

Control of the Dirac point in graphene by UV light

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It is experimentally shown that the initially shifted Dirac point in graphene-on-dielectric devices can be brought to zero by illuminating the samples with UV light. This is much easier to accomplish compared to the common procedure of annealing at high temperature. Internal photoemission is concluded to be responsible for the observed effect.

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Graphene demonstrates a unique ambipolar field effect: the graphene resistance is a symmetric function of the electric field (the gate voltage V_g). The neutrality (Dirac) point V_D of real graphene devices is however seldom at $V_g = 0$ due to extraneous doping from trapped charges in the dielectric [1], adsorbed gases [2], residues of other polar molecules at the graphene surface after processing [3], or water/oxygen redox couple [4] due to unavoidable water layer at the hydrophilic surface of oxidized silicon at ambient conditions. Such surface contaminations and trapped charges give rise to a nonuniform pattern of local electric field, which changes the overall carrier concentration in graphene. This is seen as a shift in the Dirac point along the V_g -scale. The shift can be comparable with the breakdown voltage of the gate dielectric, obviously resulting in unreliable graphene devices. The common way of dealing with this problem is to anneal graphene at temperatures from 200 to 600 °C in vacuum- or inert-gas (or hydrogen)-atmosphere, heating either in oven or by current [5]. Annealing removes surface adsorbents and organic residues which results in increased mobilities [6]. However, for graphene on SiO₂, for instance, annealing results in a stronger coupling between graphene and dielectric [7]. Graphene then conformally follows the nano-scale roughness of SiO₂ surface thereby making graphene locally bent. The increased curvature of graphene makes it susceptible to oxygenation in ambient air [7] leading to hole doping and decrease of mobility [8]. Also, annealing obviously cannot be performed when graphene is used in combination with organic underlayers (e.g. polymethylmethacrylate, PMMA) having low melting temperatures.

In this report, we show that the Dirac point can be more readily shifted to zero by illuminating graphene samples using relatively low-intensity violet/UV-light. The shift can occur in both directions by applying the gate voltage of certain sign during the illumination. This simple technique works for both exfoliated and CVD grown graphene, and also at low temperatures down to ~ 20 –50 K.

Graphene is placed on either 300-nm thick SiO₂ obtained by wet oxidation of Si or 90-nm Al₂O₃ grown by atomic-layer deposition (ALD) on doped Si wafers. The electrodes are patterned by e-beam- or photolithography, and lift-off of Au/Cr double metallization layer. The electrical measurements are made in both two- and four-probe configurations using a small ac excitation current (30–150 Hz, 50–500 nA), and with lock-in amplification of the voltage signal. The gate voltage is applied between one of the current-bias electrodes and doped Si substrate (the back-gate configuration). The range of voltages is dictated by the break-down voltage of the corresponding dielectric, which is found to vary from sample to sample and is detected by monitoring the current through the gate electrode. The Al₂O₃ gate dielectric is thinner and has higher dielectric constant than the standard 300-nm SiO₂ making gate-voltage range ≈ 6.5 times smaller in the former case.

The experiments with illumination are done in a close-cycle cryostat with optical windows. Violet laser with the wavelength $\lambda = 405$ nm or light emitting diodes (LED's, $\lambda \geq 460$) are used to illuminate samples. The effect is largely absent when using LED's with longer wavelengths. The typical light intensities are from 1 to 10 mW/cm². It is not possible to assure constant intensity for different samples with the present setup.

Fig. 1a shows how the Dirac voltage V_D of graphene on Al₂O₃, initially > 2 V, shifts after illumination done

