Patterning of Self-Assembled Pentacene Nanolayers by Extreme Ultraviolet-Induced Three-Dimensional Polymerization

Hae-geun Jee,[†] Han-Na Hwang,[†] Jin-Hee Han,[‡] Jun Lim,[†] Hyun-Joon Shin,[†] Young Dok Kim,[§] Harun H. Solak,[∥] and Chan-Cuk Hwang[†,*]

[†]Beamline Research Division, Pohang Accelerator Laboratory (PAL), Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea, [‡]Department of Physics, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea, [§]Department of Chemistry, Sungkyunkwan University (SKKU), Suwon 440-746, Korea, and [∥]Laboratory for Micro and Nanotechnology, Paul Scherrer Institute, Villigen Ch-5232, Switzerland

ABSTRACT Most researchers expect extreme ultraviolet lithography (EUVL) to be used to create patterns below 32 nm in semiconductor devices. An ultrathin EUV photoresist (PR) layer a few nanometers thick is required to further reduce the minimum feature size. Here, we show for the first time that pentacene molecular layers can be employed as a new EUV resist. Nanometer-scale dots and lines have been successfully realized using the new molecular resist. We clearly show the mechanism that forms the nanopatterns using a scanning photoemission microscope, EUV interference lithography, an atomic force microscope, and photoemission spectroscopy. The molecular PR has several advantages over traditional polymer EUV PRs. For example, it has high thermal/chemical stability, negligible outgassing, the ability to control the height and width on the nanometer scale, fewer residuals, no need for a chemical development process and thus a reduction of chemical waste when making nanopatterns. Besides, it can be applied to any substrate to which pentacene bonds chemically, such as SiO_2, SiN, and SiON, which are important films in the semiconductor device industry.

U ltraviolet lithography (UVL) has been continuously improved to make it possible to continue scaling down semiconductor devices. Currently, UVL can be used to pattern linewidths as small as 32 nm.[1] Several promising technologies, including electron beam lithography (EBL), focused ion beam lithography, scanning probe lithography, and extreme ultraviolet lithography (EUVL), have been proposed to reduce the line width below 32 nm.[2−9] EUVL is considered to be the leading postoptical lithography because of its use in mass production.[10] Because EUVL employs a shorter wavelength than UVL, it is possible to fabricate narrower linewidths. Thin EUV photoresist, whose thickness is controllable on the nanometer scale, is essential to overcome a shallow depth of focus[10,11] and make fine patterns as small as 15 or 22 nm with EUVL. For this purpose, self-assembled monolayers prepared by wet chemical treatment and single atomic layers have been studied as new photoresists.[12−18] Wet chemical self-assembling techniques can introduce EUV-reactive functional groups into molecules and make it possible to control the thickness of the photoresist on the nanometer scale by changing the molecular length.[12] This method forms a chemically stable molecular film,[19] but the film can contain impurities and a long time is required for self-assembled monolayers to form.[20] On the other hand, single atomic layers made in an ultrahigh vacuum form within a short time, are clean and have an atomically well-defined structure.[13−15] However, they are

hard to use in real device fabrication because they are easily damaged in air because of their low chemical stability.

