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Analysis of Alternative Dopants for Organic Light-Emitting Diodes Layers Using a Correlative TOF-SIMS & XPS Protocol

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INTRODUCTION

Organic light-emitting diodes (OLEDs) have made significant progress since their invention in 1989 and are now widely used for display and lighting applications. There are still improvements to be made in device lifetime, efficiency and luminance to address new applications and to compete with other LED technology. One way this is being done is by exploring new structures, molecules and dopants. To facilitate these developments, there is a need to study the degradation mechanisms in the organic layers in order to attempt to improve device performance [1]. In particular it is extremely important to be able to analyze each individual layer in a thin complex multilayer OLED stack, without damaging the fragile organic layers. Thus, the degradation of the stacks can be evaluated without the risk of confusion with damage from sample preparation or analysis. This requires the use of analysis techniques with good depth-resolution and high sensitivity to small changes in chemical structure such as time of flight of secondary ion mass spectrometry (TOF-SIMS) and X-ray photoemission spectroscopy (XPS).

STUDY OF NEW DOPANTS USING A CORRELATIVE PROTOCOL

The use of Ag to replace Ca as a dopant was recently demonstrated [2] in 2019 and has the advantage of being more air-stable and easier to handle in a production environment. We therefore decided to test Ag doped BPhen (4,7-Diphenyl-1,10-phenanthroline) to replace Ca doped BPhen in a standard OLED stack and also in a set of simplified test samples where the BPhen layer is sandwiched between two electrodes. One sample is grown with a calcium doped BPhen layer another with a silver doped BPhen layer. An undoped control sample was grown also.

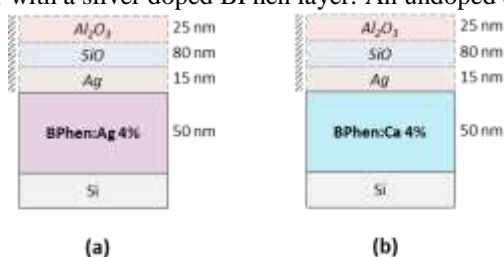


FIGURE 1. Structure of test samples of a doped BPhen layer sandwiched between two electrodes (a) the sample is grown with a Ca-doped BPhen layer and (b) the sample is grown with a Ag-doped BPhen layer.

In this study we use a correlative protocol to combine TOF-SIMS and XPS measurements on exactly the same sample area. Firstly the inorganic capping is removed using adhesive tape prior to sputtering with the argon cluster beam to avoid artefacts due to the very different sputter rates of inorganic and organic material. Then an argon cluster ion beam is used to sputter away material to access different depths within the layer of interest.

The sample is transferred between the two techniques in a dry N₂ atmosphere.

Firstly we performed TOF-SIMS mass spectrometry on the Ag doped BPhen layer to check the quality of the film deposition. A peak at a mass-to-charge ratio (m/z) of 439 is observed that could correspond to a Ag-BPhen complex. This peak was then analyzed using tandem mass spectrometry in a Physical Electronics NanoTOF II TOF-SIMS instrument. The selected peak is deviated into a collision cell where it is fragmented by collisions with argon gas atoms. The ionized fragments are then accelerated to a second time of flight detector. The spectrum shown in figure 2 shows that the peak at m/z 439 is fragmented into Ag and BPhen- H^+ molecular ions confirming the formation of a Ag-BPhen complex.

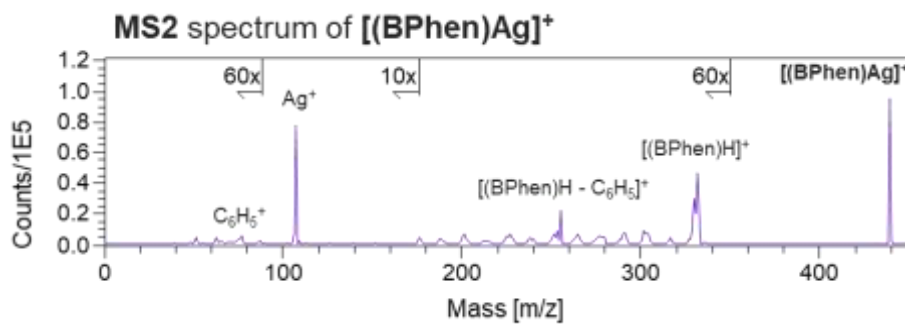


FIGURE 2. Tandem MS spectra of the peak at m/z 439 revealing the presence of Ag^+ and BPhen H^+ fragments

Then XPS analysis was performed on the same layers. The C 1s and N 1s spectra shown in Fig. 3 show a 0.6 eV peak shift to higher binding energy that is consistent with an n-type doping for both Ag and Ca doped films in comparison to the undoped BPhen film.

