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Tebyani, A.; Baalbergen, F.B.; Tromp, R.M.; Molen, S.J. van der

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Low-Energy Electron Irradiation Damage in Few-Monolayer Pentacene Films

A. Tebyani, F. B. Baalbergen, R. M. Tromp, and S. J. van der Molen*

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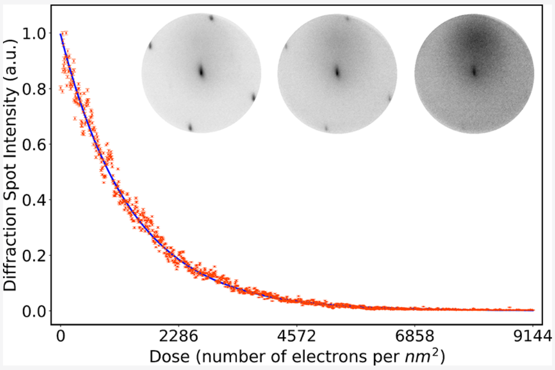
ABSTRACT: Crystalline films of pentacene molecules, two to four monolayers in thickness, are grown via in situ sublimation on silicon substrates in the ultrahigh vacuum chamber of a low-energy electron microscope. It is observed that the diffraction pattern of the pentacene layers fades upon irradiation with low-energy electrons. The damage cross section is found to increase by more than an order of magnitude for electron energies from 0 to 10 eV and by another order of magnitude from 10 to 40 eV. Close to 0 eV, damage is virtually nil. Creation of chemically reactive atomic centers after electron attachment or impact ionization is thought to trigger chemical reactions between neighboring molecules that gradually transform the layer into a disordered carbon nanomembrane. Additionally, diminishing spectroscopic features related to the unoccupied band structure of the layers, accompanied by loss of definition in real-space images, and an increase in the background intensity of diffraction images during irradiation point to chemical changes and formation of a disordered layer.



■ INTRODUCTION

Interaction of low-energy electrons (LEEs) with organic materials is of importance in several areas of research and applications. One important example is interaction of biological matter with ionizing radiation. Regardless of the radiation source (electrons or photons), exposure leads to generation of secondary electrons with relatively low energies (below 20 eV). These electrons are responsible for a substantial part of the damage to the organic sample.[1,2] Knock-on displacement of atoms and creation of structural defects occur with electrons of much higher energies (threshold of ~86 keV for knock-on displacement in graphene[3]). Techniques such as low-energy transmission electron microscopy,[4] cryo-electron microscopy,[5−8] or encapsulation[9] are attempts to reduce the damage and to extend sample lifetime.[10] An understanding of the energy dependence of interaction of LEEs with organic samples is beneficial for designing experiments that cause less damage to the sample under study. Another key example is formed by organic self-assembled monolayers (SAMs), which can be used to modify chemical, physical, and mechanical properties of surfaces. Irradiation of SAMs with LEEs can cause (desirable) chemical changes, transforming SAMs into carbon nanomembranes (CNMs) with different properties.[11−16] Hence, knowledge of the interaction of LEEs with molecules is important in designing SAMs toward the wanted functionality after exposure to LEEs. Synthesis of carbon-based (nano)materials by utilizing an electron beam is a similar application.[17−20] Another technologically important example of interaction of LEEs with organic matter is in e-beam lithography, where electrons are used to cause chemical changes in the resist film. A detailed understanding of the interaction of low-energy (secondary) electrons with the resist is essential for control over the properties of the exposed area, as well as sharpness of the written patterns and overall quality of the lithography process. Knowledge of the role of secondary electrons, which generally have low energies, is also of great importance to understand and improve extreme ultraviolet (EUV) lithography, generally considered the key lithographic technology for the next decade(s).[21,22]

In this work, we use low-energy electron microscopy (LEEM) to study the interaction of LEEs with crystalline layers of pentacene grown on a silicon (111) substrate. In LEEM, the energy of the electrons interacting with the sample can be tuned in the range 0−100 eV (with respect to the vacuum energy) with 0.25 eV energy spread. Scattering of LEEs from pentacene layers provides information about the surface structure through diffraction and also reveals spectroscopic features related to the unoccupied band structure,[23,24] as well as electronic excitations in electron

