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Researching Pentacene: The Future Revolution for Low-cost, Novel Electronics

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Abstract

Pentacene (Pn) has been researched as a novel electric material for several years using various experimental methods such as Angle-Resolved Photoemission Spectroscopy (ARPES). This paper explores the questions surrounding the growth mode of Pn on bismuth (Bi) in addition to the electric properties of Pn on silicon (Si). We gain insight on the topic of whether hole-vibration coupling is the cause of the asymmetric highest occupied molecular orbital (HOMO) peak for Pn/Si templates, or whether band structure is present in the HOMO peak. In this study, we use synchrotron radiation generated from an electron storage ring to supply the photon beam used on the different samples. As a result, we found evidence of standing Pn molecules on Bi substrates. Also, we have data that suggests possible band structure for Pn/Si samples. This implies that the Pn/Si template is an excellent candidate for the advancement of electrical products.

Key Terms:
Angle Resolved Photoemission Spectroscopy (ARPES), Highest Occupied Molecular Orbital (HOMO) peak, $k_{\parallel}$, Pentacene Monolayer, Ultra High Vacuum (UHV) chambers

Introduction

Pentacene (Pn) is a chemical that has recently been found to have possible uses in several novel electronic applications. As a solid, in powder form, pentacene is purple in color. However, because the chemical is sensitive to oxidation, it slowly turns green in the presence of air and either ultraviolet or visible light. The chemical consists of only carbons and hydrogens, making it an inorganic molecule. The chemical's twenty-two carbons and fourteen hydrogens are arranged in a way that produces a long chain of five linearly connected benzene rings. Benzene rings are chemical structures that consist of six carbon atoms and six hydrogen atoms—one hydrogen atom is attached to each of the six carbon atoms. This special arrangement causes alternation of the double bonds between carbon atoms, explained by electron delocalization. Because the double bonds can resonate to different carbon-carbon bonds, we call the benzene structure aromatic. Since pentacene is simply a linear chain of five benzene rings, pentacene qualifies as an aromatic molecule. The prefix *penta*-, in pentacene, corresponds to its characteristic of having five benzene rings.

In addition to the chemical structure of Pn, its specific crystal structure also contributes to its use in future electronics. The crystal structure of solid Pn is an arrangement of its atoms in a particular way. Pentacene's symmetrical crystal structure helps allow researchers to study and determine many of the material's electric properties. Due to pentacene's aromatic structure and its crystal structure, the compound's electrical conductivity was found to be in between that of metals and that of insulators, making it an organic semiconductor.

It is important to study Pn as a thin film transistor because of its possible application in products such as electronic wallpaper, spray-on solar cells, low-cost large-scale electronics, and even flexible computer displays. IBM scientists say that this compound is a promising material for use in electronic displays that are capable of speeds up to ten thousand times as fast as today's displays [1]. Researchers have also seen its excellent efficiency as a solar cell converting sunlight into energy. Because of its light weight and flexibility, the organic material could power society's iPods, laptops, and cell phones [2]. Pn is already being used in prototype organic thin film transistors, organic LEDs, and flexible solar cells [1]. Additional reasons to study Pn are its availability to consumers and scientists, its ability to create molecular crystals which improve material performance, and its enhancement of semi-conducting materials like silicon as the basis for electronic devices.

The specific goal of the research is to develop a better understanding of the electric properties of the organic semiconductor, Pn. In order to accomplish this goal it must be determined if Pn films show band structure. If we discover that Pn in fact does show band structure on the bismuth (Bi) substrate, for example, then we can conclude that Pn grows in a highly crystalline fashion when deposited on Bi. From this conclusion we can argue that the Pn/Bi arrangement is an ideal system for use in novel electronics. Studying the photoemission spectra also gives insight into the growth mode of Pn on various substrates, and into the interface between Pn and the various substrates. Hence, the spectra allow comprehension of the majority of pentacene's electronic properties, thereby helping us to assess the feasibility of using Pn for society's future electronic systems.

Methods

Researchers studying Pn as an organic semiconductor use various techniques for their experiments. Molecular Beam Epitaxy (MBE) and Quartz Crystal Microbalance (QCM) systems are utilized [3]. In MBE, a solid source material—Pn in this case—is placed in an evaporation cell where it slowly vaporizes from a heat source onto the substrate's surface. The QCM actually calculates the rate that Pn deposits on the substrate by measuring the frequency of a crystal's micro-vibrations caused by the effusing Pn molecules.

