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Thermal Desorption of Tris(8-hydroxyquinoline)aluminum (III) (Alq_3) on Cu(111)

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The thermal properties of tris(8-hydroxyquinoline)aluminum (III) (Alq_3), widely used in organic light-emitting diodes, have been examined on Cu(111) using temperature-programmed desorption (TPD). Two molecular desorption peaks are evident in TPD. Strikingly, the lower temperature (α) peak at ~450 K develops first, but is not saturating, whereas the higher temperature (β) peak at ~500 K appears later and grows more rapidly than the (α) peak. For the model proposed, as-deposited Alq_3 forms an amorphous phase that converts to a crystalline phase in competition with desorption during TPD and a possible crystalline formation from the deposition. Consistent with this model, annealing at 400 K slowly shifts the subsequent TPD intensity from the (α) to the (β) peak. TPD after heating to 470 K and rapidly cooling to <350 K exhibits a strong (β), but no (α), peak.

1. Introduction

Since its discovery, tris(8-hydroxyquinoline) aluminum (III) (Alq_3) has been a prominent molecule in modern organic light-emitting diodes (OLEDs) because of its electroluminescent properties and excellent stability.[1−3] Most studies to date have focused on understanding the mechanism of charge transport and the characteristics of electroluminescence of Alq_3-based OLEDs.[1−9] However, studies taking advantage of temperature-programmed desorption (TPD), to our knowledge, are not available. Thermal annealing of the polymer-based OLEDs has been a subject of recent attention.[10−15] It was found that thermal treatment results in a remarkable improvement in the long-term stability of the device.

In this paper, a novel organic molecular doser is described that allows us to reproducibly and accurately dose sublimable, low-vapor-pressure organic molecules while minimizing both the amount of source material needed and the distance between the solid source and the substrate. TPD reveals interesting changes that occur in multilayer films during thermal annealing of films deposited on Cu(111) at 90 K.

2. Experiment

2.1 UHV Chamber. All experiments were performed in an ultrahigh vacuum system with a base pressure of 3×10^{-10} Torr pumped by an ion pump and two turbo molecular pumps. The chamber contained an Auger electron spectrometer (AES) for surface analysis, a time-of-flight mass spectrometer (TOFMS) for temperature-programmed desorption (TPD) and residual gas analysis (RGA), and an ion sputtering gun for surface cleaning. A newly designed doser was positioned within the upper level for subliming organic molecules onto the substrate.

The substrate was a Cu(111) sample (0.5 in. diam) mounted on a standard sample manipulator. Liquid nitrogen cooling and resistive heating allowed access to a temperature range of 85 to 850 K. The copper surface was routinely sputtered by Ar^+ bombardment (2 to 4×10^{-6} Torr and 1.6 keV) for 15 min, followed by annealing to 800 K for 10 min. The sample's cleanliness was regularly verified using the Auger electron spectrometer.

2.2 Organic Molecular Doser. Thin organic film vapor deposition has been a long-standing issue in surface science and in industry. Here we present a novel design, Figure 1, for reproducibly dosing sublimable organic molecules that have negligible sublimation pressures at some temperature above ambient but well below the dosing temperature. The doser consists of three copper parts: (1) heater, which is a copper pipe wrapped with a heating filament and consistently maintained at a controllable elevated temperature (500 to 650 K); (2) cooler, a massive copper heat sink used to dissipate the thermal energy of the sampler and maintain the organic molecules at a temperature where they exhibit a negligible sublimation pressure; and (3) sampler, a specially designed copper container for the organic molecule that contacts the heater to initiate dosing and the cooler to terminate dosing. The first of the two thermocouples is attached to the heater (TC1) and the second contacts the sampler (TC2). The tool is designed to rapidly alter and reproduce the source temperature

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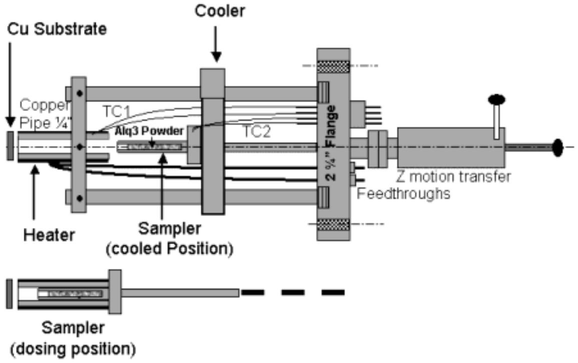

Figure 1. Schematic view of organic molecular doser.

