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Light emission enhancement from ZnO nanostructured films grown on Gr/SiC substrates

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Abstract

We report on the application of a single layer graphene substrates for the growth of polycrystalline ZnO films with advanced light emission properties. Unusually high ultraviolet (UV) and visible (VIS) photoluminescence was observed from the ZnO/Gr/SiC structures in comparison to identical samples without graphene. The photoluminescence intensity depends non-monotonically on the films thickness, reaching its maximum for 150 nm thick films. The phenomena observed is explained as due to the dual graphene role: i) the dangling bond free substrate, providing growth of relaxed thin ZnO layers ii) a back reflector active mirror of the Fabry-Perot cavity that is formed. The reported results demonstrate the potential of two-dimensional carbon materials integration with light emitting wide band gap semiconductors and can be of practical importance for the design of future optoelectronic devices.

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1. Introduction

Integration of the emerging two-dimensional materials with conventional semiconductors is a new direction in material science enabling plenty of novel potential applications [1]. Via combination of graphene (Gr) with semiconducting oxides, such as TiO_2 [2] or ZnO [3-6], hybrid composite materials and planar heterostructures with modified properties have been recently reported, facilitating novel and high performance applications.

Particularly, ZnO is a prospective semiconductor material for light emitting diodes (LEDs) due to its wide band gap (~ 3.37 eV) and high exciton binding energy (~ 60 meV at room temperature) [7]. In terms of LEDs application the light emission efficiency is of primary importance. Therefore, the possible enhancement of the light emission intensity from ZnO is a critical issue and has attracted plenty of research efforts. One of the approaches to facilitate light emission is by increasing the external efficiency, i. e. by enhancement of the light extraction from the material, via application of the special design and geometry. In parallel, the light emission may be increased via enhanced internal efficiency due to intensification of the radiative recombination processes. This may be achieved by improvement of the material structural quality and non-radiative defects elimination or using quantum wells etc. Alternatively, the radiative recombination processes and thus the light emission can be further facilitated by involvement of the phenomena such as surface plasmons [8,9] or Fabry-Perot resonance [10].

It has been earlier shown that the light emission from ZnO can be enhanced due to resonant coupling of excitons with plasmons in metals such as Au, Ag, Al or other metal-like materials [8, 9]. Recently, carbon based materials, i. e. single-walled carbon nanotubes (SWCNTs) and graphene were suggested as alternatives of the metals [3-6]. The possibility of light emission intensity increase was demonstrated by Kim et al. [3], where the SWNTs of 3–120 nm thickness were deposited on top of 100 nm ZnO films/n-type Si (100) wafer. These findings are discussed based on the surface-plasmon-mediated emission mechanism. Hwang et al. [4] reported 4-fold increase of light emission from the Gr/ ZnO structure, where a flake of graphene was put on top of the rough surface of ZnO film. The authors have explained the phenomenon observed as due to resonant coupling of excitons in ZnO with the surface plasmons possibly existing in graphene at a matching frequency. Such exciton-plasmon coupling could, in principle, enable energy transfer at the Gr/ ZnO interface and thereby intensify the radiative recombination processes due to much faster plasmon recombination rate. However, these results were criticized and the possible

plasmon-exciton coupling was ruled out due to the used geometry, where the excitation was performed from the graphene side [5]. Cheng et al reported enhancement of light emission in a composite consisting of ZnO nanorods (NRs) and reduced graphene oxide flakes. The underlying mechanism has been attributed to resonant coupling between graphene surface plasmons and the excitons in ZnO [6]. The authors noticed that the observed PL enhancement was additionally favored by the corrugated side facets of NRs. Such a corrugation (1-2 nm) was suggested as a sufficient condition for efficient exciton-plasmon coupling and therefore enhanced radiative recombination. Nevertheless, the surface plasmon-induced PL enhancement for ZnO/Gr is still very questionable and debatable issue. This is mainly due to the fact that only terahertz and mid-infrared plasmons were experimentally observed for graphene, whereas visible and UV should be damped in virtue of Landau damping mechanism. Therefore, effective exciton-plasmon coupling in the optical region is not expected. Based on the literature analysis, it is obvious that further investigations are needed to gain insight to the role of graphene in the PL enhancement phenomenon in oxides based materials systems.

