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`REGULAR ARTICLE

Ultrasonically Assisted Fabrication of Graphene/ZnO Nanocomposites with Accelerated Ultraviolet Photoresponse

A. Nadtochiy[1], A. Podolian[1,*], O. Korotchenkov[1], O. Oberemok[2], O. Kosulya[2], B. Romanyuk[2]

[1] *Faculty of Physics, Taras Shevchenko National University of Kyiv, 01601 Kyiv, Ukraine*
[2] *V. Lashkarev Institute of Semiconductor Physics NAS of Ukraine, 03028 Kyiv, Ukraine*

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This study focuses on ultrasonically assisted fabrication of the graphene/ZnO interface by placing ZnO nanorods into a graphene-tetrahydrofuran solution. This technique increases the magnitude of the photocurrent in ZnO illuminated by a 275 nm light and accelerates the photocurrent transient. A simplified model based on the charge transfer at the graphene/ZnO interface is proposed to describe the observed phenomenon. It is interpreted as a result of an enhanced injection of photogenerated electrons into graphene nanosheets accompanied by a significantly reduced concentration of oxygen atoms adsorbed on the surface of ZnO nanorods. This approach can be used to manufacture fast ultraviolet ZnO-based photodetectors.

Keywords: Surface Photovoltage, Zinc Oxide, Photocurrent Decay.

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1. INTRODUCTION

Ultraviolet radiation (UV) detectors are attractive for use in astronomy, radiation control in medical applications, flame detection, and detecting the energy emitted from missile launches [1]. Therefore, there is great demand for the manufacturing of compact and reliable detectors of UV radiation. Due to its unique properties, such as high radiation hardness, chemical stability, low manufacturing cost, large bandgap, and environmental friendliness, ZnO is a promising material for creating various sensors and, in particular, UV detectors [1-3].

UV detectors, which exploit the phenomenon of photoconductivity in ZnO thin films, and barrier-type photovoltaic detectors, in which barriers are formed in contact with metals or other semiconductors, have been widely used [1, 3, 4]. However, there is one important problem associated with the widespread use of ultraviolet detectors based on ZnO. This is due to the low speed of operation, which in turn is associated with the adsorption and desorption of atmospheric oxygen on the surface of ZnO [3].

Graphene, a 2D layered material, attracts considerable interest due to its unique properties such as high mechanical strength and flexibility, high charge carrier mobility, excellent transparency, and thermal conductivity [5]. The ZnO/graphene heterostructure is an interesting combination, as both components exhibit good electronic and optoelectronic properties, which paves the way for their application in optoelectronics and sensors [2, 6, 7].

In particular, the creation of UV photodetectors based on ZnO/graphene composite films with improved properties was demonstrated [1, 3, 6, 8, 9]. However, a complex multistep approach typically synthesized the ZnO/graphene nanohybrid. For example, the fabrication of ZnO nanowires/graphene nanohybrids employs complex chemical methods, which include the growth of graphene on a Cu substrate by the CVD method, the growth of ZnO nanorods on graphene by CVD or RF magnetron sputtering methods, coating the graphene-on-Cu sample with poly-methylmethacrylate (PMMA) followed by chemical etching of the Cu substrate [6, 7, 8, 9]. These factors significantly complicate the production of ZnO/graphene nanostructures. Due to their relative simplicity and efficiency, the sonochemical methods for obtaining nanosized ZnO [10], the aqueous liquid phase exfoliation supported by sonication of graphene nanosheets [11, 12] and ZnO-graphene nanohybrids [13] deserve special attention.

Here, we study the possibility of creating a ZnO/graphene interface by additional exfoliation of the graphene nanosheets and their deposition from a solution during ultrasonic treatment. The improved transient properties of the UV photoconductivity are obtained in the fabricated structures.

2. EXPERIMENTAL DETAILS

Photocurrent (PC) and surface photovoltage (SPV) decay curves were measured in ZnO films with a thickness of about 100 nm. The films were deposited onto glass substrates at room temperature by the RF reactive magnetron sputtering using a ceramic aluminum-doped zinc oxide (AZO) (98 wt % ZnO + 2 wt % Al_2O_3)

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[*] Correspondence e-mail: artem1976@knu.ua

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target with a purity of 99.99 %. Subsequent annealing of the ZnO film was performed at 600 °C for 30 min in an argon atmosphere to decrease the structure imperfections of the ZnO film. ZnO films synthesized on a glass substrate have been in the form of ZnO nanorods oriented along the c-axis [14].

