

## Selective Observation of Outermost Surface Layer during Epitaxial Growth by Penning-Ionization Electron Spectroscopy: Pentacene on Graphite

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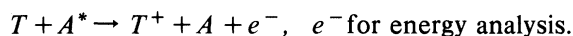
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By means of Penning-ionization electron spectroscopy the outermost surface layer of a pentacene film on a graphite substrate (cleavage plane) was selectively observed. Ultraviolet photoelectron spectroscopy was also applied to observe several layers from the surface. From the analyses of the two types of spectra the subtle changes in the electronic state and the molecular orientation of the outermost layer and also those of inner layers were probed separately during the layer-by-layer epitaxial growth of the film.

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The study of epitaxial growth of solid layers is important from both scientific and practical points of view. In particular, the characterization of the outermost layer that governs the surface properties is of fundamental significance. In this Letter we report the first selective observation of the outermost surface layer during epitaxial growth of an organic film by Penning-ionization electron spectroscopy, in which the kinetic energy of electrons ejected by collisions between targets  $T$  and metastable atoms  $A^*$  are analyzed:



The process of Penning ionization is interpreted in terms of electron transfer, in which an electron in an orbital of  $T$  fills the vacant orbital of  $A^*$  and its excited electron is ejected.<sup>1</sup> The transition probability largely depends on the overlapping of the relevant orbital of  $T$  and the vacant orbital of  $A^*$ . Therefore, an orbital spreading out of a target molecule gives a strong band, while a spatially limited and shielded orbital gives a weak band in the Penning-ionization electron spectrum (PIES). We have successfully applied this characteristic of PIES to the studies of the spatial electron distributions of *individual* molecular orbitals in various gas-phase molecules.<sup>2</sup> When metastable atomic beams are introduced onto a solid surface, an orbital distributed outside of the surface interacts with a metastable atom more effectively than an inner orbital and gives a stronger band in the PIES. Therefore, Penning-ionization electron spectroscopy not only is selectively sensitive to the outermost surface layer because metastable atoms do not penetrate into the solid,<sup>3-6</sup> but also provides information on the local electron distribution outside the surface.<sup>4,5</sup>

Pentacene was chosen as a sample because, the molecule being large and planar, we can easily prepare vapor-deposited films with controlled thickness on the substrate (graphite cleavage plane) used

in this study. The ultraviolet photoelectron spectra (UPS) were measured with an ultrahigh-vacuum (base pressure less than  $3 \times 10^{-10}$  Torr) spectrometer constructed at our laboratory.<sup>7</sup>

To measure the PIES a metastable-source chamber was attached to the analyzer chamber of the spectrometer. In the source chamber He atoms introduced through a glass capillary array were excited to the metastable states ( $2^1S$ , 20.62 eV, and  $2^3S$ , 19.82 eV) by impact of 60–70-eV electrons. To obtain pure  $\text{He}^*(2^3S)$  atoms,  $\text{He}^*(2^1S)$  metastables were quenched with a He discharge lamp.

A piece of Grafoil ( $10 \times 14 \text{ mm}^2$ , 0.4 mm thick) mounted on the substrate port was cleaned by heating at 350°C for 48 h and also at 400°C for 24 h under ultrahigh vacuum. It consists of graphite crystallites with their basal (cleavage) planes parallel to the foil plane. Pentacene films were prepared *in situ* by vapor deposition onto the Grafoil substrate. The film thickness was controlled by a quartz-oscillator monitor which had been calibrated by measuring the weight of sublimed gold films.

Figure 1 shows the PIES and UPS of pentacene layers prepared on a Grafoil substrate held at 123 K. The spectra of the clean substrate are also shown. Since the quartz-oscillator monitor gives the weight of the sample deposited, the coverage  $\theta$  shown in Fig. 1 was estimated from the density of the pentacene crystal and the thickness of the molecule, 3.4-Å (thickness of the benzene rings, approximated by the distance between successive layers of graphite), on the assumption that pentacene molecules are oriented parallel to the graphite substrate (see below). In view of the ambiguity in the value of the layer density and the error in the measurement of the sample weight, the error in the value of  $\theta$  is estimated to be about 10%.