We have fabricated structures, consisting of ZnO films and single graphene layers and investigated the light emission phenomena taking place in such structures. Graphene monolayers were grown epitaxially on the SiC substrate [11] and used as a substrate for further MOCVD growth of ZnO films of different thicknesses. The features of photoluminescence (PL) were investigated for a wide temperature range from 4 to 300 K for samples with and without graphene. We have comprehensively analyzed the structural and photoluminescence properties of ZnO films grown on graphene and suggest mechanisms responsible for the light emission enhancement in the ZnO/Gr/SiC structures.

2. Experimental

2.1 Sample preparation

Gr/SiC substrates were prepared by thermal decomposition of SiC at 2000 °C in argon atmosphere. Si-face of (0001) 4H-SiC wafers with a single crystalline orientation [0001] were used. The obtained graphene was an epitaxial monolayer on the ~93% of the substrate area, while the rest is covered with two monolayers. Earlier it was reported that such technique provides high quality large areas monolayers of graphene [11].

Growth of ZnO films on Gr/SiC substrates was realised by metal organic chemical vapour deposition (MOCVD) in a horizontal chamber setup at atmospheric pressure using a single source solid state precursor - zinc acetylacetonate ($\text{Zn}(\text{AA})_2$) and argon as transport gas [12]. During the growth the substrate temperature (T_s) was kept 550 °C, which earlier has been shown to be sufficient for obtaining ZnO films with a bright UV emission [13]. The estimated growth rate was $\sim 5 \text{ \AA/sec}$ at a constant flow of Ar 50 ml/min. Reference graphene-free 4H-SiC substrates were used simultaneously in the same growth run for comparison. ZnO/Gr/SiC and ZnO/SiC samples were grown for 3, 5, 6, 7, 10, and 30 min, providing a thickness of the ZnO films of 100, 150, 180, 200, 350 and 700 nm, respectively.

2.2 Samples characterization

Atomic Force Microscopy (AFM) was used for investigation of the graphene layer topography, using Digital Instruments Nanoscope IV. Reflectance mapping in a modified micro-Raman spectrometer as described in [14] was used for determination of the number of graphene layers on the SiC substrate. Scanning Electron Microscopy (SEM) was used to characterize the samples microstructure in a Leo 1550 Gemini SEM at operating voltage ranging from 10 kV to 20 kV and standard aperture value 30 μm . Selected Area Electron Diffraction (SAED) patterns have been taken using conventional transmission electron microscopy (TEM) by TEM JEM 120 CX. Experimental study of the crystal quality of the structures was carried out using a Philips X'Pert high-resolution x-ray diffraction (HRXRD) diffractometer via acquiring conventional θ -2 θ scans and reciprocal lattice mapping (RLM) images. The peculiarities of the light emission from the samples were studied by micro-photoluminescence at wide temperature range. Excitation was performed by frequency doubled Nd:YVO laser as continuous wave excitation source, giving a wavelength $\lambda = 266 \text{ nm}$. The laser beam was focused by UV lens, providing the excitation area of power 1 mW at circle area around 1.5 μm in diameter. The emitted luminescence was collected and mirrored into a single grating 0.45 m monochromator equipped with a liquid nitrogen cooled Si-CCD camera with a spectral resolution of $\sim 0.1 \text{ meV}$. The low temperature PL study was performed at 4 K by helium cooling of the cold-finger where the samples were placed. Via decreasing the liquid He flow and local heating of the sample holder a temperature dependent PL study was performed for the range from 10 to 300 K.

3. Results and Discussions

3.1 Microstructure characterization of Gr/SiC substrates and grown ZnO films

The Gr/SiC substrate has a terrace-stepped morphology, due to the unintentional misorientation of the SiC substrate and respectively a natural step bunching [15]. As it was observed by AFM (Fig. 1a) and reflectance mapping (Fig. 1b), the SiC surface is up to 93 ± 4 % covered by monolayer of graphene. Graphene monolayer covers densely the step on the SiC surface, while some overgrowth of bilayer is rarely observed.

