Significant improvement in the electrical characteristics of Schottky barrier diodes on molecularly modified Gallium Nitride surfaces

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III-Nitride semiconductors face the issue of localized surface states, which causes fermi level pinning and large leakage current at the metal semiconductor interface, thereby degrading the device performance. In this work, we have demonstrated the use of a Self-Assembled Monolayer (SAM) of organic molecules to improve the electrical characteristics of Schottky barrier diodes (SBDs) on n-type Gallium Nitride (n-GaN) epitaxial films. The electrical characteristics of diodes were improved by adsorption of SAM of hydroxyl-phenyl metallated porphyrin organic molecules (Zn-TPPOH) onto the surface of n-GaN. SAM-semiconductor bonding *via* native oxide on the n-GaN surface was confirmed using X-ray photoelectron spectroscopy measurements. Surface morphology and surface electronic properties were characterized using atomic force microscopy and Kelvin probe force microscopy. Current-voltage characteristics of different metal (Cu, Ni) SBDs on bare n-GaN were compared with those of Cu/Zn-TPPOH/n-GaN and Ni/Zn-TPPOH/n-GaN SBDs. It was found that due to the molecular monolayer, the surface potential of n-GaN was decreased by $\sim$350 mV. This caused an increase in the Schottky barrier height of Cu and Ni SBDs from 1.13 eV to 1.38 eV and 1.07 eV to 1.22 eV, respectively. In addition to this, the reverse bias leakage current was reduced by 3–4 orders of magnitude for both Cu and Ni SBDs. Such a significant improvement in the electrical performance of the diodes can be very useful for better device functioning. *Published by AIP Publishing.* https://doi.org/10.1063/1.5005587

Gallium Nitride (GaN), a direct wide bandgap semiconductor, is reported to have superior material properties such as higher breakdown voltage, higher electron saturation velocity, higher electron mobility, higher bandgap energy, and lower dielectric constant in comparison to other materials such as Si, SiC, and GaAs.[1] Along with this, chemical and radiation hardness and high temperature stability of GaN mitigate ecological and environmental concerns for its applications in various device technologies such as power electronics, light emitting diodes, high electron mobility transistors, and laser diodes.[2]

However, despite their benefits, GaN based transistor devices face the issue of localized surface states[3] present at the metal semiconductor interface (Gate electrode) of the devices. As a consequence, the Fermi level of the semiconductor gets pinned relative to the band edges and the Schottky barrier height (SBH) becomes nearly constant irrespective of the metal on the other side, violating the Schottky-Mott rule ($\phi_{Bn} = \phi_m - \chi_s$).[4–8] The large concentration of defects on the surface of GaN also results in tunnelling of carriers in the forward bias and large leakage current in reverse biased Schottky barrier diodes (SBDs),[9–11] degrading the device performance and reliability.

A unique method of tuning the Schottky barrier height (ϕ_{Bn}) of the Schottky barrier diodes (SBDs) was presented by Vilan *et al.* in 2000.[12] In this work, ϕ_{Bn} of gold (Au) SBDs on the n-GaAs sample was tuned by adsorption of a monolayer of variably functionalized organic molecules on the semiconductor side of the metal semiconductor interface. According to the authors, the change in functionalization of the tartaric acid derived molecules leads to the change in the dipole moment of the dipoles formed at the metal semiconductor interface, thereby tuning the interface potential which further tuned ϕ_{Bn}. The same group later continued the study to tune ϕ_{Bn} of Au SBDs on the SiO$_2$/Si sample surface in 2001.[13] In this investigation, they showed that when the molecular monolayer was chemisorbed onto the metal side of the metal-semiconductor interface, the functionalization showed reverse effects. This means that the functionalization which earlier led to the increase in ϕ_{Bn} is now responsible for the decrease in ϕ_{Bn} and vice-versa. The application of such an innovative method was also seen when the Self-assembled monolayer (SAM) of metallated porphyrin organic molecules was used as a copper diffusion barrier for SiO$_2$-Si based CMOS technologies.[14,15]

SAM adsorption on GaN has been studied to discover the scope of hybrid organic/semiconductor interfaces and apply these devices for electronic detection of specific biomolecular processes.[16–20] Adsorption of different types of organic molecules onto the GaN surface have been reported in the literature. A few of them are thiols,[16] silane,[17] organosilane,[18] and phosphonic acid.[19] These SAMs have been characterized by various techniques such as water contact angle measurement, X-ray Photoelectron Spectroscopy (XPS), and Atomic Force Microscopy (AFM) studies. In our view, incorporation of SAM to improve the electrical

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characteristics of Schottky contacts on GaN based electronic devices has not been reported anywhere in the literature.

