



A new photon source for ultraviolet photoelectron spectroscopy of organic and other damage-prone materials



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ABSTRACT

Accurate measurements of the valence electronic structures of organic semiconductors are important for the development and understanding of organic electronic devices, materials, and interfaces. Ultraviolet photoelectron spectroscopy (UPS) is a well-established technique for probing valence electronic structures; however, many organic semiconductors undergo rapid sample degradation upon exposure to traditional laboratory-based vacuum ultraviolet (VUV) photon sources. Here, we report on a novel VUV photon source for UPS measurements that utilizes H Lyman- α emission with a narrow linewidth and a widely tunable intensity, and apply it to a number of organic materials of interest to show its ability to overcome this hurdle of sample degradation. Furthermore, the H Lyman- α source displays no measurable higher energy emission lines, which significantly reduces the background over typical He I discharge sources and allows for the onset of the density of states to be clearly observed over several orders of magnitude.

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1. Introduction

Ultraviolet photoelectron spectroscopy (UPS) is a widely used technique for probing the energy of valence electronic states in semiconductor materials, work functions of metals and semiconductors, and energy level alignments across interfaces. By allowing the direct examination of these electronic states in solids this technique has enabled a better understanding of fundamental material and interfacial properties, and greatly helped aid the development of semiconducting materials and devices. Although UPS has been applied much more extensively to the study of inorganic materials, it is clearly a powerful analytical tool for studying organic materials as well [1–4]. However, UPS studies of these organic materials can be limited by significant sample damage induced by exposure to the UPS photon source [3,5]. UPS studies sometimes require illumination for long durations of time, particularly in the case where an interface is built and probed in a step-wise manner to interrogate interfacial energetics, which makes these measurements difficult or impossible in more damage-prone materials such as many organics. One means to

reduce this sample damage is through the use of alternative photon sources, particularly sources with lower energy photons and lower photon fluxes. The 10.2 eV H Lyman- α source introduced in this manuscript meets these demands and is shown to significantly reduce sample damage.

UPS is based upon the photoelectric effect, in which an incident photon with energy $h\nu$ generates a free electron with the kinetic energy, E_{kin} , given by

$$E_{kin} = h\nu - \Phi - E_B \quad (1)$$

where Φ is the work function of the material and E_B is the binding energy of the electron within the solid [6]. An ideal photon source should have a single narrow emission line, a widely adjustable photon flux, long lifetime, and easy operation. Numerous laboratory-based photon sources exist that generate the vacuum ultraviolet (VUV) radiation needed for UPS, the most popular of which are noble gas discharge lamps, with helium being the most heavily used gas.

Under different conditions the helium discharge lamps can produce mainly the He I line ($1^1S \leftarrow 2^1P$) at 21.22 eV (58.43 nm) or the He II line ($1^2S \leftarrow 2^2P$) at 40.81 eV (30.38 nm) [7,8]. These lines are the most intense of the He I and He II Rydberg line series (He I: $1^1S \leftarrow n^1P$, He II: $1^2S \leftarrow n^2P$), however several higher

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energy Rydberg lines ($n = 3, 4, 5 \dots$) are present in each [7,8]. These resonance lines vary in their relative intensity to the primary line and are shown to be highly sensitive to the operating conditions of the system [7,8]. These lines can lead to a large background, with additional components such as VUV monochromators being necessary to reduce their presence [4,7,9]. Without an expensive monochromator, care must be taken in interpreting low-intensity features observed in UPS spectra, since they may be the result of higher energy Rydberg lines [4,7,9]. The background from these higher-energy lines also limits the ability to measure features at the band edge, such as the tail and defect states that can severely affect material and device performance [4].

For organic materials, gas discharge sources can lead to issues with sample damage and charging given their high intensity and high energy [3]. Unfortunately, the intensity of these sources can only be reduced by a limited amount, as relatively high currents through the gas are required to maintain a stable electrical current. This high intensity VUV radiation can, and often will, result in sample damage by driving reactions with residual atmospheric gases, mediating photo-chemical reactions, and causing bond breaking or cross-linking [3,5,10–14]. Radiation damage is commonly observed by changes in the spectral features of the valence band, or by substantial shifts in binding energy [3,5], which makes spectral interpretation in the presence of radiation damage difficult. Besides helium, other rare gases such as xenon, krypton, and argon have been employed in plasma lamps used for laboratory based UPS [15–17]. These gases also exhibit the same problems as He I sources, including limited adjustment on the lower end of the photon flux and the presence of multiple emission lines. Xenon, for example, has eight strong emission lines in the 8.4–10.7 eV range that are emitted from the neutral and singly ionized form when excited by microwaves [15].