Here, we compare the PC and SPV decay properties of the resulting ZnO films before (untreated ZnO) and after the deposition of graphene nanosheets on ZnO nanorod surfaces. 100 mg of as-synthesized graphene derivatives was added in 20 mL of tetrahydrofuran (THF) and allowed to sonication for 60 min. THF was chosen because it is a good organic solvent for graphite nanomaterials [15]. Ultrasound treatment of graphene in a tetrahydrofuran solution was expected to contribute to additional exfoliation of graphene in monolayers of graphene, better separation, and grinding of graphene nanosheets [11, 12].

The deposition of graphene nanosheets on ZnO nanorods was carried out by immersing a glass substrate with a ZnO film in a THF solution with graphene under simultaneous ultrasonic treatment. It should be expected that, with this method of deposition, graphene nanosheets will interact more effectively with the surface of ZnO nanorods, and the resulting area of the formed ZnO/graphene heterostructure will increase. It was experimentally found that the optimal graphene nanosheet deposition time is 5 min. After removal from the solution, the sample was allowed to dry in air without a special time limitation.

For PC decay measurements, In-electrodes were slightly pressed to the surface of ZnO thin film. The current-voltage measurements showed that the In-electrodes made an ohmic contact with the ZnO surface. In one of the electrodes the reference voltage $U = 5$ V was applied and the current through the ZnO film was measured using the OP-AMP current-to-voltage converter connected to the other electrode. SPV transient curves were measured using the capacitor arrangement setup. The details of the measurement are described in the article [16]. Assuming a band gap of ZnO thin film $E_g = 3.2$-3.3 eV [17], we obtain that for the excitation of electron-hole pairs it is necessary to use light with $\lambda < 375$ nm. In our measurements, the samples are excited by light pulses with wavelength $\lambda = 275$ nm produced by UV-LED ProLight Opto PB2D-UCLA-TC. At the surface of the ZnO film light power was calculated to be of approximately 3 mW/cm^2. At a wavelength of 275 nm, the penetration depth of light into the ZnO thin film was evaluated to be of order of 70 nm [18].

3. RESULTS AND DISCUSSION

One of the main problems of UV detectors based on ZnO thin films is their low operating speed. To check the speed performance of our structures, we measured the PC rise and decay kinetics. The time dependences of photoconductivity were measured at room temperature. Typical time dependences of the photocurrent in both bare ZnO and graphene/ZnO heterostructure films are shown in Fig. 1.

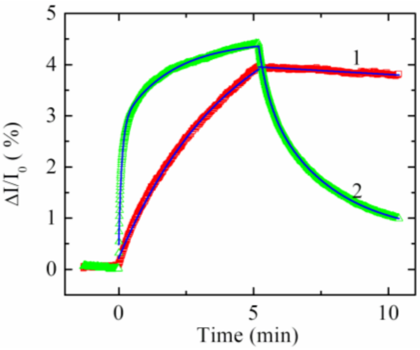

Fig. 1 – Measured PC transients in ZnO (1) and ZnO/graphene (2) films. I_0 – dark current. The duration of the exciting light pulse is 5 min

Note that the rise and decay of the photocurrent in the samples we studied was rather slow. Therefore, to clarify the details of the photocurrent rise and decay curves, the samples were illuminated with single-LED pulses for 5 min. In the sample with a bare untreated ZnO film (curve 1), during the duration of the LED light pulse, the photocurrent increases to a value that is only ~ 4 % of the dark current of the sample. From the approximation of the time dependences of the photocurrent (solid line in curve 1), it is found that in the bare sample, both rise and decay photoconductivity curves are correctly described by the monoexponential law. For the rise curve, this law can be written in the form

$$I_{on}(t) = I_{on0} + A_1\left(1 - e^{-t/\tau_1}\right), \tag{1}$$

where the calculated photocurrent rise time constant is $\tau_1 = 250$ s. After the light is turned off, the photoconductivity decay curve can also be described by a single exponent in the form

$$I_{off}(t) = I_{off0} + A_2 e^{-t/\tau_2}, \tag{2}$$

with $\tau_2 = 15000$ s.

After 5 min of exposure of the sample with a ZnO film in a solution of graphene in tetrahydrofuran under simultaneous ultrasonic treatment of the solution followed by air drying of the sample, a ~ 4.5 % increase in the PC maximum magnitude is observed. However, the most drastict sonication effect is a significant acceleration of the photocurrent rise and decay kinetics seen in curve 2 of Fig. 1. In this case, the approximation of the photocurrent rise and decay curves (solid line in curve 2) leads to the conclusion that both the rise and decay curves can be correctly described only by the sum of two exponential terms. Thus, for the photocurrent rise curve, the time dependence can be represented by a double-exponential form

$$I_{on}(t) = I_{on0} + A_1\left(1 - e^{-t/\tau_1}\right) + A_2\left(1 - e^{-t/\tau_2}\right), \tag{3}$$

where the calculated time constants for fast and slow photocurrent rise are $\tau_1 = 6.6$ s and $\tau_2 = 110$ s, respectively. Accordingly, for the photocurrent decay curve, the time dependence of the PC can be given by

$$I_{off}(t) = I_{off0} + A_3 e^{-t/\tau_3} + A_4 e^{-t/\tau_4}, \tag{4}$$

with the calculated fast and slow photocurrent decay time constants $\tau_3 = 22$ s and $\tau_4 = 150$ s, respectively.

