Synthesis of carbon nanowalls by the ICP-PECVD method and study of electron and proton irradiation for their properties

Ye. Yerlanuly[1,2,3], R.Ye. Zhumadilov[1,2], R.R. Nemkayeva[1,2], G. Akhtanova[3], T.S. Ramazanov[2], A.N. Jumabekov[3], V.V. Brus[3], M.T. Gabdullin[1,2]

[1] *Kazakh-British Technical University, Almaty, Kazakhstan*
[2] *Al-Farabi Kazakh National University, Almaty, Kazakhstan*
[3] *Department of Physics, Nazarbayev University, Astana, Kazakhstan*

Abstract: In this work, a complex experimental study of the synthesis of carbon nanowall (CNW) films is carried out in correlation with the growth time and investigation effect of electron and proton ionizing radiation on the properties of CNWs is carried out using various state-of-the-art materials characterization techniques. The morphological and structural changes in turn leads to changes in the electronic, optical, and electrical characteristics of the material, in particular changing the work function, improvement in optical transmission, an increase in surface resistance, and a decrease in the specific conductivity of the CNW films.

Keywords: carbon nanowalls, electron irradiation, proton irradiation, structure, morphology, electrical properties, optical properties

1. Introduction

Carbon nanowalls (CNWs) are one of the allotropic modifications of carbon and are three-dimensional networks of vertically oriented graphene sheets [1,2]. CNWs can be synthesized on various metallic, semiconductor and insulator substrates [3] using various techniques [4]. Carbon atoms in CNWs form covalent chemical bonds with sp^3 (C-C) and sp^2 (C=C) hybridization, which afford this unique nanostructured material to demonstrate unique structural, morphological, electrical, optical and chemical properties [1,2,5,6]. In recent years, CNWs have found many applications in various electronic devices such as solar cells [7–10], light-emitting diodes [7–12], and sensors [13,14].

Despite a wide range of applications, controlling the synthesis process and the final film morphology of CNWs remain challenging, in particular, obtaining CNWs with required morphology and material properties [15–19]. Varying synthesis parameters and irradiation CNWs leads to significant changes in morphology of CNWs, which subsequently alters the physical and chemical properties of the obtained material [20]. Gaining a better understanding of the relationship between the structural and electro-optical properties would make it extremely useful to obtain CNWs with desired properties for further practical applications. With this in mind, in this work the effect of material growth time on the physical properties of CNW films is systematically studied.

The investigated CNW films are synthesized using inductively coupled plasma enhanced chemical vapor deposition (ICP-PECVD) method. In this contribution, we revealed in details the coupling between structural, electronic, optical, and electrical properties of the obtained CNW films with the material growth time during the ICP-PECVD process. It is demonstrated that material growth time has a significant effect on the morphology of CNW films. Shorter growth time results in smaller thickness CNW films with a densely arranged maze-like structure, whereas longer growth time results in larger thickness CNW films with a petal-like structure. In addition, this contribution is devoted to the detailed study of the effect of electron and proton irradiation on the properties of CNWs, employing state-of-the-art materials characterization techniques.

2. Experimental part

Synthesis of CNW films. CNW films were synthesized on 1 cm × 1 cm quartz substrates by inductively coupled plasma chemical vapor deposition (ICP-PECVD) method using methane gas (CH_4) as a carbon source. The quartz substrate was loaded into a CVD furnace with a quartz tube. The quartz tube was pumped down to 10^{-2} Torr and heated up to 800 °C. Then, the CNW films were synthesized at a plasma power of 140 W in an Ar/CH4 and H2 mixture at flow rates of 20 and 5 cm^3/min, respectively. In the experiments, the growth time for CNW films is varied from 30 to 60 minutes with a 10 min step. The experimental setup and the CNWs growth mechanism are described in detail in our previous work [21].