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energy loss spectra.[25] The pentacene layers studied, two to four monolayers in thickness, are grown in situ in the ultrahigh vacuum (UHV) chamber of the microscope. Growth is monitored in *real time* via both LEEM and photo-electron emission microscopy (PEEM). Not only does this offer a high degree of control over pentacene thin film growth, it also ensures that the layers are not at any point contaminated due to exposure to air. The pentacene layers are exposed to electrons with a defined energy, and the main observation reported here is fading of the pentacene diffraction intensity due to beam-induced damage to the crystalline structure. To quantify the damage, line profiles of diffraction spots are analyzed over time. We obtain electron cross sections for destruction of the pentacene lattice for electron energies between 0 and 40 eV and find that the cross section becomes vanishingly small for electron energies close to 0 eV. Spectroscopic information on the unoccupied band structure and electron energy loss spectra were also obtained, and their evolution upon irradiation was investigated.

EXPERIMENTAL SECTION

A schematic of the LEEM instrument is shown in Figure 1a. Electrons traveling from the cold-field emission gun through the microscope column with a kinetic energy of 15 keV are deflected toward the sample by magnetic prism 1. The sample voltage is set at −15 kV + V_0 so that the electrons are decelerated just before they interact with the sample to a kinetic energy of $eV_0 + \Delta\Phi$, in an electric field of approximately 10 kV/mm. $\Delta\Phi$ represents the difference between the work functions of the sample and the electron gun. After interaction with the sample, some of the electrons are back-reflected. These electrons are re-accelerated by the same electric field toward the magnetic prism and are deflected toward the detector via an aberration-correcting path comprising magnetic prism 2 and the correcting electron mirror optics.[26] It is possible to project either the real-space or the diffraction-space image on the detector screen. A high-pressure Hg UV lamp attached to the sample chamber allows for imaging with photoelectrons (PEEM). In addition, a Knudsen cell evaporator is connected to the sample chamber with line-of-sight to the sample surface. By heating the cell, pentacene (purchased from Sigma Aldrich, with a purity of 99.995%) is sublimated toward the sample for in situ thin film growth. The growth of pentacene layers on silicon has been explored in detail in the literature[27−29] (see also Figure 1b,c). By placing a slit in the beam path in a diffraction plane between the objective lens and magnetic prism, electron energy loss spectroscopy data can be obtained.[25] Electrons with different energies are dispersed by the magnetic prism, and hence, spectra showing electron intensity vs energy are observed directly on the image screen.

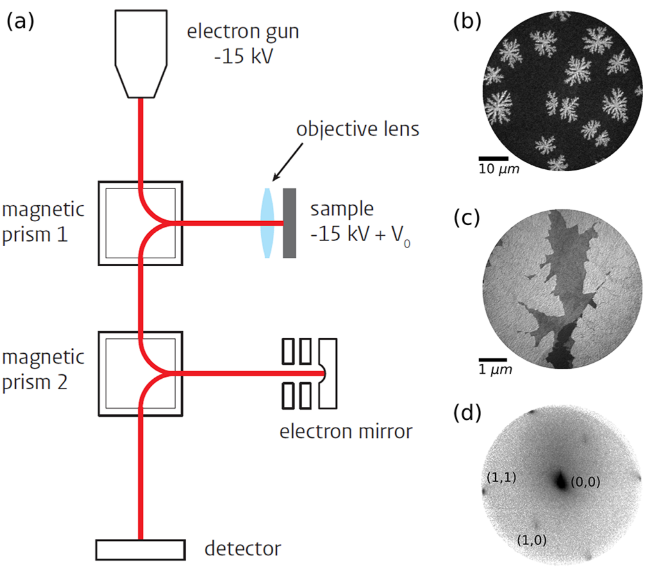

Figure 1. Low-energy electron microscopy (LEEM). (a) Schematic of the LEEM instrument. The red line shows the path traversed by the electrons from the cold-field emission gun to the detector. The electrons are decelerated to an energy close to 0 eV by the electric field between the objective lens and the sample, approximately 10 kV/mm in strength. The precise energy of the electrons upon interaction with the sample is tuned by V_0. The electron mirror corrects lowest-order aberrations. (b) PEEM image showing nucleation of pentacene molecules on the substrate surface and start of growth of the first pentacene layer with herringbone crystal structure. (c) Bright-Field LEEM image obtained with a beam of 1.3 eV electrons. The contrast indicates different layer thickness. (d) Low-energy electron diffraction (LEED) pattern of the herringbone crystal structure of a pentacene film, with different diffraction orders annotated. Intensities of diffraction spots are in logarithmic scale.

