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Anomalous diffusion of Ga and As from semi-insulating GaAs substrate into MOCVD grown ZnO films as a function of annealing temperature and its effect on charge compensation

Pranab Biswas,[1] Nripendra N. Halder,[2] Souvik Kundu,[3] P. Banerji,[1,a] T. Shripathi,[4] and M. Gupta[4]
[1]Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, India
[2]Advanced Technology Development Centre, Indian Institute of Technology, Kharagpur 721 302, India
[3]School of Electrical Engineering and Computer Science, Oregon State University, 1148 Kelley Engineering Center, Corvallis, OR 97331–5501, USA
[4]UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452 001, India

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The diffusion behavior of arsenic (As) and gallium (Ga) atoms from semi-insulating GaAs (SI-GaAs) into ZnO films upon post-growth annealing vis-à-vis the resulting charge compensation was investigated with the help of x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy. The films, annealed at 600 °C and 700 °C showed p-type conductivity with a hole concentration of 1.1×10^{18} cm^{-3} and 2.8×10^{19} cm^{-3} respectively, whereas those annealed at 800 °C showed n-type conductivity with a carrier concentration of 6.5×10^{16} cm^{-3}. It is observed that at lower temperatures, large fraction of As atoms diffused from the SI-GaAs substrates into ZnO and formed acceptor related complex, (As_{Zn}–$2V_{Zn}$), by substituting Zn atoms (As_{Zn}) and thereby creating two zinc vacancies (V_{Zn}). Thus as-grown ZnO which was supposed to be n-type due to nonstoichiometric nature showed p-type behavior. On further increasing the annealing temperature to 800 °C, Ga atoms diffused more than As atoms and substitute Zn atoms thereby forming shallow donor complex, Ga_{Zn}. Electrons from donor levels then compensate the p-type carriers and the material reverts back to n-type. Thus the conversion of carrier type took place due to charge compensation between the donors and acceptors in ZnO and this compensation is the possible origin of anomalous conduction in wide band gap materials. © *2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4876236]

I. INTRODUCTION

Zinc Oxide (ZnO) has become one of the most emerging and promising materials in semiconductor research since last couple of years. As a wide bandgap semiconducting material with large exciton binding energy of 60 meV at room temperature, ZnO has attracted the attention of device scientists for potential application in short-wavelength optoelectronics such as ultraviolet photodetectors, light-emitting diodes, laser diodes and solar cells which can be operated even above room temperature.[1–3]

However, being a nonstochiometric material, as-grown ZnO always shows n-type conductivity due to self-compensation; and a stable and reproducible p-type conductivity is difficult to achieve

[a]Author to whom correspondence should be addressed. mail: pallab@matsc.iitkgp.ernet.in (P. Banerji). Tel.: +91 3222 283984; fax: +91 3222 255303.

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without which its application in optoelectronic devices is not possible. It is found from the literature that group I (Li, Na, K, Cu and Ag) and group V (N, P, As and Sb) elements were used to dope it to achieve p-type conductivity.[4–8] Among these elements arsenic (As) is found to be capable of doping it with sufficient hole concentration. There are several techniques using which researchers were able to dope As into ZnO among which thin films of ZnO deposited on GaAs substrates, upon successive post-growth annealing, have been found to show p-type conductivity.

The origin of p-type conductivity as put forward by various researchers is not fully convincing and different opinion is available in the literature. Theoretical studies based on density functional theory have been used to predict the origin of p-type conductivity.[9,10] Most notably, Limpijumnong *et al.*[9] reported that As_{Zn}-$2V_{Zn}$ could be the major As- related acceptor complex, where As substitutes Zn and creates two more Zn vacancies. Chen *et al.*[11] on the basis of their experimental observation explained that As_{Zn}-$2V_{Zn}$ complex is the origin of hole majority in ZnO films. The authors' findings were based on an XPS peak of the As 3d core level with binding energy 45.56 eV. On the contrary, Vaithianathan *et al.*[12] reported on the basis of x-ray absorption near-edge structure that As_O could be the contributory acceptor defect in As- doped ZnO film. They observed that As substitutes O in ZnO crystal lattice and eventually it (As_O) acts as an acceptor state. In another study, using XPS, Shi *et al.*,[13] reported that the probable source of p-type conductivity could either be As_{Zn}–$2V_{Zn}$ or, As_O. The authors on the basis of As 3d spectral analysis, containing two component peaks, contended that the peak at 40.92 eV was due to As-Zn (As_O) whereas that at 44.98 eV was assigned to As-O (As_{Zn}). However, the authors assumed that As_{Zn}–$2V_{Zn}$ could be the contributory complex leading to the p-type conductivity. Most exceptionally, Du *et al.*[14] obtained As 3d peak at 41.6 eV in annealed As- doped p-type ZnO grown on n-GaAs and p-GaAs. The authors considered the peak as the identification of As_{Zn}–$2V_{Zn}$ complex. Ma *et al.*[15] and Guan *et al.*[16] assigned an XPS peak at 43.9 eV to As_{Zn}–$2V_{Zn}$ acceptor complex, though, nowhere in the literature that value is mentioned as the binding energy corresponding to As_{Zn}–$2V_{Zn}$ state. Thus it is found that the position of the XPS peak assigned to As_{Zn}–$2V_{Zn}$ acceptor complex is different for different authors.