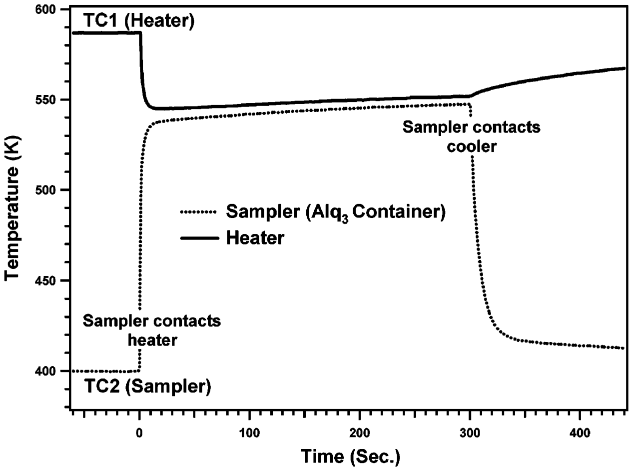

Figure 2. Temperature variation of the organic molecular doser during a typical dosing procedure. Thermocouples monitor the heater (TC1) and sampler (TC2).

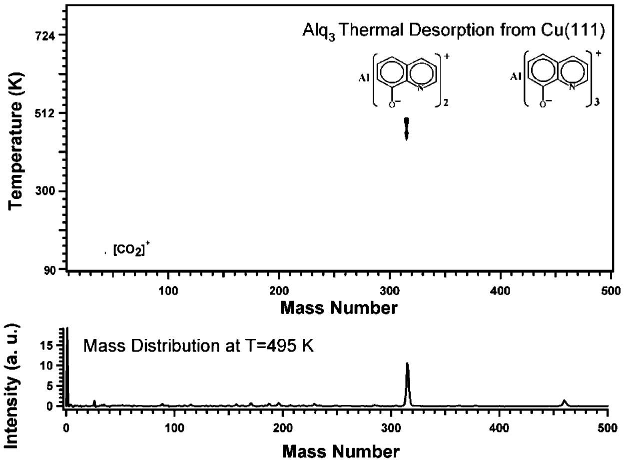

Figure 3. Upper panel: 3D thermal desorption spectrum of 20 nm of Alq$_3$ on Cu(111). Intensity is indicated by the gray scale. Lower panel: Intensity versus mass spectrum at 495 K constructed by taking a “cut” through the upper pane.

variation as indicated in Figure 2. To prepare for dosing Alq$_3$, the dosing system is stabilized over several hours. The cooler and sampler (TC2) are maintained at 400 ± 0.5 K (left side of Figure 2) and the heater (TC1) is held at 587 K. To begin dosing, the sampler is moved forward to make thermal contact with the heater (the time zero on the *x*-axis is the point of initial contact of the sampler with the heater). The temperature of the organic material rises quickly (over 110 K in 10 s), the heater temperature drops initially, then both the temperatures of the sampler and the heater rise slowly as the dosing system reequilibrates. To terminate dosing, the sampler is pulled back and brought into thermal contact with the cooler. The sampler temperature drops at least 100 K in 10 s, and the organic molecular sublimation rate becomes negligible. With the liquid-N$_2$-cooled Cu(111) surface positioned 1 mm from the end of the doser, the chamber pressure rise is not detectable during dosing.

