Current Applied Physics 16 (2016) 1120–1123

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Purine on graphene: PES and NEXAFS study of a heterocyclic aromatic organic compound

Ki-jeong Kim [a], Yong Han [a, b], Junfa Zhu [b], Jaeyoon Baik [b], Hyunjun Shin [b], Hangil Lee [c, *], Bongsoo Kim [a, **]

[a] Beamline Research Division, Pohang Accelerator Laboratory (PAL), Pohang, 790-784, Republic of Korea
[b] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, PR China
[c] Department of Chemistry, Sookmyung Women's University, Seoul, 140-742, Republic of Korea

ARTICLE INFO

Article history:
Received 2 May 2016
Received in revised form
22 June 2016
Accepted 22 June 2016
Available online 23 June 2016

Keywords:
Graphene
Purine
PES
NEXAFS

ABSTRACT

We have investigated the properties of a self-assembled purine ($C_5H_4N_4$) monolayer on epitaxial graphene (EG) on SiC by using high resolution X-ray photoemission spectroscopy (HRPES) and near-edge X-ray absorption of fine structure (NEXAFS). The monolayer of purine on graphene was prepared inside a UHV chamber. The spontaneously-assembled monolayer of purine molecules were oriented parallel to the surface of the monolayer graphene, and it reaches a charge equilibrium state on the monolayer graphene.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

A key issue for the development of multifunctional biological devices is the determination of the possible interactions of such devices with the components of biological materials so as to envisage their capabilities and limitations. Graphene's distinctive properties [1], such as its high conductivity and flexibility, and controllable permittivity and hydrophilicity, could enable the development of graphene-based biological devices [2,3]. However, the thickness, lateral extent, and surface functionalization of graphene can vary dramatically in the presence of biological materials [3–7]. Thus studies of graphene must be performed with well characterized biological materials and defined exposures.

In this study, we selected purine, which consists of a pyrimidine ring fused to an imidazole ring and is a molecule of particular interest to biotechnology and the pharmaceutical industry [8]. Many critical cell functions depend on the state of purine molecules, which is an important amino acid [9], forms part of the building blocks of DNA and RNA, and is a major component of the chemicals that store cell energy [10]. Photoemission spectroscopy (PES) is one of the most versatile methods for the investigation of surfaces on the atomic scale [11]. PES can be used to determine quantitative information about the elemental composition and chemical specificity (e.g., oxidation state) of surfaces and interfaces. Our investigation of the electronic structure and chemical state of purine on graphene was carried out with high resolution X-ray photoemission spectroscopy (HRPES) and the molecular adsorption geometry of graphene was characterized by using near-edge X-ray absorption of fine structure (NEXAFS) [12].

2. Experimental

Monolayer epitaxial graphene (EG) was grown on a SiC substrate via thermal annealing under ultra-high vacuum (UHV) conditions. Nitrogen-doped ($N_D = 9 \times 10^{17}$ cm^{-3}) Si-terminated 6H–SiC(0001) substrates were purchased from Cree Research (USA). Samples were prepared with a size of 3 mm × 12 mm and a thickness of 0.25 mm. The SiC annealing temperature was monitored with an infrared pyrometer by assuming an emissivity of 0.90. After overnight sample outgassing at 900 °C, samples were annealed at 900 °C under a Si flux (1 Å/min) for 5 min to prepare a Si-rich SiC(0001) surface. After annealing at 1150 °C, a carbon-rich

* Corresponding author.
** Corresponding author.
E-mail addresses: easyscan@sookmyung.ac.kr (H. Lee), kbs007@postech.ac.kr (B. Kim).

http://dx.doi.org/10.1016/j.cap.2016.06.014
1567-1739/© 2016 Elsevier B.V. All rights reserved.

