Solid State Communications 224 (2015) 37–40

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Metal–semiconductor–metal UV photodetector based on Ga doped ZnO/graphene interface

Manoj Kumar [a,b], Youngwook Noh [a], Kinyas Polat [b], Ali Kemal Okyay [b], Dongjin Lee [a,*]

[a] School of Mechanical Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 143-701, Korea
[b] UNAM-National Nanotechnology Research Center and Institute of Materials Science and Nanotechnology, Bilkent University, 06800 Ankara, Turkey

ARTICLE INFO

Article history:
Received 17 July 2015
Received in revised form
6 October 2015
Accepted 14 October 2015
Accepted by F. Peeters
Available online 20 October 2015

Keywords:
A. Ga doped ZnO
A. Graphene
C. Metal–semiconductor–metal
D. Surface plasmon

ABSTRACT

Fabrication and characterization of metal–semiconductor–metal (MSM) ultraviolet (UV) photodetector (PD) based on Ga doped ZnO (ZnO:Ga)/graphene is presented in this work. A low dark current of 8.68 nA was demonstrated at a bias of 1 V and a large photo to dark contrast ratio of more than four orders of magnitude was observed. MSM PD exhibited a room temperature responsivity of 48.37 A/W at wavelength of 350 nm and UV-to-visible rejection ratio of about three orders of magnitude. A large photo-to-dark contrast and UV-to-visible rejection ratio suggests the enhancement in the PD performance which is attributed to the existence of a surface plasmon effect at the interface of the ZnO:Ga and underlying graphene layer.

1. Introduction

In the recent years, there is enormous interest in fully transparent ultraviolet (UV) zinc oxide (ZnO) thin film based photodetectors (PDs) due to its various applications in environmental monitoring, large area displays and optical communications [1–4]. For UV thin film PDs, it is vital to demonstrate high response capability, good linearity of the photocurrent versus incident optical power and good rejection ratio. Moreover, it is crucial to have structural simplicity, low cost fabrication and room temperature operation for practical application.

Over the last decade, several kinds of wide bandgap semiconductors, such as GaN, SiC, diamond, CdS and ZnO, have been developed and applied to UV PDs [5–9]. Among of them, ZnO has attracted increasing interest for its particular properties such as a wide band gap of ~3.37 eV, large exciton binding energy of ~60 meV, high radiation endurability, low cost, and environmental inertness, thus emerging as one of the excellent material for next generation UV PD [10,11]. ZnO-based UV PDs is fabricated from single crystals, thin films and nanostructures in the recent past [12–15]. Performance enhancement is still one of the major issues of ZnO-based UV PDs, and continuing efforts are committed in this direction. Although, there are currently great attention paid on ZnO and graphene due to their unique and promising characteristics, there are few reports on their hybrid structure. Recent reports displayed the research efforts focused on hybrid ZnO nanostructures and graphene and their potential device applications.

At the recent past, surface plasmon has been utilized for the improvement of the device performance. The SPs can be realized by coating or decorating of metal nanoparticles on the active surface by magnetron sputtering and spin coating. The metal nanoparticles on the surface can enhance the scattering of the incident photons and make more photons reach the substrate, and thus the absorption of the photons can be enhanced [16]. Furthermore, surface plasmons can be displayed on the interface between ZnO and graphene layers [17]. Resonant plasmon modes can be induced in graphene when radiation from the ZnO film is partially trapped between the graphene and a ZnO surface. The induced plasmon can then be transformed into propagating photons through the scattering with granules on the ZnO surface and eventually result in enhanced photoemission, which provides improved performance of ZnO UV PDs.

Numerous approaches are made to enhance photoresponsivity of the ZnO based UV PDs. Kim et al. [18] have inserted MgO buffer layer to enhance the selectivity and the responsivity of the film to UV wavelengths. The highest responsivity was obtained 27 A/W. Tian et al. [19] have used surface plasmon to enhanced performance of ZnO MSM and Pt nanoparticles were coated on the surface of the ZnO film based MSM structured UV photodetectors. They have found that the responsivity of the device is enhanced by up to 56% and the obtained responsivity was 1.306 A/W. Low dark current ZnO MSM was fabricated on SiO_2/Si substrate by Calıskan

* Corresponding author.
E-mail address: djlee@konkuk.ac.kr (D. Lee).

