The electroluminescent properties based on bias polarity of the epitaxial graphene/aluminium SiC junction

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Received 13 March 2018, revised 15 May 2018
Accepted for publication 25 May 2018
Published 11 June 2018

Abstract
We investigated the electroluminescent properties of the epitaxial graphene/SiC junction. The temperature and current dependence of electroluminescence from the epitaxial graphene/SiC is measured within a temperature range of 50–300 K. The result of electroluminescence at 300 K is compared with the electroluminescent spectra from aluminium/SiC junction. The difference between the spectra is explained by the different band bending, which could lead to the tunable LED due to the semi-metal character of the graphene. We observed the electroluminescence at both bias polarities and we described the blue shift in the spectra by Franz–Keldysh effect.

Keywords: epitaxial graphene, electroluminescence, graphene/SiC junction, Franz–Keldysh effect

(Some figures may appear in colour only in the online journal)

1 Introduction

Silicon carbide is a material with an indirect broad bandgap from 2.3 to 3.3 eV depending on the SiC polytype. The unique properties of SiC, such as high saturation velocity of charge carriers or high thermal conductivity, make it a promising candidate for high-power and high-temperature applications [1].

The first LED was made of SiC material in 1927 [2]. Jan et al [3] investigated blue electroluminescence from an SiC tunneling diode. Strong electroluminescence in blue range was observed by Lebedev et al [4]. Kamiyama studied the extremely high quantum efficiency of donor-acceptor-pair emission between nitrogen (donor)–boron (acceptor) and nitrogen–aluminium (acceptor) in SiC in a range of yellow and blue color [5], which makes SiC suitable for the production of white LED with a very high color rendering index [6]. The color rendering index is a quantitative measure of the ability of a light source to reveal the colors of various objects faithfully in comparison with an ideal or natural light source. Optical emission between N and B has a wavelength at 590 nm with full width at half maximum (FWHM) ≈110 nm and between N and Al has a wavelength at 460 nm with FWHM ≈80 nm. Another prospective use of SiC is in the area of room temperature single photon emitters [7].

Graphene is a 2D crystal, consisting of a hexagonal lattice of carbon atoms. One of the methods of graphene growth is a thermal decomposition of SiC. The graphene layer is formed on the SiC surface. This growth method provides, apart from chemical vapour deposition, the highest figure of merit in terms of graphene quality and scalability, the two of several requirements for applications in electronics and optoelectronics [8–10]. There has been both intense theoretical [11, 12] and experimental [13–16] research of graphene/SiC interface. However, detailed studies of electroluminescence properties of graphene/SiC interface are rare [17].

We have studied electroluminescent (EL) properties of the graphene/SiC LED at different temperatures (50–300 K). We compared the results of an etalon sample with an Al/SiC interface and discussed differences of electrophysical properties. We verified in comparison with aluminium contacts that the electroluminescence can be altered by different electron affinity of graphene. The altered EL emission is a fingerprint

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of surface-related electron–hole recombination. We point out that, by employing semimetallicity and low density of state, graphene can be used as a suitable candidate for tunable EL diodes. We present a theory based on change of the bangap with the high inner electric field which explains the observed EL shift with applied external voltage.

2. Experimental

We grew graphene on a Si-face of the n-type conductive SiC 4H polytype (manufactured by II–VI incorporation) by thermal decomposition of SiC. The growth temperature was 1650 °C for 5 min in an argon atmosphere. More informations about the growth conditions can be found in our previous work [18]. SiC substrate was doped by nitrogen (ND ≈ 10¹⁶ cm⁻³) and its dimensions were 3.30 × 3.70 × 0.35 mm³. The SiC substrate contains small concentration of aluminium and boron, which are the natural impurities in silicon carbide [19]. The presence of graphene on the SiC surface was verified by Raman spectroscopy (figure 1). The ratio of 2D peak integrated intensity I₂D to G peak integrated intensity I_G is I₂D/I_G = 2.0 ± 0.5 and full width at half maximum (FWHM) of Lorentzian 2D peak is 33 cm⁻¹. These are the fingerprint characteristics of single layer graphene.