In the He I spectrum of graphite in Fig. 1, the peak at about 14 eV is due to  $\pi$  valence bands and the sharp peak around 3 eV is associated with  $\sigma$

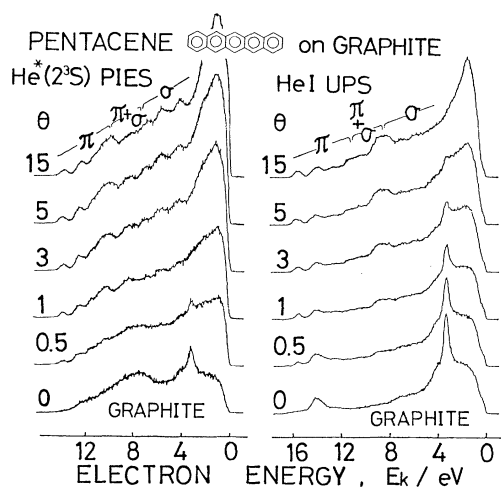


FIG. 1. Changes in the  $\text{He}^*(2^3\text{S})$  PIES and HeI UPS of pentacene layers on a graphite cleavage plane at 123 K with increasing coverage  $\theta$ .

conduction bands.<sup>8</sup> On the other hand, in the  $\text{He}^*$  spectrum of graphite almost no valence-band structure is seen and the features of the spectrum are much more diffuse than that of the UPS. This shows that  $\text{He}^*$  metastables are deexcited on the graphite surface predominantly through a combined resonance-ionization and Auger-neutralization (RI + AN) process.<sup>9</sup> Both  $\text{He}^*$  and HeI spectra of the pentacene layers show the valence-band structures due to the  $\pi$  and  $\sigma$  orbitals of pentacene (Fig. 1). The band assignment given in Fig. 1 was made on the basis of the gas-phase UPS study.<sup>10</sup> The clear appearance of the valence-band structures in the  $\text{He}^*$  spectra of the pentacene layers indicates that the metastable quenching now occurs through the effective one-electron Penning-ionization process.<sup>9</sup> The interesting point to note is that in the  $\text{He}^*$  spectra the intensity of the conduction-band peak in clean graphite is reduced to about one-half at  $\theta = 0.5$  and almost zero at  $\theta = 1$ . This finding shows that the monolayer coverage of pentacene shields the graphite substrate from metastables and that the PIES provides the information on the outermost surface layer selectively. In contrast to this, the conduction-band peak of graphite remains in the UPS even at  $\theta = 5$  (Fig. 1).

In Fig. 1 the relative intensity of the  $\pi$  and  $\sigma$  bands in the PIES is seen to change as a function of pentacene overlayer thickness. This can be accounted for as follows. As is seen in Fig. 2, if a  $\text{He}^*$  atom approaches a pentacene molecule deposited flat on the graphite surface, the  $\pi$  orbitals extending normal to the molecular plane interact with the  $\text{He}^*$  atom more effectively than the  $\sigma$  orbitals dis-

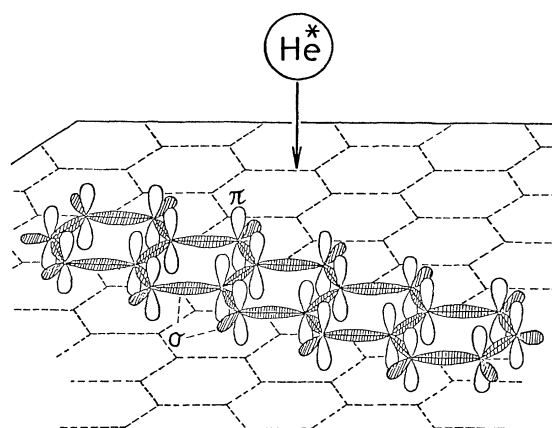


FIG. 2. Schematic diagram of a pentacene molecule deposited flat on a graphite cleavage plane interacting with a metastable He atom.