http://dx.doi.org/10.1016/j.ssc.2015.10.007
0038-1098/

et al. [20]. The dark current of the photodetector is measured as 1 pA at 100 V bias and spectral photoresponse measurement showed the usual spectral behavior and 0.35 A/W responsivity at a 100 V bias. Safa et al. [21] have demonstrated photodetection enhancement based on ZnO–reduced graphene composites fabricated by a sonochemical method. They have observed highest responsivity of 1.32 A/W with 7.5 wt% of reduced graphene oxide. Xu et al. [22] have grown ZnO nanowire on graphene layer by a hydrothermal method. The ZnO NWs revealed higher uniform surface morphology and better structural properties than ZnO NWs grown on SiO_2/Si substrate. They have obtained low dark current in the range on nA at 1 V and high responsivity of 188 A/W. The enhanced detector performance is due to the improvement of ZnO nanowire crystal quality, the increase in optical absorption, and the prevention of electron–hole recombination caused by the surface plasmon from the graphene and ZnO interface. In the present study, ZnO:Ga thin film was deposited on graphene layer in which the responsivity of the ZnO film could be enhanced due to the surface plasmon excitement at the interface. The fabricated ZnO:Ga/Graphene based MSM device revealed very low dark current and high responsivity. To the best of our knowledge, there are only few reports available based ZnO thin films grown on graphene MSM UV PD device.

In the present study, we describe fabrication and characterization of MSM UV PDs based on ZnO:Ga/graphene. The fabricated device exhibited low dark current and large photocurrent-to-dark current contrast ratio. The obtained results show that insertion of graphene layer can dramatically enhance MSM UV PD properties.

2. Experimental details

High quality single layer graphene was synthesized by CVD on Cu foil. Prior to deposit graphene, Cu foil was cleaned with acetone, isopropyl alcohol and rinsed with de-ionized water respectively. The base pressure of the chamber was maintained at 1.5 mTorr and temperature was kept at 1000 °C. After graphene growth, the graphene on Cu was spin coated with polymethylmethacrylate (PMMA). The PMMA coated Cu foil was then placed on diluted nitric acid solution for removing the bottom side of graphene and then Cu foil was dissolved in an ammonium persulphate solution and PMMA/graphene was lifted from the solution and transferred onto the water. The PMMA with graphene was then transferred on to the SiO_2/Si substrate. After completing the transfer process, the PMMA/graphene was immersed in acetone to remove the PMMA and the complete graphene transfer process is illustrated in Fig. 1.

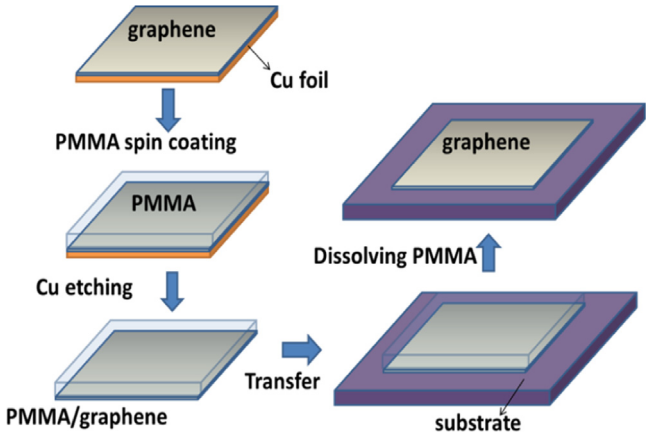

Fig. 1. Schematic diagram of graphene transfer onto substrate.

ZnO:Ga thin films were deposited on graphene/SiO_2/Si substrate using RF magnetron sputtering technique. ZnO with 1 wt% Ga_2O_3 pallets was used as a target and high purity Ar was used as the sputtering gas. The deposition was carried out in a vacuum chamber evacuated to a pressure of 6.6×10^{-6} Torr. The Ar gas pressure was maintained at 10 mTorr during deposition. ZnO:Ga thin film of 500 nm were grown with a conventional two-step growth method. A low temperature buffer layer of 50 nm deposited at substrate temperature of 150 °C and then, a high temperature growth of ZnO:Ga thin film thickness of 450 nm was deposited at 500 °C. The RF power of 100 W and deposition time of 45 min was kept constant.