To measure EL the sample was inserted between a copper plate and teflon tape. An aluminium tip was attached on the graphene layer (figure 2). The tip and Cu plate were connected to a current source Keithley 2400.

The spectrometer Princeton Instruments SpectraPro 2300i with grating 600 lines mm⁻¹ and nitrogen cooled CCD detector was used to measure the EL spectra. The EL was collected from the opposite side to which the Al tip was attached.

3. Results and discussion

We measured the EL spectrum from the sample with and without graphene contact. These spectra are shown in figure 3. It is evident that EL was observed in both polarities. The spectra of the sample with and without graphene look similar, but there is a difference between intensity and there is a small shift (∆λ ≈ 10 nm), which is caused by a different internal electric field. The internal electric field depends on the surface band bending and on the work function of the metal. This means that if we change the work function of the metal, the EL spectra will change, too. Fermi level in graphene is easily controlled by gate voltage because graphene is a semi-metal [20].

To illustrate the color in both polarities and both contacts the calculated color (CIE x,CIE y)-coordinates are shown on the Commision Internationl de l’Eclaire (CIE) 1931 chromaticity diagram in figure 4.

The difference between sample with aluminium contacts and with graphene contact in current junction is shown on figure 5. It is evident that graphene contact allows the carriers to move easily over the Schottky barrier at graphene/SiC interface. Due to the nature of the spreading electric field around the point contact, the homogeneity of the field and undefined

Figure 1. The measured Raman spectrum of epitaxial graphene (black curve). The reference spectrum of bare SiC is shown by grey curve. The insert graph shows the 2D peak with Lorentzian fit (red dashed curve). The FWHM of 2D peak is 33 cm⁻¹.

Figure 2. Schematic cross sectional view of the sample.
Figure 3. Comparison of EL spectra of SiC with (black curve) and without graphene (red dashed curve). The top graph shows the EL in the negative polarity. The EL spectra in the positive polarity is showed in bottom graph.

Figure 4. Chromaticity diagram with color coordinates for sample emission at both polarities.
contact areas do not allow to analyze the Schottky barrier parameters in details. We also point out that the electronic properties of graphene SiC interface has been intensively studied [21–25], hence we have focused on the electroluminescent properties instead.

The current dependence of the EL spectrum at 300 K is shown in figure 6. The top graph shows the EL spectra in negative polarity (negative bias at the Al contact), which consists of four broad bands. Spectral region #1 at 410 nm (3.02 eV), spectral region #2 at 520 nm (2.38 eV), spectral region #3 at 660 nm (1.88 eV) and spectral region #4 at 900 nm (1.38 eV).

The EL spectrum in positive polarity is approximately three times stronger and consists of three broader bands, spectral region #5 at 410 nm (3.02 eV) with low intensity, spectral region #6 at 660 nm (1.88 eV) and spectral region #7 at 900 nm (1.38 eV). The EL radiation was observed by naked eye.

The EL spectra in positive polarity (positive polarity on the Al contact) are shown in the bottom graph in figure 6. There are three spectral regions, spectral region #5 at 400 nm (3.10 eV) with low intensity, broad strong spectral region #6 at 660 nm (1.88 eV) and spectral region #7 at 900 nm (1.38 eV).
weaker than in negative polarity, but EL light still visible by naked eye.

The temperature dependence of EL in forward (current set to 150 mA) and backward (current set to −50 mA) biased junction is plotted in figure 7. The characteristic temperature dependence leads us to the conclusion that all the radiative transitions are caused by donor-acceptor pair (DAP) recombination because the EL intensity increases with increasing temperature due to the thermally activated electron–hole recombination between acceptor and donor levels. This is a unique fingerprint of the DAP recombination in contrast to the band-impurity transition. Although band-impurity transition could be enhanced by the increased phonon population at high temperatures, the non-radiative recombination (also caused by phonons) would be the dominant recombination channel.