Figure 1 Topography of the typical Gr/SiC substrates: a) AFM image of the Gr/SiC surface. The dark area is the monolayer of graphene, spread over the steps, while the light areas are patches of graphene bilayer; b) Reflectance map imaging the number of layers of a Gr/SiC template: one monolayer (red) with patches of bilayers (yellow) are visible. Scale bars on both images are 2 μm .

ZnO films of various thicknesses were grown on both substrates - bare SiC and Gr/SiC substrates. Films grown on both types of substrates were found to be polycrystalline, which is due to the moderate substrate temperature and rather large mismatch of the in-plane lattice parameters: $a_{\text{ZnO}} = 0.3252$ nm, $a_{\text{SiC}} = 0.3073$ nm, and $a_{\text{Gr}} = 0.246$ nm. While the polycrystalline growth of ZnO on SiC is rather trivial and can be found elsewhere [i. e. 13], growth of ZnO on Gr/SiC substrates is an original study and is therefore considered in details.

Figure 2 a), b) demonstrates the SEM images of 180 and 700 nm thick ZnO films of, respectively, grown on Gr/SiC substrates. The layers are rather uniform and the grain size tends to increase with the films thickness increase. Furthermore, with the thickness increase the films texture along c-axis also increases, which is due to the competitive grains growth [16]. Thus, due

to the lowest attachment energy on the(0001) plane, the grains oriented with their c-axis perpendicularly to the substrate, grow faster than others, providing increased c-axis texture with the films thickness increase.

Figure 2. SEM images (top view) of the nanostructured ZnO film of 180 nm (a) and 700 nm (b) thicknesses, grown on Gr/SiC substrate; c) SEM image of the thin ZnO film, partially exfoliated from the Gr/SiC substrate during the rapid cooling. Inset represents the detailed cross-section fragment of the exfoliated thin ZnO film (~180 nm), where the interface and films thickness evolution is visible. Scale bars on images a, b, inset are 200 nm; c – 200 μm .

It was also observed that the films grown on Gr/SiC substrates tend to exfoliate easily under rapid thermal cooling after the growth procedure (Fig. 2c). We relate this to the combination of in-

plane lattice mismatch and the difference in thermal expansion coefficients (TEC) of the materials: $TEC_{ZnO} = 6.51 \times 10^{-6} \text{ K}^{-1}$, $TEC_{Gr} = -7.4 \times 10^{-6} \text{ K}^{-1}$. Rapid cooling of the ZnO/Gr/SiC sample from the growth ($T_s = 550 \text{ }^\circ\text{C}$) to the room temperature causes strain at the ZnO/Gr interface, between ZnO and graphene. The SEM image of the partially exfoliated thin ZnO film from the Gr/SiC substrate is presented as the inset in Figure 2c. In order to get deeper insight into the films microstructure, we have examined the cross sections of both thin ($\sim 180 \text{ nm}$) and thick ($\sim 700 \text{ nm}$) films, exfoliated from a Gr/SiC template. A peculiar geometry of the films can be observed at a closer examination of their cross-sections (Fig. 3a, b). Such a rough interface geometry we explain as due to the combination of the deposition parameters (substrate temperature and precursors, and argon partial pressure) and the two-dimensional nature of the graphene as a substrate. Due to the dangling bonds free surface of graphene [17] and ZnO/Gr large lattice mismatch, the ZnO does not grow laterally over it, rather tends to nucleate into small grains. The nucleated grains are thereafter growing further, according to the competitive growth mode. After certain time, the grains start to form a continuous film. Films of the thickness less than $\sim 100 \text{ nm}$ are discontinuous and consist of separate grains of inversed droplet shape, not merged into a layer yet (Supplementary Figure X1a). The nucleated islands at the beginning of the growth are of a uniform size $\sim 25 \text{ nm}$ (Suppl. Figure X1b, left side). Later, they are developed into larger grains, proportional to the film thickness. Figure X1b in the Supplementary Materials demonstrates the surface of the ZnO thick film, with bulky grains of $100 - 150 \text{ nm}$ of an average size (right part of the image). The flipped fragment of the exfoliated films is evidencing the nucleation grains size (left size of the image).