Not only the identification of the acceptor complex is debatable, reports on the change in conductivity type (i.e. from n to p) as a function of annealing temperature is also available in the literature; which might apparently be thought as an anomalous behavior and need attention in the light of the effect of compensation in nonstoichiometric semiconductors. Cheng *et al.*[17] reported a hole concentration of 3.44×10^{20} cm^{-3} in ZnO grown on semi insulating GaAs by atomic layer deposition on annealing in oxygen at 700 ^{o}C which was found to decrease with annealing temperature. The authors reported type conversion in their samples at 600 ^{o}C below which n-type conductivity was observed. Ding *et al.*[18] reported p-type conductivity in ZnO/GaAs grown by metalorganic chemical vapour deposition (MOCVD) technique and then on annealing in argon ambiance for 4 h at 600 ^{o}C and 650 ^{o}C. However, Du *et al.*[14] reported the same in N_2 ambiance for 30 min at 680 ^{o}C while Ma *et al.*[15] obtained it after annealing in vacuum at 650 ^{o}C for 30 min though it is found from the literature that oxygen ambiance is the most favorable condition to achieve p-type conductivity in ZnO.[19] Again, Ryu *et al.*[20] found a conversion in conductivity from n-type to p-type in ZnO/GaAs films after annealing at 400 $^\circ$C in oxygen ambiance and Lee *et al.*[21] obtained p-type conductivity of the same after annealing the samples at 500 $^\circ$C for 1 h. However, several studies suggest that 600 $^\circ$C should be the optimized annealing temperature for As- diffusion in ZnO films.[17,18,22,23] In this context it must be mentioned that in most of the studies, a reasonably high hole concentration ranging from 10^{17} – 10^{21} cm^{-3} was obtained.[14,17,20,24] A comprehensive review on the state-of-the-art arsenic doping in ZnO is presented in a table, which can be found in the Supplemental S1.[25]

From the above discussion, it is observed that though a lot of works were reported on As-diffusion, very few studies showed interest over diffusion of Ga into ZnO from GaAs substrates.[15,26–28] It is true that As is more volatile than Ga and atomic radius of Ga (1.22 Å) is larger than that of As (1.19 Å), however, the ionic radius of Ga^{3+} (0.62 Å) is much less; and so the diffusion of Ga is expected to happen when the annealing temperature is increased. On the other hand, Zn^{2+} (0.72 Å) has a similar ionic radius to Ga^{3+} and hence it will result in a negligible lattice deformation in ZnO even for high Ga concentration.[29] It is seen from the literature that Ga

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substitutes Zn atoms (Ga_{Zn}) in the ZnO lattice and the defect acts as a source of n-type conductivity by donating one electron.[26,27] Thus on the basis of the above discussion, some relevant questions can be raised which are summarized as follows:

(i) Diffusion of As in ZnO and the resulting defect complex leading to p-type conductivity is not fully understood. Rather a lot of controversies are found in the literature so far as the ambient and annealing temperature are concerned.
(ii) Diffusion of Ga simultaneously with As in ZnO from GaAs substrates are not well documented though the diffusion of Ga leads to n-type conductivity and thus does any compensation occurs in ZnO? Is it a function of the ambient and/or annealing temperature? Otherwise, what leads to type conversion?
(iii) The diffusion kinetic is another area where one must concentrate to predict the behavior of simultaneous doping of Ga and As. Is there any competition between them to achieve p-type conductivity?

