

Short Communication

Formation of Graphite Nanostructures on the Surface of Layered n -InSe Crystal

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The possibility of the formation of graphite nanostructures on the (0001) surface of layered InSe semiconductor by the sputtering in vacuum is shown. The InSe single crystals were grown by the Bridgman method from a nonstoichiometric melts $\text{In}_{1.03}\text{Se}_{0.97}$ in silica ampoules. They had the crystalline structure of the γ -polytype, n -type conductivity, and an electron concentration of 10^{15} cm^{-3} at room temperature. The substrates for carbon deposition with dimensions of $4 \times 4 \times 0.2 \text{ mm}$ were prepared by mechanical exfoliation along the InSe layers. The deposition of the material was carried out at substrate temperatures in the range of $300\text{--}400 \text{ }^\circ\text{C}$ and upon irradiation of the growth zone with high-energy ultraviolet light. The latter was generated by halogen lamps with a quartz shell. In addition, a constant electric voltage was applied to the substrate to improve the formation of critical nuclei of carbon nanostructures. The carbon was sputtered from an electrode, which was under positive voltage of 2800 V in a vacuum of 10^{-4} Pa during 50 min. The obtained structures are long nanoformations with length about several micrometers. Their location is determined by the dislocation grid of the InSe surface. The height of the carbon nanostructures does not exceed 100 nm. This ensures their transparency in a wide spectral range. In addition, such nanostructures have high electrical conductivity, small refractive index (~ 1.5) in the spectral sensitivity range of InSe, and a heterojunction can be formed at the graphite/ n -InSe interface. Grown carbon nanostructures contribute to the propagation of incident light into the depth of crystal. The characteristic peaks of γ -InSe crystals and graphite are observed in the Raman spectrum. They indicate the absence of chemical interaction between the deposited material and the substrate, some plastic deformation of the substrate and the presence of a large number of structural defects in the carbon nanoformations.

Keywords: Nanostructures, Graphite, Indium selenide.

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1. INTRODUCTION

The development of methods for creating spatially ordered quantum-dimensional structures is an actual problem in modern nanoelectronics [1]. They can be grown on a substrate of layered semiconductors [2, 3], whose crystal structure allows to obtain an atomically smooth surfaces with a low density of dangling bonds by simple mechanical exfoliation. One of the promising materials for these purposes is graphite [4–7].

Indium selenide has high electron mobility, good photosensitivity in visible and near-infrared region of the electromagnetic spectrum [8], and photopleochromism [9]. It expands the area of practical use of graphite/InSe structures making them attractive candidates for investigating various optical effects.

In this paper, the surface morphology and optical properties of graphite nanostructures grown on the (0001) surface of InSe were investigated. The high values of the transparency of these nanostructures (several dozen nm thickness), the high electrical conductivity (important for its use as an electrical contact), small values of a refractive index (~ 1.5) in the spectral sensitivity range of InSe compared with its values for InSe crystal (~ 2.1), and the presence of a direct optical band gap in InSe (a necessary condition for light emitting semiconductor devices) provide the possibility for fabrication of nanochips for optoelectronic systems on the van der Waals surfaces of InSe.

2. EXPERIMENTAL

The substrates for vacuum deposition of carbon were prepared by mechanical exfoliation from bulk Bridgman-grown InSe crystals. They had dimensions of $4 \times 4 \times 0.2 \text{ mm}$. The high-resistance InSe single crystals had the crystalline structure of the γ -polytype, and n -type conductivity with an electron concentration of 10^{15} cm^{-3} at room temperature. The carbon was sputtered from an electrode, which was under positive voltage of 2800 V in a vacuum of 10^{-4} Pa at $390 \text{ }^\circ\text{C}$ for 50 min. The dc voltage applied to the InSe substrate provides the formation of critical nuclei of carbon nanostructures on the (0001) surface. During growth, the nanostructure was irradiated by high-energy UV radiation using halogen lamps with a quartz shell.

The surface morphology of nanostructures was studied by tapping mode atomic force microscope (AFM) in air. Micro-Raman and micro-photoluminescence spectra were measured in air at different points of the sample surface at room temperature using a Nd:YVO₄ laser ($\lambda = 532 \text{ nm}$), a confocal optical microscopic system, and an optical spectrometer (150–1200 ppm/mm) with a cooled InGaAs photodetector. The laser beam was focused by 100x lens on the surface in a light spot with a diameter of $1 \text{ } \mu\text{m}$. To exclude significant heating of the samples, the power of the light flux did not exceed 10 mW. The photosensitivity spectra of the structures were investigated using a MDR-23 monochromator.