We have used transmission electron microscopy for examination of the evolution of the films crystalline quality. The SAED pattern, acquired for thin ZnO film grown on Gr/SiC displays scattered reflection from a number of crystal planes: (0002) , $(10\bar{1}2)$, $(10\bar{1}3)$, $(10\bar{1}1)$, $(10\bar{1}0)$, $(1\bar{1}22)$ etc is shown in (Fig. 3c). This evidences that thin ZnO film on Gr/SiC is highly polycrystalline without specific texture and consists of grains with different crystal orientation. While the thick films are more textured along the c-axis, which is evidenced by the most intense (0002) reflection, with some minor contribution from $(10\bar{1}0)$, $(10\bar{1}1)$, $(10\bar{1}2)$, $(10\bar{1}3)$ (Fig.3d).

Figure 3. Cross-sectional SEM images of ZnO thin (a) and thick (b) films, exfoliated from the Gr/SiC template: their average estimated thicknesses are shown; SAED images of the films are shown respectively as c) and d), where the reflections from respective crystal planes are shown.

In order to investigate possible strain in the films and extract the lattice parameters, reciprocal lattice mapping (RLM) was performed for the ZnO films grown on both types of substrates (Supplementary Materials, Figure X2). For this, 2θ - ω scans were recorded around the symmetric (0002) and asymmetric $(11\bar{2}4)$ reflections for ZnO/Gr/SiC and ZnO/SiC structures. It was observed, that the full width at the half maximum (FWHM) of the ω -rocking curve (vertical component on RLM map) for (0002) reflection for ZnO/SiC substrate was much smaller than that for ZnO/Gr/SiC: 0.342 vs 0.756 degrees, respectively. This indicates that the growth on bare SiC provides layers with less mutual disorientation of grains (0002) crystal plane. This agrees well with the earlier observed epitaxial growth of ZnO on 4H-SiC, i. e. where the atoms of overgrowing

ZnO are rebuilding the crystal structure of SiC and resulting in both in-plane ($[10\bar{1}0]_{\text{ZnO}}/[10\bar{1}0]_{4\text{H-SiC}}$) and out-of-plane ($[0001]_{\text{ZnO}}/[0001]_{4\text{H-SiC}}$) epitaxy [13]. While the larger value of FWHM for ZnO/Gr/SiC samples we attribute as due to the case, where the substrate is not rebuilt by the overgrowing material. Thus the substrate does not define the out-of-plane epitaxial relationship and the ZnO growth occurs accordingly to the “self-texture” mechanism [16]. Thus, the crystallites in such a film can be much more disoriented and, respectively, the FWHM of the ω -rocking curve around (0002) is larger in this case.

This finding is further confirmed by the obtained value of the lattice parameters. The in-plane lattice parameter a for ZnO/Gr/SiC is 3.253 Å, while for ZnO/SiC it is 3.249 Å. Taking into account that the standard strain-free value of a for ZnO is 3.252 Å, we believe that the ZnO film grown on Gr/SiC provides more relaxed material in comparison to the identical one on SiC. In other words, while the epitaxial growth results in a polycrystalline films that are strained and then relax with creation of the non-radiative defects, the films of ZnO grown on graphene are *a priori* relaxed from the very initial thicknesses. Hence, we suggest that this promotes the efficient light emission from thin ZnO films on Gr/SiC substrate.

3.2 Photoluminescence properties of ZnO/Gr/SiC vs ZnO/SiC structures

We have investigated the room temperature PL spectra for the thin ZnO films, grown on Gr/SiC substrate in comparison to similar ones grown on bare SiC and additionally on conventional Si substrates. The PL measurement conditions (laser power, area of excitation, settings of the spectrometer etc) were the same, enabling us to compare the PL intensities from different samples on different substrates and of different thicknesses. The most intense PL was observed for the films, grown on a Gr/SiC substrate: figure 5a demonstrate the comparative PL spectra for the ZnO thin films of thickness ~150 nm that revealed the most prominent intensity difference. The spectral integral intensities of the near band edge emission ($\lambda_{\text{NBE}} = 360 - 410 \text{ nm}$) in the ultraviolet (UV) range of thin ZnO/Gr/SiC was almost 4 times higher, i. e. ~360 % of those ZnO thin films grown on bare SiC. While the PL of ZnO film on Si substrate was negligibly small in comparison to those on Gr/SiC and SiC (Fig. 5a, blue line).