In this perspective, we have investigated (i) the identity of the acceptor complex which facilitates the p-type conductivity, (ii) the behavior of both As- and Ga-diffusion in ZnO from GaAs substrates on thermal annealing, and (iii) the location of As and Ga in the ZnO lattice so that from the identification of the defect states in the band gap, the doping behavior could be predicted. This will help in understanding the role of As- and Ga-diffusion in the (charge) compensation in ZnO and thereby the type conversion in it, as is widely reported.

II. EXPERIMENTAL

ZnO films were deposited onto semi-insulating (SI) GaAs substrate by MOCVD technique having an atmospheric pressure horizontal reactor. Prior to growth, the substrates were degreased in acetone and methanol for 3 min each, successively. Then they were cleaned in piranha solution (H_2O_2–NH_4OH–H_2O in the ratio of 1:1:2) followed by rinsing in deionized water for 3 min. Finally the substrates were dried by using N_2 gun. DEZn and tert-butanol were used as Zn and O precursors, respectively, whereas, pure N_2 was used as the carrier gas. Growth temperature was optimized at 400 °C. All the growths were performed for 75 min. The thickness of the films was determined using Profilometer. Field emission scanning electron microscope (FESEM) was used to study the surface morphology and cross-sectional view.

After the growth, the samples were annealed in oxygen ambiance at three different temperatures, viz. 600 °C (sample A), 700 °C (sample B) and 800 °C (sample C) for 25 min each. To examine the structural and optical properties of the grown samples, field emission scanning electron microscope (FESEM) and UV-VIS spectrophotometer were used. Temperature dependent Hall measurements were performed under van der Pauw configuration for electrical measurements. To investigate the nature of the acceptor related complexes, XPS and time-of-flight (ToF) SIMS measurements were carried out. The latter was performed using ${O_2}^+$ as the primary ion with energy of 2 keV. The XPS measurements were done using an X-ray radiation source of AlKα (hν = 1.487 KeV) operated at 10 kV. The system equipped with an Ar+ sputtering facility. The sample chamber was evacuated at an ultra high vacuum of 10^{-10} torr. All the XPS spectra were calibrated with reference to C1s peak at around 284.60 eV to compensate the sample charging effect.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the cross-sectional FESEM image of the sample. It is observed that ZnO was uniformly deposited over SI-GaAs substrate with a thickness of 250 nm. Figure 1(b) shows the transmission spectra of the films after annealing at 600 °C. Using the Tauc relation, the optical bandgap of the material was found to be 3.37 eV and it is shown in the inset of Fig. 1(b). No change in optical bandgap was observed after annealing. Figure 2 shows low temperature Hall mobility in samples A, B and C in the temperature range 100–300 K. The electrical parameters extracted for the samples at room temperature are shown in Table I.

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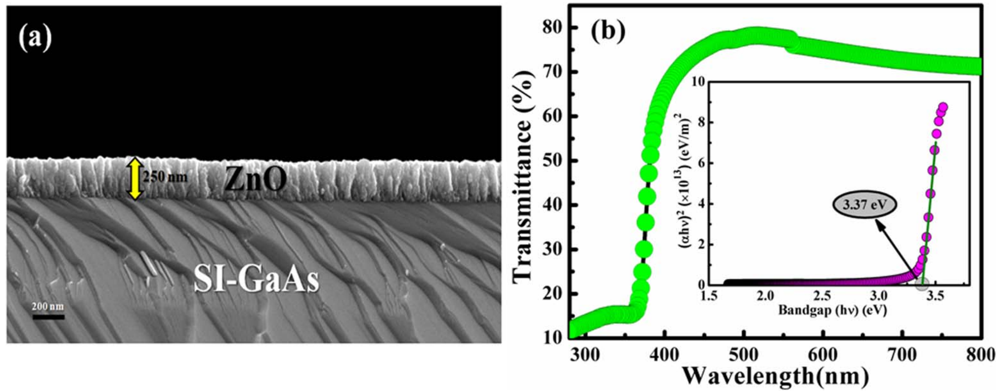

FIG. 1. (a) Cross-sectional Field Emission Scanning Electron Microscopic (FESEM) image of sample A. (b) UV-VIS transmittance spectra of the same sample. Inset of (b): Optical bandgap; calculated using Tauc relation for direct bandgap semiconductor.