In this work, we have investigated the chemisorption of SAM of hydroxyl-phenyl zinc porphyrin (Zn-TPPOH) organic molecules on the n-type Gallium Nitride (n-GaN) surface. We have reported a significant increase in ϕ_{Bn} and decrease in reverse bias leakage current in different SBDs on these molecularly modified n-GaN samples.

n-type GaN (2 μm) epitaxial layers grown on a c-plane sapphire substrate (2″ diameter) by the Metal-Organic Vapour Phase Epitaxy (MOVPE) technique was taken as the sample. The conduction properties of the sample were a Hall electron mobility of ~160 cm^2/V s, a carrier concentration of ~4.6 × 10^{17} cm^{-3}, and a sheet resistance of ~285 Ω/sq at room temperature (RT), as measured using an Ecopia Hall measurement setup (HMS 5000) at a magnetic field of 0.57 T. The wafer was cut into small pieces of 1 cm × 1 cm dimension. Thereafter, the samples were cleaned in de-ionized (DI) water, trichloroethylene, acetone, and iso-propanol for 5 min each at room temperature in an ultrasonic bath cleaner. The surface was finally rinsed-off with DI-water again. Following this, the samples were dipped in an acidic solution of hydrochloric acid mixed in DI-water at the ratio of HCl:H$_2$O::1:2 for 2 min and again rinsed off with DI-water for a prolonged time. Finally, the samples were dried using a dry nitrogen jet. The samples were immediately loaded into the thermal evaporation chamber (base pressure ~10^{-6} Torr) for deposition of ohmic contact (Indium ~100 nm) on the corners of the samples. The samples were thermally annealed at 350 °C for 60 s to finally form the ohmic contacts.

TetraPhenylPorphyrin (TPP) organic molecules were used as the basic precursors for SAM. Zinc metal complexed TPP molecules were bridged to hydroxyl (R-OH) functionalization to form functionalized TPP molecular SAM termed as hydroxyl-phenyl zinc porphyrin (Zn-TPPOH). The detailed molecular preparation is given elsewhere.[21] Zn-TPPOH molecular solute was then dissolved in toluene to form 10^{-4} M molecular solution. The cleaned ohmic-contacted GaN samples were then placed in this molecular solution for 8 h

(time decided after many optimizations) in air tight conditions to achieve the saturated surface coverage of the molecular monolayer on the sample surface.

Different Schottky contacts of Cu/Au (40 nm/100 nm) and Ni/Au (40 nm/100 nm) metal stacks were deposited on the bare contacted n-GaN samples and molecular-coated n-GaN samples as circular dots with a diameter of 500 μm using a thermal evaporation system at the base pressure of 10^{-6} Torr. The deposition rate was about 1 Å/s. The samples were characterized using Atomic Force Microscopy (AFM) (Bruker: Atomic Force Microscopy system), X-ray Photoelectron Spectroscopy (XPS) [SPECS; PHOIBOS HSA3500 150 R6 (HW Type 30:14) MCD-9 model photoelectron spectrometer], Kelvin Probe Force Microscopy (KPFM) (Bruker), and Current-Voltage (I-V) characteristics [Keithley Semiconductor Characterization System (SCS-4200)].

Self-Assembled Monolayer (SAM) is an infinite 2-dimensional periodic array of finite length organic molecules. The single layer of the self-terminating hydrocarbon film is adsorbed on the sample such that the film thickness is restricted to the angstrom level. In this work, spectroscopic ellipsometry[22] was employed to assess the thickness of the molecular layer, adsorbed on the surface of n-GaN/Sapphire samples. Ellipsometric incidence data $\Psi(\lambda)$ were collected from Zn-TPPOH SAM/n-GaN/sapphire samples and fitted using the Cauchy dispersion model. The thickness of the molecular layer was found to be 8 ± 0.79 Å. The details of the analysis are presented in the supplementary material.