Electron and Proton Irradiation. The ionizing irradiation experiments were conducted in the specialized large-scale facility of the Institute of Nuclear Physics (Almaty, Kazakhstan). Electron irradiation of the samples was carried out at the electron linear accelerator ILU-10 with an electron energy of 5 MeV and a total fluence of 7×10^{13} e/cm^2. The absorbed dose was measured using GEX B6001 polystyrene calorimeters and GEX B3002 film dosimeters based on a Genesys 30 spectrophotometer. Proton irradiation of the samples was carried out at the linear type cascade rechargeable accelerator UKP 2-1 with a proton energy of 1.5 MeV, and a total fluence of 10^{12} p/cm^2. The fluence was determined by measuring the proton beam current by a Digital Current Integrator 439 (ORTEC). For more details, see the work [22].

Characterization of the CNW Films. The morphology of the synthesized CNW films was characterized using a scanning electron microscope (SEM, ZEISS Crossbeam 540). A Raman spectrometer (LabRAM Horiba Evolution & Omega Scope with a laser wavelength of 514.5 nm) was used to study the structural properties of the samples. The electronic properties of the CNW films were characterized using an X-ray photoelectron spectrometer (XPS) with an Al-Kα monochromatic X-ray source at 1486.6 eV (NEXSA, Thermo Scientific) and an ultraviolet photoelectron spectrometer (UPS, NEXSA, Thermo Scientific) using a He1α source (21.22 eV). The optical properties of the samples were examined using a UV-Vis spectrometer (Lambda 1050, PerkinElmer Ltd.). The electrical properties were studied using a Hall effect measurement system with the van der Pauw configuration (HMS-5500, Ecopia).

3.Results and discussion

The synthesis of CNW films on quartz substrates using the ICP-PECVD method. The obtained CNW films consist of vertically oriented few-layer graphene sheets with heights varying from 60 to 190 nm. Depending on the film growth time, the morphology of the CNW films changes from a maze-like structure (30-40 min) to a petal-like structure (50-60 min). The structural, electronic and optical properties of the samples are characterized with various analytical techniques. The analysis of the Raman spectra of the samples showed that the obtained materials are CNWs with corresponding peaks at the respective Raman shift. The ratio of the I_G/I_D Raman peaks increases with the increase in film growth time. The analysis of FWHM of the G Raman peak shows a narrowing of the G peak from 37.84 cm^{-1} to 33.27 cm^{-1}, and the calculation of the degree of graphitization changes from 41% (30 min) to 52% (60 min). These data indicate an improvement in the structure quality of the obtained CNW films with increasing growth time. Also, the influence of the CNWs morphology on various optical, structural, and electrical properties of the material is revealed. In particular, the Hall and Seebeck effect measurements of the samples reveal that CNW films with a maze-like morphology (film growth time 30 and 40 min) exhibit p-type semiconducting properties, whereas CNW films with a petal-like morphology (film growth time 50 and 60 min) exhibit n-type of conductivity. For more details, see the work [21].

An integrated approach was applied to study the properties of CNWs and the effect of electron and proton irradiation treatment. The results of this study demonstrate the modification of the morphological and structural properties of the CNW samples depending on the irradiation type. The morphology of CNWs undergoes a significant change, in particular, the wall density decreases after irradiation. Our Raman and XPS analysis independently revealed that the sp^2 hybridization component increases in the CNW films after irradiation. Structural and morphological changes in CNW films after irradiation lead to an alteration in the work function of the material. UPS data analysis shows that the value of the work function of the as-prepared CNW film is - 4.8 eV, after electron irradiation, this value shifts to - 4.76 eV, after proton irradiation, the work function decreased to - 4.29 eV. The irradiation treatments also lead to changes in the optical and electrical properties of CNWs associated with modifications in their morphology and structural properties. The trend toward an improvement in optical transmission, an increase in surface resistance, and a decrease in the specific conductivity of the CNW films after the irradiation treatments is associated with a decrease in film thickness and CNW density. The obtained results clearly reveal a complex modification of the properties of CNWs after their irradiation with high-energy electrons and protons. However, the change is not very significant and CNWs themselves still exist on the substrates and remain functional as an optoelectronic material after the irradiation processes. Further experiments to study the effect of irradiation on CNWs should be conducted at different energies of electrons and protons for a better simulation of cosmic conditions. Moreover, a study on the possibility of using these carbon nanostructured films in the development of radiation-resistant optoelectronic devices for space applications is required. For more details, see the work [22].