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3. RESULTS AND DISCUSSION

At temperatures up to 300 °C, nanosized surface defects are formed on the InSe surface due to plastic deformation along the pyramidal glide planes of dislocations in hexagonal crystals. They pass through the chalcogen atoms in the (0001) plane and are located in this plane at an angle of 60° relative to each other. Such defects cover several layers and pass into the crystal bulk at an angle $\alpha = 30^\circ$ to the C crystal axis. The appearance of these planes is accompanied by rupture of the atomic bonds between metal and chalcogen in the InSe crystal lattice and formation of nanosized In droplets along the straight lines on the van der Waals surfaces, where nanostructures grow [3]. Nanosized In droplets act as a catalyst in the formation of nanostructured graphite. The irradiation of the growth zone of carbon nanostructures by high-energy ultraviolet radiation also facilitates the graphitization of carbon nanostructures. They grow at a certain angle relative to the C crystal axis of InSe in nano-cavities on its surface (see Fig. 1).

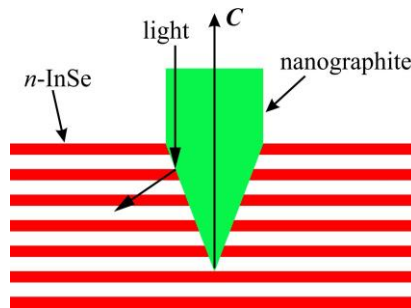


Fig. 1 – Schematic representation of the graphite/*n*-InSe nanostructure

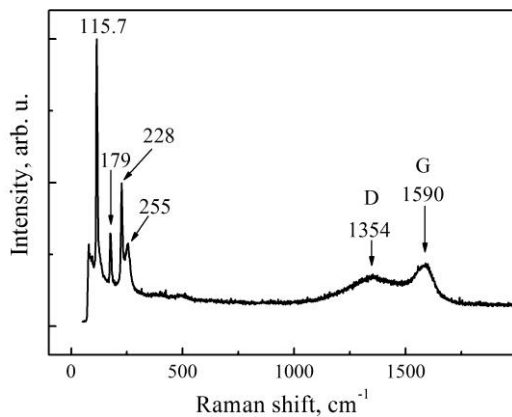
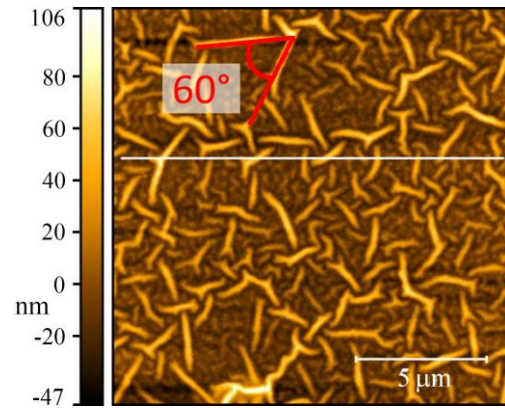


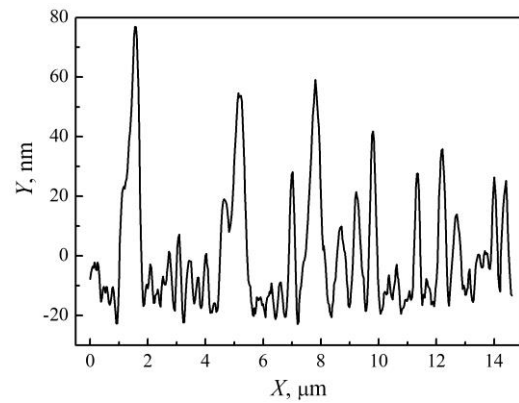
Fig. 2 – Raman spectra of the graphite/*n*-InSe nanostructure ($T = 300$ K)

Fig. 2 shows the Raman spectra of grown nanostructures in the range of 50-2000 cm^{-1} . The strong and narrow bands at 115.7, 179, and 228 cm^{-1} are observed. They are typical for a rhombohedral γ -InSe crystal, which is used as substrates for the growth of nanostructures. This means that when carbon is deposited, there is no chemical interaction between the deposited material and the substrate. However, the presence of a peak at 255 cm^{-1} , belonging to amorphous selenium, indicates plastic deformation of the substrate at heating that leads to the rupture of atomic bonds between metal and chal-

cogen in InSe crystal. The D and G bands in the Raman spectra at 1354 cm^{-1} and 1590 cm^{-1} confirmed the formation of nanosized graphite on the (0001) van der Waals surface [10]. The D band indicates a large number of structural defects.



a



b

Fig. 3 – Surface morphology of the graphite/*n*-InSe nanostructure: a) two-dimensional AFM image; b) height distribution of a rough surface