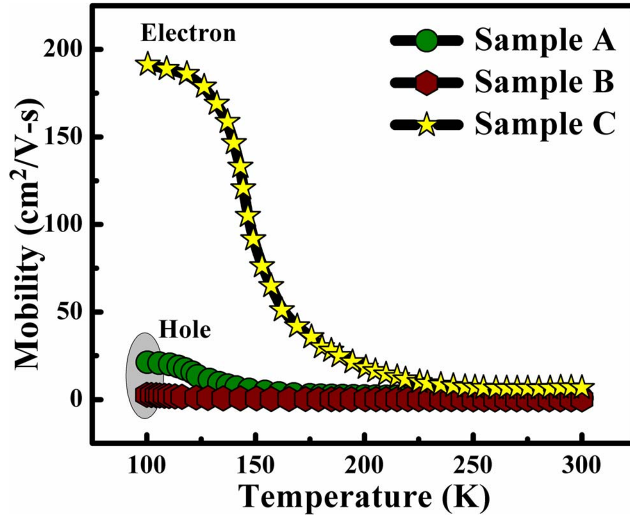

FIG. 2. Temperature dependent Hall mobility in the range 100 - 300 K for all three samples A, B, and C. In samples A and B, the conductivity was due to majority hole carriers, whereas, in sample C it was due to electrons.

TABLE I. Room temperature carrier concentration, resistivity and charge carrier type of ZnO films grown on semi-insulating GaAs by MOCVD.

Sample	Annealing temperature (°C)	Carrier concentration (cm^{-3})	Resistivity (Ω-cm)	Charge carrier type
A	600	1.1×10^{18}	6.84	p
B	700	2.8×10^{19}	2.98	p
C	800	6.5×10^{16}	14.52	n

Hall measurements revealed that the type of charge carriers changed from p-type (samples A and B) to n-type when annealing temperature was increased to 800 °C (sample C). Distinct change in carrier concentration and its type is also found from (p-type) 1.1×10^{18} cm^{-3} to (n-type) 6.5 $\times 10^{16}$ cm^{-3} when the temperature is increased from 600 °C to 800 °C. To investigate this anomalous behavior in electrical properties (change in conductivity) of the samples, obtained XPS data have been analyzed. Full scan XPS spectra of the ZnO thin films of all the three samples are shown in

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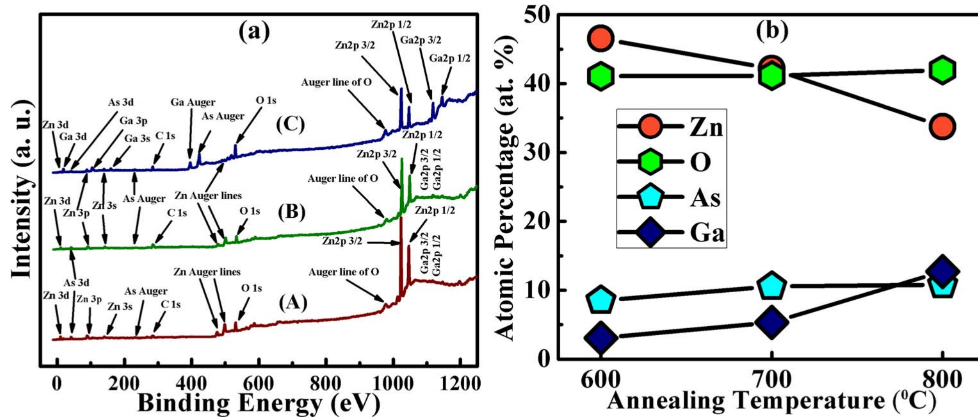

FIG. 3. (a) Full scan X-ray photoelectron spectra of the annealed ZnO fims grown onto semi-insulating GaAs substrates. The spectrum A shows the peaks related to the elements present on the surface of the films annealed at 600 °C. Similarly spectra B and C correspond to samples B and C which were annealed at 700 °C and 800 °C, respectively. All the spectra indicate presence of As and Ga along with Zn and O. (b) Atomic fraction (at. %) of Zn, O, As, and Ga elements at the surface of the films obtained from XPS data is plotted against the annealing temperature.