Herein, we show that a pentacene layer, which is widely used as a representative material in organic devices,[21] can be employed as a new EUV resist, combining the strong points of both methods. When the pentacene layer is exposed to EUV radiation, quasi-polymerization occurs through cross-linking between the molecules. While the pentacene molecules in the non-EUV-irradiated regions are easily removed upon annealing up to 500 K, those in the EUV-irradiated regions are stable up to 1100 K. Therefore, selective EUV exposure followed by annealing allows molecular nanopatterns to be fabricated on the surface.
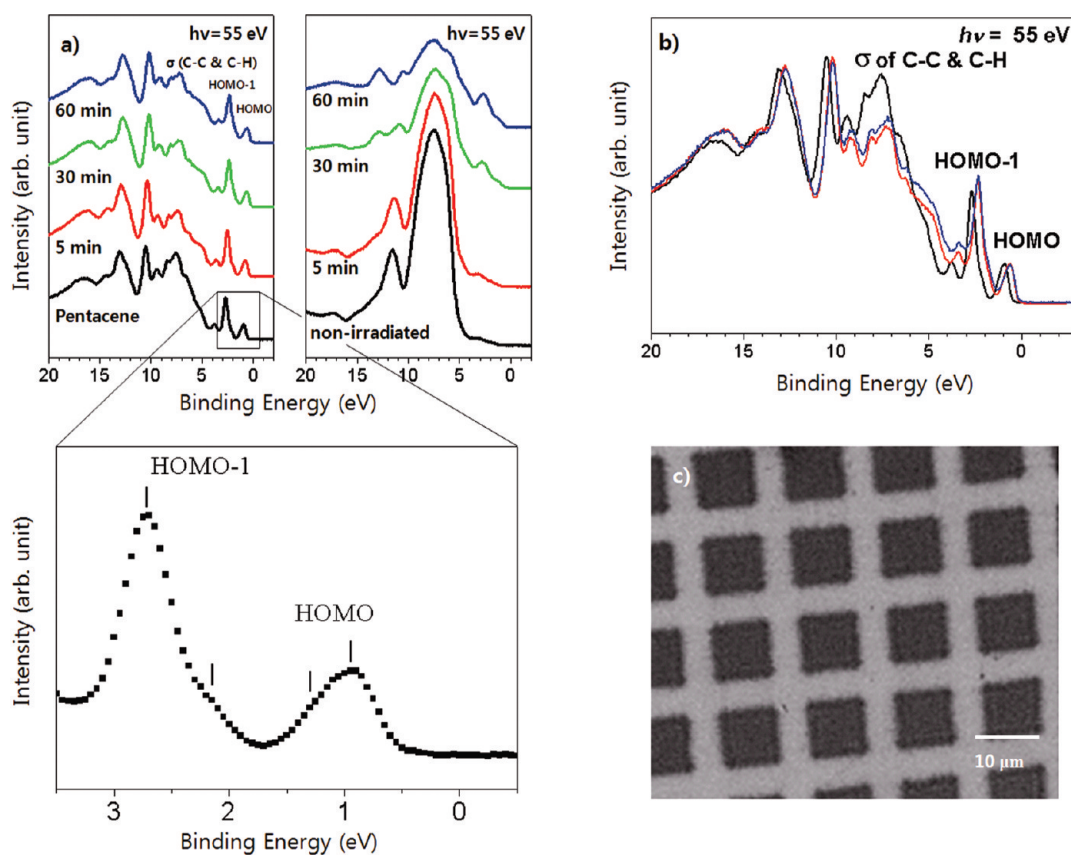
Figure 1. (a) Valence-band spectra of an EUV-irradiated samples for different irradiation times before (left panel) and after (right panel) annealing at about 500 K. (b) Valence-band spectra of samples irradiated for 0 min (black line), 30 min (red line), and 60 min (blue line), which were selected from panel a for comparison. (c) An SEM image of a sample that was exposed to EUV radiation through a gold mesh (10 × 10-μm^2 hole, 5-μm-wide line) and then annealed using direct resistive heating.

RESULTS AND DISCUSSION

The valence-band spectra in Figure 1a (left panel) show how a pentacene layer reacts with EUV light with a wavelength of 13.4 nm ($E = 92.5$ eV). The bottom spectrum was taken from a 300-Å pentacene/SiO$_2$ layer. The EUV exposure time was increased from the bottom to the top (0−60 min). Four structures appeared at ∼0.94, 1.29, 2.14, and 2.71 eV in the expanded view of the spectrum because of intermolecular $\pi-\pi$ interactions[22] from the pentacene/SiO$_2$ layer. The two structures at ∼0.94 and 1.29 eV originate from the highest occupied molecular orbital (HOMO) and the others correspond to HOMO-1.[23] The spectrum of the pristine molecular layer was almost unchanged when the surface was exposed to EUV radiation in the initial stage. However, we found the following spectral changes after about an hour of exposure (top spectrum in Figure 1a, left). The spectrum of the pentacene layer shifted by about 0.35 eV toward a lower binding energy. After aligning the spectra with respect to the HOMO states before exposure, we found that the structures between 5.5 and 10.0 eV decreased, those around 3.7 eV increased, and the π bonds maintained their intensities and shapes. This suggests that EUV exposure leads to cleavage of the C−H bonds and the formation of new