Interdigitated metal electrodes were fabricated by standard photolithography and liftoff process. Fig. 2 demonstrates the schematic structure of the fabricated ZnO:Ga/graphene MSM UV PD device. Magnetron sputtered 10/90 nm thick Ni/Au interdigitated fingers were employed as the metal contact in order to form MSM UV PD on ZnO:Ga/graphene. The optical active area was $10 \times 100\ \mu m^2$ with spacing of 10 μm. The vacuum chamber was evacuated at base pressure of 5.0×10^{-6} Torr. A Rigaku x-ray diffraction (XRD) system was employed to study crystallographic orientation of the film. The surface morphology and microstructure of the films were observed by a Hitachi S-4700 scanning electron microscope (SEM). The current–voltage (*I–V*) measurements were performed using standard probe station and a semiconductor parameter analyzer (Keithley 4200) at room temperature. The spectral response was obtained by using a lock-in amplifier with an optical chopper and a monochromator from 300 to 450 nm with a 150 W xenon arc lamp.

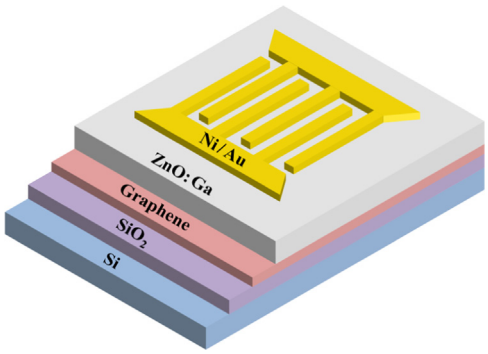

Fig. 2. Schematic illustration of fabricated ZnO:Ga/graphene MSM UV PD device.

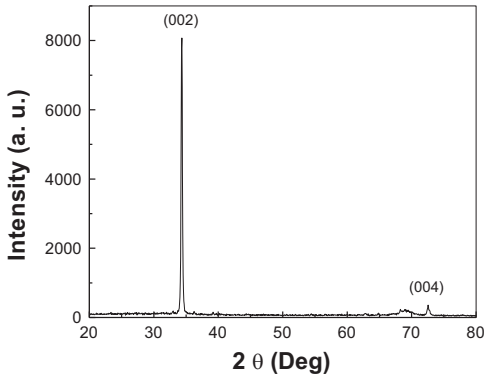

Fig. 3. XRD spectrum of ZnO:Ga/graphene thin film.

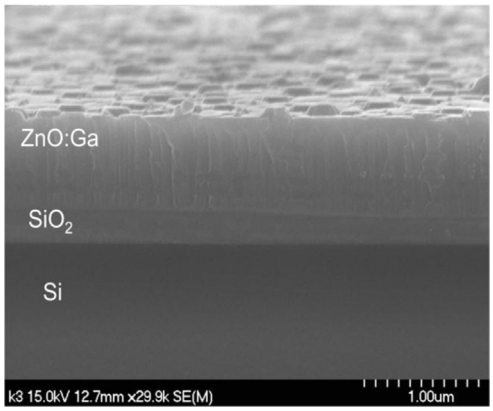

Fig. 4. SEM cross-section image of ZnO:Ga/graphene/SiO_2/Si.

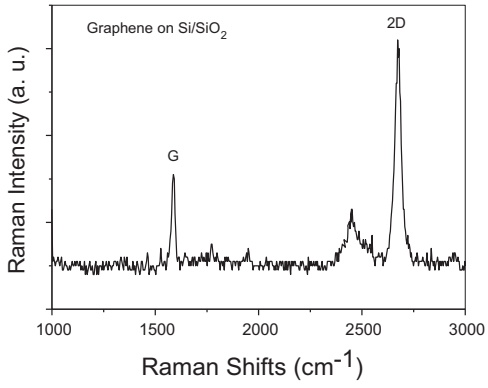

Fig. 5. Raman spectrum of graphene transferred onto SiO_2/Si substrate.

3. Results and discussion

Fig. 3 shows XRD spectrum of ZnO:Ga/graphene thin films grown on SiO_2/Si substrate. The XRD spectrum exhibits only (002) and (004) diffraction peaks, indicating highly preferred *c*-axis orientation. No other phases corresponding Ga_2O_3 were seen. The stronger (002) diffraction peak obtained from the ZnO:Ga films grown on graphene layer suggests that the high quality of the ZnO:Ga thin film was grown on the graphene layer.