The final procedure used in the research is Angle Resolved Photoemission Spectroscopy (ARPES). ARPES uses the phenomenon known as the photoelectric effect. In the late 1880s this phenomenon was discovered and observed in experiments conducted by the scientists Heinrich Hertz and Wilhelm Hallwachs [3]. The newly discovered process involved the use of ultraviolet light to produce what is known as a photon (a massless subatomic particle with electromagnetic force). Within a vacuum, a beam of photons are directed toward the surface of a solid sample. When the photons have enough energy they will excite some of the electrons on the sample's surface causing the excited electrons to "bounce" out off of the surface. The photoelectric effect explains how electrons are emitted from a material when the material absorbs enough electromagnetic radiation. So, when photon light, for example, is directed onto a material, energy from the light excites electrons in the material, sometimes causing the electrons to gain enough energy to escape the material. In order for the excited electrons to escape the material, their energies—gained from incident photon energy—must overcome the work function or binding energy of the specific material. This relation can be represented in the algebraic equation:

$$h\nu = \O + E_{k,max} \qquad \text{(Equation 1)}$$

where h is plank's constant, ν is the frequency of the incident photon, $E_{k,max}$ is the maximum kinetic energy of the ejected electrons, and $\O$ is the work function or binding energy—the minimum amount of energy required to remove a delocalized electron from the surface of the given material.

Now, scientists are using the photoelectric effect in the process called Photoemission Spectroscopy (PES) [4]. In this method, the light source for the photons is vacuum ultraviolet radiation, soft x-ray radiation, or synchrotron radiation. PES uses the emitted electrons by capturing them in a hemispherical electrostatic analyzer which has a detector at the end.

After Pn molecules are deposited onto the substrate surface using MBE, the last process takes place. Using ARPES, a beam of photons is released onto the sample at a given angle and energy, causing electrons to escape the material and travel into an analyzer which counts the number of electrons emitted at a given angle and at a given kinetic energy. The electron analyzer can be rotated to different positions in the azimuthal (horizontal) direction, polar (vertical) direction, or a combination of both. The graphs produced by the analyzer, called photoemission spectra, allow comprehension of the majority of pentacene's electronic properties. The ARPES method allows researchers to obtain photoemission spectra taken with different conditions. For example, spectra can be taken with different Pn film thicknesses (measured in angstroms), different photon energies, temperatures, substrates, and at different emission angles.

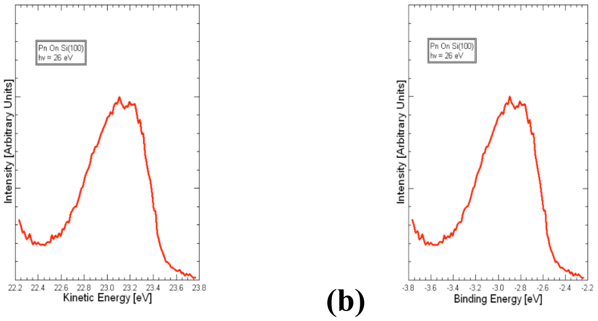
A specific example of the techniques used in experimentation is given below. These methods are referenced from the research paper titled, "An Analysis of Substrate Dynamics and Dependence with Pentacene Films" [4]. The procedures used in this experiment involve two different ultra-high vacuum (UHV) chambers, one preparation chamber and an analysis chamber. At the Synchrotron Radiation Center (SRC) in

Stoughton, WI, synchrotron radiation (~10 eV-32 eV) from the 4m NIM beam-line was used. Once the substrate is placed in the preparation chamber, with an ideal pressure in the average × 10^{-11} atm, it is "flashed" by sending a steady, regulated current through the material that is high enough to cause it to glow bright orange. This process should only last a maximum of 10 seconds to prevent any melting of the substrate. Pn is then deposited onto the flashed substrate, using standard molecular beam epitaxy (MBE) techniques, and the thickness is determined by a quartz crystal microbalance (QCM). Using a linear manipulator the sample is transferred under ultra high vacuum (UHV) to the analysis chamber. The sample may be rotated to a given angle. With the analysis chamber at approximately 4.5×10^{-11} atm, the photon beam is opened onto the sample. Depending on the chosen photon energy, the photon beam line must use either the low energy grating for energies ≤ 21 eV, or the high energy grating for energies > 21 eV. The final procedure used in the experiment is ARPES. Applying this method, we not only compare photoemission spectra relative to different horizontal (azimuthal) and vertical (polar) angles, but also on photon energy dependence, film thickness dependence, and on sample temperature dependence. In order to assure that the sample's surface receives the absolute minimal amount of radiation damage from prolonged photon exposure, the photon beam is shut off from the sample immediately after each completed scan, and multiple spots on our relatively large samples are used.