Growth of the pentacene layers in situ in a UHV pressure of ∼1.0×10^{-9} mbar and keeping them in the same pressure during the entire measurements ensures cleanliness of the surface. For obtaining the data presented here, an aperture is placed along the illuminating beam path to confine the beam to a smaller, more homogeneous area (below 2 μm in diameter) on the pentacene layer. The diffraction pattern corresponding to the chosen area is recorded over time as the layer is exposed to the electron beam. Recordings are made for exposures to electrons with incident energies in the range 0−40 eV. The measurements are carried out at room temperature.

The total emission current of the electron gun is measured via an anode aperture that transmits about 0.1% of the emitted electrons. The ratio between the beam current that passes through this aperture and the total emission current was determined by placement of an aperture along the magnetic prism diagonal and measurement of the aperture current with a Keithley Picoammeter when the aperture blocked the beam. Electron beam current densities used are 3−45 pA/μm^2, corresponding to ∼19−281 e$^-$/nm^2/s. The surface density of pentacene molecules is about 4.74 molecules/nm^2.[29]

RESULTS

Pentacene layers grow on silicon (111) substrates in a thin-film phase with a herringbone crystal structure.[29] The corresponding diffraction pattern is shown in Figure 1d. In Figure S1 and the inset in of Figure 2, we show a measurement of a typical diffraction spot and its line profile. The line profile is taken in the direction orthogonal to that of the magnetic prism dispersion (which is in vertical direction in Figure S1) in order to avoid asymmetric broadening of the line profile. Next, the background is removed from the images by the following procedure: first, a Fourier transform of the diffraction image for each frame of the recording is generated. Then, a median filter is applied to the Fourier-transformed image. This operation removes the low-frequency noise and the background present in the diffraction image. Finally, the filtered image is transformed back and a new diffraction image with reduced noise and background is obtained. The full process is

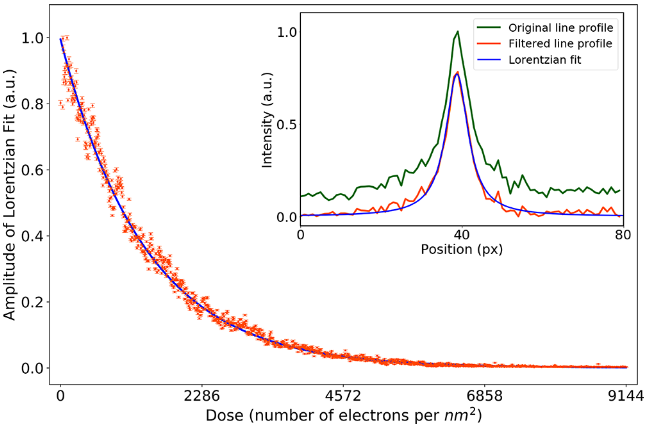

Figure 2. Orange points: Amplitudes of Lorentzian fits to a (1,1) diffraction peak as a function of dose. The latter is proportional to irradiation time. Solid line: exponential fit of the form $Ae^{-\sigma \cdot \text{dose}} + B$ to the decay of the peak amplitude. A and B are constants. From the fit, we determine the damage cross section, defined as σ in the exponent. The pentacene film is 4 monolayers thick and is irradiated with 10 eV electrons. The beam current density is 2.96 pA/μm^2. The inset shows the line profile of a (1,1) diffraction peak before and after filtering, corresponding to Figure S1. Lorentzian fit to the diffraction peak after filtering is also depicted.

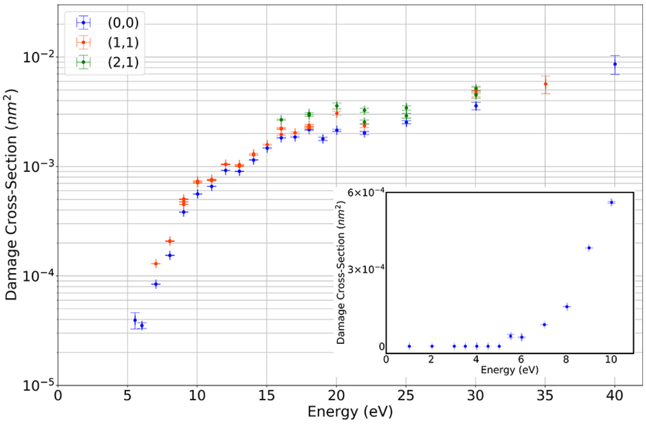

Figure 3. Damage cross sections (see Figure 2) of different-order diffraction peaks versus incident electron energy for a pentacene sample with thickness of 4 monolayers. The beam current density used for obtaining the cross sections is 2.96 pA/μm^2. The inset shows the damage cross section for datapoints up to 10 eV in linear scale, including energies for which no decay in diffraction intensity was observed.

