Carbon 113 (2017) 237–242

Contents lists available at ScienceDirect

Carbon

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

Van-der-Waals-gap tunneling spectroscopy for single-wall carbon nanotubes

Dong-Hwan Choi [a, b, 1], Seunghun Jang [c, 1], Du-Won Jeong [a, c], Jeong-O Lee [c], Hyunju Chang [c], Dong-Han Ha [b], Seung Mi Lee [b], Jongwoo Kim [c], Yung Doug Suh [c, d], Myung-Ho Bae [b, e, *], Ju-Jin Kim [a, **]

[a] Department of Physics, Chonbuk National University, Jeonju 54896, Republic of Korea
[b] Korea Research Institute of Standards and Science, Daejeon 34113, Republic of Korea
[c] Korea Research Institute of Chemical Technology, Daejeon 34114, Republic of Korea
[d] School of Chemical Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea
[e] Department of Nano Science, University of Science and Technology, Daejeon 34113, Republic of Korea

ARTICLE INFO

Article history:
Received 20 September 2016
Received in revised form
11 November 2016
Accepted 20 November 2016
Available online 21 November 2016

ABSTRACT

As a consequence of their unique electronic band structures, low-dimensional materials such as one-dimensional (1D) single-wall carbon nanotubes (SWCNTs), 2D graphene and various 2D transition-metal dichalcogenides have exhibited intriguing electrical transport properties when incorporated into field-effect transistors. Meanwhile, the van-der-Waals (vdW) interfaces between top-contacted metals and low-dimensional materials have become a challenging issue for future high-performance electronics. Here, we report a new aspect of vdW interface that offers vdW-gap tunneling spectroscopy by adopting indium (In) as a top-contacted metal on SWCNTs without an artificial insulating tunnel barrier. We show that multiple differential conductance peaks for varying bias voltages correspond to the van Hove singularities existing in the electronic density of states of SWCNTs. Our first-principles calculations reveal that In forms a physisorption interface with a considerable vdW gap, which causes little disruption to the density of states of the SWCNTs near the metal interface and which thus allows vdW-gap tunneling spectroscopy.

1. Introduction

Various semiconducting nanostructures of one-dimensional (1D) single-wall carbon nanotubes (SWCNTs) [1,2] and layered 2D materials (e.g., graphene [3,4] as well as transition-metal dichalcogenides (TMDC) [5,6]) including nanowires [7] have been explored toward future energy-efficient and high-performance semiconducting electronics. One outcome has been the design of a field-effect transistor (FET) with the source and drain metal electrodes in contact with low-dimensional materials and with the gate electrodes capacitively coupled to these materials to apply electrostatic potential. A proper understanding of the interface between the metal and the materials in the FET design is critical if seeking to utilize their low-dimensionality characteristics fully [8]. It is known that the interface of the top-contact configuration on the surface of atomically thin TMDC semiconductors creates a van der Waals (vdW) gap in many cases, which suppresses the charge carrier injection from metals and limits the development of TMDC-based electronics [9]. In fact, this type of vdW gap has been intensively studied in SWCNT electronics and is known as the physisorption interface. Gold and aluminum can serve as physisorption-induced metals for SWCNTs [10]. Good ohmic contact in SWCNTs has been realized in the form of strong-bond contacts with metals that offer good wettability, such as palladium (Pd) and titanium [11,12]. We note that such strong bonding significantly alters the electronic density of states (DOS) of the SWCNTs at the interface, creating what is known as a chemisorption interface. On the other hand, the DOS of SWCNTs at the physisorption interface with a vdW gap remains nearly unchanged, thus there has

* Corresponding author.
** Corresponding author.
E-mail addresses: mhbae@kriss.re.kr (M.-H. Bae), jujinkim@chonbuk.ac.kr (J.-J. Kim).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.carbon.2016.11.053
0008-6223/

been a suggestion of detection of the DOS by measuring the conductance with the physisorption contacts [10].

In this study, we demonstrate vdW-gap tunneling spectroscopy based on physisorption interface materials without an artificial insulating tunnel barrier to determine the electronic structures of SWCNTs. To form the physisorption interface, we deposited indium (In) electrodes onto SWCNTs. Low-temperature transport measurements revealed multiple conductance peaks for varying the bias voltage, which were subsequently translated into van Hove singularities (vHSs) in the SWCNTs. To elucidate the properties of the interface barrier that enables exploration by tunneling spectroscopy, we undertook first-principles calculations based on density functional theory (DFT). A comprehensive understanding of the interface between In and the SWCNTs is required to uncover key factors pertaining to vdW-gap tunneling spectroscopy, which thus far remains unrealized.

2. Experimental

2.1. Sample preparation

Carbon nanotubes were grown at 915 °C on a 500-nm-thick SiO_2/Si substrate with catalysts using the chemical vapor deposition process in a gas mixture of CH_4:H_2 = 5000:500 (sccm). In was deposited via a thermal evaporator at ~10^{-6} Torr to define electrodes on a CNT after electron beam lithography on a PMMA (poly(methyl methacrylate)) layer and a development process, in which the temperature of the sample stage was maintained at 100 K during the evaporation process. See Section 1 in the Supplementary Data for details of the sample preparation method used.

2.2. Experiments

The devices were placed in a cryo-free system with a base temperature of 4 K. The two-probe setup was used to measure the devices electrically with a Keithley 213 device as a voltage source and an Ithaco 1211 instrument to supply an amplifying current. After measuring the current-voltage (I-V_{sd}) characteristics, the dI/dV_{sd}–V_{sd} curves were ascertained by means of numerical differentiation.