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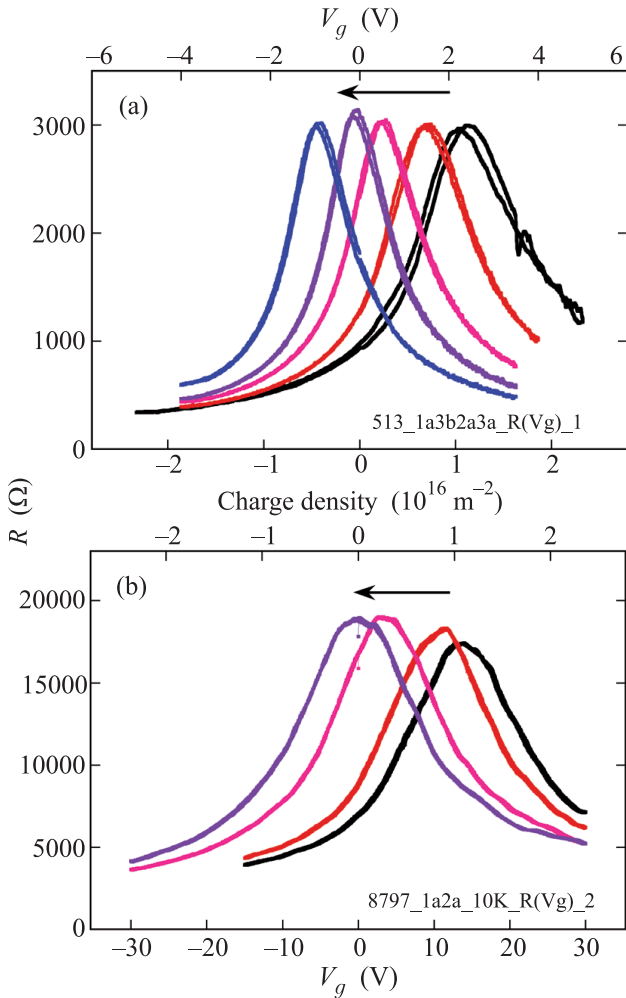


Fig. 1. (Color online) $R(V_g)$ -curves of graphene on $\text{Al}_2\text{O}_3/\text{Si}$ substrate at room temperature $T = 293 \text{ K}$ (a) and graphene on SiO_2/Si substrate at $T = 10 \text{ K}$ (b). The arrows indicate shift of the Dirac voltage (corresponding to the maximum of the $R(V_g)$ -curves) after successive illumination doses at $V_g = 0$

at zero gate voltage. It is seen that the curves continuously move in voltage to the left with the Dirac point eventually ending up at $V_g \approx -1 \text{ V}$ after ≈ 290 min of accumulated exposure time at $\approx 2 \text{ mW}/\text{cm}^2$ of light intensity. Similar behavior were reported for high-mobility CVD graphene [9]. This illustrates usefulness of the method for removing (or compensating for) extraneous doping in graphene. Fig. 1b demonstrates that the effect is also present at low temperature. In this case the sample of graphene on SiO_2/Si substrate at $T = 10 \text{ K}$ is measured. The total light-exposure time is 100 min. The intensity of light ($\approx 10 \text{ mW}/\text{cm}^2$) is several times higher than in Fig. 1a, which might result in excess heating of the sample to an estimated temperature of $\lesssim 30 \text{ K}$.

The time evolution of the sample resistance, $R(t)$, is nearly exponential in time, with sometimes two time constants (~ 20 – 200 s), which depend on both the initial conditions and particular sample. However, no clear pattern of this dependence could be revealed. For the majority of Al_2O_3 -samples, the shift in the Dirac point is reversible. Also, the shift and its time evolution are not symmetric: in some cases it is found that the Dirac point shifts only to negative voltages, irrespective of the gate voltage during the illumination.

It is interesting to note that the charge mobility μ appears to correlate with the position of Dirac point in the Al_2O_3 -samples. The more negative V_D , the higher the mobility (see Fig. 2). The mobility noticeably in-

