Scalable Sub-micron Patterning of Organic Materials Toward High Density Soft Electronics

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The success of silicon based high density integrated circuits ignited explosive expansion of microelectronics. Although the inorganic semiconductors have shown superior carrier mobilities for conventional high speed switching devices, the emergence of unconventional applications, such as flexible electronics, highly sensitive photosensors, large area sensor array, and tailored optoelectronics, brought intensive research on next generation electronic materials. The rationally designed multifunctional soft electronic materials, organic and carbon-based semiconductors, are demonstrated with low-cost solution process, exceptional mechanical stability, and on-demand optoelectronic properties. Unfortunately, the industrial implementation of the soft electronic materials has been hindered due to lack of scalable fine-patterning methods. In this report, we demonstrated facile general route for high throughput sub-micron patterning of soft materials, using spatially selective deep-ultraviolet irradiation. For organic and carbon-based materials, the highly energetic photons (e.g. deep-ultraviolet rays) enable direct photo-conversion from conducting/semiconducting to insulating state through molecular dissociation and disordering with spatial resolution down to a sub-μm-scale. The successful demonstration of organic semiconductor circuitry promise our result proliferate industrial adoption of soft materials for next generation electronics.

Recently developed high-performance organic and carbon-based materials have demonstrated charge carrier mobilities and conductivities greater than 10 cm² V⁻¹ s⁻¹ and 10⁻³–10⁴ S cm⁻¹, respectively, which are superior to those of industrial standard materials such as amorphous silicon and indium-tin-oxide. Although the outstanding electrical properties of such soft materials position them as promising building blocks for next-generation flexible electronics, reliable and scalable fine-patterning technology should also be accompanied for the realization of high-density and multi-functional soft electronics. Typically, proper isolation/patterning of the functional materials is required to suppress parasitic and off current, leading to less cross-talk between neighboring devices and minimum power consumption in high-density integrated systems. Fluorinated photoresists using an orthogonal solvent, photochemical dimerization of specific organic molecule, pre-patterned self-assembled monolayers, and many other techniques have been proven to be efficient methods for patterning organic and carbon-based materials. In this report, we demonstrate a facile, general, and high-throughput patterning method that is applicable to all organic and carbon-based materials with spatial resolution down to a sub-μm-scale. The success of this method is attributed to the properties of deep-ultraviolet irradiation, which is capable of direct photo-conversion from conducting/semiconducting to insulating state on spatially selective areas.

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and various direct printing techniques have been used to pattern such soft materials; however, several drawbacks, such as the process complexity, limited choice of materials, low throughput, and the resolution limit, have proven problematic for industrial realization. Mainly based on photo-oxidation, the photobleaching of light emitting materials have been applied for the high-resolution patterning of organic light emitting diode (OLED) devices. Although the photobleaching process was quite successful for the monochromatic OLED device patterning, the approach was only demonstrated for controlling fluorescence of π-conjugated materials. Here, we report a facile and general route to achieve scalable high-resolution (sub-micron) patterning of organic and carbon-based materials for device and material integrations via photochemically induced molecular disordering. Upon deep-ultraviolet (DUV) irradiation, the soft matters experienced dissociation of specific chemical bonds within molecules as well as the loss of inter-molecular ordering, transforming them into a non-functional state. Spatially selective DUV irradiation enables large arrays of patterned functional devices on a substrate. Various organic and carbon-based thin-film-transistors were fabricated using this patterning approach; the resulting transistors exhibited well-defined active material isolation (current on/off ratio: >10^7) and minimized parasitic current (on the order of pA). The transistors were used to fabricate low-power consumption integrated circuits on both rigid and flexible substrates without compromising their individual device performance.

