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Determination of Schottky barrier heights and Fermi-level unpinning at the graphene/n-type Si interfaces by X-ray photoelectron spectroscopy and Kelvin probe

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ABSTRACT

The interface characteristics of graphene/n-type Si samples using X-ray photoelectron spectroscopy (XPS) measurements are investigated. XPS makes it possible to extract a reliable Schottky barrier value. For graphene/n-type Si samples with (without) sulfide treatment, the Schottky barrier height is 0.86 (0.78) eV. The Schottky barrier height was increased from 0.78 to 0.86 eV, indicating that sulfide treatment is effective in passivating the surface of Si (owing to the formation of Si–S bonds). To determine the Fermi-level pinning/unpinning at the graphene/n-type Si interfaces with sulfide treatment, an analysis is conducted according to the Schottky–Mott limit and the actual work function of graphene is examined with the Kelvin probe. It is shown that the Fermi energy level is unpinned and the Schottky barrier value is dependent on the work function of graphene. Investigation of graphene/n-type Si interfaces is important, and providing the other technique for surface potential control is possible.

1. Introduction

Graphene, the two-dimensional counterpart of three-dimensional graphite, has attracted vast interests in solid-state physics, materials science, and nanoelectronics. Graphene is a zero-gap semiconductor and has a very large intrinsic carrier mobility, which makes it a very promising material for incorporation into devices ranging from diodes to transistors [1–5]. Many efforts have been made to investigate the physical properties of Schottky contacts and their interfacial properties of graphene on semiconductors, such as GaN, AlGaN, GaAs, SiC, Si, SnS_2, and MoS_2 [6–22]. Due to the technological importance of Schottky diodes which are among the most simple of the graphene–semiconductor contact devices, a full understanding of the nature of their electrical characteristics is of great interest. In this paper, we report transfer of epitaxial graphene layers onto the n-type Si (n-Si) surfaces with and without sulfide treatment. Investigation of graphene/Si interfaces is important, and providing the other technique for surface potential control is possible. The formation of Schottky and ohmic contacts between graphene and Si is crucial to their wide application in the area of electronic and optoelectronic devices [3,6–9,16]. However, the behavior of Schottky barriers at the graphene/Si interfaces is complicated and not well understood. In general, the Schottky barrier height is extracted through traditional current–voltage and capacitance–voltage measurement methods. However, X-ray photoelectron spectroscopy (XPS) makes it possible to extract a reliable Schottky barrier value. The interface characteristics of graphene/n-Si samples using XPS measurements are investigated in this study. The actual work function of graphene is examined with the Kelvin probe. We found that the Fermi energy level (E_F) is unpinned and the Schottky barrier value is dependent on the work function of graphene.

2. Experimental details

Four-inch n-Si (100) wafers purchased from Woodruff Tech Company were used in the experiment. The n-Si wafer thickness was about 525 μm. Using Hall measurement at room temperature, the electron concentration was determined to be 2×10^{15} cm^{-3}. The n-Si samples were first cleaned with chemical solutions of acetone and methanol, then rinsed with deionized water, and immediately blow dried with N_2. Next, the n-Si sample was chemically etched with a diluted HF solution for 1 min, rinsed with deionized water, and blow-dried with N_2 (referred to as as-cleaned n-Si samples). Then, some of the as-cleaned n-Si samples were dipped into a yellow $(NH_4)_2S_x$ solution (with 6% S, Nippon Shiyaku Co., Ltd.) for 5 min (referred to as sulfide-treated n-Si samples). The graphene sheet was grown by chemical vapor deposition

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(CVD). Before the CVD growth of graphene onto Cu, the copper foil (90 μm thick) was pre-annealed at 1000 °C for 30 min under a flow of H_2 = 9 SCCM (SCCM denoted standard cubic centimeter per minute) in order to prepare a high-density terrace structure on Cu. A gas mixture of CH_4 (120 SCCM) and H_2 (40 SCCM) was used for the growth of graphene at 66.7 Pa. After 40 min of growth, the system was cooled to room temperature under H_2. To transfer the as-grown graphene sheets, a polymethylmethacrylate (PMMA) layer was spin-coated on the graphene/Cu sample. The PMMA/graphene/Cu sample was then baked at 100 °C for 1 min. The procedures from coating to drying were repeated five times. Next, the sample was immersed in $FeCl_3$ solution (0.1 g/cm^3) for 6 h overnight to remove the Cu substrates. The PMMA/graphene layers were respectively transferred to the as-cleaned and sulfide-treated n-Si substrates. The PMMA/graphene/as-cleaned n-Si and PMMA/graphene/sulfide-treated n-Si samples were then dried at 50 °C for 30 min on a hotplate. Next, the PMMA layer was dissolved by acetone. The graphene/as-cleaned n-Si and graphene/sulfide-treated n-Si samples were then inserted into a furnace and annealed in pure nitrogen ambient at 200 °C for 1 min. The graphene area is 0.25 cm^2. The structural property of graphene was examined using Raman spectroscopy (Ramboss 500i, Dong-Woo Optron). A 532-nm laser was used for excitation. Atomic force microscopy (AFM) is used for measurement of the thickness of graphene. The graphene work function was examined with the SKP5050 Scanning Kelvin probe (KP Technology). Relative methods make use of the contact potential difference between the probe and a reference material (that is, Au) or between the probe and graphene. Au is used as a reference material for obtaining the work function of graphene, owing to its high chemical stability. Systems offer very a high work-function resolution of 1–3 meV (2 mm tip). The XPS study is used to determine the band-structure lineup of the graphene/n-Si heterojunction structure. XPS measurements (ULVAC-PHI, PHI 5000) were performed using a monochromatic Al Kα X-ray source. We took an Au $4f_{7/2}$ peak at 83.86 eV for energy reference purposes. Curve-fitting of the C 1s, Si 2p, and S 2p spectra was performed using a Gaussian–Lorentzian peak shape after performing a Shirley background correction.