The qualitative difference in PL spectra of the films is evident also: not only UV emission is more intense, but also the visible (VIS) band intensity is much more prominent for the sample of ZnO/Gr/SiC. We have calculated the enhancement factor for a number of samples from different

locations over the films surface for both UV and VIS luminescence. Indeed, the average value of UV PL enhancement at RT is 3.6 (360%) with standard deviation $\pm 15\%$. While for the DLE the PL enhancement was up to 6.5 (650%) with the deviation reaching up to $\pm 50\%$ (Suppl. Fig. X3)

The UV emission enhancement was studied as a function of the ZnO films thickness (Fig. 4 b,c). Generally, the PL intensity from polycrystalline films increases with their thickness, due to evolutionary improvement of the films crystal quality, i.e. increase of the grains size, reduction of the grain boundaries concentration etc. Indeed, for the ZnO films grown on bare SiC we have observed a monotonous increase of the PL intensity (Fig. 4b, black squares). However, the PL intensity from the films grown of Gr/SiC has different behaviour and *depends non-monotonically* on the films thickness. Initially the weak PL intensity (for the films thicknesses ≤ 100 nm) starts to increase rapidly for the films with thicknesses ranged 150 – 200 nm (Fig. 4b, red circles). It undergoes a maximum for the film ~ 150 nm and then decreases, approaching the same value as for those grown on bare SiC with thicknesses ranging 200 - 700 nm.

Figure 4. a) Comparison of the PL intensity from the ZnO thin films (~ 150 nm) grown on Gr/SiC, bare SiC and Si substrate. The respective regions of excitonic ultraviolet (UV) and visible (VIS)

emission are shown; b) enhanced UV and c) VIS luminescence from the ZnO films of different thicknesses, grown on Gr/SiC (circles) and bare SiC (squares). The lines are only guides for eyes; d) schematic, demonstrating the laser beam excitation and phenomena that occur in case of thin vs thick films.

In order to validate that graphene does not introduce additional levels of PL in ZnO, we have investigated the nature of the light emission from thin ZnO films on graphene by temperature dependent photoluminescence (PL) at 4 – 300 K. The PL spectra for the wavelength 300 – 700 nm for thin ZnO film are shown on Figure 5. At low temperature, the PL spectrum is dominated by donor bound exciton (D^0X) emission peak at 3.3618 eV. At the energy range 3.12 – 3.25 eV a number of peaks, which originate from the SiC substrate is present at low temperature [13]. With the temperature increase the peak of the free excitonic emission (FX) of ZnO starts to appear from the high energy side of the spectrum and becomes completely dominant after 120 K.

Toward the lower energy of the spectrum, the weak peak is located at 3.327 eV, which is attributed to the two electron satellite peak (TES). The energy difference between D^0X and TES is around 34 meV, what is close to two electron satellite separation energy reported for ZnO earlier [18]. The peak origin is confirmed by the fact that the intensity of TES decreases with temperature decrease in the same way as D^0X peaks intensity does, and it is totally vanished after 60 K. The respective temperature dynamics and the peaks energy positions are represented in the inset of Fig. 5. It is also observed, that both the D^0X line and the FX line showed red shifts with temperature increase as well as the total PL intensity rapidly decreases. At the same time, with temperature increase above 150 K, the additional band of luminescence in the visible range appears (450 - 550 nm), which is due to the defects available, as it was reported earlier [19]. Thus, at room temperature the PL spectrum of ZnO/Gr/SiC is dominated by free excitonic emission peak centered at ~3.3 eV followed by wide band of visible luminescence centered at 2.5 eV, which suggests that graphene does not contribute to appearance of any additional peaks in the PL spectrum.

Figure 5. Temperature dependent photoluminescence of ZnO/Gr/SiC: the respective peaks of neutral donor bound ($D^{\circ}X$) and free exciton (FX) emission along with the two electrons satellite emission are shown. Inset represents the temperature dependence of the energy positions of the respective peaks, fitted by Varshni formulae (solid lines).