Result and Discussion
Room-temperature photochemical routes via deep-ultraviolet (DUV) irradiation have been known to be effective in cleaving specific chemical bonds, which inspired us to explore the possibility of the chemical-free fine-patterning of organic and carbon-based functional materials using high-energy photon irradiation. Figure 1a shows a schematic of the direct photochemical patterning of the soft materials via DUV exposure through a quartz photomask. The high-energy photons, from low pressure mercury lamp (LPML) [90% 4.88 eV (254 nm) and 10% 6.70 eV (185 nm)] or radio frequency (RF) discharge excimer lamp [7.21 eV (172 nm)], exceed the typical dissociation energies of the molecular bonds of soft materials.
materials, such as the dissociation energies of C–S (2.69 eV), C–C (3.65 eV), C–H (4.25 eV), and C–C (6.32 eV)\(^2\). In organic and carbon-based electronic materials, this DUV irradiation can be expected to induce chemical bond dissociation and the subsequent loss of carrier transport mechanisms, such as molecular packing for \(\pi-\pi\) interactions\(^2\), crystalline domain interconnections\(^2\), and electron delocalization within extended carbon materials\(^2\). Although we typically applied low cost LPML irradiation for chemically weak organic semiconductors, the strong internal chemical bonding in carbon materials requires high energy excimer lamp irradiation with residual oxygen. Figure 1b shows the cross-polarized optical microscopy (CPOM) images of DUV-patterned 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) line arrays on a silicon substrate with an exposure time of 30 min. The C8-BTBT films in unexposed areas exhibit strong birefringence, which is indicative of molecular ordering, whereas DUV-irradiated regions don't respond to the polarized light (Supplementary Fig. 1). This result suggests that the crystalline molecular structures change into an amorphous phase via the photochemical deactivation route. Fine patterning of the C8-BTBT organic films to sub-micron linewidths is also shown in the bottom of Fig. 1b. As shown in Fig. 1c, this photochemical route can be applied to various organic and carbon-based materials, including poly(3-hexylthiophene) (P3HT), poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), graphene and poly(3-dodecylthiophene) (P3DDT)–wrapped carbon nanotube (CNT) films, thereby creating a periodic change of contrast. The full utilization of this approach at the device and system levels would be greatly facilitated by the development of a scalable fabrication method that overcomes the resolution limitation while providing uniform patterned structures. Figure 1d shows a photograph of a DUV-patterned C8-BTBT film on a 4-inch silicon wafer. The residue-free and uniformly developed organic patterns over the entire wafer are clearly demonstrated in the four-quadrant high-magnification CPOM images in Fig. 1d.

Grazing incidence X-ray diffraction (GIXRD) profiles of the organic semiconductor films were collected to investigate the effect of DUV irradiation on the high degree of inter-molecular ordering within organic semiconductors. As shown in Fig. 2a–c, the as-prepared films of C8-BTBT and P3HT and poly-[2,5-bis(2-decyltetradecyl)pyrrolo[3]pyrrole-1, 4-(2H,5H)-dione-(E)-(1,2-bis(5-thiophen-2-yl) selenophen-2-yl)ethene] (P-29-DPPDTSE)\(^2\) showed apparent out-of-plane Bragg diffraction peaks at each Qz vector; these peaks represent the well-ordered alkyl chain stacking distance normal to the substrate. With increasing DUV irradiation time, the diffraction peaks obviously decreased in intensity and

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\begin{align*}
Q_z (\text{Å}^{-1}) & = 1.80, 1.00, 0.20, 0.04, 0.02, 0.01 \\
\text{a} \quad Q_z (\text{Å}^{-1}) & = 1.00, 0.40, 0.10, 0.04, 0.02, 0.01 \\
\text{b} \quad Q_z (\text{Å}^{-1}) & = 1.00, 0.40, 0.10, 0.04, 0.02, 0.01 \\
\text{c} \quad Q_z (\text{Å}^{-1}) & = 1.00, 0.40, 0.10, 0.04, 0.02, 0.01
\end{align*}
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Figure 2. Intermolecular disordering and chemical-bond dissociation of DUV-exposed small molecule, polymer, and carbon-based films. GIXRD patterns of Bragg diffraction peaks of (a) C8-BTBT (small molecule), (b) P3HT (polymer), and (c) P-29-DPPDTSE (high-performance polymer) in the Qz direction (reciprocal space) as a function of DUV irradiation time. Gradual decreases in the intensity of Bragg diffraction peaks are clearly visible with increased DUV exposure time. Raman spectra of (d) C8-BTBT, (e) P3HT, and (f) P3DDT-wrapped CNTs, indicating the disappearance of organic-related characteristic peaks after DUV irradiation.