Cross-section SEM image of the grown film is shown in Fig. 4, indicating that the micrograph of the ZnO:Ga film was grown in island-growth mode as very dense columnar structure, vertically aligned high aspect ratio grains. This type of growth leads to very high surface area/volume ratio through the film.

Raman spectrum of graphene layer grown on SiO_2/Si is illustrated in Fig. 5. The graphene layer recognized by Raman measurements displayed a large 2D to G intensity ratio. The Raman spectrum obtained a strong 2D peak centered at 2671 cm^{-1} and G peak located at 1589 cm^{-1}. The absence of D mode in the Raman spectrum suggests a small number of defects. The number of graphene layer is associated with the intensity ratio of the 2D and G modes. The Raman intensity ratio of the 2D to G modes is found to be nearly 2, indicating the graphene is deposited in single layer [23].

A typical RT dark and photocurrent *I–V* characteristics of ZnO:Ga/graphene MSM UV PD is demonstrated in Fig. 6. The resulting curve shows non-linear rectifying behavior. The dark current measured from the fabricated ZnO:Ga/graphene MSM UV PD remains in the nA up to the bias voltage of 3 V. The device exhibited low dark current in the range of 8.68 nA at bias voltage of 1 V. An abrupt increase in the current is observed under illumination with UV light. When the device is illuminated at 370 nm,

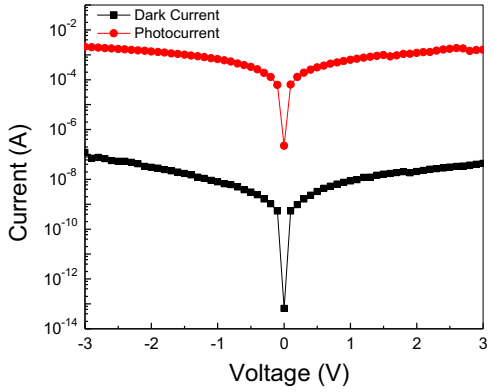

Fig. 6. Typical room temperature dark and photo *I–V* characteristics of ZnO:Ga/graphene MSM UV PD device.

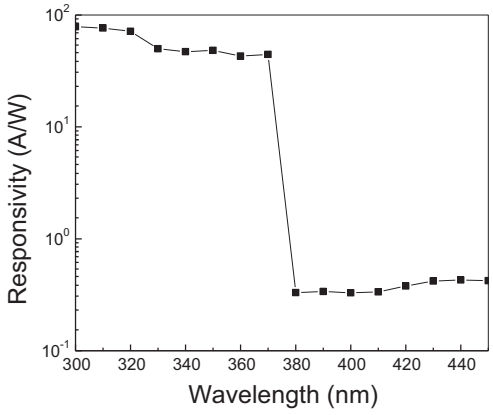

Fig. 7. Spectral responsivity of the ZnO:Ga/graphene MSM UV PD device.

the photo current increased to 6.27×10^{-4} A at 1 V bias. The photo-to-dark current contrast ratio was found to be about 2.22×10^5 at bias voltage of 3 V, which is attributed by the excitation of surface plasmons at the interface between ZnO:Ga and graphene layer [24].

I–V characteristics of the ZnO:Ga/graphene MSM PDs is analyzed by thermionic emission theory to calculate electrical parameters using the following diode equations [25]

$$I = I_0\left[\exp\left(\frac{qV}{nkT}\right) - 1\right] \tag{1}$$

where I_0 is saturation current expressed as

$$I_0 = AA^*T^2 \exp\left(-\frac{q\varphi_b}{kt}\right) \tag{2}$$

where q is electron charge, V applied voltage, A the effective diode area, A^* the Richardson constant, which is 32 A cm^{-2} K^{-2} in case of ZnO [26], R_s series resistance, T absolute temperature, ϕ_b the effective barrier height, and n is ideal factor. The barrier height and ideality factor are determined by fitting the forward *I–V* curve and the obtained values are 0.81 eV and 1.78, respectively.