The enhanced PL from the thin films on Gr/SiC substrates can be explained due to their relaxed nature, as it was demonstrated earlier. However, the PL intensity on films thickness dependence cannot be explained by the films crystal quality only. Apparently, this phenomenon is caused by additional factors, influencing the light emission processes in thin ZnO films grown on Gr/SiC. We explain it as due to the laser beam excitation depth and the role of graphene at the interface.

It is obvious, that the PL enhancement occurs when the entire film – including the graphene interface is excited. The laser penetration depth in ZnO is reported to be $\sim 50 \div 70$ nm for polycrystalline ZnO films [20]. Thus, via excitation of the thin film the entire films volume is excited, reaching the Gr/SiC interface (Fig. 5d) For thicker films (≥ 200 nm) the PL intensity is limited by the laser beam penetration depth. Thus, the excitation and the radiative recombination processes occur in the top part of the film, without involvement of the Gr/SiC interface. Therefore, the PL intensity of thick ZnO films on Gr/SiC substrates is similar to those ones grown on SiC and no light emission enhancement is observed. Meanwhile the films thinner than ~ 100 nm did not reveal any PL enhancement, rather vice versa. It is because such films were observed to be

discontinuous and were in fact separate grains coating the Gr/SiC substrate. Their total volume is basically not enough to provide the intense radiative recombination.

When the laser excitation is penetrating the entire volume of the film, the graphene is involved into the light emission process. To be specific, the planar hybrid structure, at a rough approximation, bears a strong resemblance to Fabry-Perot resonator composed of natural ZnO cavity with two interfaces (air/ZnO and ZnO/Gr/SiC), which play the role of Bragg reflectors (Fig. 6). If we assume that each Bragg mirror has the same product of optical thickness and refractive index, then the following equation is valid:

$$2n_1d_1 = 2n_2d_2 = \frac{n_c d_c}{m} = \frac{\lambda_c}{2}$$

where d_1 and d_2 are the thickness of Bragg reflector, n_1 and n_2 are refractive indices of Bragg reflector, m is the mode number of cavity-photon modes, n_c and d_c are refractive index and thickness of resonator layer, respectively, and λ_c is the central wavelength where the reflectivity occurs. Inserting the central wavelength $\lambda_c=375$ nm (UV FX emission), the refractive index of ZnO ($n \approx 2.45$) at UV range and mode number $m=2$ into the equation, we calculated the cavity thickness to be about 153 nm. In principle, such a value of cavity thickness correlates with results presented in Fig. 4, where the enhancement effect is observed at the thicknesses not exceeding 200 nm. In this regime, the exciting $e-h$ pairs or excitons can interact with the confined optical field (cavity photons) in the ZnO microcavity, thereby improving radiative recombination efficiency [10]. It is interesting to note that equation predicts that in the case of central wavelength as large as $\lambda_c=550$ nm (visible luminescence) the optimal cavity thickness for the first cavity mode ($m=1$) is approximately equal to 120 nm with consideration of wavelength-dependent refractive index of ZnO ($n \approx 2.3$ for $\lambda_c=550$ nm). It explains why we observed the PL enhancement not only within UV region, but also in the visible at the appropriate thicknesses.

Figure 6. Schematics of the Fabry-Perot cavity formed in the ZnO/Gr/SiC structure, comprising the self-organized Bragg reflectors based on the interfaces: ZnO/Gr/SiC and ZnO/air.

4. Conclusion

We have studied the photoluminescence phenomena in ZnO films grown on Graphene/SiC in comparison to conventional SiC substrates. It is demonstrated, that the growth on graphene was affected by its two-dimensional nature and resulted in obtaining of relaxed polycrystalline films with an intense UV and VIS photoluminescence. The most intense PL signal was observed from ZnO films as thin as ~150 nm and is 3.6 (UV) and 6.5 (VIS) times stronger in comparison to the samples grown at identical conditions but without graphene. We explain the observed phenomena as due to formation of the Fabry-Perot cavity in the structure ZnO/Gr/SiC, where graphene plays an additional role as a back reflector. The results obtained are of practical importance for the design of future optoelectronic devices and may facilitate the eventual graphene integration into semiconductor industry.

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