3. Results and discussion

Fig. 1a shows the Raman spectra of graphene films. Graphene displays a band at ~1345 cm^{-1}, a band at ~1580 cm^{-1}, and a band at ~2700 cm^{-1} corresponding to the well-documented D, G, and 2D bands [16,23,24]. The G band is assigned to the E_{2g} mode of the relative motion of sp^2 carbon atoms. The intensity of the 2D band is related to the layer numbers of graphene. The ratio of the 2D to G peak intensities was calculated to be close to 1, suggesting that four layers of graphene formed [23,24]. The D band is disorder-induced and caused by phonon scattering at defect sites and impurities. The ratio of the D to G peak intensities (I_D/I_G) is usually used to evaluate the disorder of graphene. The observed I_D/I_G value (0.42) in this study is larger than the reported value by Luo et al. [25]. The Raman spectrum is sensitive to growth conditions. The different growth conditions may lead to the change in the I_D/I_G ratio. Fig. 1b shows the C 1s core-level spectra of graphene films. The signal of the C 1s was divided into two major peaks near 284.5 and 286.0 eV, corresponding to the sp^2 hybrid (C–C) and the sp^3 hybrid (C–O) bonds, respectively [26,27]. It is shown that the structural imperfection induced by incorporating oxygen induces the increased I_D/I_G ratio. In addition, we performed an AFM measurement in a cracked region of graphene on Si and measure the step height to get an independent estimation of the number of layers. Fig. 1c shows line

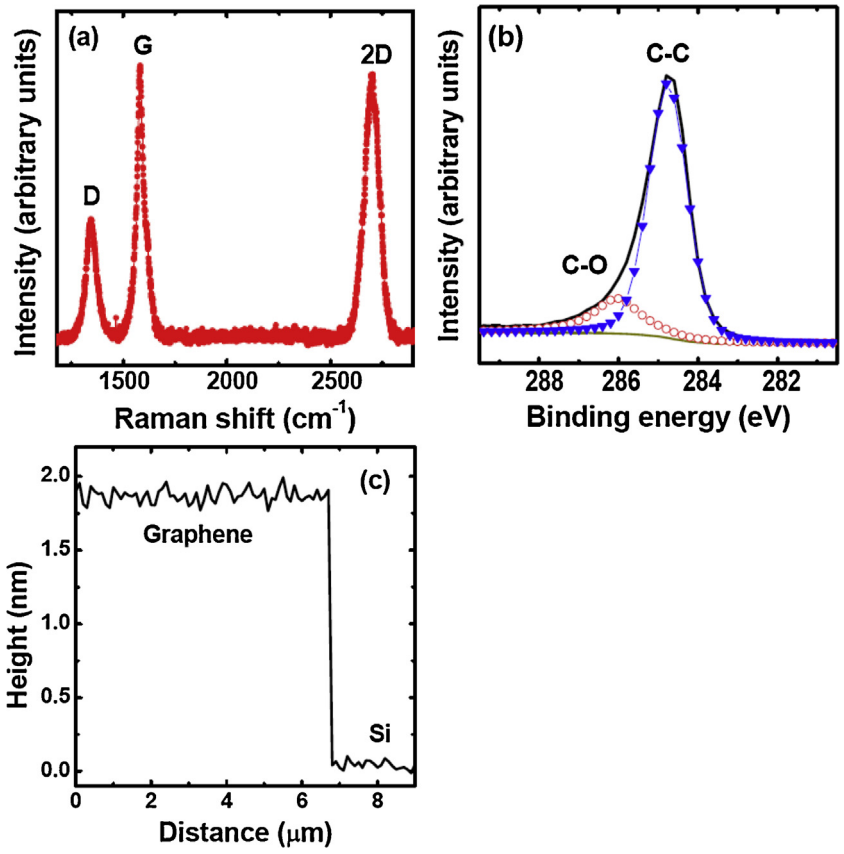

Fig. 1. (a) Raman spectra and (b) C 1s core-level spectra of graphene films. (c) Line scan data at the edge of graphene on Si.