Fig. 3(a). The peaks related to Zn, O, As, and Ga are found to be present in the spectra which indicate that both As and Ga have indeed diffused in the films. Strong presence of the Ga related peaks are observed in the XPS spectrum of sample C compared to that in samples B and C which is due to considerable amount of Ga-diffusion on raising the annealing temperature to 800 °C. The sample surface composition of the elements (at. %) has been determined from the XPS data using the following relation[30]

$$X_i = 100\frac{A_i}{\sum_{j=1}^{m} A_j}.$$

Here the atomic percentage of the ith element, X_i, is determined by using the adjusted intensity A_i of the same element where

$$A_i = \frac{I_i}{T(E_i)R_i {E_i}^n},$$

I_i is the peak intensity, T (E_i) is the transmission function which depends on kinetic energy E_i, R_i is the relative sensitivity factor for the ith element, n is the escape depth exponent, and index j is varied from 1 to total number of elements (m). The calculated values of atomic percentage (at. %) of the elements are plotted in Fig. 3(b) against corresponding annealing temperatures. A notable variation in the ZnO stoichiometry is observed. According to the quantitative XPS analysis Sample A has oxygen vacancies (V_O) whereas sample C shows zinc vacancies (V_{Zn}). The sample A contains large fraction of As and it is eventually larger in sample B and C. High thermal energy together with oxygen ambiance makes the samples oxygen rich which thus in turn introduces zinc vacancy at higher annealing temperatures. The atomic percentage of As that has been diffused from the SI-GaAs substrates is found to increase when the annealing temperature is raised from 600 °C to 700 °C. However on further increased to 800 °C, it remains almost constant whereas the same for Ga is found to enhance significantly.

To investigate further the reason behind the conversion in carrier type and to find different chemical states present in the films, XPS narrow scans for Ga, As, O and Zn were performed. Figure 4(a) shows the XPS spectra of Zn 2p obtained in all the three samples (A, B and C). The peak corresponding to Zn $2p_{3/2}$, located at a binding energy of 1021.6 eV, can be attributed to Zn atom tetrahedrally bonded with four O atoms. The Zn $2p_{3/2}$ spectrum observed in sample C shows a small shoulder peak at 1023 eV unlike in samples A and B. This may be assigned to V_{Zn}.[31] Possibly annealing at high temperature in oxygen ambience leads to Zn vacancies in sample C and thus V_{Zn} is not observed in samples A and B. According to Li *et al.*,[32] this zinc vacancy acts as a stable

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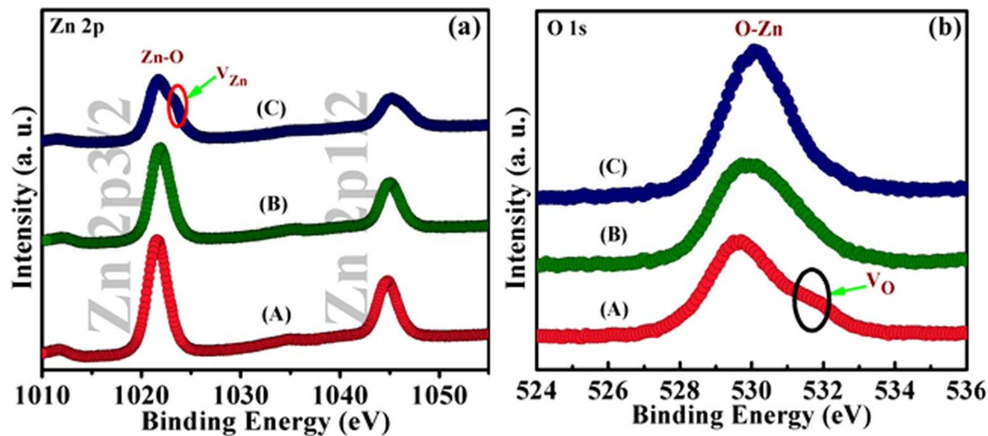

FIG. 4. (a) Narrow scan surface X-ray photoelectron spectra of Zn $2p_{3/2}$ obtained in the samples annealed at: (A) 600 °C; (B) 700 °C; and (C) 800 °C. (b) Surface X-ray photoelectron spectra of O 1s orbital of the ZnO films annealed at: (A) 600 °C; (B) 700 °C; and (C) 800 °C.

defect near the surface. This is also supported by the XPS core level spectra of O 1s, which is shown in Fig. 4(b). The peak at a binding energy of 530.3 eV, found in all the samples, is attributed to O_2^- ions bonded with Zn^{2+} in normal hexagonal wurtzite matrix of ZnO whereas shoulder peak at 531.5 eV, observed in sample A only, is associated with O_2^- under oxygen deficiency (oxygen vacancy, V_O).[33] Therefore, it can be assumed that as the annealing temperature is increased in presence of oxygen ambiance, V_O decreases and particularly in sample C, zinc vacancies (V_{Zn}) is formed in the ZnO lattice.

