Examination of nanostructures inside organic thin films

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A combination of surface analysis techniques and in situ cluster ion slicing can be used to show the link between nanostructures and properties of organic electronics.

The properties of optoelectronic devices are significantly affected by the nanoscale structure of the materials used to make them. For organic electronic devices, segregation of amorphous and oriented phases of polymers can occur in a manner highly sensitive to the fabrication process. Furthermore, while the active layer in these devices is often a mixture of molecules that have different chemical structures, additional phase separation can occur. This changes the nanostructure inside organic electronic devices, crucially affecting performance. Phase separation can be controlled by modifying the fabrication conditions. However, the exact link between a device’s properties and the fabrication process used to make it is still unclear because of the difficulties in characterizing the nanostructure.

Unlike inorganic semiconductors, which are usually crystalline, organic materials are mostly amorphous. As a result, it has been difficult to analyze the nanostructure inside organic electronics using well-established analytical techniques with high enough spatial resolution. Transmission electron microscopy, for example, gives poor contrast, mainly from the lack of difference in diffraction power (which creates the image contrast) in an amorphous material. Furthermore, typical organic electronic devices consist of soft materials as the active layer and hard materials as electrodes and substrates. Preparing the sample for observation therefore poses a challenge.

To probe the structure of multilayered devices directly, we use in situ ion sputtering. In this scheme (shown in Figure 1), the ion sputtering serves as a slicing tool that removes the surface in a controllable manner. We can use information gathered at different depths to reconstruct a depth profile indicating the distribution of materials.

Atomic ion sputtering is generally used with surface analysis techniques, including x-ray photoelectron spectrometry (XPS), Auger electron microscopy, and secondary ion mass spectrometry (SIMS), to generate a depth profile. However, by bombarding organic materials with energetic particles, the molecular structure of the materials can also change. In other words, ion beams can induce chemical transformations and alter the chemical composition. Unless the removal rate is higher than the accumulation of damage to the molecular structure, the information gathered below the surface may not represent the real structure. Consequently, this technique is not suitable for analyzing organic materials. Successful examination of organic electronics requires a high ion sputtering rate to remove the altered material so that damage will not accumulate.

Rather than atomic ions, which are more liable to alter the surface before ejecting material from it, we use cluster ions such as C$_{60}^+$, a hollow ball of pure carbon atoms called buckminsterfullerene. These cluster ions break into atoms or smaller ions when they collide with the surface. The kinetic energy of collision is more evenly distributed across a larger surface and enhances the removal of materials. As each fragment has a low kinetic energy, it is less likely to alter the chemical structure of the sub-surface. C$_{60}^+$ cluster ion sources show great potential for profiling organic materials. However, the inevitable carbon deposition associated with their use limits their application. To overcome this problem, we apply a stream of low-energy argon

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ions (Ar\(^+\)) alongside a high-energy C\(_{60}^+\) beam to suppress carbon accumulation.\(^1\) The low-energy argon ions remove the surface slowly and cause limited damage to the chemical structure.

Using XPS and in situ C\(_{60}^+\)-Ar\(^+\) slicing, we have studied the degradation of organic LEDs by profiling devices operated for different times. Using this information, we have identified a new degradation mechanism based on direct observation of small-molecule migration under direct current. We also found that using host materials with higher steric hindrance could suppress the migration of electron-injecting materials and enhance the device lifetime.\(^2\) The knowledge gained in this work is crucial to the success of organic electronics with sufficient lifetimes for real applications.

To gain high spatial resolution in 3D, the C\(_{60}^+\)-Ar\(^+\) co-sputtering technique that provided excellent depth resolution was combined with scanning probe microscopy, which has high lateral (in-plane) resolution. We found that the fabrication parameters affect the resulting nanostructure significantly. For solar-cell devices, phase separation is desirable. It forms a bulk heterojunction that provides an adequate path for the removal of charge carriers, in turn enhancing device efficiency.\(^3\) On the other hand, phase separation inside LEDs is less efficient at trapping the charge carriers, leading to efficiency drops with the development of a nanostructure. This is shown in Figure 2.\(^4\)

Our previous work focused on profiling different elements or structures associated with various organic materials that remain on the surface during depth profiling of fabricated devices. Using our C\(_{60}^+\)-Ar\(^+\) co-sputtering method, we have found that we can profile nanostructures at different depths by analyzing the ejected material using SIMS. Since these secondary ions ejected by C\(_{60}^+\)-Ar\(^+\) co-sputtering can have high molecular weight and are characteristic of the chemical structure, our next steps will be to expand from organic electronics to biomedical materials,\(^5\) where fewer inorganic elements are available for XPS to monitor.

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References


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