C−C bonds without any considerable change in the π bonds. It is difficult to tell whether the process is cycloaddition-mediated or due to direct C−H bond cleavage. When annealed up to 500 K for a few seconds (Figure 1a, right), the molecular layer remained on the surface in the case where sufficient EUV irradiation was provided (upper spectrum). However, the valence-band spectrum of the non-EUV-irradiated surface (bottom spectrum) is almost the same as that of the SiO$_2$ substrate before pentacene deposition, which means that the silicon oxide substrate is revealed by the desorption of pentacene in the non- or briefly irradiated regions. The C 1s core level spectra show the same result as the valence-band spectra (not shown here). The C 1s peak intensity is almost unchanged in the EUV-irradiated regions, but it almost totally disappears in the nonirradiated regions upon annealing. To determine whether fine patterns can be made, a pentacene layer with a thickness of about 300 Å was selectively exposed to EUV radiation through a gold mesh.[14,15] Figure 1c shows a scanning electron microscope (SEM) image of the molecular layer after selective EUV exposure and subsequent annealing up to 500 K. The white lines are the regions where pentacene desorbed. The black squares indicate the regions covered with penta-
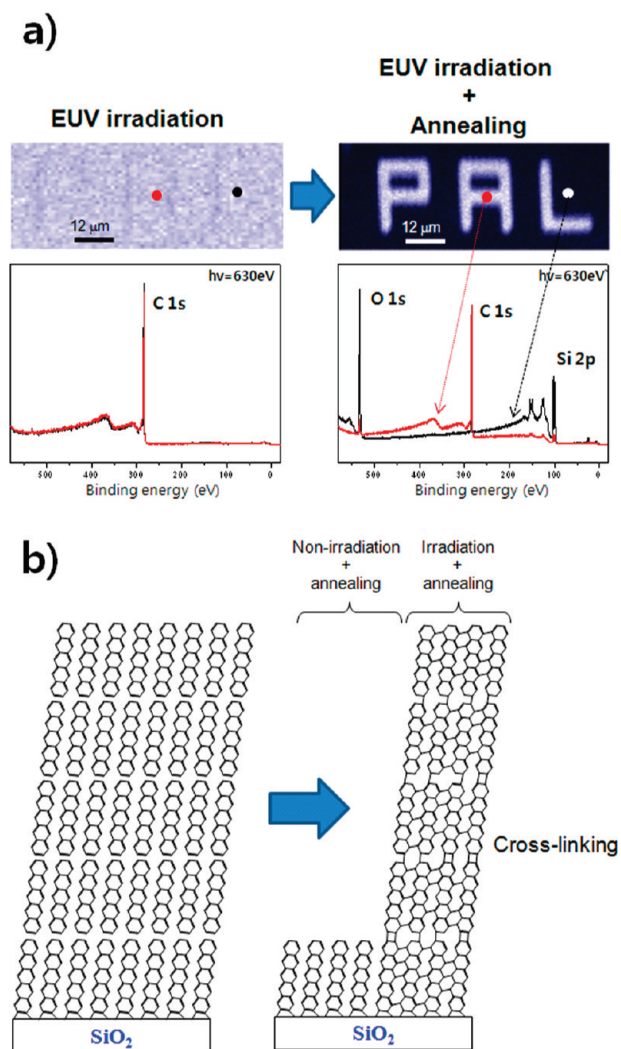
Figure 2. (a) SPEM image and μ-PES spectra of a sample that was exposed to finely focused EUV radiation to write the characters "PAL" before (left panel) and after (right panel) sample heating. Survey spectra (bottom graphs) from EUV-exposed (red) and -unexposed (black) regions. (b) Schematic diagram of the patterning process based on EUV-induced cross-linking between pentacene molecules.

cene. The regions where the pentacene desorbed were full of secondary electrons, although their real height was lower than that of their surroundings. These results demonstrate that a pentacene molecular layer can be applied as a negative EUV resist.

A finely focused EUV beam with a wavelength of 1.9 nm (E = 630 eV) was used to write arbitrary characters directly on a pentacene layer with a thickness of about 300 Å.[13,14] Scanning photoemission microscope (SPEM) images were taken for the C 1s core level before and after annealing the sample that was selectively exposed to focused EUV radiation, as shown in Figure 2a (upper image). To analyze the differences between the EUV-exposed and -unexposed regions, we obtained μ-photoemission spectroscopy (PES) data, as shown in Figure 2a. It is difficult to see the written characters before annealing because the PES spectra are almost the same for both regions. However, the pentacene is des-

orbed in the non-EUV-irradiated regions but remains in the EUV-irradiated regions after annealing. This renders the three characters—PAL—clearly visible. Figure 2b shows the process by which fine patterns are fabricated by EUV irradiation. The pentacene makes chemical bonds with the underlying Si oxide in the initial adsorption stage, but physisorption takes place from the second layer. Previous X-ray absorption spectroscopy and X-ray diffraction studies show that a pentacene layer on silicon oxide has a good crystalline structure, as illustrated in the left side of Figure 2b.[22,24] The molecular layer of pentacene is linked together in both the lateral and vertical directions upon EUV irradiation. If the sample exposed selectively to EUV radiation is annealed up to 500 K, the physisorbed pentacene desorbs completely, but the cross-linked molecules remain on the surface, resulting in fine molecular patterns on the surface, as displayed in Figures 1c and 2a. Because a spot size of 15 nm can be achieved using a Fresnel zone plate,[25] it may be possible to pattern pentacene layers on the nanometer scale.