Figure 5 shows the core level XPS spectra of As 3d observed in samples A, B and C. It consists of two components with peaks at 40.9 eV and at 44.7 eV. The one with low binding energy can be assigned to As atoms bonded with Ga atoms, (As–Ga).[34] As the annealing temperature increases from 600 °C to 800 °C, the peak intensity increases significantly showing an increase in As –Ga in ZnO films, which in turn indicates an increase in Ga concentration in samples annealed at higher temperature. The peak located at 44.7 eV can be assigned to the As atoms substituting Zn atoms (As_{Zn}) and bonded with O atoms (As–O).[35] The intensity of this peak is found to decrease with increase in annealing temperature. The corresponding atomic percentage of As in samples A, B and C are shown in Fig. 3(b). It is found from the literature that diffusion of As in ZnO can lead to three types of defects, viz. As_i, As_O, and As_{Zn}. In the present study, the XPS spectra provide evidence of As_{Zn} in ZnO films; whereas, there is no significant observable peak found showing presence of As_O and As_i. The acceptor defect, As_O, has a formation energy of 9.87 eV which is larger than that of As_{Zn} (1.59 eV), and more so the O-rich ambiance provides favorable condition to suppress its formation.[36] The result is found to be consistent with the study of Wahl *et al.*[37] In Table II various defects along with their ionization energies are presented on the basis of their presence in the XPS spectra. The formation of oxygen vacancy (V_O) in sample A and zinc vacancy (V_{Zn}) in sample C (ref. to Table II) are found to be consistent with the atomic composition of the respective samples is shown in Fig. 3(b). Janotti *et al.*[38] and Zhang *et al.*[19] reported that though there are native acceptor defects such as V_{Zn}, O_i and O_{Zn} at both Zn-rich and O-rich environments, the donor defects, viz. V_O, Zn_i and Zn_O, having low formation enthalpies form readily and act as ''hole killers''. As a fact, as-grown ZnO always have n-type conductivity and via native defects we cannot obtain p-type conductivity in it.

So, the question that remained unanswered is that in spite of the defect, As_{Zn}, which was supposed to act as a donor, why the Hall measurements show p-type conductivity in samples A and B. Thus there should be some stable acceptor complex which will give rise to the p-type conductivity in the films. First-principle calculations reveal that As_{Zn}–$2V_{Zn}$ is the complex behind this conduction type in ZnO films.[9] Here As atom diffused into the ZnO films and occupies the Zn antisite which is energetic enough to generate two zinc vacancies (V_{Zn}) and form the above-mentioned complex. The

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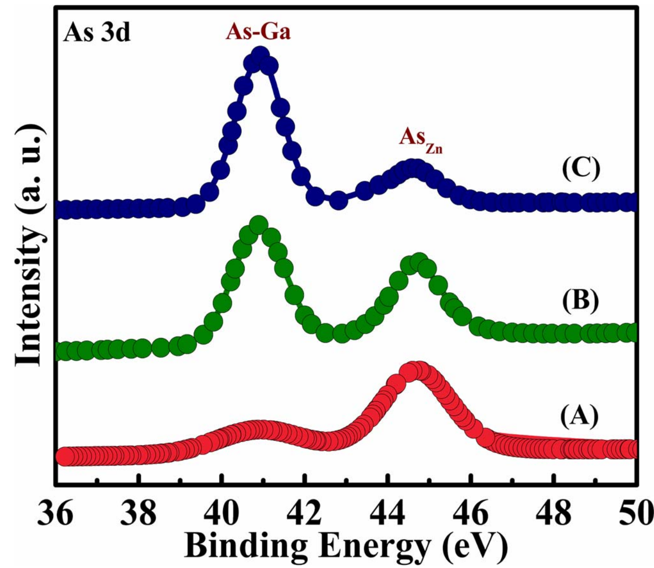


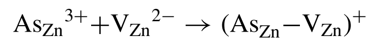
FIG. 5. Core level X-ray photoelectron spectra of As 3d in the ZnO films annealed at: (A) 600 °C; (B) 700 °C; and (C) 800 °C.