Results and Discussion

All of the data and results are referenced from the research titled, "An Analysis of Substrate Dynamics and Dependence with Pentacene Films" [4]. The photoemission graphs, or spectra, obtained from the electron analyzer are thoroughly studied for characteristics of band structure or other significant electric properties. All materials have their own characteristic spectra shapes, and researchers normally focus on the first main peak (going from right to left) in the spectra. This main peak that usually characterizes the material is known as the highest occupied molecular orbital (HOMO) peak. The x- and y-axes on the graphs show that the spectra are usually taken with the intensity as a function of the material's binding energy. Intensity, on the y-axis, is the amount of electrons captured in the analyzer; its units are arbitrary. The negative binding energy quantities along the x-axis can be explained by the algebraic equation representing the photoelectric effect—Equation 1. As researchers collect the data from the analyzer they normally receive one spectrum at a time, as shown in Figure 1.

<u>Figure 1</u>



(a) **(b)**

FIG. 1 (color). Photoemission spectrum of Pn on Si(100) taken with a photon energy of 26 eV at normal emission (meaning the analyzer was perfectly facing the surface of the sample, collecting electrons emitted normal to the sample's surface at the angle Θ = 0°). The spectrum was taken with a certain thickness of Pn molecules on the Si substrate at room temperature (RT). (a) One photoemission spectrum with intensity as a function of the kinetic energy of the photoemitted electrons. (b) The same spectrum shown with intensity as a function of the binding energy overcame by the photoemitted electrons. The axes setup in (b) is the preferred method in the PES research field.

In order to study and compare the spectra of the samples, numerous spectra are taken with various Pn film thicknesses, for example. After taking several of these spectra, each with a different measure of Pn thickness, they can be "stacked" on top of one another to examine any differences or similarities that have occurred as a result of the different Pn film thicknesses. Examples of Pn thickness dependent spectra are shown in Figure 2.

Figure 2

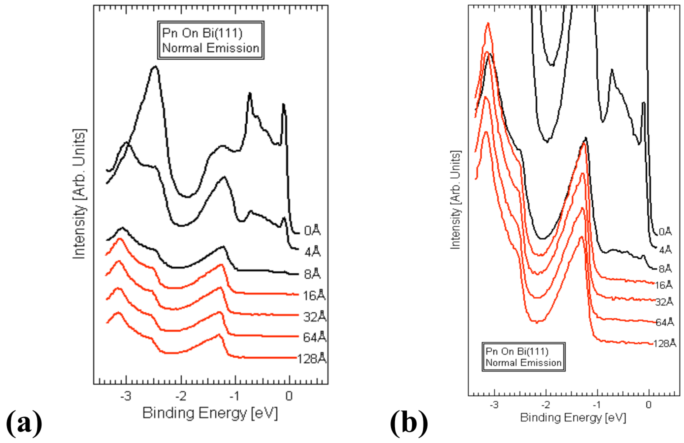
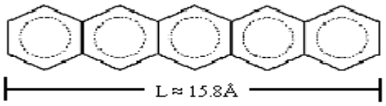


FIG. 2 (color). (a) Pn on Bi(111) thickness dependence spectra taken at Θ = 0° with hv = 15 eV and sample temperature at room temperature (RT). Spectra are stacked from top to bottom increasing in Pn thickness. Background subtraction achieved by subtracting the respective photon current for each individual spectra.

Figure 2 (a) shows spectra of Pn thickness dependence on the Bi(111) surface. The stacked spectra are arranged with increasing Pn thickness from top to bottom. The top spectra at 0 Å of Pn clearly shows two distinctive peaks around -0.7 eV and -0.1 eV from pure Bi(111). Depositing additional Pn onto the Bi substrate for each scan reveals gradual dissipation of the Bi features in the spectra. Figure 2 (b) shows that dissipation more clearly. Looking at the spectra taken at 8 Å, it is evident that Bi characteristics still exist.