Although this very simple doser design can be used for numerous materials, the limitations are obvious. By adding a rotatable flag to the front of the doser, the temperature variations during dosing could be minimized. Although the source temperature was not constant, TPD peak areas were reproducible to within 5% so further improvement was not needed for dosing Alq$_3$. There is one major inherent limitation: the source materials cannot have significant sublimation rates at any temperature up to the bakeout temperature of the UHV system. Furthermore, source molecules that react with copper cannot be dosed.

2.3 Amounts of Alq$_3$ Adsorbed. While TPD after dosing Alq$_3$ at 90 K indicates negligible thermal decomposition, the spectra do not exhibit identifiable monolayer and multilayer features. Thus, assessing coverages requires calibration using other means, e.g., AES. Keeping in mind the potential electron-induced decomposition of Alq$_3$, we minimized the electron beam flux and measured AES spectra for clean Cu(111) and for a small dose (45 s) of Alq$_3$. From the attenuation of the Cu AES signal at 920 eV and an inelastic mean free path of 2.55 nm in Alq$_3$, the calculated thickness of the Alq$_3$ was 0.43 nm.[16] This factor was used to convert all Alq$_2^+$ TPD peak areas to film thicknesses. Considering a single layer of Alq$_3$ would be ~1 nm thick, this calibration dose involves submonolayer coverage.

3. Results

3.1 TPD Study. Figure 3 displays a three-dimensional (3D) TPD spectrum for 20 nm of Alq$_3$ on Cu(111). The *x*-axis is the *m*/*e* and the *y*-axis is the surface temperature, and the *z*-axis (gray scale) denotes the intensity. This 3D plot involves a single dose of Alq$_3$ and samples every mass from 1 to 500 amu. The parent (Alq$_3^+$) ion at 459 amu exhibits two regions of peak intensity (~450 and 500 K) that are tracked faithfully by many other ions taken to be fragments formed by electron impact in the ion source of the TOFMS. The Alq$_2^+$ fragment at 315 amu is most intense and is used to monitor the desorption kinetics (see below). There are weak signals for several low masses (particularly 28 and 44 amu) between 120 and 170 K. These are attributed to desorptions from nonsample surfaces and from some background accumulation on the sample. We find no TPD evidence of significant Alq$_3$ dissociation or other impurity accumulation. Confirming that dissociation is negligible, Auger spectra taken before and after 10 TPDs, without cleaning between experiments, revealed minor carbon and nitrogen accumulation (<5 atom %).

TPD spectra (Figure 4) taken after dosing with the substrate held at 90 K, are striking in that the low-temperature feature (α) peaking at 450 K fills first and continues to grow slowly after a rapidly growing peak (β) appears at 500 K. Evidently, the common and somewhat arbitrary definitions of monolayers and multilayers in terms of TPD peaks are not applicable in this case.

We use the combination of AES and TPD to define Alq$_3$ surface coverage; the results are indicated in the graphs. The lowest coverage, 0.35 nm, is submonolayer. Focusing on the development of the α peak, the inset

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[16] Powell, C. J.; Jablonski, A. *NIST Electron Effective Attenuation Length Database*; http://www.nist.gov/srd/nist82.htm; Version 1.0, 2001.

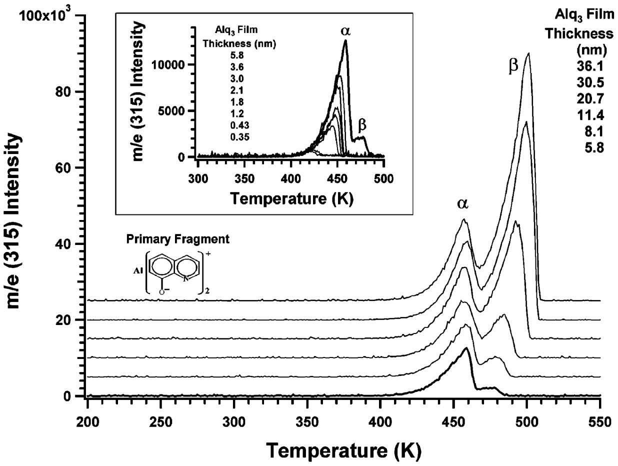

Figure 4. TPD spectra of various Alq$_3$ coverages on Cu(111), surface coverages are indicated; the insert is the low coverage regime. TPD heating rate was 2 K s^{-1}.

