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Patterning of an amine-terminated nanolayer by extreme ultraviolet

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The adsorption of NH_3 molecules on the $Si(100)2 \times 1$ surface constructs a cleaner and more well-defined amine layer than self-assembled monolayer such as aminosilylated layer, which make it possible to study photoinduced reactions between amines and monochromatic light with shorter wavelength than ultraviolet, i.e., extreme ultraviolet and soft x ray. We report that the molecular layer of amine groups reacts with extreme ultraviolet and soft x ray, which can be used to make fine patterns on the amine-terminated layer. The amine patterning with the leading postoptical lithography using extreme ultraviolet could be applied to fabricating future molecular nanodevices. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2803216]

Amine group-terminated surfaces have been used as substrate for fixating nanoparticles[1] and biological molecules, such as DNA,[2] enzymes,[3] and antibodies,[4] and finally, they can be applied to fabricating molecular nanodevices. Patterning amine layer in micro- or nanoscale is a key process to reach the final goal. Ultraviolet lithography (UVL) has been a standard tool in patterning process for several decades. However, its ability to make nanopatterns on a wafer is now limited to a feature size of 45 nm.[5] In order to overcome the limit, extreme ultraviolet lithography (EUVL) has been proposed as a leading postoptical lithography.[6,7] Therefore, the interaction of amines with EUV is a fundamental issue for making future molecular nanodevices based on EUVL.

Polymer films with a thickness of micrometer to several hundreds of nanometers have been employed as photoresist (PR) for manufacturing practical devices in UVL.[8] However, their application to EUVL has significant drawbacks such as shallow penetration depth of EUV by high optical absorbance, blur of patterned images due to smaller depth of focus than PR thickness and due to back scattering of electrons at PR surface.[9] Thin polymer films with a thickness of tens of nanometers or self-assembled monolayers (SAMs) with monomolecular thickness have been suggested as a new platform to overcome these problems. Some research groups reported their possibility as PR and practical applications in lithography.[8,10] These monomolecular layers are formed by immersing a substrate into a solution of surface-active materials or by spin coating. To our knowledge, impurities in solution and atmosphere can cause several undesired problems such as nonuniform density, irregular orientation, and height fluctuation during the formation. From long experience in surface science field, the adsorption of NH_3 on the $Si(100)2 \times 1$ surface is well known to construct uniform and structurally well-defined amine groups, because the molecules adsorb softly on the underlying crystalline surface, where broken bonds are regularly distributed. Therefore, this system was chosen as a model system in this work to study the interaction between amines and EUV. The clean and well-ordered amine layer was observed to react with mono-

chromatic light with shorter wavelength than UV, i.e., EUV and soft x ray. We used EUV near the 13.4 nm wavelength, which is being applied to practical EUVL in device industry. The EUV-induced surface modification at this wavelength has not been reported for the NH_3/Si, amine-terminated SAMs, and other representative well-defined molecular systems, such as H/Si (Ref. 11) and Cl/Si.[12] We report that the surface modification can be used to make fine patterns of amine groups.

Figure 1 is a schematic diagram of the amine groups patterning on the Si(100) surface. First, the Si(100) sample was put inside the chamber with a base pressure of $\sim 2 \times 10^{-10}$ Torr. The sample was directly heated up to 1250 °C by passing dc through it and the temperature was maintained for a few seconds to remove the native SiO_2 layer and some
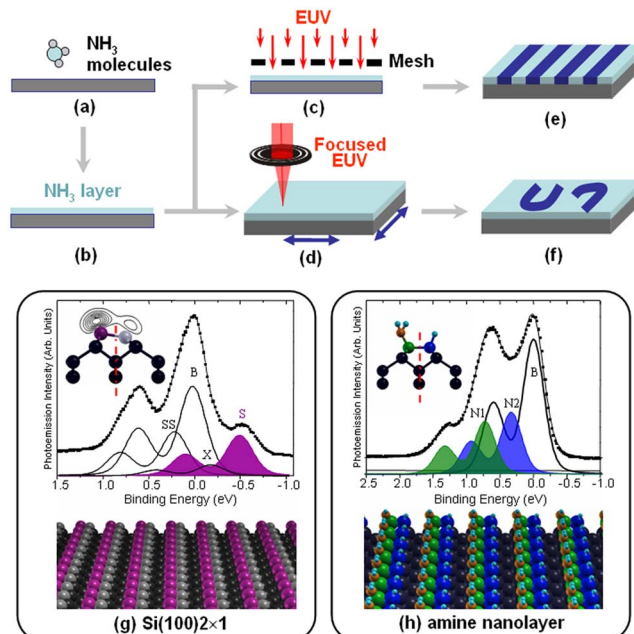