To understand the adsorption behavior, pentacene, with a thickness of ~1 monolayer (ML), was adsorbed on a clean silicon oxide formed in UHV (see Supporting Information). The pentacene seemed to chemically bond to the surface because the peaks from the suboxides shifted toward higher binding energies in the Si 2p core level spectrum and did not completely desorb when the sample was heated at ~500 K (see Supporting Information). When the pentacene multilayers are adsorbed and then heated at ~500 K, all of the physisorbed pentacene is completely removed from the surface, except for the initially chemisorbed layer. However, when the pentacene multilayers are exposed to EUV radiation, the C 1s satellites and valence-band structures of the multilayers are changed, and the layers are not removed after annealing at ~500 K. This results from quasi-polymerization of the molecular layer through a 3-dimensional cross-linking process between the pentacene molecules. The pentacene layers, which make chemically strong bonds with the surface because of polymerization, remain on the surface even after annealing up to 500 K, while hydrogen atoms are desorbed upon annealing at temperatures higher than 500 K. This cross-linking process is independent of the incident photon energy, which indicates that it originates from EUV-induced secondary electrons.[26] This suggests that previously observed contributions from secondary electrons to the patterning of aromatic organothiol and organosiloxane monolayers using e-beam and X-ray exposure tools may be a dominant mechanism in high-energy patterning.[27−29] Therefore, one could also uti-
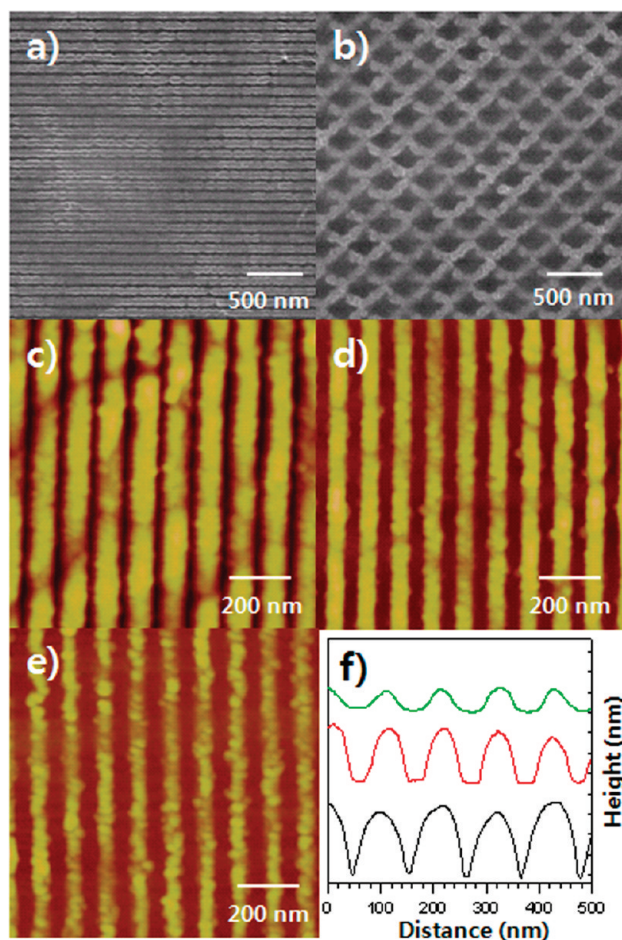
Figure 3. SEM images of (a) nanowires and (b) nanodots fabricated by EUV-IL. The black regions are the places where the pentacene remained after EUV irradiation and subsequent annealing. AFM images of nanowires fabricated with (c) long, (d) medium, and (e) short EUV irradiation times. (f) Line profiles of nanowires in (c) (black), (d) (red), and (e) (green), where the vertical distance between the sticks is 5 nm.

lize other electromagnetic waves such as ultraviolet waves and X-rays, as well as electron sources, for patterning the pentacene layer.

