Proceeding Paper

Gallium Selenide, and Rubidium Iodide Filling of Single-Walled Carbon Nanotubes as p, and n-Dopant Chemical Compounds †

Marianna V. Kharlamova 1,2

1 Centre for Advanced Materials Application (CEMEA), Slovak Academy of Sciences, Dúbravská Cesta 5807/9, 845 11 Bratislava, Slovakia; mv.kharlamova@gmail.com or dr.marianna.kharlamova@gmail.com
2 Moscow Institute of Physics and Technology, 9 Institutskiy per., 141700 Dolgoprudny, Russia

Abstract: I filled the single-walled carbon nanotubes (SWCNTs) with gallium selenide (GaSe), and rubidium iodide (RbI) as p, and n-dopant chemical compounds. The filling was confirmed by high-resolution transmission electron microscopy. I investigated the electronic properties by Raman spectroscopy, optical absorption spectroscopy, near edge X-ray absorption fine structure spectroscopy, and X-ray photoelectron spectroscopy. I proved the p-doping of SWCNTs by the introduced GaSe. The data featured the n-doping of carbon nanotubes in RbI-filled SWCNTs.

Keywords: gallium selenide; rubidium iodide; carbon nanotubes; electronic properties; doping; Raman spectroscopy; optical absorption spectroscopy; near edge X-ray absorption fine structure spectroscopy; and X-ray photoelectron spectroscopy

1. Introduction

The interest to single-walled carbon nanotubes led to many interesting applications, such as nanoelectronics, thermoelectric power generation devices, optoelectronics, biomedicine, sensors, catalysis, electrochemical energy storage devices. The filled SWCNTs are promising components of these devices. An approach to tailor the properties of SWCNTs by filling was started in our works [1–8]. After that the SWCNTs were filled with chalcogenides, halogenides of metals, and the modified properties were studied by Raman spectroscopy, optical absorption spectroscopy, X-ray absorption spectroscopy, and photoemission spectroscopy. It was shown that electron donors, and electron acceptors modify the properties of SWCNTs [9–21]. Modifications of spectra are changes in peak positions, and profiles of bands, appearance of new peaks [22]. The methods of filling of SWCNTs were developed to fill SWCNTs with large ratios. Among them are liquid phase methods of filling with metals, melt method of filling with metal halogenides, gas method of filling with molecules. It is difficult to fill metal chalcogenides inside SWCNTs in a single step process, because they have large melting points. In this work, I fill the SWCNTs with gallium selenide by the single-step process. The melting point of GaSe is 960 °C, and this is a unique case of filling of high melting compound in SWCNTs by the melt method. I investigate the electronic properties of filled SWCNTs by spectroscopic techniques to study the influence of encapsulated compound on SWCNTs.

The filler inside SWCNTs leads to electron donor, or electron acceptor doping effect. There are many compounds that were encapsulated inside SWCNTs. Among them are metal halogenides, metal chalcogenides, metals. The influence of substances on the electronic properties of SWCNTs is determined by its work function (WF). There are three cases. If the work function of substance is larger than the WF of SWCNTs, the p-doping of
carbon nanotubes is observed. If the work function of substance is smaller than the WF of SWCNTs, the n-doping of SWCNTs occurs. If the work function of substance equals the WF of SWCNTs, no modification of the electronic properties is observed [22]. Typical donors of electrons are metals with the WF that is significantly smaller than the WF of SWCNTs. Molecules can also lead to donor doping of SWCNTs. Among metal halogenides, rubidium iodide has smaller WF than the value of SWCNTs. It is expected to have n-doping effect on SWCNTs. The filling of SWCNTs with rubidium iodide is convenient way of n-doping of SWCNTs. This is caused by several reasons. Firstly, the filling of SWCNTs with Rbl is made by single-step melt method, which is simple, and it leads to clean samples. Secondly, Rbl has low melting point, which simplifies the combinations of synthesis, and integration processes at lab, and industrial scale. Thirdly, Rbl has very low WF (about 1 eV lower than the value of SWCNTs). This can result in very large modifications of Fermi level of SWCNTs. The downshift of several hundreds of meV is expected [22].