Sample charging is another common problem with measuring UPS of organic semiconductors, with the low electrical conductivity of typical organic semiconductors limiting the film thicknesses that can be measured for many materials to only 10 nm [3]. A few methods for alleviating charging have been shown; however, the primary method for alleviating sample degradation with He sources is to simply reduce exposure time by taking quick measurements [3,5]. This severely reduces the signal-to-noise ratio and is not applicable for all samples. Utilizing filters or apertures to attenuate the emission intensity is also an acceptable solution, though introduction of these components to existing systems can be difficult. For example, the Amassian group at KAUST recently purchased a custom designed aperture system to integrate with their gas discharge source to reduce the photon flux at the sample.

Another class of sources for UPS emit in the VUV to UV region and take advantage of the photon sources and monochromators developed for UV-Visible spectroscopies [6,18]. These sources typically operate with a sealed gas cell containing deuterium or xenon and the photon energy is low enough to pass through available viewport materials into a UHV system, thus they do not require differential pumping systems like the gas discharge lamps do. They cover a spectral range from 115 to 400 nm, though below 180 nm the atmosphere in the system must be kept free from water vapor and oxygen. These sources, such as a monochromated low-energy deuterium lamps, have been successfully operated at low intensities in order to reduce sample charging and probe buried interfaces at depths greater than that achieved by He I sources [18,19]. Furthermore, the use of a double monochromator can result in a low background that allows for gap states to be observed [18,19]. Deuterium sources also emit from the Lyman- α transition at 121.6 nm (10.2 eV), although the efficiency for this emission is on the order of 0.1% [20]. To take advantage of this 121.6 nm emission, a vacuum monochromator is required to remove the lower energy

emission without significantly attenuating the Lyman- α emission line.

In this paper we present the application of a new photon source that emits monochromatic photons at 10.2 eV with no higher-energy emission lines and without the use of a monochromator. The source produces H Lyman- α ($1s^2S \leftarrow 2p^2P$) emission at 10.2 eV (121.6 nm) and the intensity of the source can be readily adjusted over a wide range to reduce sample damage and charging. It can produce up to 2×10^{18} photon/s in the continuous wave mode, can be separated from the UHV system by a MgF₂ window to eliminate differential pumping requirements, is small in size allowing for easy outfitting to existing systems, has a long lifetime, and is relatively easy to operate (i.e. no precise adjustment of pressure and no need for differential pumping).

2. Materials and methods

2.1. Materials

Ag (99.99%) was purchased from Angstrom Engineering, Au foil (99.95%) from Alfa Aesar, NPD (sublimed grade, 99%) from Sigma Aldrich, C₆₀ from nano-C (99.5%), regioregular P3HT (electronic grade) from Rieke Metals, and the DPP containing polymers were synthesized by the Mei group using their previously published procedure [21]. All materials were used as received.

2.2. VUV lamp spectra and intensity characterization

The Hydrogen Lyman- α lamp was characterized using two McPherson 218 VUV-monochromators with 1200 L/mm, Al/MgF₂ gratings, and blazed at 150 nm. The monochromators were equipped with an ET Enterprises 9130/350 B photomultiplier tube, specially equipped with a MgF₂ window for VUV applications, operating in photon counting mode for high resolution spectroscopy (as e.g. in Fig. 2) and a MgF₂-S20 image intensified diode array camera (EP&S Karger Elektronik) for overview spectra (as e.g. in Supporting Information Fig. S1).

2.3. UPS and XPS measurements

All UPS and XPS measurements were performed in a PHI 5600 UHV system containing an 11-inch diameter hemispherical electron energy analyzer with a multichannel plate detector. UPS measurements were performed using the Excitech H Lyman- α photon source (E-LUX™121) coupled with a 90° ellipsoidal mirror (E-LUX™ EEM Optical Module). Samples were negatively biased (–5 V) during UPS measurements and the pass energy was 5 eV. With the exception of the beam path environment experiments, all UPS measurements were carried out with a dry house nitrogen purge of the beam path at 8 Torr. For the beam path environment experiments, the region between VUV source and UHV chamber was either pumped using a turbomolecular pumping unit or purged with a low pressure of ultra-high purity oxygen or nitrogen (Scott Gross, both 99.999% purity). The He I UPS data was recorded in the Amassian laboratory at KAUST with an HIS 13 gas discharge source in an Omicron UHV system with a SPHERA hemispherical electron energy analyzer with a pass energy of 2.5 eV. XPS measurements were performed using a Mg K α source (1253.6 eV). The binding energy scale was calibrated using the Au 4f peak position, the spacing between the Au 4f and Cu 2p peaks, and the Fermi edges of Au and Ag (all sputter cleaned with Argon).

2.4. Silver and C₆₀ film preparation

Silver samples were made by thermally evaporating 50 nm of

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