shows that all the spectra have a common onset near 400 K, superimposable leading edges that extend to higher temperature as the dose increases, and a sharp decay after the peak. This is characteristic of zero-order kinetic behavior. The β peak exhibits similar characteristics.

To explore why the α peak emerges before the β peak, TPDs of 3.0-nm-thick Alq$_3$ films prepared at 90 K were compared with and without annealing at 400 K for 30 min and recooling (Figure 5a). Without annealing (solid line) there is no β peak. With annealing (dotted line) a small β peak is clearly evident, and the leading edge of the α peak (but not the trailing edge) shifts to higher temperature by 5 degrees. Confirming the absence of desorption during the annealing, the total integrated intensities are the same for both TPDs. This comparison indicates that by thermal activation at 400 K, Alq$_3$ is converted slowly to a more stable configuration (β peak).

To further examine this interesting behavior, quite thick (30 nm) films formed at 90 K were compared (Figure 5b). Dosing followed by TPD gives the expected α and β peaks. The same dose annealed at 400 K for 30 min gives a different profile: the α peak is suppressed while the β peak is enhanced. In a third experiment, the system was heated to 470 K (from 90 to 470 K in 35 s) and promptly recooled to 90 K. The TPD (thin solid line) exhibits no α peak and a slightly less intense β peak.

Taken together, these TPD data suggest an irreversible structural transition occurs in competition with desorption of Alq$_3$ in the α peak. We take this up in more detail below.

4. Discussion

Alq$_3$ Interaction with Copper Substrate and Its Surface Morphology. Except for background gases, all the ions follow the same profile (Figure 3) indicating that Alq$_3$ does not dissociate on Cu(111). The desorption features, exponentially increasing leading edges, and sudden high-temperature cutoffs are characteristic of zero-order desorption kinetics for both the α-peak and the β-peak. This is in accord with the expectation that aromatic organic molecules have strong van der Waals intermolecular interactions that are competitive with adsorbate−substrate interactions.