The spectral regions at 3.02 eV and 3.10 eV are caused by the donor-acceptor transition between N and Al [26, 27]. The spectral region at 2.38 eV is ascribed to donor-acceptor-pair recombination between N donors and Al acceptors levels, too [3]. The transitions between N donors and B acceptors is responsible for EL at 1.88 eV [5]. The last spectral region at 1.38 eV could have its origin from the transition between energy levels of a silicon vacancy [28].

All radiative transitions take place in close proximity to the graphene/SiC interface where the tip is attached because there is the highest voltage gradient. When the negative polarity is applied, the electrons are injected from the graphene to the SiC and they can be trapped at nitrogen levels. The minority holes are drawn from the volume to the interface, where they are captured on the acceptor levels and then they are radiatively recombined with electrons from nitrogen levels. In applied positive bias, the electrons are injected from the back contact and attracted from volume to the interface. However, the holes are blocked at the interface and pass through the barrier in a small quantity from the graphene. They are immediately trapped on the boron levels, which have greater capture cross sections than the other levels. Then the captured holes recombine with electrons bound on nitrogen donors and cause the EL at 1.88 eV (660 nm) with FWHM about 0.44 eV (160 nm).
The EL peak positions are determined as centers of mass (COM). The spectral ranges for COM calculations are depicted in table 1 for reverse polarity and at table 2 for positive polarity. The ‘band centers of mass’ show a small blue shift (figure 8 for reverse polarity and figure 9 for positive polarity). This shift is caused by the change of the bandgap as a function of the internal electric field. The maximal inner electric field $E_{\text{max}}$ at the interface is described by the formula [29]

$$E_{\text{max}} = \sqrt{\frac{2eN_D V}{\varepsilon}},$$

(1)

where $V$ is the voltage, $N_D$ is a donor concentration, $e$ is the elementary charge and $\varepsilon$ is the absolute permittivity. The electric field varies in the range of $10^7 - 10^8$ V m$^{-1}$ in our case of applied bias (1–12 V). The change of the bandgap $\Delta W^{\text{exp}}(E)$ with the electric internal field $E$ is described by Franz–Keldysh effect [30].

Figure 8. Bar chart of the center of mass as a function of the current in the sample.

Figure 9. Bar chart of the center of mass as a function of the current in the sample.
\[ \Delta W(E) = W^{\text{exp}}(E) - W(0) = \frac{3}{2} \left( \frac{e\hbar E_{\text{max}}}{(m^*)^{1/3}} \right)^{2/3}, \]

where \( W(0) \) is the position of the EL COM without applied bias, \( \hbar \) is the reduced Planck constant and \( m^* \) is the effective mass. The theoretical curve \( (N_D \approx 10^{16} \text{ cm}^{-3}, m^* = 0.15m_0, \varepsilon \approx 10 \times \varepsilon_0) \) and experimental data are plotted in figure 10. We obtain a good agreement between experimental data and theory equation (2).

4. Conclusions

We have experimentally studied EL from SiC/graphene junction, and, we have compared its transport and emission characteristics to the Al/SiC Schottky point contact. The EL was observed in both positive and negative bias polarity and its color perception is significantly altered in the chromaticity diagram. We have determined the dominant contribution of Franz–Keldysh effect on the band gap of SiC as a function of externally applied bias. The spectral shift of the EL peaks between graphene and AI contacts, both metals with different work function, brings up a perspective of a tunable EL diode based on graphene and its tunable Fermi energy.

Acknowledgments

The study was supported by the Charles University, project GA UK No.932216 and by the Czech Science Foundation, project No. 16-15763Y. This work was supported by the grant SVV–2018–260445. Raman spectroscopy has been measured as part of Project No. VaVPl CZ.1.05/4.1.00/16.0340.
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