However, once 16 Å of Pn is reached, all Bi features have been suppressed, meaning electrons from the Bi substrate are no longer being emitted due to Pn coverage.

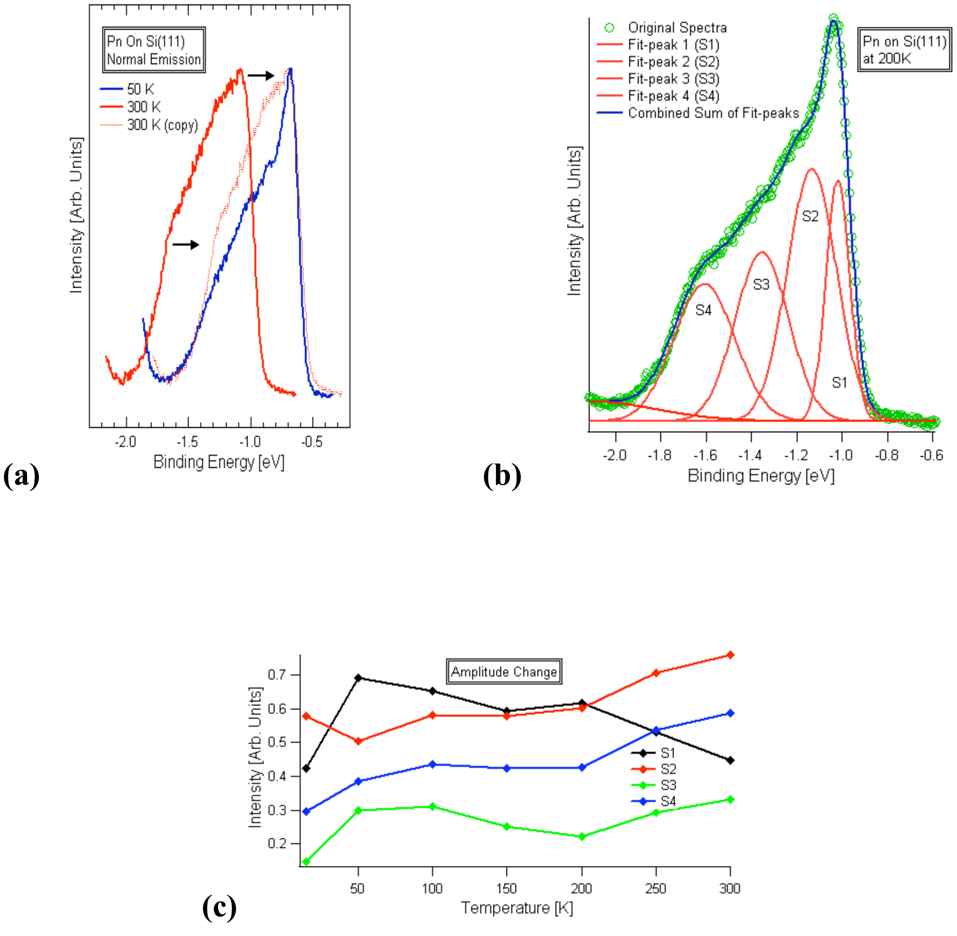
Length of the Pn Molecule



$C_{22}H_{14}$

Since the length of one Pn molecule is ~15.8 Å, it is indicated that one monolayer of Pn was deposited on the Bi substrate. This data suggests that the growth of Pn on Bi(111) is characterized by “standing” Pn molecules.