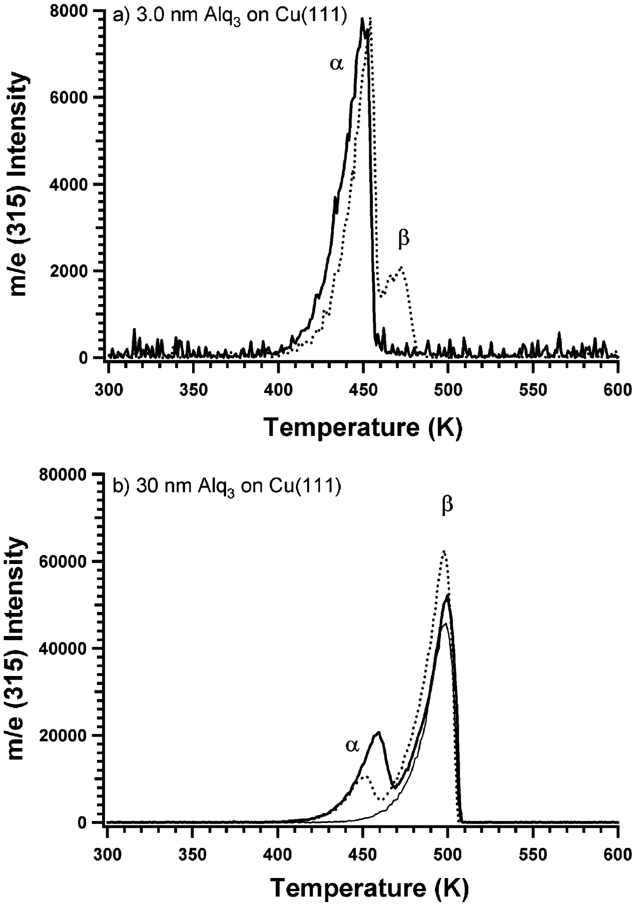

Figure 5. (a) TPD spectra of 3.0-nm-thick Alq$_3$ film on Cu(111). The thick solid line is dosed at 90 K. The dashed line is dosed at 90 K and annealed at 400 K for 30 min. (b) TPD spectra of 30-nm-thick Alq$_3$ film on Cu(111). The thick solid line is dosed at 90 K. The dashed line is dosed at 90 K and annealed at 400 K for 30 min. The thin solid line is dosed at 90 K but annealed to 470 K briefly.

Alq$_3$ TPD spectra in Figure 4 are surprising and rather unique. For a multilayer, the molecules at the adsorbate−vacuum interface must leave the surface before the molecules at the adsorbate−substrate interface. This is reflected in typical TPD; desorption peaks at lower temperature for high coverage (multilayers) compared to low coverage (monolayer or submonolayer) including, in our system, benzene on Cu(111)[17] and naphthalene on Cu(111).[18] The opposite is indicated by Figure 4, and neither layer-by-layer growth nor island models provide sufficient interpretations. Rather, an irreversible structural rearrangement occurring in competition with desorption is indicated.

We propose the following model. As-dosed at 90 K, Alq$_3$ forms an amorphous overlayer formed in “hit-and-stick” fashion, i.e., the molecule does not move laterally from the point of collision with the substrate. The forces operating between Alq$_3$ molecules are nearly equal to those between Alq$_3$ and Cu. As the substrate is heated, desorption sets in above 400 K (α desorption) and peaks

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at 450 K. In only those areas where the Alq_3 layer is more than one molecule thick, structural rearrangement to form a more stable, locally crystalline state competes with desorption. As this irreversible transformation occurs, the desorption rate drops briefly but recovers as the temperature rises. The net effect in TPD is a second TPD peak at 500 K.

In the framework of this model, low doses of Alq_3 give no β peak for two reasons. First, there are few areas where the Alq_3 layer is more than one molecule thick. Second, even where the layer is locally two molecules thick, the rate of thermal desorption from the amorphous phase dominates. At the other extreme, very thick layers of Alq_3 showing no regions that are one molecule thick still exhibit an α peak because this peak is dominated by desorption from the Alq_3−vacuum interface regardless of coverage. Consistent with this model, there is very slow, multilayer conversion from α to β during annealing at 400 K, and, once heated into the 470 K region and recooled, subsequent TPD shows no α state.

These results may be of importance for the preparation of Alq_3-based OLEDs in the sense that their performance may well be influenced by the structures taken at interfaces and within the bulk of the film. Alq_3 has a well-known drawback; there is a phase transformation from amorphous to crystalline during operation that suppresses performance.[19−22] The thermal properties of Alq_3 powder and vacuum-deposited thin films have been studied by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).[23−25] These reveal a glass transition temperature (T_g) of Alq_3 at 448 K. This is consistent with our observations; the phase transformation would take a long time at 400 K and ramping the temperature to 470 K would result in a single-phase film produced by phase conversion in competition with desorption.

5. Summary

Temperature-programmed desorption (TPD) has been employed to study tris(8-hydroxyquinoline) aluminum (III) (Alq_3) interactions with a Cu(111) surface. The TPD spectra show two desorption peaks and, in relatively unique fashion, the lower temperature desorption (α-peak) dominates at low coverages while the higher temperature desorption (β-peak) appears and dominates at higher coverages. This is accounted for by a model involving desorption from amorphous (α) and locally crystalline (β) forms of Alq_3. The transition from α to β occurs in competition with desorption from the α state and requires local multilayer coverage.

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