Fig. 7 shows the responsivity spectrum of ZnO:Ga/graphene MSM UV PD at a bias voltage of 1 V. The responsivity is estimated using a calibrated detector. It can be clearly seen from the figure that the device reveals sharp cut off above the band edge of ZnO at wavelength of 370 nm. The responsivity is significantly higher for the wavelength range of 300–370 nm and gradually decreases when the device is shined with a longer wavelength. The measured peak responsivity of ZnO:Ga/graphene MSM UV PD is achieved 48.37 A/W at 350 nm. The measured responsivity of the device is larger than the theoretical value of a ZnO based UV PDs

supporting internal gain in the device. It is noticed that the obtained results are better than those of previously reported ZnO thin films based MSM PDs [27,28]. Furthermore, the fabricated device revealed superior responsivity to those of the reported UV PDs, such as graphene/p-Si PDs, mixed-phase ZnMgO based PDs and dual band MgZnO UV PDs integrated on Si [25,29,30]. The fact that PD response dropped from 48.37 at 0.32 A/W at wavelength 350–400 nm across the cut-off region also indicates that high quality ZnO:Ga thin film is grown on graphene/SiO_2/Si. The detectivity of the ZnO:Ga/Graphene MSM UV PD is determined using the following equation [31]

$$D = R\left(\frac{R_0 A}{4 k T}\right)^{\frac{1}{2}} \tag{3}$$

where R is the zero bias reponsivity, R_0 is the differential resistance at zero bias and A is the detector area. The differential resistance of the MSM UV PD is calculated by taking the (dV/dI) derivative and obtained values of 5.44×10^{10} Ω, resulting in the R_0A product of 5.44×10^6 Ω-cm^2. The detectivity performance of the ZnO:Ga/Graphene MSM UV PD of 1.83×10^{11} cm Hz$^{1/2}$ W^{-1} is achieved.

The MSM UV PD fabricated on ZnO:Ga/graphene demonstrates better results in terms of low dark current, larger photo-to-dark current ratio and UV-to-visible rejection ratio in comparison to the device fabricated without inserted graphene into the Si substrate (data not shown here). It is assumed that the enhancement of the performance of UV PDs based on hybrid structure of ZnO:Ga/graphene originates from the excitation of surface plasmons at the interface between ZnO:Ga and graphene layer. The surface plasmon excites an electromagnetic field in ZnO:Ga and the peak amplitude of the field are expected to be much larger than that of the incident electromagnetic field. It is supposed that the increased field amplitude and interaction time between the field and the ZnO:Ga might be likely to increase absorption. It is evident that in the presence of graphene, photocurrent response increases at the wavelength corresponding to those of the graphene surface plasmon resonances. When device is illuminated photons are transformed from surface plasmons graphene through the scattering with corrugated ZnO surface. The photo-excited electrons in the conduction band of ZnO:Ga can transfer to the graphene side, which acts as an electron sink due to the Schottky barrier at the ZnO:Ga/graphene interface. Consequently, separation of the charges at the interface prevents the recombination of electrons and holes, hence, more and more photo-generated carriers can be collected which results in terms of responsivity enhancement.

4. Conclusion

MSM UV PDs on ZnO:Ga/graphene is fabricated and characterized. The obtained device achieved low dark current and larger photo-to-dark current contrast ratio. The dark current was found to be in the range of nA up to bias voltage of 3 V. The measured peak responsivity value of 48.37 A/W at 350 nm was achieved. The performance enhancement of the device caused by the generation of surface plamons at the interface between ZnO:Ga/graphene layer. The obtained results indicate that this approach may be very useful in fabricating high performance ZnO thin film based UV PDs.

Acknowledgment

This research was supported by Basic Science Research Program (2015R1C1A1A02037326 & NRF-2010-00525) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning and by Ministry of Education.