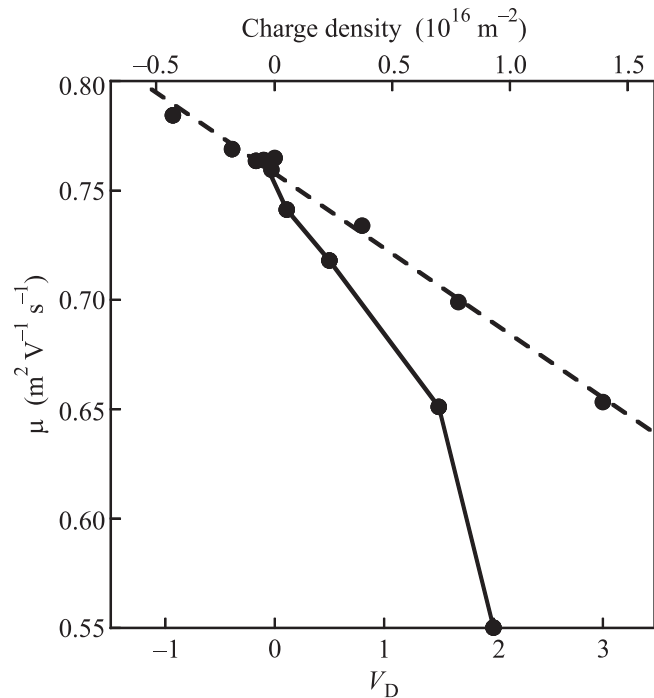


Fig. 2. The charge mobility μ versus the Dirac voltage V_D for a number of experiments with UV-illumination, when V_D is shifted in both directions by applying the gate voltage of certain polarity. Note that after the initial increase, the mobility becomes a reproducible linear function of V_D

creases while the Dirac point shifts towards negative voltages immediately after starting the illumination. During subsequent experiments when V_D is positive and then negative again, the mobility becomes a reproducible linear function of V_D , although not repeating the initial increase. This indicates that the mobility is at least partly limited by the charged scatterers in the vicinity of graphene [10].

The initial position of the Dirac point $V_D \neq 0$ is obviously caused by some charges or polar molecules in

the vicinity of graphene surface. These can be charges trapped in the oxide layer or molecules adsorbed at the graphene surface and/or interface with underlying substrate. The photoeffect seen in the present- and a few other works [7, 9, 11] is then due to photodesorption of these molecules or neutralization of the trapped charges. Ref. [9] only ascertains the effect of UV-light at room temperature and SiO_2 , while Refs. [7, 11] focus on the role of molecular oxygen in doping of graphene and only mention the effect of UV-light, without analyzing it in detail or discussing other possibilities.

The mechanism of graphene doping by oxygen [7, 11] does not seem to agree well with our experiments done in helium gas and in a wide range of temperatures. Once being photodesorbed, oxygen molecules are unlikely to diffuse back and be adsorbed altogether again on the small graphene area. During the experiments at cryogenic temperatures, oxygen is much likely to end up being adsorbed at the cold walls of the cryostat. At last, the direction in which the charge-neutrality point moves under UV-light can depend on the polarity of gate voltage during the illumination, which is also impossible to reconcile with the oxygen-doping model.

A layer of water with some oxygen dissolved in it is always present in graphene-on-oxide samples prepared at ambient conditions [12–14]. Oxygen dissolved in water gives rise to O_2 -water redox reactions involving the transfer of electrons and a few intermediate reactions yielding peroxide (H_2O_2) and hydroxyl radical ($\bullet\text{OH}$). The latter can form charge traps accumulating a net negative charge at the surface of oxide and attracting a net positive charge to graphene (*p*-doping). This has very convincingly been demonstrated experimentally in Ref. [4]. The UV-light induced changes can then be associated with the internal photoemission removing trapped electrons possibly resulting in inverse redox reactions. There are however several questions that need to be addressed before ultimately deciding on the very mechanism of the UV-induced changes in graphene doping.

First, assuming that the effect has the same origin for both Al_2O_3 and SiO_2 gate insulators, we note that the conduction-band offset (E_{CO} , see Fig. 3) is probably not important for the observed effect. E_{CO} for SiO_2 is slightly larger than the energy of photons of our 405-nm laser (3.06 eV), while it is smaller than that ($E_{\text{CO}} = 2.4$ eV) for Al_2O_3 [15]. This means that if the effect were to include E_{CO} , it would be much stronger in the case of Al_2O_3 . Although indeed, it is somewhat clearer for Al_2O_3 , the corresponding time scales of the doping change under the illumination are yet not much different for Al_2O_3 and SiO_2 gate insulators.

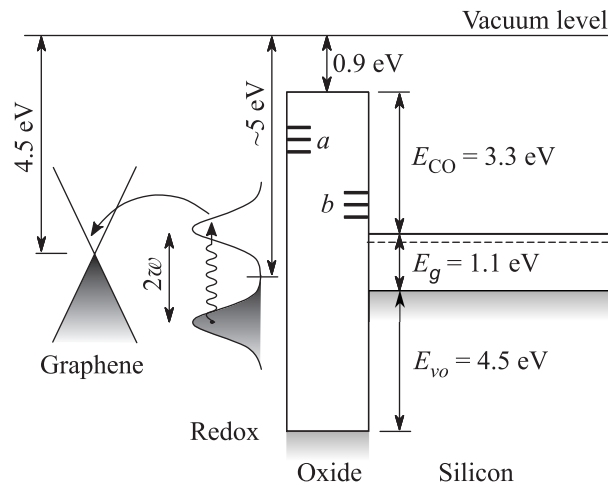


Fig. 3. Schematic of the flat-band diagram of the graphene/oxide/silicon device. w is the reorganization energy (~ 1 eV). The band-energy offsets shown are for SiO_2 [15]. a and b – schematically mark the energy levels of oxide electron traps. The suggestive electron transfer under the action of UV-light is denoted by the dashed line