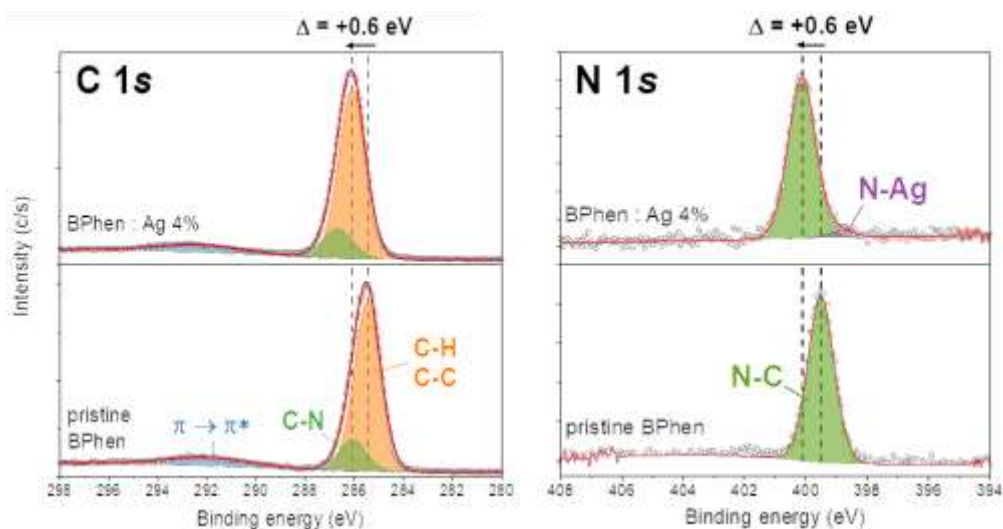


FIGURE 3. XPS data: high resolution C 1s and N 1s core level spectra of Ag (top), undoped (bottom) BPhen films showing a shift towards higher binding energy ($\Delta = +0.6$ eV) characteristic of n type doping

In order to assess the stability of the Ag-doped film compared to that of the Ca-doped one, both films were depth profiled after different air exposure times ranging from a few minutes to several hours. The silicon interface width in the depth profile is plotted in figure 4(a). In the case of the Ca doped films the interface width with the silicon interface increases rapidly due to roughening of the BPhen film. For the Ag doped film this roughening happens over a much longer timeframe. To investigate whether more subtle changes are occurring we used the detection of backscattered Argon clusters as this has been shown to give information on the mechanical properties of polymer films [3, 4]. Fig. 4b shows the ratio of $Ar^2/Ar^+ + Ar^n$ where $n = 3$ or 4 increases, consistent with a

hardening of the film, after 4 hours of air exposure. These results confirm an improved stability of Ag-doped vs Ca doped films.

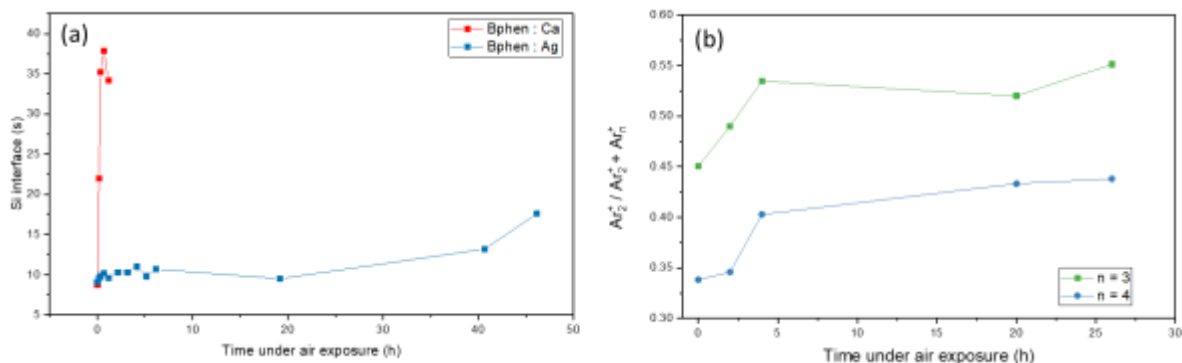


FIGURE 4. (a) evolution of the silicon interface width as a function of time, (b) evolution of the backscattered Argon cluster signal showing an increase in the $Ar_3^+/Ar_2^+ + Ar_n^+$ where $n = 3$ or 4 indicating a hardening of the layer with time.

CONCLUSIONS AND PERSPECTIVES

A correlative approach using TOF-SIMS and XPS has been used to investigate the use of Ag as an alternative dopant to Ca in the BPhen layer of an OLED device. The interest of Ag as a dopant is confirmed and work is in progress to study electrical ageing in Ag doped devices using a bevel crater approach in order to limit damage to the organic layers [5]. The air exposure experiments also highlight the importance of performing such correlative work using a vacuum or protective environment transfer system.

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KEYWORDS

OLEDs, TOF-SIMS, XPS, bevel crater, Argon cluster sputtering, tandem MS