FIG. 1. (Color online) [(a)–(f)] Schematic illustration of the patterning of an amine-terminated nanolayer through an EUV-induced surface modification. Structural models and Si 2p core level spectra of (g) the bare $Si(100)2 \times 1$ and (h) the amine nanolayer on the Si(100) surface.

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carbon contaminants. This procedure was repeated under 2×10^{-9} Torr to prevent carbon and oxygen contaminations by residual gases inside the chamber. After the heating procedures, the clean Si surface was obtained. Then it was exposed to ammonia (NH_3) gas of 10 L (for 100 s at the partial NH_3 pressure of 10^{-7} Torr, 1 L $= 10^{-6}$ Torr s) to make the ammine layer at room temperature [Fig. 1(a)]. At room temperature, NH_3 molecules are dissociated into amine ($-NH_2$) and hydrogen ($-H$), then the dissociated species bond easily with the reactive dangling bonds revealed on the clean Si(100) surface.[13] As a consequence, a thin amine-terminated layer is formed on the Si(100) surface [Fig. 1(b)]. The clean and ammine terminated surfaces were confirmed by synchrotron radiation photoemission spectroscopy (PES). After the base pressure was recovered, EUV or soft x ray was irradiated on the amine ($-NH_2$) nanolayer. Here, two irradiation methods were used; projection printing by irradiation through a gold mesh (hole of 250×250 μm and wire of 20 μm thickness), as shown in Fig. 1(c), and direct writing to make arbitrary patterns using focused beam [Fig. 1(d)]. In direct writing, EUV ($\lambda = 1.9$ nm) is focused into ~ 1 μm to pattern one pixel at a given time. The amine-terminated layer is chemically transformed into silicon nitride on EUV-exposed regions.[14] Different chemical properties between exposed and unexposed regions make a chemical pattern on the surface [Figs. 1(e) and 1(f)]. Surface core level shift was employed to confirm whether the clean and amine-terminated surfaces were realized in these experiments. The most striking characteristic of the Si(100) surface is asymmetric dimers with reactive broken bonds [Fig. 1(g)].[15] Since up dimers (purple atoms) have rich valence electrons, their Si 2p core level (S) appears at a lower binding energy of ~ 500 meV than the bulk peak (B).[16] The asymmetric dimers become symmetric as the broken bonds are saturated with the amines and the hydrogens, as shown in Fig. 1(h),[13] where the structures are slightly exaggerated for simplicity. Actually, the building block in the side view and their inverse structure for the plane indicated with dashed line are randomly distributed at room temperature. The Si 2p peak from the Si dimers bonded with nitrogen (denoted by N1) is clearly separated from the bulk peak due to the large difference in electronegativity between silicon and nitrogen. The strong N1 component indicates that Si$-$NH$_2$ was widely formed on the surface.

All experiments in this paper were carried out in UHV environment. The base pressure of the system was $\sim 2.0 \times 10^{-10}$ Torr and background gases such as H_2O, H_2, CO_2, and CO were maintained below 5×10^{-11} Torr, as confirmed by a residual gas analyzer. The chamber pressure was increased to $\sim 9 \times 10^{-10}$ Torr during the irradiation through a Au mesh and $\sim 5 \times 10^{-9}$ Torr during the focused beam irradiation. Gases desorbed from the Au mesh, pin hole, or zone plate in front of the sample may be responsible for the increase of the chamber pressure.