4.Conclusions

In conclusion, a complex experimental study of the synthesis of carbon nanowall (CNW) films is carried out in correlation with the growth time and investigation effect of electron and proton ionizing radiation on the properties of CNWs is carried out using various state-of-the-art materials characterization techniques. A shorter growth time results in thinner CNW films with a densely spaced labyrinth structure, while a longer growth time results in thicker CNW films with a petal structure. These changes in morphology further lead to changes in the structural, optical, and electrical properties of the CNW. Also, CNW layers on quartz substrates were exposed to 5 MeV electron and 1.8 MeV proton irradiation with accumulated fluences of 7×10^{13} e/cm^2 and 10^{12} p/cm^2, respectively. It is found that depending on the type of irradiation (electron or proton) the morphology and structural properties of CNWs change, in particular, the wall density decreases, and the sp^2 hybridization component increases. The morphological and structural changes in turn leads to changes in the electronic, optical, and electrical characteristics of the material, in particular changing the work function, improvement in optical transmission, an increase in surface resistance, and a decrease in the specific conductivity of the CNW films. Lastly, this study highlights the potential of CNWs as nanostructured functional material for novel high-performance radiation-resistant electronic and optoelectronic devices.

5.Acknowledgments

YY and MTG thanks Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP09260730, AP08856684). RTS thanks Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. XXXX).VVB thanks Nazarbayev University Collaborative Research Grant (grant number: 11022021CRP1505) and Nazarbayev University Faculty

Development Competitive Research Grant (grant number: 11022021FD2915). ANJ thanks Nazarbayev University Collaborative Research Grant (grant number: 021220CRP1922).

6. References

[1] Wu, Y., Qiao, P., Chong, T. & Shen, Z. Advanced Materials, **14,** 1 (2002).
[2] Hiramatsu, M. & Hori, M. Carbon nanowalls: Synthesis and emerging applications. Carbon Nanowalls: Synthesis and Emerging Applications (2010). doi:10.1007/978-3-211-99718-5.
[3] Ghosh, S. et al. Applied Surface Science **349,** 576-581 (2015).
[4] Bo, Z. et al. Nanoscale **5**, 5180-5204 (2013).
[5]Hiramatsu, M., Shiji, K., Am,ano, H. & Hori, M. Applied Physics Letters, **84**, 4708 (2004).
[6] Kawai, S. et al. Japanese Journal of Applied Physics, **49**, 060220 (2010).
[7] Liu, J. et al. Applied Physics Letters, 106, 043904, (2015).
[8] Yang, C. et al., Journal of Materials Chemistry A, **1**, 770-775 (2013).
[9]Lin, G. et al., Functional Materials Letters, **11**,1 (2018).
[10] Wei, W., Sun, K. & Hu, Y. H., Industrial & Engineering Chemistry Research, **56**, 7, 1803–1809, (2017).
[11] Han, T. H. et al., Nature Photonics, **6**, 105–110 (2012).
[12] Ci, H. et al., Advanced Materials, **31**, 29, (2019).
[13] Seo, D. H. et al. Nature Communications, **8**, 14217 (2017).
[14] Tomatsu, M. et al. Japanese Journal of Applied Physics, **56,** 06HF03 (2017).
[15] Jiang, N., Wang, H. X., Zhang, H., Sasaoka, H. & Nishimura, K., Journal of Materials Chemistry, **20**, 5070-5073 (2010).
[16] Fang, J., Levchenko, I., Van Der Laan, T., Kumar, S. & Ostrikov, K., Carbon **78**, 627-632 (2014).
[17] Yerlanuly, Y. et al. Applied Surface Science, **523**, 146533 (2020).
[18] Ichikawa, T., Shimizu, N., Ishikawa, K., Hiramatsu, M. & Hori, M., Carbon, **161**, 403-412, (2020).
[19] Choi, H., Kwon, S., Kang, H., Kim, J. H. & Choi, W., Energies **12**(24), 4759 (2019).
[20] Kim, S. Y., Choi, W. S., Lee, J. H. & Hong, B., Materials Research Bulletin, **58**, 112-116 (2014).
[21] Yerlanuly, Ye. et.all, Scientific Reports, **11**, 19287 (2021).
[22] Y. Yerlanuly et.all, ACS Omega, **7**, 51, 48467–48475, (2022).