tributed on the molecular plane and should give stronger bands in the PIES. On the other hand, if a  $\text{He}^*$  atom approaches a pentacene molecule tilted on the substrate, the  $\sigma$  bands should also appear with appreciable intensity in the spectrum. In Fig. 1 the  $\sigma$  bands are much weaker than the  $\pi$  bands in the PIES for thin layers and their intensities gradually increase with increasing overlayer thickness. This points out that pentacene molecules are deposited flat onto the substrate at low coverage and gradually tilted in subsequent layers with increasing coverage. Thus, in thin layers the molecular orientation is determined mainly by the interaction between the molecules and graphite substrate, whose hexagonal network causes the pentacene rings to lie flat on it. With increasing thickness the effect of the substrate-molecule interaction gradually becomes weaker. We have observed a similar change in molecular orientation for benzene adsorbed on graphite on the basis of the PIES study.<sup>11</sup> The flat molecular orientation at low coverage is also supported by the fact that the graphite substrate is shielded from metastables at 1 monolayer that is estimated from the flat molecular deposition as described above. If molecules were to be arranged as in the bulk crystal having its  $ab$  plane parallel to the substrate,<sup>12</sup> the coverage would be 0.20 at "1 monolayer" defined above. Although surface molecules in thick films in Fig. 1 are tilted, the degree of tilting is much lower compared with the case of those in crystalline films prepared on a metal substrate. This was confirmed by the fact that in the PIES the intensity of the  $\sigma$  bands relative to that of the  $\pi$  was much larger in the latter case.<sup>13</sup> Thus, a subtle change in molecular orientation during the epitaxial growth has been detected

in Fig. 1.

Figure 3 shows the first ( $3b_{2g}, \pi$ ) bands in the PIES and UPS of pentacene layers. The first band is well separated from the other bands and therefore allows an analysis to be made in more detail. In the figure the background due to scattered electrons and those emitted from the substrate (for UPS) is subtracted in each spectrum. In the PIES no change in the peak position and the shape of the band is seen with increasing layer thickness because electrons only from the outermost surface layer contribute to the spectra, while in the UPS involving inner layers as well as the outermost, the peak position and the band shape change with increasing thickness. For the coverage  $\theta=2$  to 4 the UPS bands are decomposed to derive the electron-emission curves for the outermost layer (solid curves) and those for the inner layers (broken curves). When an electron is emitted from a molecule in the solid phase, the state of the remaining molecular ion is stabilized because of the polarization of neighboring molecules. Since the stabilization energy for a molecular ion in the outermost layer (corresponding to a dielectric half-space) is smaller than that for an ion in an inner layer, the

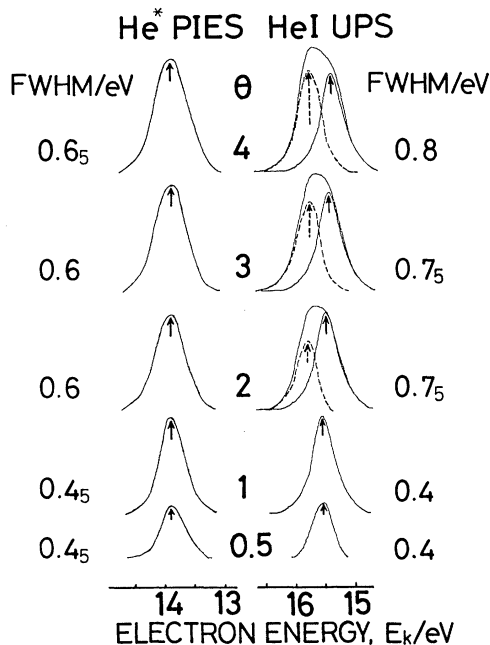


FIG. 3. Changes in the first bands in the  $\text{He}^*(2^3S)$  PIES and HeI UPS of pentacene layers on a graphite cleavage plane with increasing coverage  $\theta$ . For  $\theta=2$  to 4 the UPS bands are decomposed to derive the electron emission curves for the outermost layer (solid curves) and those for the inner layers (broken curves).