The amine-terminated layer was exposed to EUV ($\lambda = 1.9 \sim 11.8$ nm, photon flux of 3×10^{12} photons/s cm^2) from the 7B1 bending magnet beamline in Pohang Accelerator Laboratory for 1 h, but no change was observed. This is a natural consequence if we consider that EUV or soft x ray is generally used to analyze solid surface without destroying its state. The amine-terminated nanolayer then was exposed to highly brilliant EUV of $\lambda = 11.8$ nm (photon flux of 2×10^{14} photons/s cm^2) from the 8A1 undulator beamline
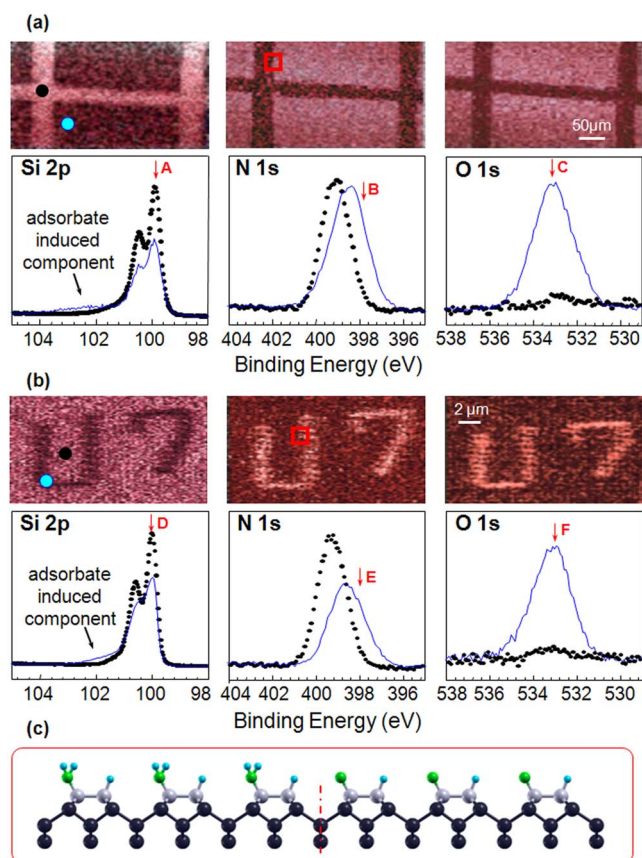

FIG. 2. (Color online) SPEM images of fine patterns and μ-PES spectra obtained from exposed (blue dot in SPEM image) and unexposed regions (black dot in SPEM image) for (a) $\lambda = 11.8$ nm and (b) $\lambda = 1.9$ nm. The PES spectra from exposed and unexposed regions are represented by blue solid line and black dot, respectively. (c) Atomic model of the boundary between exposed (right side) and unexposed (left side) regions as marked with red rectangle.

through a gold mesh for 1 h [Fig. 1(c)]. Scanning photoelectron microscopy (SPEM) images for Si 2p, N 1s, and O 1s core levels show that mesh patterns were formed on the surface [Fig. 2(a)]. μ-PES were recorded at both exposed and unexposed regions. Notice that the N 1s core level binding energy is lowered by ~ 0.7 eV, indicating that the amino group ($-NH_2$) is transformed to silicon nitride upon EUV irradiation.[14] A similar experiment was also performed at a shorter wavelength of $\lambda = 1.9$ nm. A Fresnel zone plate was used to increase the photon flux per unit area by focusing monochromatic beam into ~ 1 μm^2. Figure 2(b) shows the patterns fabricated by the focused EUV. Desired patterns could be directly written on the substrate by the fine control of the sample stage, as shown in Fig. 1(d). In this case, two characters, U7 standing for the undulator with 7 cm periodicity, were written. SPEM images for Si 2p, N 1s, and O 1s core levels clearly show the letters written on the molecular nanolayer. μ-PES was used to analyze the chemical differences between the irradiated and unirradiated regions. The N 1s core level shift of ~ 0.7 eV was also observed. Thus, the bright regions in the N 1s image reflect that silicon nitrides were formed at the exposed regions. The appearance of the adsorbate-induced component in the Si 2p spectrum and the increase of the O 1s peak after irradiation indicate that silicon nitrides and oxides (or oxynitrides) were formed on the regions exposed to EUV probably due to residual H_2O inside the chamber. As shown in the structural model of Fig. 2(c),