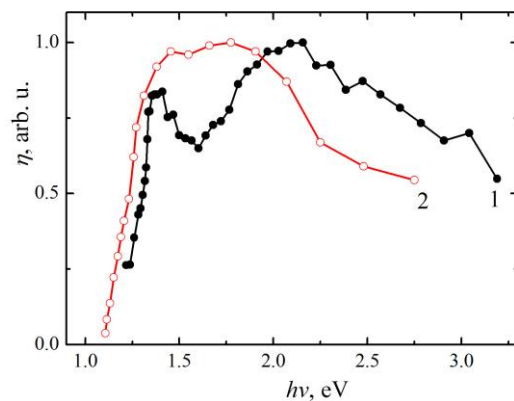


Fig. 4 – Photoresponse spectrum of the graphite/*n*-InSe nanostructure (curve 2) and *n*-InSe (curve 1) ($T = 300$ K, photocurrent flow along the C crystal axis)

As can be seen from the AFM images (see Fig. 3), the carbon structures are long (about several micrometers) nanoformations. They have a height less than 100 nm and are located in the sites of exit of plastic deformation planes on the (0001) surface. At such height, they pass

over 80 % of the incident radiation in the fundamental absorption region of InSe. The light incident on the nanostructure surface propagates along these transparent channels into the crystal bulk. The refractive index is greater in InSe than in nanographite. When light passes through the graphite/*n*-InSe interface, the light is deviated and then propagates at a smaller angle relative to the plane of InSe layers (see Fig. 1). Therefore, the contribution to the photoconductivity of light component with polarization of $\mathbf{E} \parallel \mathbf{C}$ (\mathbf{E} is the electric field vector of the light wave) increases. This leads to a change of the size and shape of the photoresponse spectrum (Fig. 4) [11]. Such polarimetric structure can be used to measure the parameters of polarized optical radiation by changing the angle of incident beam relative to the (0001) plane of the layered crystal. The advantage of such

measurements is that they do not require the presence of electrical contacts at the end face of the sample.

It is known that the heterojunction may be formed at the interface between graphite and InSe [12]. As can be seen from Fig. 4, the same situation takes place in our case. This gives additional opportunities for the practical use of the obtained structures in electronics.

4. CONCLUSIONS

A new, technologically simple way of growing graphite nanostructures on the InSe substrate is proposed. They are photosensitive within the range of 1.2-3 eV. The obtained carbon nanotubes can be used to make heterojunctions and also can act as a selective coating material for photoconverters.

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Формування графітових наноструктур на поверхні шаруватого кристалу *n*-InSe

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Показано можливість формування графітових наноструктур на поверхні (0001) шаруватого напівпровідника InSe розпиленням у вакуумі. Монокристали InSe вирощувалися у кварцових ампулах методом Бріджмена із розплаву нестехіометричного складу $\text{In}_{1.03}\text{Se}_{0.97}$. Вони мали кристалічну структуру γ -політипу, *n*-тип провідності та концентрацію електронів $\sim 10^{15} \text{ см}^{-3}$ при кімнатній температурі. Підкладки для осадження вуглецю розміром $4 \times 4 \times 0.2$ мм виготовлялися механічним сколюванням вздовж шарів InSe. Осадження матеріалу проводилось при температурах підкладки 300-400 °C і при опроміненні зони росту високоенергетичним ультрафіолетовим випромінюванням. Останнє генерувалося за допомогою галогенних ламп з кварцовою оболонкою. Додатково, для покращення формуванню зародків вуглецевих наноструктур, до підкладки прикладалася постійна електрична напруга. Вуглець розпилювався з електрода, який знаходився під позитивною напругою ~ 2800 В у вакуумі $\sim 10^{-4}$ Па протягом 50 хвилин. Отримані структури представляють собою протяжні нанотворення довжиною декілька мкм. Їх розташування задається дислокаційною сіткою поверхні InSe. Висота вуглецевих наноструктур не перевищує 100 нм. Це забезпечує їх прозорість в широкому спектральному діапазоні. Крім того, такі наноструктури мають високу електричну провідність, малий коефіцієнт заломлення світла (~ 1.5) в області спектральної чутливості InSe, а на інтерфейсі графіт/*n*-InSe може утворюватися гетероперехід. Вирощені вуглецеві наноструктури сприяють розповсюдженню падаючого на поверхню InSe світла в глибину кристалу. В раманівських спектрах присутні піки, що характерні для кристалів γ -InSe та графіту. Вони вказують на відсутність хімічної взаємодії між осадженим матеріалом і підкладкою, деяку пластичну деформацію підкладки та наявність великої кількості структурних дефектів у вуглецевих нанотвореннях.

Ключові слова: Наноструктури, Графіт, Селенід індію.