X-ray Photoelectron Spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that is used to analyse the surface chemistry of a material. In order to investigate whether the Self Assembled Monolayer (SAM) of organic molecules is chemisorbed or physisorbed on the n-GaN surface, XPS measurements were done on the SAM coated n-GaN samples with Al Kα X-ray excitation in an ultra-high vacuum environment. Since XPS measures the elemental composition of the sample surface, XPS peaks of Ga, N, C, O, and Zn elements were considered. The spectra were processed using CasaXPS software where the Shirley background correction was employed. Deconvoluted XPS
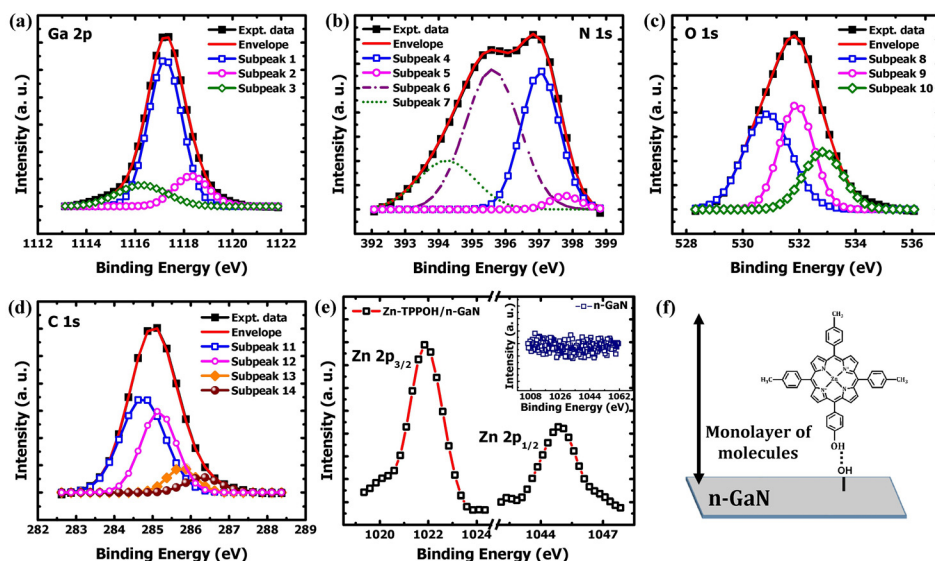

FIG. 1. XPS measurement data for the Zn-TPPOH SAM/n-GaN sample showing (a) Ga peak, (b) N peak, (c) O peak, (d) C peak, and (e) Zn peak. (f) A schematic to explain the bonding between Zn-TPPOH SAM and the n-GaN sample.

TABLE I. Experimentally observed binding energies of deconvoluted XPS peaks for different elements of the Zn-TPPOH/n-GaN sample structure illustrating the corresponding bonds formed at the SAM/semiconductor interface (as compared from their respective references).

Element	Subpeak no.	Observed binding energies (eV)	Bonds formed	References
Ga 2p [Fig. 1(a)]	1	1117.12	Ga-N	23
	2	1118.37	Ga-O (N-Ga-OH)	24
	3	1116.37	contribution from N core level	25
N 1s [Fig. 1(b)]	4	397.17	N element in N-tetraphenylporphyrin	27
	5	397.83	N-Ga	24
	6	395.57	Auger Ga peaks	26
	7	394.24	Auger Ga peaks	26
O 1s [Fig. 1(c)]	8	530.82	O-Ga (Ga-OH)	28
	9	531.82	OH hydrogen bonds	28
	10	532.82	C-O-H	29
C 1s [Fig. 1(d)]	11	284.74	C 1s in the molecular monolayer	29
	12	285.12	C-H (CH$_3$)	30
	13	285.87	C-N-H	29
	14	286.37	C-OH (phenol)	29
Zn 2p [Fig. 1(e)]	…	…	Present	…

peaks of different elements for Zn-TPPOH/n-GaN are plotted in Fig. 1 and summarized in Table I. The analyses not only confirmed the presence of Zn-TPP molecules and the phenol functionalization (subpeaks 4 and 10–14) but also explained that the SAM was not bonded to either Ga or N atoms (subpeaks 1–3 and 5–7) on the n-GaN surface. Further, the SAM was bonded to the hydroxyl molecules present on n-GaN (subpeaks 2 and 8) *via* the OH (subpeak 10) functionalization due to strong intermolecular forces [hydrogen bonds (subpeak 9)] [Fig. 1(f)]. The detailed explanation interpreting the XPS peaks is presented in Sec. 2 of the supplementary material.