Second, the surface chemistry is expected to be different for the two oxides. Little is known for Al_2O_3 , but in SiO_2 the redox bands are some 4.8–5.7 eV below the vacuum level, depending on acidity of water [4]. The SiO_2 conduction- or valence band edges are, again, quite distant from the redox states, not allowing the photoexcited electrons climb over either energy barriers associated with oxide band structure. In the case of Al_2O_3 , the situation is better, and the photoexcited electrons can, in principle, be thrown into the conduction band of the oxide. Again, this would mean that the effect has different mechanism for Al_2O_3 and SiO_2 .

The reorganization energy w (the diabatic energy which is required to arrive at the final state of a chemical reaction without rearrangement of other molecules around) is about 1 eV [4]. Photoexcited transitions between the reduction and oxidation states become very plausible, requiring photons with energy $\gtrsim 2w$ only. We note, however, that this energy is a bit low to explain the wavelength threshold for the effect observed in the experiment: the blue- and green LED's ($\lambda = 460$ nm $\leftrightarrow 2.7$ eV and $\lambda = 523$ nm $\leftrightarrow 2.3$ eV, respectively) produced no visible effect. Finally, it is not exactly clear how the reactions are affected by the low temperature. Naively, when water is frozen the redox chemical reactions involving reorganization of water molecules are obviously becoming unlikely. However, several photochemical reactions in ice have long been known and discussed in connection with Earth pollution studies [16–18]. It is also known that the surface layer of water is solid at

room temperature anyway [12, 14]. This means that the electron and proton exchange (or tunneling) are possible under UV-illumination even at low temperature. The diabatic energy is then expected to be higher ($w \sim 1.5$ eV) than in liquid solutions, also taking into account the presence of another (graphene) surface which the water molecules are in contact with.

Another possible explanation for the observed effect is neutralization of the trapped charges inside SiO₂ and Al₂O₃ by internal photoeffect (see levels *a* and *b* schematically shown in Fig. 3). Indeed, the crystallographic structures of SiO₂ and Al₂O₃ are not simple, having many possible defects which could be responsible for trapping of both positive and negative charges [19, 20]. Many scenarios – some controversial – surround the nature of charge trapping, charge neutralization, and UV-induced reactions in SiO₂. These have been discussed in regards to the performance and reliability of MOSFET-transistors. Examples of these proposed mechanisms include the appearance of defects (*E'*- and *V*₀⁺-centers), injection of photoemitted electrons from the valence or conduction band of Si into conduction band of SiO₂, and UV-induced water- and oxygen dissociation inside SiO₂. However, the majority of experiments related to studies of radiation-induced changes in SiO₂ have been done using vacuum UV ($\lambda \sim 250$ nm). The energy of such photons (≥ 4.8 eV) well exceeds an offset between conduction bands (CB's) of SiO₂ and Si (3.3 eV) allowing for internal photoemission. Photons in our experiments ($\lambda = 405$ nm \leftrightarrow 3.0 eV) almost reach the band offset, with resort to the fact that the band edge is not sharply defined in disordered SiO₂. Moreover, oxygen vacancies in the thermally grown SiO₂ can reach densities of 10^{19} cm⁻³ [19]. Such vacancies introduce an empty level at ~ 0.8 eV below the conduction band which is broadened by the randomness of vacancy positions and uneven mechanical strain [21]. CB offsets in ALD-Al₂O₃/Si thin films can also be sufficiently small (2.2–2.8 eV), making the internal photoemission even more plausible [20]. Furthermore, a high density of charge traps were found at the oxide-Si interface for such thin films [22].

To study oxide charging, we use a few mm² large CVD graphene in qualitative capacitance versus dc gate voltage (*C-V*) measurements. The CVD graphene is grown on a copper foil and transferred onto 7×7 mm² SiO₂/Si after the foil is wet-etched away. The Dirac point of this sample is far above the voltage limit (40 V) which we normally use in our measurements (see Fig. 4b, two-probe measurements).

