ag amount leading to a linear increase of the SERS effective surface area [17]. This mechanism influences the Raman signal enhancement up to ~1 nm Ag coverage. When the cluster size exceeds a critical limit their coupling with the electromagnetic field decreases. The modelling of the signal decay as a function of film thickness matched the experimental points only when a sum of two exponentials was used. The first exponential function with a decay constant of 1.2 (±0.2) nm dominates the region below 2 nm nominal thickness, while beyond that a second exponential takes over. The value of the latter decay constant (6.7 (±0.5) nm) corresponds well to half of the penetration depth of the 2.34 eV light for bulk Ag (~6.5 nm). This indicates that at ~2 nm a percolation of clusters takes place, and the signal attenuation is thereafter governed predominantly by absorption of light in a Ag film which has a granulate closed structure as revealed by scanning electron microscopy.

4. Summary

Thermal evaporation of Ag onto thin Alq_3 films was monitored in situ by means of Raman spectroscopy. Internal vibrational modes of Alq_3 were probed to deduce information on the metal/organic interface formation. The moderate spectral changes reveal that the chemical structure of molecules is preserved, and no pronounced charge transfer takes place from or towards the metal atoms. Moreover, the Raman response of the molecular film is significantly enhanced upon the silver deposition via electromagnetic effects. It is therefore proposed that Ag when used in combination with other metals can be an ideal probe for the investigation of their interface formation with molecular thin films.

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