Atomic Force Microscopy (AFM) was used to examine the surface coverage of the molecular layer and to find the change in the roughness of the sample after the SAM adsorption. AFM was done using a Bruker Atomic Force Microscopy system in the tapping mode on different parts of the sample at a scan size of 5×5 μm^2. Figures 2(a) and 2(b) compare the AFM surface images of the bare cleaned n-GaN sample and the Zn-TPPOH SAM/n-GaN sample. It was observed that the RMS surface roughness (R_q) of the n-GaN sample was 0.98 nm, but R_q increased to 1.25 nm after the adsorption of SAM on the sample surface. The slight change in the RMS roughness of the sample surface after the surface assimilation confirms the presence of a monolayer of the organic molecules. In continuation of the study of surface properties, the effect of SAM on surface electronic properties was determined by the measurement of surface potential using Kelvin probe force microscopy (KPFM). KPFM was done on both bare n-GaN and SAM/n-GaN samples on various locations at a scan size of 1×1 μm^2. The absolute value of the surface potential was calculated by taking the mean of different values calculated using Nanoscope Analysis software and is shown in Figs. 2(c) and 2(d). The value of the surface potential was found to be 950 ± 18 mV for the bare cleaned n-GaN sample surface and 608 ± 8 mV for the molecular coated n-GaN sample surface. It can be seen that the surface potential of the GaN sample decreases by $\sim$350 mV when the surface is modified by the SAM of organic molecules. This significant change in the surface potential has resulted in

an improvement in the electrical characteristics of Schottky barrier diodes on SAM/n-GaN samples.

Current-Voltage (I-V) characteristics of Copper (Cu) and Nickel (Ni) Schottky barrier diodes (SBDs) on the molecularly modified n-GaN samples were measured and compared with those of SBDs on the bare n-GaN sample. The data are plotted and shown in Fig. 3. From the figure, it can be seen that the reverse bias leakage current has decreased significantly by 3–4 orders of magnitude at ± 5 V when the SAM of organic molecules was sandwiched between the metal and the semiconductor, in both the Cu and Ni cases.

For thermionic emission (TE) and V > 3 kT/q, the general diode equation is given by[31]
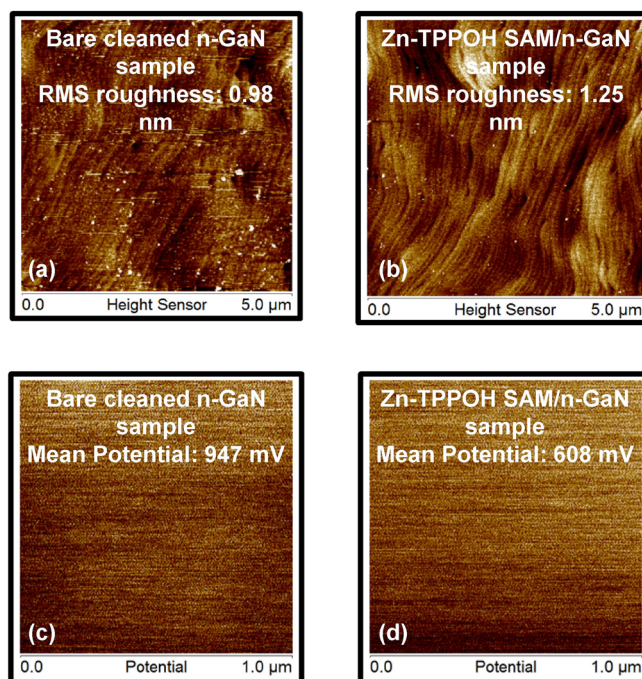

FIG. 2. AFM image of (a) bare cleaned n-GaN sample and (b) Zn-TPPOH SAM/n-GAN sample. KPFM image of (c) bare cleaned n-GaN sample and (d) Zn-TPPOH SAM/n-GaN sample.
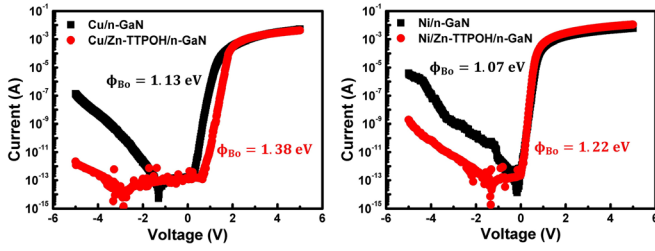
FIG. 3. Current-Voltage (I-V) measurements of Cu/n-GaN, Cu/Zn-TPPOH SAM/n-GaN, Ni/n-GaN, and Ni/Zn-TPPOH SAM/n-GaN Schottky barrier diodes.

