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# Ubiquitous Pentacene Monolayer on Metals Deposited onto Pentacene Films

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Received June 22, 2007. In Final Form: September 3, 2007

Photoelectron spectroscopy (XPS and UPS) was used to study the deposition of metal layers (Ag, Cu, and Au) onto pentacene films. Very low work functions were measured ( $\Phi_{\text{Ag}} = 3.91$  eV,  $\Phi_{\text{Cu}} = 3.93$  eV, and  $\Phi_{\text{Au}} = 4.3$  eV) for all of the metals, in agreement with results from the literature. The intensities of the C 1s core-level signals from pentacene that were monitored during stepwise metal deposition leveled off at a value of about 30% of a thick pentacene film. This C 1s intensity is comparable to that of one monolayer of pentacene deposited onto the respective metal. The valence band spectra of metals deposited onto pentacene and spectra collected for pentacene deposited onto bare metal surfaces are very similar. These findings lead to the conclusion that approximately one monolayer of pentacene is always present on top of the freshly deposited metal film, which explains the very low work function of the metals when they are deposited onto organic films. We expect similar behavior with other nonreactive metals deposited onto stable organic layers.

## I. Introduction

Organic semiconductors have attracted considerable attention in past years because of their successful application in organic electronic devices (refs 1–4 and references therein). Among the various organic semiconductors studied, pentacene attracted the most interest. Pentacene, a planar polyaromatic hydrocarbon (PAH), has remarkably high charge-carrier mobilities, making it a suitable candidate for organic thin film devices.<sup>5</sup>

All semiconducting devices require either front or back contacts to inject charge carriers into the active semiconducting layer. A straightforward device design is to sandwich the semiconducting layer between metals A and B. As with inorganic ohmic contacts, barrier heights for electron and/or hole injection can be obtained by using the appropriate metal. Various metals were studied as contact for pentacene-based devices. The barrier height for pentacene when changing the metal work function is changed by 0.36 eV for a 1.0 eV change in the metal work function.<sup>6–8</sup> The deposition of a metal onto a thick pentacene layer typically leads to the measurement of a very low metal work function. Watkins et al.,<sup>9</sup> Kampen et al.,<sup>10</sup> and Popinciuc et al.<sup>11</sup> showed that the deposited metallic film never reaches a work function associated with a clean bulk metallic substrate. Watkins et al.<sup>9</sup> pointed out that the metal atoms diffuse into the pentacene layer during deposition, which might lead to a longer deposition time in order to cover the pentacene with a continuous metallic film. However, even metal films with thicknesses ( $> 100$

Å) that are 5 to 10 times the escape depth of photoemitted C 1s core-level electrons still have these low metal work functions. Kampen et al.<sup>10</sup> showed that thick layers of 3,4,9,10-perylene-tetracarboxylicdianhydride (PTCDA) or 3,4,9,10-perylene-tetracarboxyimine (PTCDI) can template the growth of different orientations of the metal films and metal work functions are a function of crystal orientation. However, in these experiments the obtained metal work function values were still lower than expected.

Herein we systematically study the deposition of different metals onto polycrystalline pentacene films and provide an explanation for the observed low metal work function.

## II. Experimental Setup

All experiments were performed in a commercial Omicron Multiprobe ultrahigh vacuum (UHV) system with a base pressure of  $5 \times 10^{-10}$  mbar. The system is equipped with X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS). Electron detection is achieved using a VSW EA125 single-channel hemispherical analyzer. Binding energies are calibrated to the Fermi edge and to the Au 4f, Ag 3d, and Cu 2p core-level emissions using literature values.

Thick pentacene films were deposited by physical vapor deposition from a home-built resistively heated source ( $T \approx 225$  °C), leading to a deposition rate of  $\sim 20$  Å/min. For this study, pentacene films with a thickness of 300–400 Å were prepared on Ag(111) and Au(111) to use as substrates. The pressure in the deposition chamber during film preparation was usually better than  $1 \times 10^{-8}$  mbar.

Gold, copper, and silver films were deposited stepwise from a home-built source onto the thick pentacene film at room temperature at a rate of 4 to 5 Å/min. To reduce the effect of sample heating, the metal source-to-sample distance was set to more than 25 cm. After each metal deposition step, the sample was immediately transferred in situ into the measurement chamber and analyzed with XPS and UPS.