illustrated in Figure S1. Next, Lorentzian functions are fitted to the line profiles of the diffraction spots for each frame of the recording; see the inset of Figure 2. To quantify the rate of fading of the diffraction pattern, we plot the amplitudes of the Lorentzian fits as a function of the cumulative electron dose (number of electrons per nm^2). Fitting an exponential function to these amplitudes yields the cross section for damage to the pentacene crystal lattice at the incident electron energy corresponding to the recording; see Figure 2. The fitted function has the form $Ae^{-\sigma \cdot D} + B$, where D is the cumulative dose in units of number of electrons per nm^2, σ is the damage cross section in nm^2, and A and B are constants. By repeating the procedure described above for recordings corresponding to different incident electron energies, we obtain damage cross sections as a function of electron energy. Figure 3 shows the results of this analysis on diffraction peaks of different orders, obtained from a representative sample, four pentacene monolayers in thickness. Note again that electron energies are determined with respect to the vacuum energy.

Figure 3 shows that the damage cross section decreases sharply below 10 eV. A similar behavior is reproduced in data sets from several other samples (Figures S2−S4). For the data set represented in Figure 3, the intensity of the diffraction peaks did not decrease during the duration of the recording for electron energies below 5.5 eV. In some of the other data sets, decays were observed down to about 2 eV, with the damage cross section becoming vanishingly small for few-eV electrons. In all cases, a sharp decrease (in an almost exponential manner) in damage cross section is observed, as the energy of the incident electrons decreases below 10 eV. Changes in damage cross section span up to 2 orders of magnitude for electron energies starting from the observed damage threshold for the data set up to 10 eV. The damage cross section increases by about another order of magnitude for electron energies between 10 and 40 eV and in general shows a monotonic behavior. Finally, damage cross sections obtained from higher-order diffraction peaks are consistently higher than those obtained from lower-order diffraction peaks, as shown in both Figure 3 and the results from several other samples with very few exceptions. This observation indicates that high-resolution information, that is, short-range order, is lost before loss of order across the entire irradiated area. Faster fading of higher-order diffraction peaks has also been reported in the literature.[10,30] For completeness, Figure S5 shows a typical example of changes in the width of the Lorentzian fits over time, exhibiting a generally increasing trend.

Changes induced in the film upon irradiation are also observed in real space. During irradiation, the structure of the layer gradually loses definition and sharpness and becomes darker in bright-field images. To obtain bright-field images, a contrast aperture is placed around the 0th-order diffraction peak to exclude all the electrons which are not specularly reflected, including secondary electrons. After a sufficiently long exposure time and disappearance of the diffraction pattern, the irradiated areas look very dark for all incident electron energies in bright-field images (Figure S6). This change in the irradiated regions is also reflected in the spectroscopic features, as described below.

In general, the number of electrons reflected from an area of the sample, and hence the image intensity, is a function of the incident electron energy. By plotting the intensity versus the incoming beam energy, we obtain an intensity-vs-voltage plot, or in short, a LEEM-IV curve. A LEEM-IV curve is a spectroscopic fingerprint of the probed area and is largely determined by the unoccupied band structure of the sample above the vacuum energy.[23,24] The reflected specular intensity is directly related to the density of states (DOS) in the solid along the surface normal. A low density of unoccupied states lowers the probability that incoming electrons enter the solid, resulting in higher reflectivity. Conversely, a high DOS leads to a low reflectivity. Figure 4 shows LEEM-IV curves of a crystalline pentacene film, three monolayers in thickness, measured repeatedly on the same area. These LEEM-IV curves follow the intensity variations of the 0th-order diffraction peak, corresponding to specularly reflected electrons. After each subsequent measurement, the features of the LEEM-IV curve are diminished, meaning that a smaller fraction of the incident