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\begin{align*}
\text{Intensity (a.u.)} & = 1300, 1500, 1600, 1700, 1800, 1900 \\
\text{Raman shift (cm}^{-1}) & = 1300, 1500, 1600, 1700, 1800, 1900 \\
\text{d} \quad \text{Intensity (a.u.)} & = 1300, 1500, 1600, 1700, 1800, 1900 \\
\text{e} \quad \text{Intensity (a.u.)} & = 1300, 1500, 1600, 1700, 1800, 1900 \\
\text{f} \quad \text{Intensity (a.u.)} & = 1300, 1500, 1600, 1700, 1800, 1900
\end{align*}
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Undoubtedly, DUV-exposed device exhibits a negligible IDS as a consequence of photochemical degradation, which is confirmed by the transfer curves of Fig. 3a–d and Supplementary Fig. 7, which are almost identical to the physical isolation cases. The photochemical reaction of relatively poor UV sensitive organic materials can be used to isolate the channel region. CPOM images of small-molecule-based OTFTs clearly indicate the isolated channel region (Supplementary Fig. 6 and the inset of Fig. 3a). Figure 3a–d and Supplementary Fig. 7 clearly show improvements in the transfer curves of these soft-material-based TFTs after their semiconducting layer was isolated via spatially selective DUV exposure. Without proper isolation of the semiconducting layers, the off-state current (I_\text{off}) is roughly one-tenth of the drain current (I_D) and relatively low current on/off ratios (~10^4) were observed in most of the devices. These undesired/parasitic currents are often associated with cross-talk between adjacent devices in high-density integrated circuits, which becomes increasingly problematic when device dimensions are downscaled. Apparently, photochemical isolation enables a substantial decrease of I_GS by more than 4 orders of magnitude while simultaneously increasing the field-effect mobility (\mu) of organic semiconductors. The high UV dose requirements were also reported on complete organic-patterned devices could be achievable with our chemical-free DUV irradiation (Supplementary Fig. 12). Figure 4a shows a simple inverter circuit and its characteristics measured from P-29-DPPDTSE OTFTs with a β of 60%.
10 on a PI film before and after DUV isolation. We observed an approximately 3 orders of magnitude smaller supply current (I_on) and noticeable reduction of supply current (I_DD) while maintaining almost identical or enhanced gain in the inverter by active layer isolation via DUV irradiation (Supplementary Fig. 13). Figure 4b shows a relation of the oscillation frequency and the single-stage propagation delay as a function of supply voltage, exhibiting an oscillation frequency up to 7.21 kHz at V_DD = −20 V. The corresponding output waveforms at the low and high supply voltage of V_DD = −3 V and −20 V are shown in Fig. 4c,d, respectively. Figure 4e shows the flexible high-performance organic circuits wrapping around the steel rod (R = 1 mm), highlighting the successful isolation of devices packed at fairly high density (approximately 3.8 × 10^3 cm^−2). Additionally, based on an AIM-SPICE simulation, the power consumption of a 7-stage ring oscillator can be reduced by about 20% after the organic channel isolation due to the reduction of leakage current (Supplementary Fig. 14).

In summary, we demonstrated that spatially selective DUV irradiation can enable high-density fine pattern formation for a wide range of organic and carbon-based films, including small molecules, polymers, CNT, and graphene. This single-step, chemical-free DUV deactivation takes advantage of atomic-level bond dissociation and loss of inter-molecular ordering within the soft functional materials. Therefore, we envision that this selective DUV irradiation could offer an innovative scientific and technological approach to the low-cost and large-volume patterning of high-density organic and carbon-based electronics with excellent uniformity and resolution.
Methods

We prepared the organic and carbon-based films using simple solution processes (see the supplementary information for details). For the LPML DUV irradiation, a DUV generator (SAMCO UV-1) equipped with a low-pressure mercury lamp, which emitted main peaks at 253.7 nm (90%) and 184.9 nm (10%), was used; the radiation intensity was 18–23 mW cm\(^{-2}\). For the 172 nm high energy irradiation, RF discharge excimer lamp (Hamamatsu Photonics K.K. EX-mini L12530) was used; the radiation intensity was 50 mW cm\(^{-2}\). The DUV irradiations were performed with chrome-patterned quartz masks under N\(_2\) atmosphere.

The crystalline nature of DUV-patterned C8-BTBT small-molecule organic films was visualized using cross-polarized optical microscopy. Other patterned films of soft materials, including P3HT, PEDOT:PSS, and graphene were visualized using optical microscopy. Grazing incidence wide-angle X-ray scattering (GIWAX) measurements were performed at the X9 beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. Surface morphologies of organic films before and after DUV irradiation were examined using AFM system in non-contact mode. Raman spectra of organic films were obtained with a confocal Raman spectroscopy system.

For the fabrication of various OTFTs, organic semiconductor films were contacted by 50-nm-thick thermally evaporated Au electrodes on a heavily doped silicon wafer (gate) bearing a 200-nm thermal oxide. For individually addressable OTFTs and circuit fabrication, a 50-nm-thick sputtered Cr film as a gate electrode on a glass substrate and on a PI film were patterned by conventional photolithography. 35-nm-thick Al\(_2\)O\(_3\) as a gate insulator was vacuum-deposited using atomic layer deposition system at 100°C. Source and drain electrodes with Cr/Au (3/50 nm) were formed by a lift-off process. All devices and circuits measurements were performed with an Agilent 4156 C semiconductor parameter analyzer under dark and ambient-air conditions.

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Author Contributions
S.K.P. designed the project and supervised the experiments. J.K., M.-G.K., S.J., J.K., J.-W.J., W.L. and C.H. carried out the experiment and data analysis. J.M. and L.Y. performed the grazing incidence X-ray diffraction measurement and interpreted the results. Y.-H.K., Y.-Y.N., J.Y.J. and Y.-H.K. provided the materials and in-depth analysis of results. J.K., M.-G.K., Y.-H.K. and S.K.P wrote the manuscript. All authors read and commented on the manuscript.

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