References

[1] E. Monroy, F. Omnes, F. Calle, Semicond. Sci. Technol. 18 (2003) R33.
[2] W. Yang, R.D. Vispute, S. Choopun, R.P. Sharma, T. Venkatesan, H. Shen, Appl. Phys. Lett. 78 (2001) 278.
[3] L. Peng, L. Hu, X. Fang, Adv. Mater. 25 (2013) 5321.
[4] H.W. Lin, S.Y. Ku, H.C. Su, C.W. Huang, Y.T. Lin, K.T. Wong, C.C. Wu, Adv. Mater. 17 (2005) 2489.
[5] D. Li, X. Sun, H. Song, Z. Li, Y. Chen, G. Miao, H. Jiang, Appl. Phys. Lett. 98 (2011) 011108.
[6] F. Zhang, W. Yang, H. Huang, X. Chen, Z. Wu, H. Zhu, H. Qi, J. Yao, Z. Fan, J. Shao, Appl. Phys. Lett. 92 (2008) 25110.
[7] M. Liao, X. Wang, T. Teraji, S. Koizumi, Y. Koide, Phys. Rev. B 81 (2010) 033304.
[8] L. Li, H. Lu, Z. Yang, L. Tong, Y. Bando, D. Golberg, Adv. Mater. 25 (2013) 1109.
[9] R. Liu, D. Jiang, Q. Duan, L. Sun, C. Tian, Q. Liang, S. Gao, J. Qin, Appl. Phys. Lett. 105 (2014) 043505.
[10] M. Razeghi, A. Rogalski, J. Appl. Phys. 79 (1996) 7433.
[11] K.W. Liu, M. Sakurai, M. Aono, Sensors 10 (2010) 8604.
[12] K. Moazzami, T.E. Murphy, J.D. Phillips, M.C.K. Cheung, A.N. Cartwright, Semicond. Sci. Technol. 21 (2006) 717.
[13] M.J. Liu, H.K. Kim, Appl. Phys. Lett. 84 (2004) 173.
[14] S. Kumar, V. Gupta, K. Sreenivas, Nanotechnology 16 (2005) 1167.
[15] S. Liang, H. Sheng, Y. Liu, Z. Huo, Y. Lu, H. Shen, J. Cryst. Growth 225 (2001) 110.
[16] W. Zhang, J. Xu, W. Ye, Y. Li, Z. Qi, J. Dai, Z. Wu, C. Chen, J. Yin, J. Li, H. Jiang, Y. Fang, Appl. Phys. Lett. 106 (2015) 021112.
[17] S.W. Hwang, D.H. Shin, C.O. Kim, S.H. Hong, M.C. Kim, J. Kim, K.Y. Lim, S. Kim, S. H. Choi, K.J. Ahn, G. Kim, S.H. Sim, B.H. Hong, Phys. Rev. Lett. 105 (2010) 127403.
[18] D.C. Kim, B.O. Jung, J.H. Lee, H.K. Cho, J.Y. Lee, J.H. Lee, Nanotechnology 22 (2011) 265506.
[19] C. Tian, D. Jiang, B. Li, J. Lin, Y. Zhao, W. Yuan, J. Zhao, Q. Liang, S. Gao, J. Hou, J. Qin, Appl. Mater. Interfaces 6 (2014) 2162.
[20] D. Calıskan, B. Butun, M. Cihan Cakır, S. Ozcan, E. Ozbay, Appl. Phys. Lett. 105 (2014) 161108.
[21] S. Safa, R. Sarraf-Mamoory, R. Azimirad, J. Sol–Gel Sci. Technol. 74 (2015) 499.
[22] Q. Xu, Q. Cheng, J. Zhong, W. Cai, Z. Zhang, Z. Wu, F. Zhang, Nanotechnology 25 (2014) 055501.
[23] T. Yu, Z. Ni, C. Du, Y. You, Y. Wang, Z. Shen, J. Phys. Chem. C 112 (2008) 12602.
[24] B.L. Sharma, Metal–Semiconductor Schottky Barrier Junctions and Their Applications, Plenum, New York, 1984.
[25] Y.N. Hou, Z.X. Mei, H.L. Liang, D.Q. Ye, C.Z. Gu, X.L. Du, Appl. Phys. Lett. 102 (2013) 153510.
[26] K.U. Hasan, N.H. Alvi, J. Lu, O. Nur, M. Willander, Nanoscale Res. Lett. 6 (2011) 348.
[27] S.J. Young, L.W. Ji, R.W. Chuang, S.J. Chang, X.L. Du, Semicond. Sci. Technol. 21 (2006) 1507.
[28] D. Caliskan, B. Butun, M.C. Cakir, S. Ozcan, E. Ozbay, Appl. Phys. Lett. 105 (2014) 161108.
[29] Y. An, A. Behnam, E. Pop, A. Ural, Appl. Phys. Lett. 102 (2013) 013110.
[30] M.M. Fan, K.W. Liu, Z.Z. Zhang, B.H. Li, X. Chen, D.X. Zhao, C.X. Shan, D.Z. Shen, Appl. Phys. Lett. 105 (2014) 011117.
[31] M. Kumar, B. Tekcan, A.K. Okyay, Curr. Appl. Phys. 14 (2014) 1703.