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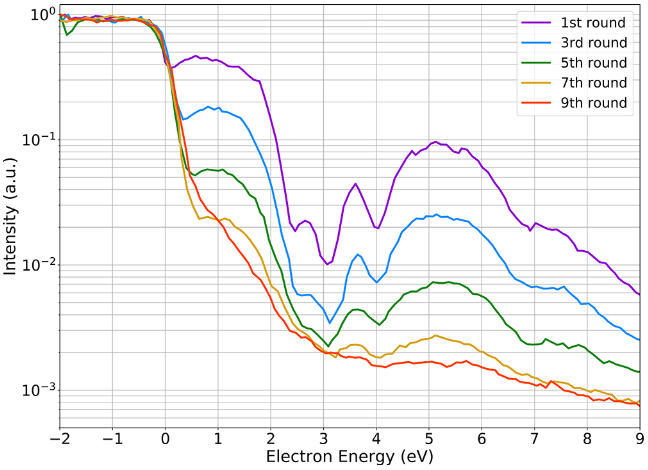

Figure 4. Diminishing of LEEM-IV features through consecutive measurements. The LEEM-IV curves correspond to the intensity of the (0,0) diffraction peak of a sample with film thickness of three monolayers. The beam current density for the measurements is 5.3 pA/μm^2.

electrons undergo specular reflection. The latter is consistent with our previous result that irradiated areas appear gradually darker in real-space images. For an area exposed to the electron beam for a sufficiently long time, all the IV curve features are lost, as can be seen in Figure 4. This indicates that the states associated with the original pentacene layer disappear, suggesting that a new material with a broad set of unoccupied states is being formed. This is the reason irradiated areas appear very dark with no intensity change in bright-field real-space images obtained by incident electrons of any energy. In a related observation, the background intensity in diffraction images is noted to increase during irradiation (Figure S7), indicating that more electrons are scattered incoherently after a period of exposure to the beam.

Finally, Figure S8 shows the changes in the electron energy loss spectra after a period of exposure to the beam. It can be inferred that the energy distribution of the secondary electrons is such that the vast majority of them have an energy of less than ~4 eV. Considering our observations about the damage cross section in pentacene layers, it can be concluded that the secondary electrons generated during irradiation contribute minimally to the damage cross sections for the incident electron energies in our study.

■ DISCUSSION

To analyze the full energy dependence of the damage cross-section curve depicted in Figure 3, we consider possible mechanisms of interaction of molecules with incoming electrons having different energies. At few-eV incident energies, "electron attachment" is regarded as the primary mechanism. It can lead to either autodetachment of the electron, leaving the molecule in an excited state, or fragmentation of the molecule, that is, the case of dissociative electron attachment (DEA), or formation of reactive negatively charged centers via rearrangement of charge within the molecule. The relative probability of each of these scenarios depends on the energetic landscape (potential energy surfaces) of the molecule. Electron attachment and formation of anions at low electron energies has been investigated with different techniques and reported for pentacene and similar molecules in the literature. In particular, mass spectroscopic studies of vapors of pentacene molecules bombarded with LEEs found that singly charged anions of pentacene could be detected for electron energies in the range 0−3 eV, demonstrating electron attachment at such energies.[31] In the same study, neutral pentacene molecules were detected, also up to 3 eV. In another similar mass spectroscopic study,[32] singly charged anions of pentacene molecules with one hydrogen missing were detected starting from ~5 up to ~11 eV, with much smaller quantities (about 100 times lower) found in the range 3−5 eV. Singly charged negative anions of other polycyclic aromatic hydrocarbons with one hydrogen missing were also detected in several other studies,[33,34] showing a distribution centered around 8 eV and becoming increasingly smaller above 10 eV and below 6 eV. In a study of vibrational states of gaseous benzene molecules probed with incident electrons, the cross section for excitation of the carbon−hydrogen bond is shown to have a resonance between 5.5 and 10 eV, with a peak at 8 eV, accompanied by a smaller resonance between 4 and 5.5 eV.[35] Electron bombardment of an aromatic thiol (Au−S−$CH_2C_6H_5$) was found to result in creation of H_2 molecules, with the yield becoming drastically smaller below ~6 eV.[36] Irradiation of *p*-terphenylthiol SAMs with LEEs was found to show a resonance centered at 7.2 eV for excitation of carbon−hydrogen bonds.[37,38]

