



Micro-orientation control of silicon polymer thin films on graphite surfaces modified by heteroatom doping



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ABSTRACT

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is applied to study orientation structures of polydimethylsilane (PDMS) films deposited on heteroatom-doped graphite substrates prepared by ion beam doping. The Si *K*-edge NEXAFS spectra of PDMS show opposite trends of polarization dependence for non irradiated and N₂⁺-irradiated substrates, and show no polarization dependence for an Ar⁺-irradiated substrate. Based on a theoretical interpretation of the NEXAFS spectra via first-principles calculations, we clarify that PDMS films have lying, standing, and random orientations on the non irradiated, N₂⁺-irradiated, and Ar⁺-irradiated substrates, respectively. Furthermore, photoemission electron microscopy indicates that the orientation of a PDMS film can be controlled with microstructures on the order of μm by separating irradiated and non irradiated areas on the graphite surface. These results suggest that surface modification of graphite using ion beam doping is useful for micro-orientation control of organic thin films.

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1. Introduction

Organic electronic devices (OEDs) have many potential functionalities due to their huge variety of constituent organic molecules. The formation and application of OEDs using organic thin films have been studied extensively because of the versatility derived from their lightness, softness, and ease of enlargement, which are in contrast to conventional silicon-based inorganic devices [1,2]. However, the miniaturization of orientation structure remains a challenge for achieving the large-scale integration and functional improvement of OEDs. The intra- and inter-molecular charge mobilities depend strongly on the molecular orientation as most organic molecules used for OEDs have anisotropic electronic structures depending on their symmetries [3–5]. Thus, many studies have attempted to control the orientation of organic thin films utilizing techniques based on electric fields [6], magnetic fields [7], drawing [8], temperature [9], friction transfer [10], rubbing [11], and polarized light [12]. These methods are useful for forming homogeneous films with lying or standing orientations on a substrate, but these orientations are difficult to miniaturize due to the influence of homogeneous external fields.

Conversely, many methods have been proposed for micropatterning of OEDs using shadow masking [13], inkjet printing [14], screen printing [15], lithography stamping [16], UV irradiation [17], orthogonal solvents [18], and selective chemical modification [19]. These enable the production of micropatterns on the order of several μm. These methods rely on the selective adsorption or desorption of organic molecules for patterning; however, it is difficult to control lying/standing/random orientations freely on an arbitrary substrate using these methods. Although a thickness dependence has been proposed for lying- and standing-orientation control [20], precise thickness control is necessary for organic thin films with micropatterns and many technological problems still exist for large-area films prepared by coating or evaporation.

Directed self assembly (DSA) is a promising method proposed for achieving both orientation control and micropatterning for block co-polymer thin films [21,22]. DSA enables the formation of regularly patterned structures on the order of a few tens of nm by combining the self-assembly of block co-polymers and artificial guides. Because the formed thin films create oriented structures along the guides, DSA can provide micro-orientation control to some extent. This interesting method has many advantages, but it also has some drawbacks. First, the formation of specific irregular microstructures requires considerable ingenuity because DSA utilizes regular structures derived from self-assembly for patterning [23]. Second, it is difficult to form micropatterns on the order of several μm because the periodic structures of block co-polymer

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thin films tend to be lost when they are distant from the artificial guides by a few μm [24]. Finally, it is also difficult to apply DSA to simple organic molecules besides block co-polymers, and there is no micro-orientation control method presently available for arbitrary organic materials.

We focus on orientation control of polysilane thin films in this work. Polysilane is regarded as a one-dimensional direct-transition type semiconductor because σ electrons are delocalized along the main chain due to the σ conjugation along the Si–Si bonds. To date, several unique characteristics have been reported for polysilane molecules including intense UV absorption [25], high quantum efficiency of photoluminescence [26], high hole mobility [27], and strong non-linear optical properties [28]. Thus, polysilane is very attractive as an organic device material. In addition, because hole mobility depends on orientation structure for polysilane thin films, orientation is an important factor for functional improvement [29]. With regard to orientation control of polysilane films, lying-orientation films have been produced by drawing [30], Langmuir–Blodgett method [31], friction transfer [32], and rubbing [33]. Meanwhile, vacuum evaporation has been used to form standing-orientation films, and it has been reported that a polydimethylsilane (PDMS) film with standing-orientation evaporated on a quartz substrate [34]. However, these methods have not succeeded in achieving micro-orientation control of polysilane films.

Our group also investigated the orientation of PDMS thin films deposited by vacuum evaporation, finding standing orientations on an indium tin oxide (ITO) and a Cu polycrystalline substrates [35]. Meanwhile, we found that PDMS thin films adopted lying orientations on highly oriented pyrolytic graphite (HOPG) [36]. These results reveal that the orientation of polysilane thin films prepared by vacuum evaporation depends on the substrates; furthermore, graphite substrates interact strongly with polysilane films, whereas ITO and Cu substrates interact weakly with these films. Recently, graphene has attracted much interest as a transparent electrode and the formation of organic thin films on graphene has been studied intensively [37–40]. Because graphite and graphene are closely related in terms of surface interactions involved in molecular adsorption, graphite surfaces present an interesting research subject, and many studies have investigated organic thin films on graphite substrates [41–45].