2. Experimental

I put the SWCNTs and GaSe in a quartz ampoule, seal it under vacuum, and heat to temperature of 1060 °C, which is higher by 100 °C than melting point of GaSe. The SWCNTs were pre-opened by annealing in air at 500 °C for 30 min. The diameter of SWCNTs is 1.4 nm. The quartz ampoule was cooled down to room temperature to crystallize the compound inside SWCNTs. Rbl was placed inside quartz ampoule where SWCNTs were located. The system was maintained at temperature that is 100 °C higher than the melting point of Rbl (T_{melting}(Rbl) = 656 °C). The samples were cooled slowly to room temperature. The electronic properties of SWCNTs filled with GaSe, and Rbl were investigated by Raman spectroscopy, optical absorption spectroscopy, near edge X-ray absorption fine structure spectroscopy (NEXAFS), and photoemission spectroscopy (X-ray photoelectron spectroscopy, XPS).

3. Results

It was found that GaSe is filled inside SWCNTs. Figure 1 shows the high resolution transmission electron microscopy (HRTEM) image of GaSe-filled SWCNT bundle. It is visible that the channels of carbon nanotubes are filled. The homogenous filling of carbon nanotubes is confirmed. The filling materials is recognized inside the inner cavities of carbon nanotubes.
Figure 1. The HRTEM image of bundle of GaSe-filled SWCNTs.

Figure 2 presents the HRTEM image of individual filled SWCNTs. In this image, one can see the two filled SWCNTs in the bottom. It is visible that there is the filler within the walls of carbon nanotubes. For comparison, the two unfilled SWCNTs are visible in the middle of the image. It is visible that the space inside the channels is not filled. Thus, it is obvious that GaSe is filled inside SWCNTs.

Figure 2. The HRTEM image of individual GaSe-filled SWCNTs.
Here, I show the HRTEM data of RbI-filled SWCNTs. Figure 3 shows the low-magnification image of the filled SWCNTs. It is visible that there are encapsulated materials in channels of carbon nanotubes. They are filled throughout the sample. White contrast lines correspond to filler within SWCNTs.

Figure 3. The HRTEM image of bundles of RbI-filled SWCNTs.

Figure 4 presents the high-magnification image of filled SWCNTs. The atoms of introduced salt are visible inside carbon nanotubes. The atoms are white dots. They are located in two columns, and atoms in columns are periodically positioned. There are pairs of atoms that are symmetrically located within the SWCNTs. The walls of SWCNTs are also visible, and it is obvious that the diameter of atomically-thick crystals is smaller than the diameter of SWCNTs. The crystals inside SWCNTs have cubic structure, as in the case of bulk compound [23].
The data of Raman spectroscopy shows that GaSe has an electron acceptor effect on SWCNTs (Figure 5a). The NEXAFS shows no formation of chemical bonds between SWCNTs and GaSe. The data of XPS shows the shift by 0.28 eV to lower binding energies. This testifies about the p-doping of SWCNTs by the introduced compound. The electronic properties of SWCNTs filled with RbI were investigated by Raman spectroscopy, and X-ray photoelectron spectroscopy. It was shown that RbI has n-doping effect on SWCNTs (Figure 5b). This is a unique case of n-doping of SWCNTs by metal halogenide, and the success of this experiment opens new ways to applications of filled SWCNTs in nanoelectronics, including p-n transitions with similar morphology, and atomic structure compounds, and simple preparation methods, integration routes, cleaning procedures, manipulation in devices. This filling is very important achievement, which opens new chapter in applications of filled SWCNTs, because it gives lots of information on chemical, and physical properties.
4. Conclusions

In this work, I filled SWCNTs with GaSe, and investigated the electronic properties by spectroscopic techniques. The HRTEM data proved the filling of SWCNTs, and the data of four spectroscopic methods confirmed the p-doping of SWCNTs by encapsulated GaSe. I filled SWCNTs with RbI by the melt method. I investigated the atomic structure of filled SWCNTs by HRTEM. It was shown that the channels of SWCNTs are filled. The electronic properties of filled SWCNTs were investigated by Raman spectroscopy, and X-ray photoelectron spectroscopy. The introduced compound leads to n-doping of SWCNTs. This leads to easy preparation, integration, and applications of RbI-filled devices.

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References


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