Figure 3



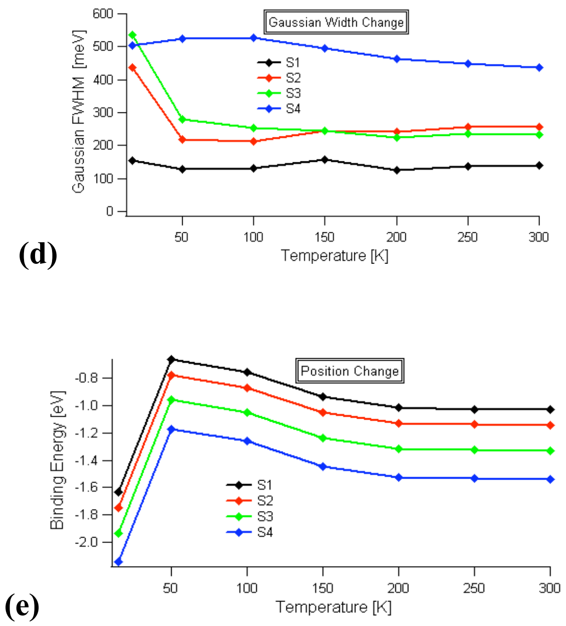


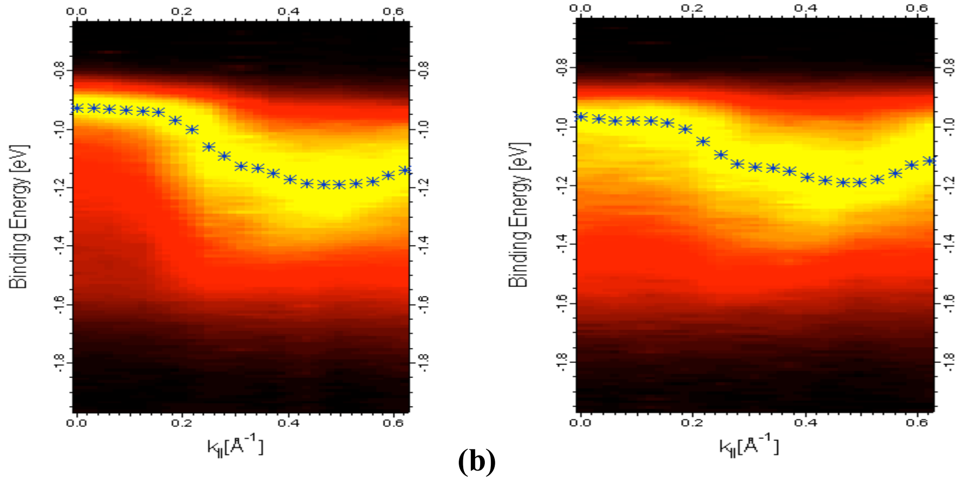
FIG. 3 (color). (a) Pn on Si(111) temperature dependence spectra taken around the Pn HOMO peak range at Θ = 0° with hν = 18 eV. Background subtraction achieved through Shirley background removal. The figure displays a comparison of a RT spectra with a 50 K spectra without repositioning. (b) 200 K Spectra obtained from the same temperature dependence study as in (a). The 200 K spectra in (b) is fitted with four main peaks labeled S1 through S4. (c) Mapping of the change in amplitude of the fit peaks (S1-S4) as temperature changes. (d) Mapping of the change in width of the fit peaks (S1-S4) as temperature changes. Width is measured from the fit peaks' width at half the amplitude (FWHM) of the individual fit peak. (e) Mapping of the change in position of the fit peaks (S1-S4) as temperature changes.

An additional experiment carried out in this research is a temperature dependence study on the Pn/Si template, where we scanned from 300 K to 50 K in 50 K increments with an additional scan at 15 K. Two specific results are shown in Figure 3 (a), which summarize the outcome. In the spectra, as temperature decreases, the HOMO peak steadily loses intensity in the left-hand side of the peak. It was also observed how a strong peak develops on the right-hand side of the HOMO peak. In addition, one should note that as temperature decreases the binding energy of the material decreases—this is seen in Figure 3 (a).

Peak fitting is a mathematical technique where several smaller peaks are used to estimate the "shape" of the obtained HOMO peak. So, adding all of these smaller "fit peaks" should result in one HOMO peak. We chose to run a peak fit on the HOMO peaks and found four Gaussian fit peaks would give the best fit to the spectra. This fit is shown on the 200 K spectra in Figure 3 (b). The fit peaks labeled S1 through S4 change slightly in their dimension and position as a function of temperature change. Amplitude differences can be seen in Figure 3 (c). In Figure 3 (d) the width of S1 through S4 show very little deviation, indicating that there is very weak interaction between electrons and vibrations within the Pn film structure. Figure 3 (e) is a mapping of the change in position of fit peaks S1 through S4. From this graph we can see that each of the fit peaks change position by the same amount with every temperature change. This allows us to see an average bandwidth of approximately 0.5-0.6 eV. Bandwidth is a measure of the length between the end fit peaks (in this case it's the length between S4 and S1). This parameter can be seen using the 200 K spectra in Figure 3 (b) as a base model.