2.3. AFM and Raman characterization

The Park Systems XE-100 AFM was used to obtain the AFM images in the tapping mode. The Raman spectra were obtained on a LabRAM HR system (Horiba Scientific) equipped with a 514.5 nm laser and a 100 × objective lens. The beam exposure time was 10–15 s.

3. Results and discussion

3.1. Concept of vdW-gap tunneling spectroscopy

Fig. 1a shows a schematic of a SWCNT field-effect transistor (FET) on a SiO_2/Si substrate with the back-gate geometry. The band diagram of the semiconducting (*sm*-) SWCNT is shown in Fig. 1b, aligned to the Fermi levels of the drain (E_{FD}) and source (E_{FS}) with inherent Schottky barriers. Here, SC*n* (SV*n*) denotes the *n*th sub-bands in the conduction (valence) bands of a SWCNT. The properties of the interfaces between the metals and *sm*-SWCNT as indicated by the vertical red lines are mainly determined by the charge redistributions between them. Fig. 1c and d shows two typical metal/SWCNT interfaces: chemisorption (with Pd) and physisorption (with In) interfaces. The chemisorption interface in Fig. 1c forms covalent bonds between Pd and SWCNT, resulting in good ohmic contact. When a bias voltage (V_{sd}) is applied to the drain, electronic bands in the SWCNT nearly linearly incline along the channel and electrons are injected from the metal to the SWCNT through the Schottky barrier at the drain, as indicated by the arrows in the figure. This is a general concept of a SWCNT FET including bulk semiconductors with Schottky barriers.

On the other hand, the physisorption interface in Fig. 1d forms a vdW gap, which is expressed as a tunnel barriers between the metals and the SWCNT as shown in Fig. 1f (two vertical green bars). With a bias voltage at the drain, the SWCNT bands are nearly flat along the channel, except for the drain region, as shown in Fig. 1f. In that case, the electron injection through the tunnel barrier is enhanced when E_{FD} is aligned to the flat sub-bands of the SWCNT due to the vHS in the DOS at each sub-band. This suggests that vdW-gap tunneling spectroscopy could be used to elucidate the electronic structure of low-dimensional materials in the FET geometry.

3.2. vdW-gap tunneling spectroscopy on SWCNTs

Fig. 2a and b shows AFM images of the SWCNTs with In electrodes as investigated here, where both diameters, D, equal approximately 1.15 nm (see Section 2 in the Supplementary data for details including representative Raman data taken from the *m*-SWCNT). Fig. 2c shows the drain current (I) as a function of the back-gate voltage (V_{bg}) at V_{sd} = 1.5 V and −1.5 V at T = 4 K for the SWCNT in Fig. 2a, which shows *sm*-behavior with the band-gap region indicated in Fig. 2c, i.e., *sm*-SWCNT. The I-V_{bg} curve in Fig. 2d obtained at V_{sd} = 1 V and −1 V from the SWCNT in Fig. 2b shows quasi-metallic behavior without a gap feature, i.e., metallic (*m*-) SWCNT.

Fig. 3 shows the vdW-gap tunneling spectroscopy results for the *sm*-SWCNT and *m*-SWCNT samples shown in Fig. 2a and b, respectively. Fig. 3a shows a dI/dV_{sd} map as a function of V_{sd} and V_{bg} for the *sm*-SWCNT, where the dashed lines indicate the depletion boundary. The dI/dV_{sd} map shows main four conductance-peak curves, as indicated by the arrows in the hole-doped region for V_{bg} < −20 V, whereas the electron-doped region for which V_{bg} > 10 V is rather unclear. The black curve in Fig. 3b indicates a typical dI/dV_{sd}-V_{sd} curve at V_{bg} = −41 V, showing four pronounced conductance peaks, denoted by the vertical arrows, corresponding to those in Fig. 3a. For comparison, we added the electronic DOS with two different diameters depending on their chiral indices of (10, 6) and (7, 5) in Fig. 3b, where the DOS was calculated via the tight-binding method with a tight-bonding energy level of 3 eV and a carbon-carbon distance of 1.42 Å [13,14]. Here, V_{sd} corresponding to the conductance peaks as indicated by the blue, black and green arrows with E_g ~ 0.75 eV is in good agreement with the vHS locations in the (10, 6) chiral index, corresponding to SC1, SV1 and SV2, respectively, as indicated by the blue dashed lines with D = 1.1 nm, also comparable to what measured by AFM. Another distinct conductance peak appears at V_{sd} ~ −0.38 V, as indicated by the orange arrows in Fig. 3a and b. The peak location corresponds to a SWCNT with D = 0.82 nm of a chiral index, (7, 5), with an E_g value of approximately 1.05 eV. Although further study of the origin is needed, it could be related to our geometry with two indium contacts. For instance, if the diameter along the SWCNT changes [15], the two tunnel barriers will have different electronic bands, resulting in such side peaks. Another *sm*-SWCNT with a similar diameter also exhibited the same trend, as shown in Section 3 in the Supplementary data.

An *m*-SWCNT is expected to display a wider space between the first sub-bands than a *sm*-SWCNT with a similar diameter. Fig. 3c shows the dI/dV_{sd} map as a function of V_{sd} and V_{bg} for the *m*-SWCNT device, which shows weak gate-dependence conductance and