Therefore, it is important to note that although the slower photocurrent rise time increases only by a factor of ~ 2.3 [τ_1 in Eq. (1) and τ_2 in Eq. (3)], the slower PC decay rate decreases by 2 orders of magnitude [τ_2 in Eq. (2) and τ_4 in Eq. (4)].

In general, it is believed that the slow rise and decay of UV photoconductivity in ZnO under normal atmospheric conditions is due to the slow atmospheric oxygen adsorption and desorption processes [19, 20, 1, 4, 8, 10]. In the dark, on the surface of ZnO nanorods, O_2 is chemisorbed to surface oxygen vacancy states by capturing conduction electrons (e^-) from the ZnO volume followed by the formation of negative ions on the surface according to the reaction

$$O_2\ (g) + e^- \rightarrow O_2^-.$$

As a result, low conductivity depletion layers are formed near the ZnO nanorod surfaces. When UV light is turned on, the photocurrent should initially increase rapidly due to the generation of electron-hole pairs

$$h\nu = e^- + h^+$$

Later, a slow increase in the photocurrent should occur. This is due to the migration of photogenerated holes to the surface of ZnO nanorods, their capture by adsorbed O_2^- ions, and oxygen desorption described by

$$h^+ + O_2^-(ad) \rightarrow O_2\ (g).$$

As a result, the width of the depletion layer is reduced, which, along with increasing the free carrier rate, thereby enhances conductivity.

After UV light is turned off, a fast photocurrent decay should first occur due to the recombination of electron-hole pairs at fast defect recombination levels, accompanied by a slow decay of photoconductivity via the capture of electrons by the re-adsorbed O_2 on the surfaces of ZnO nanorods [4]. Therefore, it should be expected that the photoconductivity rise and decay rates in ZnO nanorods will depend on the ratio of the concentrations of fast-defect recombination levels and oxygen adsorbed on the surface. Reducing the possibility of oxygen adsorption on the ZnO nanorod surfaces can be expected to increase the speed of ZnO-based photoconductive-type photodetectors.

When creating a graphene/ZnO interface, an ohmic contact is formed between ZnO and graphene [9]. The formation of a graphene/ZnO interface should prevent the adsorption of oxygen on the surfaces of ZnO nanorods. In addition, because of the ohmic contact, there is a high possibility of rapid separation of photogenerated in ZnO nanorods carriers via the transfer of electrons to graphene. The mobility of electrons in graphene will be high enough to additionally increase the speed of ZnO-based photoconductive type photodetectors.

In the present work, we attempted to create a large area of the graphene/ZnO interface by deposition of graphene nanosheets on the surface of ZnO nanorods from a sonicated THF solution with graphene. The sonication of the graphene derivatives in tetrahydrofuran for 60 min is expected to lead to an additional exfoliation of graphene into graphene monolayers and better grinding and separation of individual nanosheets [11, 12]. When a sample with a ZnO film is sonicated in the solution, the surface of ZnO nanorods should be cleaned from adsorbed oxygen due to cavitational treatment. Furthermore, nanosheets in the form of graphene monolayers dispersed in tetrahydrofuran due to sonication of the solution can effectively interact with ZnO nanorods, creating a graphene/ZnO interface; see Fig. 2.

As a result, there is a significant decrease in the concentration of oxygen adsorbed on the surfaces of ZnO nanorods, and the possibility of efficient transfer of photogenerated electrons to graphene nanosheets occurs. The photogenerated charge carriers recombine faster and move faster to the electrodes, which thus explains the significant acceleration of PC transients observed in our experiments.

Because the formation of the graphene/ZnO interface should significantly reduce the concentration of oxygen adsorbed on the surfaces of ZnO nanorods, the thickness of the near-surface depleted layer in ZnO nanorods should also decrease. If we also take into account the ohmicity of the graphene/ZnO interface, the efficiency of the separation of photogenerated charge carriers along the c-axis of ZnO nanorods should also increase due to the rapid transfer of photogenerated electrons to graphene nanosheets.