From these results, we conclude that at energies in the range from 0 eV up to about 10 eV, the incoming electrons can attach to the pentacene molecules; however, toward the lower end of the range, the molecules most probably autodetach the extra electron, and the temporary attachment is much less likely to lead to fragmentation of the molecule. Toward the upper end of the 0−10 eV range, electron attachment will leave the molecule in a chemically reactive state with consequences that are discussed further below. The new reactive state of the molecule can be a result of scission of the carbon−hydrogen bond and the subsequent removal of a hydrogen atom from the molecule, charge reorganization after electron attachment, or an energetically excited state after detachment of the electron. The increased resistance toward damage at very low electron energies is in contrast to results from similar LEEM experiments on PMMA and the molecular organometallic EUV resist known as tin-oxo cage;[21,22] for both, it was found that electrons with energies all the way down to 0 eV (with respect to vacuum energy) can cause chemical changes in the resist layer. Lower susceptibility of aromatic organic molecules toward irradiation damage, compared to their derivatives which contain also single bonds, such as the case of pentacene and bis(triisopropylsilylethynyl) pentacene,[39,40] or compared to saturated molecules,[41] has already been reported in various studies. In agreement with our observations on pentacene layers, an inverse photo-emission spectroscopy study on pentacene films also found no remarkable change in the spectra when electrons with kinetic energy of 5 eV were used, in contrast to the case for 10 eV electrons, for which spectral changes were observed.[42]

As the incident energy of the electrons increases above a few eV, other mechanisms for interaction between the incoming electrons and the pentacene molecules become possible. For pentacene molecules bombarded with electrons, a threshold of 6.6 eV has been experimentally measured for ionization of pi-electrons of pentacene,[43−47] with more ionizations as the incident electron energy increases.[44] Ionization of sigma bonds in pentacene is identified to start at approximately 11 eV,[44] with the ionization leading to scission of carbon−hydrogen bonds starting at 15.2 eV.[43] In a related study, the ionization cross section in benzene shows a steep rise from incident electron energy of ∼9 eV (the ionization threshold in benzene) up to around 100 eV.[48] A similar behavior is expected to be the case for pentacene but starting from a lower ionization threshold. The availability of more pathways for interaction between the incident electrons and the molecules is manifested in the continuous increase of the damage cross section versus electron energy observed in Figure 3. However, DEA is assumed to contribute to damage in pentacene mostly for electron energies below ∼11 eV, given the diminished amounts of singly charged anions of pentacene molecules with one hydrogen missing detected at energies higher than ∼11 eV, as found in Ref 32. Indeed, electron attachment and formation of a transient negative ion are expected to happen for electron energies below 15 eV.[1,2,49] At higher incident electron energies, impact ionization is expected to be the dominant interaction mechanism.

The cross sections for damage to the pentacene crystal lattice obtained here are within the range of cross sections reported in the literature for interaction of electrons with gaseous benzene.[48,50−53] A lower damage cross section for pentacene films could be expected due to higher irradiation damage resistance of pentacene compared to benzene, as a result of a higher degree of electron delocalization within both the molecule and the layer with neighboring molecules.

Irradiation with electrons has been reported in various studies to lead to cross-linking within the organic layer, such as the case of 4′-nitro-1,1′-biphenyl-4-thiol SAM (incident electron energies 2.5−100 eV),[54] 1,1′-biphenyl-4-thiol SAM (incident electron energies 50 eV),[55] $CH_3(C_6H_4)_2(CH_2)_nSH$ SAM (incident electron energies 10 eV),[56] and *p*-terphenylthiol SAMs (incident electron energies 6 and 50 eV).[37,57] Hence, we propose that the mechanism behind damage to the pentacene crystalline structure is the formation of chemical bonds between nearby molecules initiated by reactive atoms. The reactive atoms are created as a result of either (dissociative) electron attachment at lower energies or impact ionization at energies higher than thresholds for scission of various bonds. This process, repeated many times across the layer, will eventually result in polymerization of the molecular film and creation of a CNM. At higher electron energies, scission of different bonds, fragmentation of molecules, and drifting away of the fragments are also possible.

