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Graphene/diamond (carbon sp^2-sp^3) heterojunctions as novel photoelectronic devices

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Abstract

We demonstrate *in-situ* growth of carbon nanowalls (CNWs) on diamond semiconductors by microwave plasma assisted CVD. The resulting CNW/diamond junctions have both photo-controllable multiple resistance states and nonvolatile memory functions. The resistance state (high or low resistance state) can be selected by light irradiation with the application of a bias voltage, giving a large resistance switching ratio of ~10^5. These results indicate CNW/diamond (carbon sp^2-sp^3) junctions could have applications in novel photo-controllable devices, which have photo-sensing, memory, and switching functions.

1. Introduction

Diamond and graphene are common carbon allotropes and have numerous potential applications in electronic devices. Although both diamond and graphene are important electronic materials individually, more recently the interface between graphene (including vertically aligned graphene) and diamond, that is, the sp^2 – sp^3 interface, has attracted much attention because of the various electronic phenomena associated with it. Many theorists suggest that interfaces between graphene and diamond (carbon sp^2-sp^3 interfaces) exhibit interesting electronic characters such as high-efficiency photoelectric conversion, highly spin-polarized states, etc. Diamond and graphene are important not only individually in electronic devices but also as building blocks for innovative electronic devices using carbon sp^2-sp^3 interfaces. However, despite these interesting theoretical considerations, experimental results regarding the electronic properties of such interfaces have rarely been reported [1, 2]. To the best of our knowledge, there are no empirical data concerning the electronic properties of diamond/vertically aligned graphene (carbon nanowalls (CNWs)) heterojunctions, although there have been a few reports regarding the growth of CNW layers on diamond.

In this study, toward fabrication of novel electronic devices using carbon sp^2-sp^3 interfaces, vertically aligned graphene (carbon nanowalls: CNW)/diamond heterojunctions were fabricated and their electronic properties were examined in detail [3].

2. Experimental

Unintentionally boron-doped diamond semiconductors were homoepitaxially grown on diamond (100) substrates by microwave plasma CVD [4]. To reduce the amount of residual B in the diamond layers, O_2 gas was also introduced (O_2/H_2 flow ratio of 0.25%). Hall measurements showed typical room temperature (RT) acceptor concentrations and mobilities in the resulting diamond layers is ~10^{16} cm^{-3} and ~1000 cm^2/Vs, respectively. By tuning growth conditions, CNW were able to be formed in-situ on diamond semiconductors in the same microwave plasma reactor as shown later in this abstract. Junctions using the CNW/diamond heterostructures were fabricated (area: 20-160 μm ϕ) and their current-voltage (*I-V*) characteristics were examined under photo and heat irradiation.

3. Results and Discussion

By optimizing the *in-situ* growth conditions of CNW on diamond, we found that using a higher CH_4/H_2 ratio (~25%) with a lower microwave power (~500 W) and higher growth temperature (~900°C) compared to those employed for diamond (~1%, 1300 W, and ~700°C) is the key to obtain high quality CNW layers on diamond. In the case for CNW

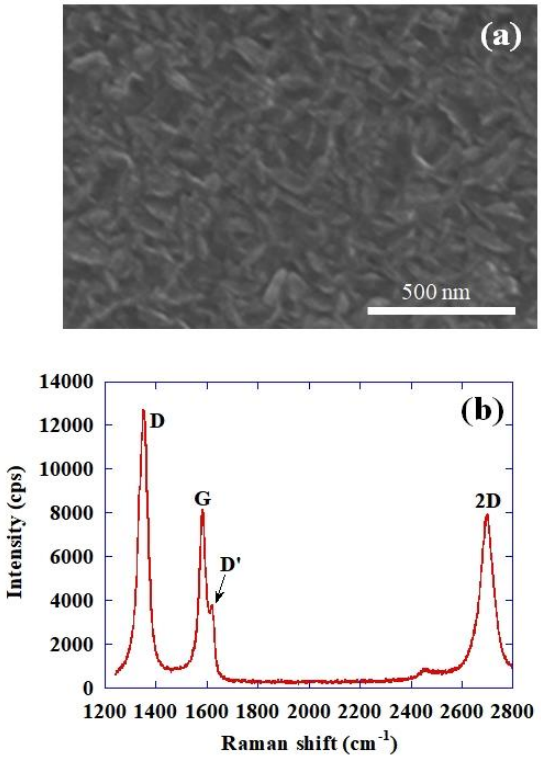

Fig. 1: Typical (a) SEM image and (b) Raman spectrum of the CNW layers on diamond semiconductors.

on diamond formed at substrate temperature of 900°C and microwave power of 500 W, many wall-like structures with length and width of ~1 μm and ~10 nm were observed by SEM measurements. In the Raman spectrum of the CNW, three major peaks were observed: G peak (~1580 cm^{-1}) and 2D peak (~2700 cm^{-1}), which are typical of graphene layers, and a D peak at 1350 cm^{-1}. Intensity ratio of D to G peak, which was related to the in-plane sp^2 crystalline size, was ~2, indicating smaller grain size of the graphene layers in the CNW on diamond. The G peak was accompanied by a shoulder peak at ~1620 cm^{-1}, which is characteristic of CNW. These SEM and Raman results indicate high quality CNW layers were successfully formed on diamond semiconductors.