$$I_n = \left[AA^*T^2 \exp\left(-\frac{q\phi_{BnTE}}{kT} \right) \right] \left[\exp\left(\frac{qV}{\eta kT} \right) - 1 \right], \quad (1)$$

where A is the area of the Schottky diode, A^* is the effective Richardson coefficient, T is the absolute temperature, q is the fundamental electronic charge, ϕ_{BnTE} is the barrier height, k is Boltzmann's constant, V is the applied voltage, and η is the ideality factor. Taking the log of Eq. (1), the Schottky barrier height was calculated using the relation

$$\phi_{bo} = \frac{kT}{q} \ln\left(\frac{AA^*T^2}{I_s} \right), \quad (2)$$

where I_s is the saturation current. ϕ_{bo} for the Cu/n-GaN Schottky barrier diode (SBD) was calculated to be 1.13 ± 0.06 eV at room temperature (RT), and for Ni/n-GaN SBD, ϕ_{bo} was found to be 1.07 ± 0.01 eV. The effect of insertion on the molecular monolayer was seen when ϕ_{bo} of both Cu and Ni SBDs increased to 1.38 ± 0.04 eV and 1.22 ± 0.03 eV, respectively. This remarkable increase in ϕ_{bo} and decrease in reverse bias leakage current in the SBDs can be very useful for better device operation and reliability. The ideality factor for Cu and Ni Schottky barrier diodes changed from 1.7 ± 0.26 to 1.16 ± 0.02 and 1.5 ± 0.12 to 1.05 ± 0.02, respectively, after the insertion of Zn-TPPOH SAM between the metal and the semiconductor.

It is noteworthy that the increase in ϕ_{bo} is in spite of the problem of Fermi level pinning, which is common in III-Nitride semiconductors (because of the presence of surface/interface states and defects). This is because the molecular monolayer plays with the interface potential at the metal semiconductor interface, thereby tuning the Schottky barrier height. This may be understood with the help of the energy band diagram, as shown in Fig. 4. n-GaN suffers from localized surface states that have a continuous distribution of energy within the forbidden gap. If the energy of the states does not coincide with the Fermi level, there is a net charge on the surface, leading to the formation of surface potential V_s [Fig. 4(a)]. When the metal is deposited, the charge on the surface of the semiconductor together with its image charge formed on the surface of the metal constitutes a dipole layer which yields an interface potential V_i.[32] The interface potential upsets the Schottky-Mott equation $\left(\phi_{B,n} = \phi_m - \chi_s \right)$ for calculating the Schottky barrier height (SBH) and resets it into $\phi_{B,n} = \phi_m - \chi_s - eV_i$ as illustrated in Fig. 4(b). This interface potential hinders the proper functioning of the SBDs. One of the ways to reduce V_i is to insert organic molecules at the metal-semiconductor interface. This is because molecules have a dipole moment of their own.
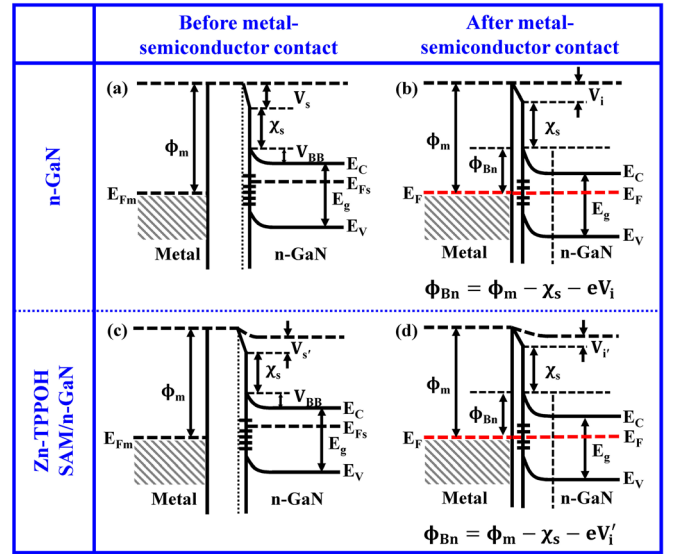

FIG. 4. Energy band diagram when (a) metal and bare semiconductor are separate, (b) metal and bare semiconductor form contact, (c) SAM is adsorbed on the surface of n-GaN (effect of SAM on the surface potential of the semiconductor before metal contact), and (d) metal forms contact with the molecularly modified n-GaN surface.