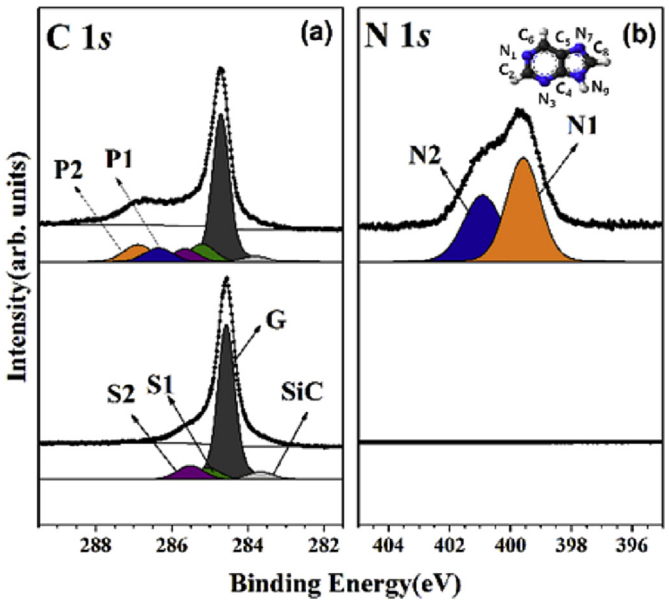

Fig. 1. C 1*s* (a) and N 1*s* (b) core level spectra of EG (bottom) and purine/EG (upper). Each spectrum was recorded at a photon energy of 510 eV. Also the inset shows the molecular structure of purine with the numbers. Black, gray and blue colors indicate carbon, hydrogen and nitrogen, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$(6\sqrt{3} \times 6\sqrt{3})R30^{\circ}$ electron diffraction pattern was observed. A well-reconstructed 1×1 surface was found after further annealing at 1200 °C [13]. Lastly, purine (Aldrich, USA) was evaporated onto the monolayer graphene. A Ta filament with a thickness of 0.25 mm was wound around the quartz crucible and a K-type thermocouple was used to control the temperature. We tested various purine molecule evaporation times: 10 s, 30 s, and 60 s. The C 1*s* and N 1*s* core-level spectra were recorded before and after purine evaporation at a photon energy of 510 eV with a total resolution of 200 meV at the 8A2 HRPES beamline at the Pohang Accelerator Laboratory (PAL) [14]. The binding energies and the spectral resolutions were calibrated by recording the Au $4f_{7/2}$ core-level spectrum. Secondary electron emission spectra (−20 V sample bias) and valence-band spectra were recorded at photon energies of 130 eV. All spectra were obtained in the normal emission mode. The photoemission spectra were carefully analyzed by using a standard nonlinear least-squares fitting procedure with Voigt functions [15,16].

3. Data and results

We could prepare the self-assembled purine monolayer very easily inside vacuum chamber. Purine was evaporated using the thermal evaporation inside organic molecular deposition chamber. Its base pressure was 5×10^{-7} torr. Purine molecules was put in the quartz crucible wounded by Ta filaments. The crucibles and graphene distance was 15 mm and the base pressure of the evaporation chamber was 5×10^{-7} torr. Purine molecule was evaporated on the EG on SiC for 30 s. We could see the multi-layered purine circle, as soon as the evaporation. After then, we monitored the gradual change of the circle, waiting for 60 s, 120 s, and 180 s after evaporation in the evaporation chamber. And then, we transferred the sample to the analysis chamber whose base pressure was 1×10^{-10} torr. Eventually, the multi-layered purine circle disappeared after 600 s evaporation. During transferring the sample to UHV chamber for measuring HRPES and NEXAFS, the multi-layered

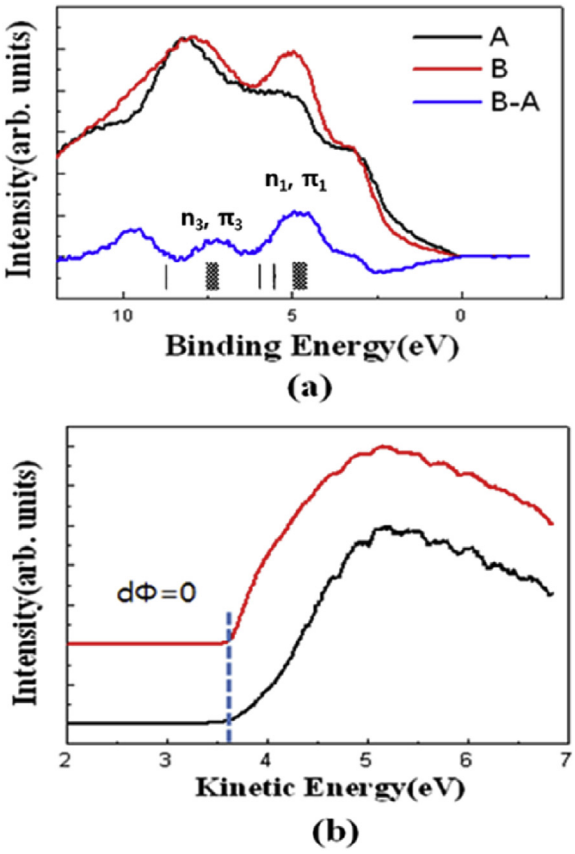

Fig. 2. (a) Valence-band spectra and (b) work function changes determined from the variations in the secondary edge upon the adsorption of purine molecules onto monolayer graphene under a sample bias of −20 V: as-grown graphene (black), purine on graphene (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

purine molecules were desorbed. So, we like to know that if the all of purine molecules was desorbed or what is existed on the surface. So, we measured high resolution X-ray photoemission spectroscopy (HRPES) to investigate the electronic structure and the chemical state analysis of purine on graphene. Also, the molecular adsorption geometry on graphene was measured through the angle resolved near-edge x-ray absorption of fine structure (NEXAFS).

Fig. 1 shows the C 1*s* (a) and N 1*s* (b) core level spectra, which were obtained at a photon energy of 510 eV. We focus here on the changes in the C 1*s* and N 1*s* core-level spectra with purine exposure, because the Si 2*p* spectrum does not undergo significant changes upon purine adsorption. However, the amount of adsorbed purine could be estimated by measuring the change in the Si 2*p* intensity; the attenuation length was 3.2 Å. C 1*s* core-level spectra were obtained before and after purine evaporation onto the monolayer EG. As shown in Fig. 1(a), there are four distinct peaks due to monolayer EG at 285.5, 285.1, 284.7, and 283.6 eV, which are assigned to *sp* [2] carbon atoms at the interface layer weakly interacting with the carbon atoms of the underlying substrate (S2), the $(6\sqrt{3} \times 6\sqrt{3})R30^{\circ}$ interface/buffer layer (S1), the EG layer (G), and SiC, respectively [17–19]. After exposure to purine molecules, two new peaks are evident in the upper spectrum in Fig. 1(a) with binding energies of 286.3 eV (P1) and 286.8 eV (P2). The chemical shifts of P1 and P2 indicated that these species incorporated the N atoms [20].

Fig. 1(b) shows the N 1*s* core-level spectra before (bottom) and after (upper) exposure of the monolayer graphene to purine. The

Download English Version:

https://daneshyari.com/en/article/1785504

Download Persian Version:

https://daneshyari.com/article/1785504

Daneshyari.com