Depth Profiling of an Organic FET with XPS and Argon Cluster Ions

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Key Words
MAGCIS, XPS, Argon Clusters, CuPc, Depth Profiling, Organic Electronics, Polymer Electronics FET

The Thermo Scientific™ K-Alpha™ XPS instrument, with the Thermo Scientific™ MAGCIS™ dual mode ion source, was used to depth profile a copper phthalocyanine-based organic FET material. Argon clusters were employed to profile the organometallic layer while preserving important chemical information in the XPS data, then monatomic argon ions were used to profile into the silicon substrate.

Introduction
The drive towards thin, low-cost, flexible electronic systems had led to the design of many organic microelectronic components, including field effect transistors (FETs). Early organic FET designs tended to be based on aromatic organic semiconducting materials, while recent developments have explored organometallic species, which potentially offer greater performance. Copper phthalocyanine (CuPc, Figure 1) is of significant interest as an organometallic semiconductor, and was used as the basis for the device under study.

The composition and thickness of the organic/organometallic layers in organic FETs are critical to the device’s performance. X-ray photoelectron spectroscopy is an analytical technique that provides detailed chemical compositional information from within 5–10 nm of the surface of a sample, and so is ideal for the chemical analysis of surfaces. Combined with a depth profiling technique, XPS can be used to monitor the composition of a coated or layered material to greater depths (hundreds of nm or even µm scales). Traditional ion sputtering depth profiling techniques cause significant damage to the subsurface of “soft” organic materials, this is visible in the XPS data as a loss of structure and chemical information. The new MAGCIS argon cluster ion source from Thermo Scientific addresses this problem. The gentle, shallow sputtering from argon cluster ions does not cause subsurface damage, so the XPS data preserve chemical state information through the entire profile. The MAGCIS source can also generate the traditional monatomic ion beams for profiling inorganic materials, so it is possible to profile through an organic layer with the cluster ions, then switch to monatomic ions to profile into a harder substrate.
Method or Experiment
A schematic of the structure of the organic FET is shown in Figure 2.

The Thermo Scientific K-Alpha XPS instrument, fitted with the MAGCIS cluster ion source, was used to acquire depth profiles from the CuPc FET. The CuPc sample was attached to a standard K-Alpha sample holder using a clip to ensure good top-surface electrical contact. The CuPc material was profiled with 4 keV argon cluster ions, with an average cluster size of 2000. The source was then switched to monatomic ion generation to profile through the SiO₂ isolation layer into the silicon substrate. The two profiles were combined to give a single depth profile through the entire organometallic/inorganic stack.

Results
A comparison of surface XPS carbon 1s spectra from the CuPc device and from a reference CuPc sample is shown in Figure 3. The spectra are similar, but the device sample has more hydrocarbon signal from surface contaminants at 285 eV. This confirms that the surface chemistry of the organic layer approximates CuPc.

Figure 4 shows a C1s spectrum acquired from the device after the removal of about 6 nm of material by cluster ion sputtering. This is in much better agreement with the reference data, showing that the device has pure CuPc in the semiconducting layer. The MAGCIS cluster ion sputtering has successfully removed material without causing subsurface damage, so the XPS spectrum resembles a pure material. This is a primary strength of the cluster ion technique, which allows the depth profile analysis of organic materials without visible damage in the XPS data. The spectral quantification in Table 1 confirms that the exposed CuPc is an excellent match to the expected composition.

<table>
<thead>
<tr>
<th>Expected At%</th>
<th>Observed At%</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>78.0</td>
</tr>
<tr>
<td>N</td>
<td>19.5</td>
</tr>
<tr>
<td>Cu</td>
<td>2.4</td>
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Table 1: Quantification of MAGCIS-cleaned CuPc
The spectrum has been deconvoluted by peak fitting to show how the XPS data reflects the sample chemistry. The red peak corresponds to the 6-membered ring carbon atoms, while the blue peak is from the carbon atoms bonded to nitrogen in the 5-membered rings. The green peaks arise from a complex set of loss features due to the aromatic ring systems. Preservation of these loss features is a characteristic indicator of the minimal damage effects from the cluster ion beam.

By sputtering through the CuPc with cluster ions, and through the SiO₂ with monatomic ions, it is possible to build up a profile of the entire device stack, as shown in Figure 5. After removal of surface contamination and modification, the CuPc has the correct stoichiometry through the profile, due to the damage-free cluster ion sputtering. After switching to monatomic ions, the SiO₂ also has the correct stoichiometry, until the Si substrate is reached. This complete quantitative profile, obtained using a single ion source, is not feasible by other means.

**Summary**

The MAGCIS ion source, attached to a Thermo Scientific K-Alpha, was used to depth profile an organo-metallic semiconductor layer on an SiO₂/Si substrate. The MAGCIS source was used in cluster ion mode for damage-free profiling of the CuPc layer, and in monatomic ion mode for profiling of the SiO₂ insulation layer. XPS spectra acquired in between etch cycles allowed quantitative determination of the sample chemistry in the layers, and showed that the composition was preserved through the profile.

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![Figure 5: MAGCIS profile of organic FET](image-url)