When they are subjected to an external opposing electric field, there is depolarization (reduction in dipole moment) due to which the potential is reduced. Following this phenomenon, when SAM of organic molecules is adsorbed on the surface of n-GaN, it comes in the vicinity of the electric field generated by the surface charge. The depolarization of the layer forming molecules leads to the reduction in the surface potential V_s [to V_s', Fig. (4c)], which is also evident from the KPFM study. Further, as the metal comes in contact with the molecular coated semiconductor, the interface potential also changes to a lower value V_i' [Fig. 4(d)]. The change in the potential due to the molecular monolayer is mathematically written as $\Delta V = N\mu \cos\theta / \varepsilon\varepsilon_o$, where N is the surface density of the dipoles (m^{-2}), μ is the dipole moment (C m), θ is the tilt angle of the dipoles with respect to the surface normal, ε is the molecular layer's dielectric constant, and ε_o is the permittivity of vacuum (Fm^{-1}).[33] The decrement in interface potential leads to an increase in ϕ_{Bo}, which was shown experimentally for both the metals, Cu and Ni.

It may be noted that the performance of Cu/Zn-TPPOH/n-GaN SBDs is a little better than that of Ni/Zn-TPPOH/n-GaN SBDs (talking in terms of increment in the barrier height). The plausible reason may be the difference in the interaction of Cu and Ni metals with the SAM of porphyrin organic molecules. The aromatic rings of SAM of porphyrin molecules act as steric hindrance for copper, and thus, it prevents the diffusion of Cu between the molecules through the SAM layer.[34] Lesser is the diffusion of the metal, better is the gate performance. Now, when the metal/Zn-TPPOH/n-GaN diodes are given a reverse bias, the electrons do not have sufficient energy to cross over the high Schottky barrier. In addition, the molecular monolayer coverage on the semiconductor surface acts as a passivation layer which does not allow the electrons to tunnel through the metal semiconductor interface. This was confirmed by Photoluminescence (PL) measurements, where the band-to-band peak for n-GaN (at ∼365 eV) was enhanced by 7–8 times,

after the adsorption of SAM. Thereby, a major reduction in the reverse bias leakage current is observed experimentally.

In conclusion, the Self-Assembled Monolayer (SAM) of hydroxyl-phenyl zinc Porphyrin (Zn-TPPOH) organic molecules was adsorbed onto the n-GaN surface. The adsorption of the molecules was in the form of bonding between OH functionalization of SAM and the native oxide on the n-GaN sample. The SAM negligibly affected the surface roughness but reduced the surface potential of n-GaN by ∼350 mV. When metal was deposited on the SAM coated semiconductor, the interface potential reduced, which resulted in a significant increase in the Schottky barrier height. This further resulted in the reduction of reverse bias leakage current by three to four orders of magnitude. The improvement in the electrical characteristics can be very useful for n-GaN based high power and high frequency devices.

See supplementary material for a detailed explanation of how Zn-TPPOH organic molecules form a monolayer on n-GaN following the concept of Self-Assembly. The detailed explanation of XPS measurements on Zn-TPPOH/n-GaN samples has also been presented.

[1]U. K. Mishra, P. Parikh, and Y. F. Wu, Proc. IEEE **90**, 1022 (2002).

[2]R. Siddharth and J. Debdeep, Semicond. Sci. Technol. **28**, 070301 (2013).

[3]J. Bardeen, Phys. Rev. **71**, 717 (1947).

[4]A. M. Cowley and S. M. Sze, J. Appl. Phys. **36**, 3212 (1965).

[5]S. Arulkumaran, T. Egawa, G. Y. Zhao, H. Ishikawa, T. Jimbo, and M. Umeno, Jpn. J. Appl. Phys. **39**, L351 (2000).

[6]C. G. V. de Walle and D. Segev, J. Appl. Phys. **101**, 081704 (2007).

[7]S. Jung, S. N. Lee, and H. Kim, Appl. Phys. Lett. **102**, 151603 (2013).