Figure 2 shows the *I-V* characteristics of the CNW/diamond junctions at 150 °C under blue light irradiation for ~30 s at ±10 V. The junction showed hysteretic *I-V* behaviors and the resistance changed between a low-resistance state (LRS) and a high-resistance state (HRS) based on the application of a negative or positive bias. This hysteresis was observed between RT and 200 °C, although the conductivity change ratio gradually decreased as the temperature decreased. The transition between the HRS and LRS resulting from irradiation was maintained even after the irradiation was stopped, suggesting that these junctions could function as nonvolatile memory. This resistive switching behavior is a unique feature of so-called memristors, which have multiple resistance states and can act as nonvolatile memory. This phenomenon is exhibited by numerous oxides, including TiO_2, Nb-$SrTiO_3$, etc. However, in a typical memristor, the resistance state can be switched only by the application of a bias without photoirradiation. The photo-induced resistance switching is quite rare and has only been observed in a few materials and heterostructures, all of which have demonstrated relatively lower photoresponsivity values on the order of ~10^2. The characteristics of our results is that this is the first report on photomemristive behaviors of CNW/diamond junctions, which showed extremely large conductivity change (~10^6). The current change ratio of ~10^5 exhibited by our junctions are much larger than the previously reported values, and thus these junctions have significant potential for optical applications. It is therefore probable that CNW/diamond junctions have the capacity to act as photo-controllable memristors (photomemristors) with photo-switchable resistance states and multiple nonvolatile memory functionalities. The mechanism for the conductivity change was under investigation, however we consider components in air such as oxygen play important roles for the behaviors because air exposure for several days was needed for inducing the largest current change.

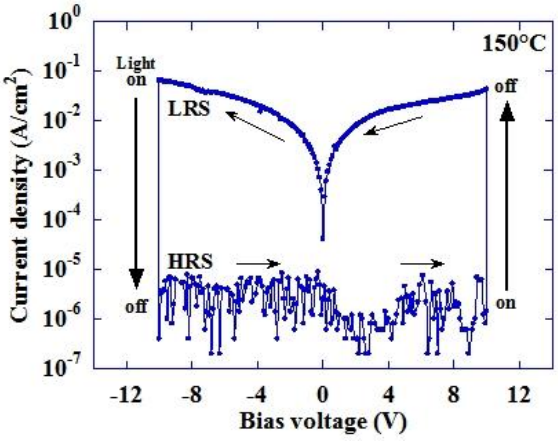

Fig 2: *I-V* characteristics of the CNW/diamond junctions measured at 150°C under blue light irradiation at ±10 V for 30 s.

These results indicate CNW-diamond, carbon sp^2-sp^3 heterojunctions can be used as novel photo-controllable devices with both photo- switching and memory functions.

As a note, recently, we tried fabricating high quality graphene layers (normally oriented, not vertical) on diamond semiconductors by CVD annealing method of spin coated graphene oxide layers [5] to clarify orientation effects of graphene layers to their electronic properties. By the method, formation of graphene layers on diamond was confirmed by Raman measurements. Their structural and electronic properties will be also discussed in this presentation.

4. Conclusions

This work demonstrated *in-situ* growth of CNWs on diamond semiconductors by microwave plasma CVD and the resulting CNW/diamond junctions have both photo-controllable multiple resistance states and nonvolatile memory functions. The conductivity change ratio between the HRS and LRS of the junctions became quite large (> 10^5) at ~150 °C. The data obtained in this study indicate that CNW/diamond heterojunctions could find applications as high-sensitivity optical devices intended for use as photo-controllable nonvolatile memory with switching functions.

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References

[1] J. Yu, G. Liu, A. V. Sumant, V. Goyal, and A. A. Baladin, Nano Letters, 12 (2012) 1603.

[2] K. Ueda, S. Aichi, and H. Asano, Appl. Phys. Lett., 108 (2016) 222102.

[3] K. Ueda, H. Itou, and H. Asano, J. Mater. Res. 34 (2019) 626.

[4] K. Ueda, K. Kawamoto, T. Soumiya, and H. Asano, Dia. Relat. Mater. 38 (2013) 41.

[5] M Chen et al., Carbon 50 (2012) 2581.