The reference films were prepared on freshly cleaved, annealed, highly orientated pyrolytic graphite (HOPG) and on a freshly deposited, thick, annealed Ag film on mica.

## III. Experimental Results and Discussion

The deposition of gold, copper, and silver onto polycrystalline pentacene films was studied with a both XPS and UPS. Figure 1 shows the C 1s emission intensity trends for overlayers of the three metals as a function of the deposited nominal film thickness.

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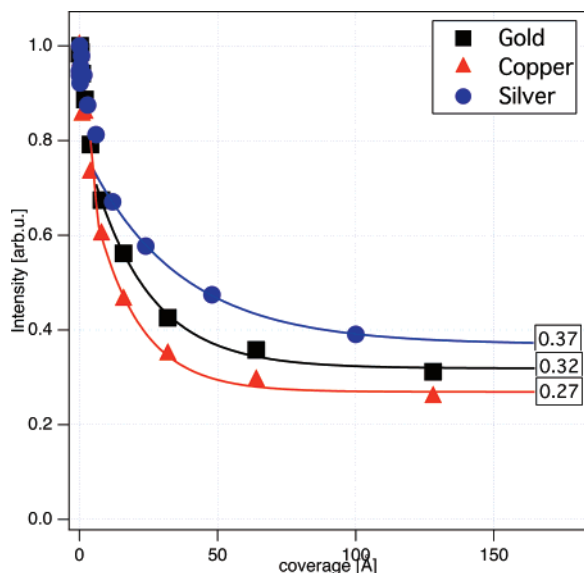
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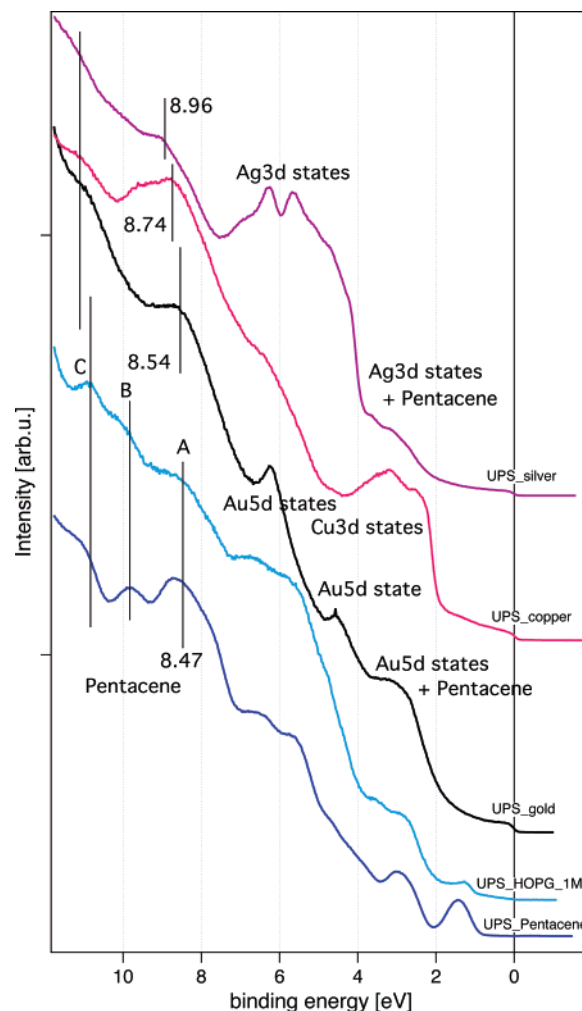
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**Figure 1.** Plot of the normalized intensities obtained for the C 1s emission during the deposition of the various metals. In all cases, the intensity levels off at a value of  $\sim 0.3I_0$ , which corresponds closely to the emission intensity of pentacene on a metallic substrate.