Much research has also been conducted for the surface modification of graphite and graphene by heteroatom doping [46–50]. Theoretical approaches have indicated that if a carbon atom of graphene is substituted for another heteroatom, the adsorption of small molecules, e.g., H_2O , SO_x , and NO_x , depends strongly on the dopant atom [51,52]. We observed that the adsorption properties of thiophene differed greatly upon nitrogen or phosphorus doping in graphite [53], and proposed that heteroatom doping may be an efficient means of controlling the adsorption properties of polymer molecules. The advantage of this method is that a variety of micropatterns can be freely designed by scanning focused ion beam drawing. If organic molecules align along the micropatterns formed by ion beam drawing, this method will improve a novel means of orientation control.

In this work, we study the orientation change of PDMS thin films deposited on HOPG substrates with and without surface modification by a N_2^+ ion beam using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. Si K -edge NEXAFS is employed to clarify electronic structures and orientation of PDMS thin films because of element specificity due to Si 1s core excitation and polarization dependence. We also study the orientation of a PDMS thin film on an HOPG substrate irradiated by Ar^+ ions to compare the effect of the radiation damage induced by the ion beam. These NEXAFS spectra are interpreted by first-principles calculations and discussed in terms of the conformation of PDMS. Furthermore, we

deposited PDMS onto an HOPG substrate on which a micropattern was formed by ion beam irradiation to confirm whether the orientation of the PDMS thin film on a substrate can be controlled using the micropattern.

2. Experimental

2.1. Sample preparation

HOPG samples (10 mm \times 10 mm \times 2 mm) were purchased from Optigraph (STM-grade) and introduced into an ultra-high-vacuum (UHV) chamber with a base pressure of approximately 5×10^{-7} Pa after surface peeling. Ion beam irradiation was performed using a cold-cathode ion gun (Omegatron, OMI-0045CK) equipped in the UHV chamber. N_2 or Ar gas was introduced in the ion gun at approximately 5×10^{-4} Pa and ionized species were accelerated at 3 keV and irradiated onto the HOPG surface at room temperature. The fluences of the N_2^+ and Ar^+ ions were 7.6×10^{16} and 1.0×10^{17} ions/cm², respectively.

The irradiated samples were extracted from the UHV chamber to atmosphere and placed in a preparation vacuum chamber for PDMS deposition. The base pressure of the preparation chamber was approximately 5×10^{-6} Pa. PDMS powders were purchased from GELEST Inc. The average molecular weight was approximately 2000, and the average number of Si atoms in this molecule estimated from the molecular weight is approximately 34. We used an evaporator (Omegatron, OMB-0051EB) positioned approximately 15 cm from the HOPG sample. In the evaporator, a tantalum crucible under an applied voltage of +1.5 kV was heated by electron bombardment using a surrounding tungsten filament, and PDMS molecules were evaporated from the crucible. Because some of the PDMS molecules become ions due to surface ionization, we controlled the amount of deposition by monitoring the ion current with a shutter at the top of the evaporator and controlling the shutter opening time. For the non irradiated and Ar^+ -irradiated substrates, PDMS thin films were simultaneously deposited with a shutter current of 500 pA for 10 min. For the N_2^+ -irradiated substrate, a PDMS thin film was deposited with a shutter current of 2 nA for 3.5 min.

Two additional samples were prepared to attempt the formation of PDMS thin films with different orientations on an HOPG substrate. Fig. S1 shows schematic representations of the sample preparation. In the case of the left-hand sample, half of an HOPG plate was masked by a stainless-steel plate and the HOPG was irradiated by a N_2^+ ion beam with a fluence of 1×10^{17} ions/cm². After irradiation, the mask was removed and PDMS was deposited on the HOPG with a shutter current of 2 nA for 3.5 min. In the case of right-hand sample, a small HOPG flake on an aluminum plate was masked by a nickel grid (Nisshin EM, 1000 mesh) of 25 μm periodicity (9 μm blank and 16 μm space) and irradiated by a N_2^+ ion beam with a fluence of 1×10^{17} ions/cm². After irradiation, the Ni grid was removed, and PDMS was deposited on the HOPG flake with a shutter current of 2 nA for 3.5 min.

2.2. XPS and NEXAFS analysis

All experiments were performed at the BL27A beamline of the Photon Factory of the High Energy Accelerator Research Organization (KEK-PF). This beamline has an InSb(111) double crystal monochromator and the energy resolution at the Si K -edge (1.84 keV) is approximately 0.9 eV [54]. For the X-ray photoelectron spectroscopy (XPS) measurements, 3-keV monochromatic X-ray and a hemispherical analyzer (VSW, Class 100) were used. NEXAFS spectra were obtained by measuring the total electron yield. Because the soft X-rays emitted from BL27A are horizontally polarized, the surface normal of HOPG was directed toward the

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