The *C-V* measurements at 75 kHz shown in Fig. 4a reveal a step-like dependence indicating accumulation,

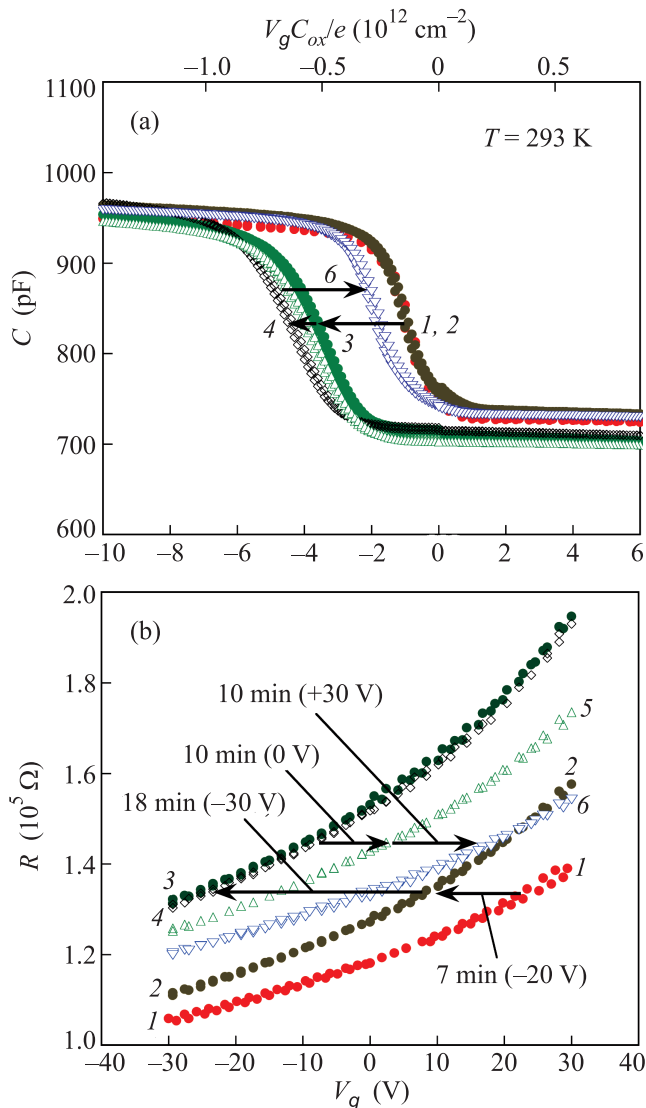


Fig. 4. (Color online) The capacitance C of a parallel-plate capacitor made of a CVD graphene on Si/SiO₂ substrate (a) and the graphene resistance (b) as functions of the back-gate voltage V_g after an intense broad-spectrum illumination. The device is illuminated at room temperature in steps of ~ 10 min at different V_g 's indicated in parenthesis. $C(V_g)$ (at 75 kHz) and $R(V_g)$ (at 37 Hz) are measured after each step. The arrows and numbers marking the curves illustrate a sequence of illumination events resulting in the shown curves

depletion, and inversion regimes typical for metal-oxide-semiconductor (MOS) structures. The flat-band voltage V_{FB} corresponding to the *C-V* step witness to the presence of trapped charges in the oxide layer [23]. We illuminate the graphene-electrode capacitor in periods of 5–10 min by using an ultra-high-pressure mercury lamp from a common LCD projector. The lamp produces a broad-band light with wavelengths down to

300 nm. The illumination is done at non-zero V_g , allowing shifts of the Dirac point in both directions. Fig. 4 shows the obtained dependencies.

V_B appears to qualitatively correlate with the changes in $R(V_g)$ after the illumination steps. The kink moves to the left or right after the illumination at $V_g < 0$ or $V_g > 0$, respectively. Assuming a uniform distribution of the oxide-layer charges, we can estimate their total areal density from V_{FB} (the upper abscissa of Fig. 4a). Such photo-induced charging- and neutralization of dielectrics were reported in the literature earlier [24, 25].