For the deposition of copper and gold, a leveling off at an intensity of  $\sim 30\%$  of the initial intensity ( $I_0$ ) is measured. These intensity values are comparable to the C 1s photoemission intensity observed for approximately a monolayer of pentacene deposited onto the same metal surface.<sup>8,17</sup> The slightly higher C 1s intensity for the silver interfaces might be due to slightly different packing densities resulting from different 2D structures in the monolayer regime. A slightly higher monolayer intensity for silver was also visible in the pentacene deposition experiments on Ag(111), where a monolayer equals  $\sim 0.35I_0$ .<sup>8</sup>

Figure 2 shows a comparison of UPS data for thick metal films deposited onto a thick pentacene layer, a monolayer of pentacene deposited onto HOPG, and a freshly prepared, thick pentacene layer on Ag(111) that acts as a reference spectrum for pure pentacene. Thick pentacene films on other metals with (111) orientation show the same emissions as the presented example. HOPG was used as a monolayer coverage reference because HOPG has no strong valence band emissions in the region between 12 eV binding energy and the Fermi level (0 eV); therefore, all emissions in this region can be attributed to pentacene HOMO (highest occupied molecular orbital) emissions. This is in contrast to the metals because they have strong d-state emissions between the Fermi level and approximately 7.0 eV (Ag,<sup>13</sup> Cu,<sup>14</sup> and Au<sup>15</sup>), and a comparison in the region between 6.0 eV and the Fermi level is therefore not reliable. No strong metal emissions are present in the energy region between 12.0 and 7.0 eV (see ref 16), making this region suitable for comparison of the UPS spectra. HOPG shows three emissions at energies of A = 8.47 eV, B = 10.05 eV, and C = 10.90 eV. The two higher binding-energy emissions are closer together and might show only one broad emission if the pentacene molecules are not aligned flat on the surface. This scenario is very likely on these metal films because



**Figure 2.** Comparison of the final spectra obtained for the metal deposition onto pentacene. Similarities in the region between 6 and 12 eV are evident.

they are polycrystalline and not well oriented, as they would be on a mica substrate.

A close examination reveals that at least two features are present in the spectra of the deposited metal films (Figure 2A,C) that are also present in all presented spectra. These emissions are an indication that the measured C 1s intensity is associated with intact pentacene molecules. This is surprising because more than 100 Å of the metals was deposited, a thickness that is more than 5 times the escape depth of photoelectrons from the C 1s core level. Another demonstration of the existence of intact pentacene molecules is the binding-energy shift in the observed emissions. (See lines labeled A with the given binding energies in Figure 2.) These shifts reflect the different Schottky barrier heights and the different strengths of photogenerated hole screening by the metal. The obtained binding energies for the HOMO levels for pentacene floating on the metallic film are slightly higher than for the deposition of pentacene onto the metal.<sup>8,9</sup> This shift is basically in agreement with earlier observations in the literature where different barrier heights were also obtained for metals deposited onto pentacene.<sup>8,9,11</sup> This shift to higher binding energies might be attributed to a non-abrupt interface due to the diffusion of the metal into the organic layer.

The last observed indication for pentacene molecules floating on top of the metallic film comes from a comparison of the work functions measured on the metal films deposited on pentacene with work functions measured at approximately one monolayer of pentacene coverage on the corresponding metallic substrate

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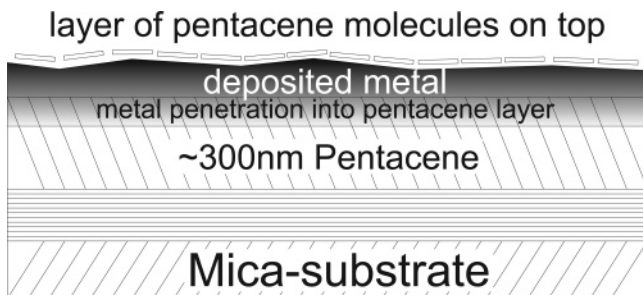
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**Figure 3.** Schematic representation of the final result of metal deposition onto polycrystalline pentacene films.