the N–H bonds of the amines, which act as a passivation layer against the chemisorption of adsorbates, may be broken by the EUV in an intermediate step, after which the unstable nitrogen atoms form silicon nitrides and water molecules are adsorbed on the revealed broken bonds.

In order to understand how EUV influences on the other dissociated species, Si–H, synchrotron radiation was irradiated on the silicon monohydride.[11] We could not find any change induced by monochromatic photons with wavelength of 1.9 to 11.8 nm generated from the undulator. Therefore, the Si–H species on the NH_3-adsorbed Si surface seem not to be affected by EUV irradiation. They act as only spacers defining the distance between the amines. The distance may be also controlled by changing substrate orientation or by the surface treatment suggested by Finstad *et al.*[17]

The surface modification by EUV or soft x ray is not a general phenomenon that applied to every molecular system. While the destruction of SAMs or polymer layers frequently has been an issue,[18] simple molecules on silicon surface are known to be stable for the EUV or soft x-ray irradiation. Other well-ordered molecular nanolayers, such as H/Si and Cl/Si, show different behaviors upon EUV or soft x-ray irradiation. The hydrogen atoms on the H/Si surface are well known to be desorbed with scanning tunneling microscope (STM) tip,[19] electron gun[20] or UV light,[21] while EUV or soft x ray makes no effect on the surface.[11] On the other hand, the Cl/Si surface is affected by STM tip,[22] electron gun,[23] UV light,[24] or focused soft x ray,[12] but no change was observed upon unfocused EUV irradiation near 13.4 nm. The EUV-induced amine group modification near 13.4 nm has not been reported for amine-terminated SAMs, other well-defined molecular nanolayers, such as H/Si (Ref. 11) and Cl/Si,[12] and even the same NH_3/Si system. The well-defined structure of the present system and brilliant light source make it possible to observe clearly such results.

SPEM was used in this work to image chemical patterns induced by EUV irradiation. Because of its restricted spatial resolution, the feature size was in micrometer scale[25] and thus the resolution must be improved for practical nanofabrication. A variety of methods are currently being developed to fabricate nanopatterns using EUV (or soft x ray) without complex and expensive lithographic tools, i.e., steppers and scanners. Considerable effort has been made to focus EUV or soft x ray into nanometer scale. Recently, ~15 nm focusing was achieved by using the zone plate lens.[26] Owing to the development of the EUV focusing technique, direct writing in nanometer scale or medium volume production of fine patterns is possible through the zone plate array lithography.[27] On the other hand, EUV interference lithography is applicable to fabricating patterns of regular shape such as nanowire and nanodot by using Lloyd's mirror or transmission grating.[28,29] The functional group patterning combined with these frontier techniques will provide considerable usefulness in surface functionalization and therefore could be applied in the manufacture of future molecular nanodevices. Since our system is intrinsically ultrathin, consisting of one or two atomic layers, better resolution can be expected when it is patterned with these techniques.

In summary, we report that the well-defined amine layer on the Si surface is chemically transformed by EUV or soft x ray with a shorter wavelength than UV. The EUV-induced surface modification was used to make fine patterns on the amine-terminated nanolayer. The patterned surface could be applied as a template for future molecular devices.

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