Lastly, we did an angle dependent study of the Pn/Si(100) sample. Instead of "stacking" the spectra, as seen previously with thickness dependent spectra (Figure 2), researchers usually represent the differences in spectra (due to different emission angles) in what is known as intensity maps—seen in Figure 4. The intensity maps are simply another way of comparing each spectrum's HOMO peak position, taken at a range of angles. Using intensity maps, each spectrum is assigned colors that appear brighter at the higher points of the spectrum and darker at lower points. You can think of the spectra as being stacked against each other side-by-side (where they read from left to right in thickness dependent graphs, they now read from bottom to top in intensity maps). So, we are now looking "down" onto our spectra peaks. Note the axes labels. Binding energy is now a vertical axis and $k_{\parallel}$ is the horizontal axis, where $k_{\parallel}$ is the momentum of the photoemitted electrons measured parallel to the sample's surface. The $k_{\parallel}$ quantity is actually related to the emission angle Θ. Researchers again prefer to use the momentum quantity instead of emission angle.

Figure 4



(a) **(b)**

FIG. 6 (color). Intensity maps of angular dependent Pn on Si(100) taken with a Pn film 200 Å thick with hv = 18 eV and sample temperature at 200 K. The blue markers indicate peak positions by their highest intensity point. Map (a) shows spectra taken in 2° steps starting at Θ = 0° and ending at 20° off normal emission. Map (b) shows spectra taken in 2°

steps starting at 20° off normal emission and ending at Θ = 0°. (20° corresponds to $k_{\|} \approx 0.612$ Å^{-1})

Angular dependent intensity maps were taken of Pn on Si(100), and can be seen in Figure 4 (a) and (b). Since map (a) was taken from 0° to 20° in 2° steps, a fair amount of radiation damage is evident from approximately 0.3 Å^{-1} to $k_{\|}$ final. Therefore a second map was taken at a new spot scanning from 20° to 0° also in 2° steps. Using angle dependent intensity maps, researchers can measure a material's dispersion. Dispersion is measured by finding the greatest amount of deviation of the peak position. The blue markers indicate peak position in the spectra as emission angle changes. From this data we see dispersion of the HOMO peak that is approximately 100-200 mV.

Conclusion

Thus far, scientists using ARPES claim they see the electric property called band structure at the HOMO peak in the spectra of Pn on Bi(001) [5], while other researchers say the asymmetrical HOMO peak of Pn on highly oriented pyrolytic graphite (HOPG) arises from hole-vibration coupling and not from band structure [6]. Band structure is an electric property that can be confirmed by showing data that has the necessary bandwidth and dispersion. Our research on Pn has helped gain insight on this matter. Using scanning tunnel microscopy (STM), reflection high energy electron diffraction (RHEED), X-ray diffraction, low-energy electron microscopy (LEEM), and near edge X-ray absorption fine structure (NEXAFS) systems, other researchers have found that Pn grows standing up on Bi films with smooth even coverage, opposed to the crystallite (island-like) coverage on Si surfaces [7].

Based on previous experimental research, the referenced data has further developed the knowledge related to the electric properties of Pn by studying its photoemission using various substrates. The substrates that were tested in the referenced project include Pn on Bi and Pn on several different surfaces of crystalline Si. The experiments in this study have revealed several electric properties of Pn. Analyzing temperature dependent spectra and angular dependent spectra from Pn/Si samples, we have found evidence of bandwidth in peak fitting data and proof of dispersing peak positions in intensity maps of angle dependent spectra. Since Si(100) spectra and Si(111) spectra show very similar characteristics, the information obtained from Figures 3 and 4 indicate that Si substrates for Pn films indeed show band structure rather than the affect of hole-vibration coupling.

Researchers now expect to find varied electronic properties for Pn films grown on these different substrates arising from diverse Pn crystal polymorphs. Prospective experiments involve the study of Pn on other substrates in addition to Bi(111), Si(100), and Si(111), like highly oriented pyrolytic graphite (HOPG). Now that scientists have found evidence of band structure in Pn films it is agreed that the material can be used in future electrical products with much less expense to manufacturers and consumers. IBM researchers say the Pn films enable fabrication of low-cost, low power organic transistors and light emitters. Pn molecules have been deposited onto various materials to produce flexible electronics. Scientists at IBM state that the next steps toward commercial production are to fabricate the improved devices in new large grain Pn films. In order to build the flexible transistors on a mass scale, IBM teams are looking into techniques that produce them at low temperatures using a technique of "painting-on" the transistors. The researchers go on to say that this could lead to a very simple manufacturing technique similar to printing documents on laser printers [8].

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