**Table 1. Comparison of the Work Function of the Metal Film Deposited onto Pentacene with the Work Function Obtained for an Approximate Monolayer of Pentacene Deposited onto a Clean Metal Surface**

	$\Phi_{1 \text{ ML on metal}}$ (eV)	$\Phi_{\text{thick metal}}$ (eV)	$\Phi_{(111)}$ (eV)	$\Phi_{\text{poly}}$ (eV) <sup>a</sup>
Au	$4.45 \pm 0.1^{17}$	$4.3 \pm 0.1$	$5.4 \pm 0.1^{17}$	$5.1 \pm 0.1^{18}$
Cu	$4.11 \pm 0.1^8$	$3.91 \pm 0.1$	$4.9 \pm 0.1^8$	$4.6 \pm 0.1^{19}$
Ag	$3.92 \pm 0.1^8$	$3.93 \pm 0.1$	$4.5 \pm 0.1^8$	$4.3 \pm 0.1^{19,20}$

<sup>a</sup> Work function trends between (111)-oriented films and polycrystalline material.

with a preferred (111) orientation. Table 1 shows a comparison of these values and also includes values for clean (111)-oriented crystal surfaces and clean polycrystalline surfaces. The trends in Table 1 reflect the change in the metal work function from the high work function material gold ( $\sim 5.4 \text{ eV}^{12}$ ) to the lower work function material silver ( $\sim 4.5 \text{ eV}^8$ ). It is clear from Table 1 that the work functions of the three metals with a monolayer of deposited pentacene are within experimental error, of those measured on thick metal films deposited onto pentacene. The slightly lower values for the work function of the deposited metal films are due to the fact that polycrystalline metal films can be expected. The investigated metals typically show a lower work function for polycrystalline films when compared to films with a predominate (111) orientation ( $\Phi_{\text{poly}} < \Phi_{(111)}$ ; see the last two columns of Table 1).

The findings are summarized with the sketch given in Figure 3. The metals (Au, Cu, and Ag) partially diffuse into the pentacene layer.<sup>9</sup> A thick metallic layer is eventually formed on top of this mixed pentacene/metal layer. The thick metal layer is usually used for contacting devices. The reported low work function during the deposition of metals onto organic layers can then be understood in terms of a floating pentacene layer on top of the thick metal film. A similar surprising observation was made decades ago during the deposition of gold onto silicon surfaces.<sup>21–23</sup> There a thin gold–silicide layer is formed that remains on top of the thick deposited gold film.

The driving force to form this floating layer is mainly a minimization of the surface free energy of the metal. At early stages of the metal deposition, the nucleation of metal islands occurs and will minimize their surface area and thus surface energy. These nuclei can further reduce their surface energy by covering their surface with a lower-surface-energy organic layer. When the nuclei grow and coalesce into a continuous metal film, the low-surface-energy organic layer is retained at the surface. We attempted to overwhelm the movement of pentacene by continuously depositing a metal film at a much higher rate (20–25 Å/min) to a final thickness of more than 120 Å. However, even at this high metal deposition rate the surface pentacene layer was still retained.

Checking the mechanism of evaporation and readsorption of pentacene due to the heat of the metal source might be investigated in a future study by mounting two samples (a thick pentacene layer and a fresh metal film) close to each other and then checking the carbon contaminations and the UPS spectra on the metal surface. From our experiments, we think that this mechanism will have only a minor impact on the thickness of the floating pentacene layer.

#### IV. Conclusions

The results of photoelectron spectroscopy (XPS and UPS) give conclusive evidence that pentacene is on top of even thick metal films that are freshly deposited onto pentacene layers. The measured C 1s core-level intensities for thick metal films level off at approximately 30% of the initial carbon signal. This amount of carbon nearly equals the measured C 1s intensity of one pentacene monolayer in the reverse experiment—a pentacene monolayer deposited onto a clean metal surface. The collected valence band spectra of the thick metal films show features assignable to pentacene in the region between 7.0 and 12 eV that were also found in spectra where pentacene is deposited onto a clean metal surface. The presence of a pentacene surface layer explains the observation that metals deposited onto an organic layer typically have very low work function values; however, these values are close to those obtained for a monolayer of pentacene deposited onto a clean metal surface.

The presence of the pentacene layer on top of the deposited metal is due to the mobility and chemical and thermal stability of pentacene and the lowering of the surface energy of the system by always covering the high-surface-energy metal with a low-surface-energy organic layer. We expect similar behavior for other nonreactive metals deposited onto any stable organic substrate because the energetics of these systems will be similar.

**Acknowledgment.** This work was supported by NSF grant no. CHE-0518563.

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