This conclusion is also compatible with the LEEM-IV measurements, presented in Figure 4. In the first measurement, the LEEM-IV curve shows reflection maxima at about 2 and 5.5 eV, separated by a pronounced minimum (low reflectivity) at about 3.5 eV. As shown previously,[23,24] high electron reflectivity corresponds to a gap in the electronic band structure, that is, low DOS in the conduction band above the vacuum level. The disappearance of the reflection maxima at these energies with consecutive exposures indicates a loss of crystal order and thereby a loss of electronic structure, including these band gaps. Given that orbital energies are affected/shifted corresponding to their environment, creation of a disordered CNM is expected to lead to a more dispersed set of energies for unoccupied orbitals. This in turn results in low reflectivity and featureless LEEM-IV curves for irradiated pentacene areas compared to pristine areas showing clear dips and peaks. Polymerization of the layers, resulting in a more rugged surface, also explains loss of definition in the real-space images upon irradiation, as well as the increase in the background intensity (noncoherent scattering) in diffraction images observed in Figure S7.

■ CONCLUSIONS

Crystalline thin films consisting of two to four pentacene monolayers are grown on silicon substrates in situ in the UHV chamber of a LEEM instrument. It is observed that irradiation of the films with low-energy electrons leads to fading of their diffraction pattern at a rate that depends on the energy of the incident electrons. Cross sections for damage to the crystalline structure of the thin films are obtained by analysis of the evolution of the diffraction peaks over time. The results indicate that the damage cross section increases by more than an order of magnitude for electron energies from 0 to 10 eV and by another order of magnitude from 10 to 40 eV. Spectroscopic LEEM-IV measurements also show gradual disappearance of the unoccupied band structure as a result of continued irradiation. These observations are explained by the different mechanisms that govern the interaction of pentacene molecules with incoming electrons having different energies. Electron attachment is proposed as the dominant mechanism at low energies and a contributing factor to damage up to ∼10 eV. It can lead to scission of carbon−hydrogen bonds and removal of hydrogen (with a higher likelihood above ∼5 eV), or otherwise leave the molecule in a chemically reactive state. Impact ionization plays a bigger role as the energy of the electrons increases beyond various ionization thresholds. Scission of various other bonds and fragmentation of the molecule are assumed to happen at higher energies. The fading of the diffraction pattern and the spectroscopic LEEM-IV features is proposed to be a result of polymerization of the layer and its transformation into a CNM, triggered by scission of molecular bonds and creation of radicals. Loss of definition in real-space images and increase in background intensity in diffraction images also indicate a more disordered surface landscape, likely as a result of polymerization of the layer. From electron energy loss measurements, secondary electrons generated during exposure were found to have energies mostly below ∼4 eV and, as a result, have a negligible contribution to the damage cross sections.

The implications of these results should be taken into account in experiments and processes that expose organic samples and materials to low-energy electrons in the form of either a primary beam or as secondaries produced upon exposure of the sample to high energy electrons or photons. Note that such secondaries would possess energies within the range studied here. Given the lower damage rate at few-eV incident electron energies, experiments can be designed such that the sample is not destroyed or lasts longer during the experiment. The results can also point to the possible use of aromatic systems as electron resists with a significant energy threshold in order to reduce the effects of low-energy secondary electrons in resist exposure. This may reduce the sensitivity of the resist but also improve resolution and line edge roughness.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c06749.

Filtering procedure to remove the background from diffraction images; damage cross sections of more samples; evolution of widths of Lorentzian fits during irradiation; irradiation damage in real-space images; increase of background intensity in diffraction images due to irradiation; changes in electron energy loss spectra due to irradiation; and irradiation experiment on a HOPG flake (PDF)

AUTHOR INFORMATION

Corresponding Author

S. J. van der Molen − *Huygens-Kamerlingh Onnes Laboratorium, Leiden Institute of Physics, Leiden University, NL-2300 RA Leiden, The Netherlands*; Email: molen@physics.leidenuniv.nl

Authors

A. Tebyani − *Huygens-Kamerlingh Onnes Laboratorium, Leiden Institute of Physics, Leiden University, NL-2300 RA Leiden, The Netherlands;* orcid.org/0000-0001-8086-0067

F. B. Baalbergen − *Huygens-Kamerlingh Onnes Laboratorium, Leiden Institute of Physics, Leiden University, NL-2300 RA Leiden, The Netherlands*

R. M. Tromp − *Huygens-Kamerlingh Onnes Laboratorium, Leiden Institute of Physics, Leiden University, NL-2300 RA Leiden, The Netherlands; IBM T. J. Watson Research Center, New York, New York 10598, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.1c06749

Notes

The authors declare no competing financial interest.

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