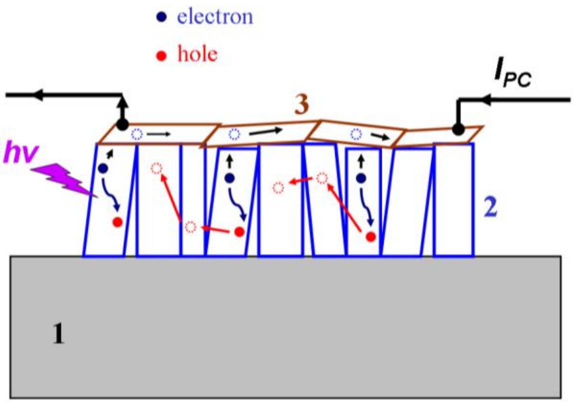

Fig. 2 – Photocurrent formation in graphene/ZnO interface. 1 – glass substrate, 2 – ZnO nanorods, 3 – graphene monolayers

To determine the efficiency of the spatial separation of photogenerated charge carriers due to the electron transfer from ZnO nanorods to graphene nanosheets, we additionally measured fast SPV transient kinetics. The time dependences of SPV were measured under illumination with short LED light pulses of only 100 μs, since we were interested in the fast photogenerated carrier spatial separation processes in the direction perpendicular to the surface of the glass substrate, that is, mainly along the c-axis of ZnO nanorods. SPV transient curves are shown in Fig. 3.

This experiment shows that in the sample with the graphene nanosheets deposited on the surfaces of the ZnO nanorods, the amplitude of the SPV (curve 2 in Fig. 3) increases compared to the sample with the bare ZnO film (curve 1). This result can confirm our assumption of the more effective separation of photogenerated

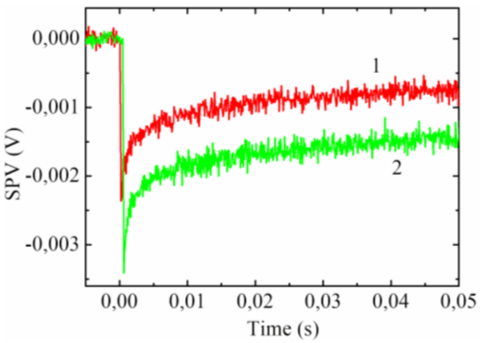

Fig. 3 – Measured fast SPV transients in ZnO (1) and ZnO/graphene (2) films. The duration of the exciting light pulse is 100 μs

charge carriers in ZnO nanorods because of the reduction of the near-surface electron-depleted layer and the transfer of photogenerated electrons from ZnO nanorods to graphene nanosheets. At the same time, the analysis of the SPV transient curves shows that the SPV rise and decay rates practically do not change, which is indicative of the fact that the concentration of fast defect recombination levels on the surface of ZnO nanorods almost does not change during the formation of the graphene/ZnO interface.

4. CONCLUSIONS

The ultrasonically-assisted deposition of graphene nanosheets onto the surface of ZnO nanorods from the graphene-tetrahydrofuran solution has increased the magnitude of the photocurrent in ZnO illuminated by a 275-nm light and accelerated the photocurrent transient. A simplified model based on the formation of a large area of the graphene/ZnO interface is proposed to describe the observed phenomenon. It is interpreted as a result of an enhanced injection of photogenerated electrons into graphene nanosheets accompanied by a significantly reduced concentration of oxygen atoms adsorbed on the surface of ZnO nanorods. The result can be used to manufacture fast UV ZnO-based photodetectors.

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Стимульоване ультразвуком виготовлення нанокомпозитів графен/ZnO з прискореним фотовідгуком в ультрафіолетовому діапазоні світла

А. Надточій[1], А. Подолян[1], О. Коротченков[1], О. Оберемок[2], О. Косуля[2], Б. Романюк[2]

[1] *Фізичний факультет, Київський національний університет імені Тараса Шевченка, 01601 Київ, Україна*
[2] *Інститут Фізики напівпровідників ім. В. Є. Лашкарьова НАН України, 03028 Київ, Україна*

Осадження графенових нанопластинок за допомогою ультразвуку на поверхню нанострижнів ZnO з розчину графен-тетрагідрофурану дозволяє збільшити величину фотоструму в ZnO, освітленому світлом з довжиною хвилі 275 нм, і прискорити перехідні процеси фотоструму при імпульсному освітленні. Для опису спостережуваного явища запропоновано спрощену модель, засновану на формуванні межі поділу графен/ZnO. Отримані дані пояснюються посиленою інжекцією фотогенерованих електронів у графенові нанопластинки, що супроводжується значно зниженою концентрацією атомів кисню, адсорбованих на поверхні нанострижнів ZnO. Результат може бути використаний для виготовлення швидких УФ фотодетекторів на основі ZnO.

Ключові слова: Поверхнева фото-Е.Р.С., Оксид цинку, Релаксація фотоструму.