UPS peak due to the outermost layer appears on the lower-energy side of the peak due to inner layers. The separation of the two peaks is 0.3–0.35 eV for  $\theta=2$  to 4 in Fig. 3. Salaneck measured the angle-dependent photoemission from an anthracene film (thickness 20 Å), in which planar molecules lay on a gold substrate.<sup>14</sup> He obtained the difference in the relaxation energy between the bulk and the outermost layer to be 0.3 eV, which is close to our values.

Table I shows the relative integrated intensity of the first band in the UPS as a function of the coverage  $\theta$ . The value of  $I(\theta)/I(1)$  increases with increasing  $\theta$  because of the successive contributions from inner layers. If photoemitted electrons giving the first band from an inner layer can escape in the proportion  $\rho$  when they pass through one overlayer, the intensity of the band due to the  $n$ th layer becomes  $I_n = I(1)\rho^{n-1}$ , where  $I(1)$  corresponds to the intensity due to one monolayer or the outermost layer. The total intensity of the first band relative to  $I(1)$  at the coverage  $\theta$  is given by

$$\frac{I(\theta)}{I(1)} = \sum_{n=1}^{\theta} I_n/I(1) = \sum_{n=1}^{\theta} \rho^{n-1}.$$

Using a least-squares fit, we obtained 0.53 as the value of  $\rho$ , the escape probability of photoelectrons through one overlayer. In Table I the values of the observed  $I(\theta)/I(1)$  are in good agreement with those of the calculated ones. From the value of  $\rho$  we can calculate the escape depth of photoelectrons giving the first band. It is 18 Å after the correction of the emission angle 60°.

Finally we wish to discuss the width of the first band. At  $\theta=0.5$  or 1 the FWHM (full width at half maximum) is 0.4 eV for the UPS and 0.45 eV for the PIES (Fig. 3). The latter value is slightly larger because of the interaction between the colliding partners in Penning ionization, as is usually observed in gas-phase spectra.<sup>15</sup> After two monolayers the FWHM for the UPS increases because of

TABLE I. The observed and calculated (see text) relative intensities of the first bands in the UPS of the pentacene layers as a function of coverage  $\theta$ .

$\theta$	$[I(\theta)/I(1)]_{\text{obs}}$	$[I(\theta)/I(1)]_{\text{calc}}$
1	1.00	1.00
2	1.55	1.53
3	1.79	1.81
4	1.96	1.96
5	2.06	2.03

the contribution of photoelectrons from inner layers. Also in the PIES which detects only the outermost layer the bandwidth for  $\theta \geq 2$  is larger than that for  $\theta = 1$  by 0.15–0.2 eV. This broadening can be ascribed to the site inhomogeneity of the first-surface-layer molecules which occupy various nonequivalent positions on the second-layer molecules.

The above results clearly demonstrate the usefulness of Penning-ionization electron spectroscopy in probing the outermost layer of the solid surface. Besides, it has been shown that the present method of applying Penning-ionization electron spectroscopy together with photoelectron spectroscopy to a solid film with controlled thickness allows us to probe both the outermost surface layer and inner layers separately.

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<sup>9</sup>In the RI + AN process the electron in the 2s level of a He\* atom tunnels into an empty level (conduction-band level) in graphite (RI) and the He<sup>+</sup> ion thus formed is then neutralized through an Auger process (AN). In this case the spectrum gives broad self-convoluted features, because the energy of the He<sup>+</sup> ion formed in the RI process is shared by two electrons from graphite in the AN process. On the other hand, in the effective one-electron Penning-ionization process the spectrum shows the appearance corresponding to UPS. As for the deexcitation mechanisms of metastables on solid surfaces, see H. D. Hagstrum, *Phys. Rev. Lett.* **43**, 1050 (1979).

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