[8]A. Kumar, M. Kumar, R. Kaur, A. G. Joshi, S. Vinayak, and R. Singh, Appl. Phys. Lett. **104**, 133510 (2014).

[9]A. Kumar, S. Vinayak, and R. Singh, Curr. Appl. Phys. **13**, 1137 (2013).

[10]A. Kumar, K. Asokan, V. Kumar, and R. Singh, J. Appl. Phys. **112**, 024507 (2012).

[11]M. Garg, A. Kumar, S. Nagarajan, M. Sopanen, and R. Singh, AIP Adv. **6**, 015206 (2016).

[12]A. Vilan, A. Shanzer, and D. Cahen, Nature **404**, 166 (2000).

[13]Y. Selzer and D. Cahen, Adv. Mater. **13**, 508 (2001).

[14]M. A. Khaderbad, K. Nayak, M. Yedukondalu, M. Ravikanth, S. Mukherji, and V. R. Rao, in *IEEE-2008 8th IEEE Conference on Nanotechnology (IEEE-NANO), Arlington, TX, USA*, 18–21 August 2008, pp. 167–170.

[15]M. A. Khaderbad, R. Pandharipande, V. Singh, S. Madhu, M. Ravikanth, and V. R. Rao, IEEE Trans. Electron Devices **59**, 1963 (2012).

[16]V. M. Bermudez, Langmuir **19**, 6813 (2003).

[17]B. Baur, G. Steinhoff, J. Hernando, O. Purrucker, M. Tanaka, B. Nickel, M. Stutzmann, and M. Eickhof, Appl. Phys. Lett. **87**, 263901 (2005).

[18]R. M. Petoral, G. R. Yazdi, A. Lloyd Spetz, R. Yakimova, and K. Uvdal, Appl. Phys. Lett. **90**, 223904 (2007).

[19]T. Ito, S. M. Forman, C. Cao, F. Li, C. R. Eddy, Jr., M. A. Mastro, R. T. Holm, R. L. Henry, K. L. Hohn, and J. H. Edgar, Langmuir **24**, 6630 (2008).

[20]V. M. Bermudez and J. P. Long, Surf. Sci. **450**, 98 (2000).

[21]T. R. Naik, V. Singh, M. Ravikanth, and V. R. Rao, IEEE Trans. Electron Devices **63**, 2009 (2016).

[22]F. Schreiber, Prog. Surf. Sci. **65**, 151 (2000).

[23]Y. J. Lin, H. Y. Lee, F. T. Hwang, and C. T. Lee, J. Electron. Mater. **30**, 532 (2001).

[24]X. Zhang and S. Ptasinska, Sci. Rep. **6**, 24848 (2016).

[25]V. Matolín, S. Fabík, J. Glosík, L. Bideux, Y. Ould-Metidji, and B. Gruzza, Vacuum **76**, 471 (2004).

[26]G. Moldovan, I. Harrison, M. Roe, and P. D. Brown, Inst. Phys. Conf. Ser. **179**, 115 (2004); http://eprints.nottingham.ac.uk/1444/.

[27]D. K. Lavallee, J. Brace, and N. Winograd, Inorg. Chem. **18**, 1776 (1979).

[28]X. Zhang and S. Ptasinska, Phys. Chem. Chem. Phys. **17**, 3909 (2015).

[29]S. J. Kerber, J. J. Bruckner, K. Wozniak, S. Seal, S. Hardcastle, and T. L. Barr, J. Vac. Sci. Technol. A **14**, 1314 (1996).

[30]L. Chen, Z. Xu, J. Li, Y. Li, M. Shan, C. Wang, Z. Wang, Q. Guo, L. Liu, G. Chen, and X. Qian, J. Mater. Chem. **22**, 13460 (2012).

[31]E. H. Rhoderick and R. H. Williams, *Metal—Semiconductor Contacts*, 2nd ed. (Clarendon, Oxford, UK, 1988), p. 98.

[32]R. T. Tung, Phys. Rev. B **64**, 205310 (2001).

[33]G. Ashkenasy, D. Cahen, R. Cohen, A. Shanzer, and A. Vilan, Acc. Chem. Res. **35**, 121 (2002).

[34]M. A. Khaderbad, K. Nayak, M. Yedukondalu, M. Ravikanth, S. Mukherji, and V. R. Rao, in *8th IEEE Conference on Nanotechnology (IEEE-NANO) 2008, Arlington, TX, USA*, 18–21 August 2008, pp. 167–170.