We tried to form nanopatterns on a pentacene layer using EUV-interference lithography (EUV-IL).[30] SEM and atomic force microscope (AFM) images were taken after the sample was exposed to interfering EUV beams through transmission gratings and then annealed up to 500 K. Figure 3 panels a and b show the SEM images of the nanowires and nanodots fabricated with EUV-IL, using two- and four-beam interference, respectively.[31] The black regions are the places where the pentacene remained after EUV irradiation and subsequent annealing. The period of the line pattern and the size of the dots were about 105 nm and 200 × 200 nm^2, respectively. Figure 3 panels c−e display topographic images of the nanowires that were fabricated with different EUV dosages (11000, 6100, 3400 mJ/cm^2). Their line profiles are drawn in Figure 3f. The line widths were 65, 60, and 35 nm and the average heights were 15, 10, and 8 nm for the long (c and black line in f), middle (d and

red line in f), and short (e and green line in f) irradiation times, respectively. The height and width of the line pattern became larger with increasing irradiation time because of enhanced cross-linking between the pentacene molecules at higher exposure times. This means that the height and width of the nanopatterns can be adjusted by changing the irradiation time and, thus, controlling the degree of polymerization.

As shown in this work, pentacene has the potential to be used as an EUV resist for fabricating nanopatterns. While impurities are easily included in the general photoresist coating process, there is a negligible amount of contaminants on the pentacene layer, as confirmed by PES. Besides, the molecular layer does not show any detectable outgassing. The resolution of the pattern could be maximized using pentacene because one can manipulate the thickness of the pentacene layer on the nanometer scale by controlling the deposition rate and time. Because the pentacene layer is chemically stable, clean nanopatterns can be formed even if the sample exposed to EUV radiation is kept in air for several days. Fine patterns fabricated with EUV radiation show high thermal stability up to 1100 K. One can also manipulate the width and height of the patterns by changing the irradiation time and, thus, controlling the degree of polymerization. In general, wet development is used in the semiconductor industry to remove resists by immersing the sample in developing agents,[32] but it is very difficult to remove the residuals of the resists and exclude contamination originating from the liquid developing solutions.[33] When pentacene is used as a resist, the cleanliness of the sample can be assured because there is a relatively small amount of residual remaining after heating the sample and no developing solution is needed. Furthermore, not needing wet chemical development makes the process simple and reduces chemical waste during patterning. It may also be possible to functionalize the molecular patterns using dangling bonds generated after the desorption of hydrogen upon annealing. It was previously reported that pentacene does not bond directly to SiO$_2$ substrate.[34] On the contrary, we observed that it forms direct bonding with SiO$_2$, which makes it possible to generate nanopatterns. If the pentacene is not anchored, the cross-linked molecules will not be attached to the substrate. This means that patterning with pentacene can be applied to a variety of substrates to which pentacene bonds chemically, in particular, to SiO$_2$, SiON, and SiON, which are important in the device industry. Because cross-linking originates from secondary electrons, the same process can be applied to UVL, EBL, and X-ray lithography using shorter wavelengths than EUVL.

METHODS

All experiments except for the EUV-IL were carried out at the 3A2, 7B1 and 8A1 beamlines of the Pohang Accelerator Laboratory (PAL) in Korea.[35] The base pressures of the systems were below 3.0×10^{-10} Torr, and the pressures of background gases such as H_2O, H_2, CO_2, and CO were maintained below 5×10^{-11} Torr, as confirmed by quadrupole mass analyzers. Pentacene, with a thickness of about 300 Å, was deposited on a silicon oxide substrate, and its adsorption was characterized by synchrotron radiation PES. EUV radiation with energies of 92.5 eV ($\lambda = 13.4$ nm) and 650 eV (1.9 nm) was irradiated onto the pentacene layer. Here, we used three irradiation methods: projection printing through a gold mesh (square holes with a size of 250×250 μm^2 and wires with a thickness of 20 μm) in front of the sample,[14,15] direct writing to make arbitrary patterns using a focused beam,[13,14] and EUV-IL. In the case of direct writing, EUV radiation ($\lambda = 1.9$ nm) was focused into a beam with a diameter of ~1 μm to pattern one pixel at a time. The EUV-IL exposures were performed at the XIL beamline of the Swiss light source,[22] where fully coherent EUV radiation could be utilized.

Supporting Information Available: Survey spectra showing pentacene desorption behavior and Si 2p core level spectra before/after ~1 ML pentacene adsorption on clean SiO_2/Si. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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