However, there is no exact one-to-one correspondence between the changes in $R(V_g)$ and $C(V_g)$. We can observe an increase in resistance but no change in V_{FB} (compare curves 1 and 2 in both panels). While the resistance change saturates, $|V_{FB}|$ continues to increase with illumination dose (e.g. curves 3 and 4). Light from the 405-nm laser only affects $R(V_g)$ but not $C(V_g)$. All this tells us that also charges at the graphene surface are important, as outlined above. To make an exact distinction between various contributions would require a rigorously characterized graphene surface.

In conclusion, we routinely use UV-illumination to bring the Dirac point of graphene-on-dielectric devices to zero gate voltage from an initial non-zero state. This easy method works for both Al_2O_3 and SiO_2 gate dielectrics, and for both CVD- and exfoliated graphene. It bypasses the need to anneal graphene devices which, in many cases, either cannot be used because of e.g. low melting point of materials used in the devices or can even damage graphene itself. The most probable explanation for the effect is an internal photoeffect involving oxygen/water redox couples at the interface between graphene and oxide gate insulator of the silicon substrate. We believe that our experiments might also contribute to studies of photoinduced charge transfer in oxides and their surfaces by using graphene as a charge-sensitive material.

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1. P. Samanta, *Solid State Electron.* **52**, 255 (2008).
2. F. Schedin, A.K. Geim, S.V. Morozov et al., *Nat. Mater.* **6**, 652 (2007).
3. C. Coletti, C. Riedl, D.S. Lee et al., *Phys. Rev. B* **81**, 235401 (2010).
4. P.L. Levesque, S.S. Sabri, C.M. Aguirre et al., *Nano Lett.* **11**, 132 (2011).
5. K.I. Bolotin, K.J. Sikes, Z. Jiang et al., *Solid State Commun.* **146**, 351 (2008).
6. D.C. Elias, R.V. Gorbachev, A.S. Mayorov et al., *Nat. Phys.* **7**, 701 (2011).
7. S. Ryu, L. Liu, S. Berciaud et al., *Nano Lett.* **10**, 4944 (2010).
8. Z. Cheng, Q. Zhou, C. Wang et al., *Nano Lett.* **11**, 767 (2011). "Wet-Chemical Treatment of SiO_2 -Supported Graphene Devices"
9. Z. Luo, N.J. Pinto, Y. Davila, and A.T.C. Johnson, *App. Phys. Lett.* **100**, 253108 (2012).
10. L.A. Ponomarenko, R. Yang, T.M. Mohiuddin et al., *Phys. Rev. Lett.* **102**, 206603 (2009).
11. J.-M. Aubry, C. Pierlot, J. Rigaudy, and R. Schmidt, *Acc. Chem. Res.* **36**, 668 (2003).
12. H.A. Al-Abadleh and V.H. Grassian, *Langmuir* **19**, 341 (2003).
13. R. Williams and A.M. Goodman, *Appl. Phys. Lett.* **25**, 531 (1974).
14. D.B. Asay and S.H. Kim, *J. Phys. Chem. B* **109**, 16760 (2005).
15. E. Bersch, S. Rangan, R.A. Bartynski et al., *Phys. Rev. B* **78**, 085114 (2008).
16. M.P. Bernstein, S.A. Sandford, L.J. Allamandola et al., *Science* **283**, 1135 (1999).
17. P. Klán and I. Holoubek, *Chemosphere* **46**, 1201 (2002).
18. K. Kim and W. Choi, *Environ. Sci. Technol.* **45**, 2202 (2011).
19. D. Bauza, in *Handbook of Surfaces and Interfaces of Materials*, ed. by H.S. Nalwa, Academic Press, San-Diego (2001), v. 1, p. 115.
20. J. Robertson, *Eur. Phys. J. Appl. Phys.* **28**, 265 (2004).
21. J.K. Rudra and W.B. Fowler, *Phys. Rev. B* **35**, 8223 (1987).
22. R. Ludeke, M.T. Cuberes, and E. Cartier, *Appl. Phys. Lett.* **76**, 2886 (2000).
23. S.M. Sze, *Physics of Semiconductor Devices*, 2nd edition, Wiley-Interscience (1981).
24. B.J. Mrstik, V.V. Afanas'ev, A. Stesmans et al., *J. Appl. Phys.* **85**, 6577 (1999).
25. D.A. Mehta, S.R. Butler, and F.J. Feigl, *J. Appl. Phys.* **43**, 4631 (1972).