TABLE II. Chemical states present in the samples and their ionization energy[22,23,38–41] under oxygen-rich annealing conditions.

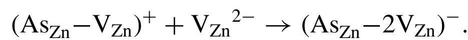
	Chemical states	Type of states	Ionization Energy[a] (eV)	Trace in XPS spectra		
				Sample A	Sample B	Sample C
NATIVE	V_{Zn}	Acceptor	0.87	–	–	√
	O_i	Acceptor	1.59	–	–	–
	O_{Zn}	Acceptor	1.77	–	–	–
	V_O	Donor	2.51	√	–	–
	Zn_i	Donor	3.65	–	–	–
	Zn_O	Donor	3.91	–	–	–
INDUCED	As_O	Acceptor	0.93 (Deep)	–	–	–
	As_{Zn}	Donor	0.95 (Deep)	√	√	√
	As_{Zn}–$2V_{Zn}$	Acceptor	0.15 (Shallow)	√	√	√
	Ga_{Zn}	Donor	0.055 (Shallow)	–	√	√

[a]For acceptor transition (−/2−) and for donor transition (2+/+).

resulting complex is stable and has low ionization energy of 0.15 eV. The complex forms through the following steps:



$$As_{Zn}{}^{3+} + V_{Zn}{}^{2-} \rightarrow (As_{Zn} - V_{Zn})^{+}$$



$$(As_{Zn} - V_{Zn})^{+} + V_{Zn}{}^{2-} \rightarrow (As_{Zn} - 2V_{Zn})^{-}.$$

The complex $(As_{Zn}$–$V_{Zn})^+$ is a result of Coulombic force between two oppositely charged components, whereas, subsequent complex $(As_{Zn}$–$2V_{Zn})^-$ is formed due to optimization of Madelung energy and because of certain energy states.[9] Here As atoms act as triple donor by donating all the three electrons to two V_{Zn}, each of which can accept two electrons. The complex $(As_{Zn}$–$2V_{Zn})^-$ is stable in nature, easier to form, prevalent and dominant As- related acceptor in the ZnO lattice compared to other defects. It has a remarkably low formation energy of 1.59 eV with ionization energy of 0.15 eV and migration energy of 1.60 eV.[9,10] Since the obtained XPS data shows a major peak related to As_{Zn}, the p-type character of the samples is due to the presence of $(As_{Zn}$–$2V_{Zn})^-$.

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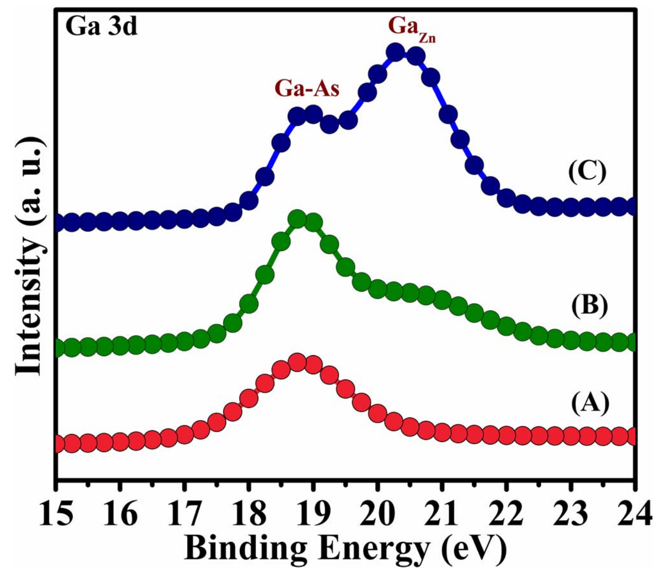

FIG. 6. Ga 3d core level X-ray photoelectron spectra obtained in the ZnO films annealed at: (A) 600 °C; (B) 700 °C; and (C) 800 °C.

However, the Hall measurements showed n-type conductivity in sample C (Table I), though As_{Zn} peak was observed in the As 3d XPS spectrum of that sample.

The answer lies in Fig. 6, where XPS spectra of Ga 3d are shown for all the three types of samples (A, B and C). The spectra consist of two different peaks. The low binding energy component located at 18.8 eV can be attributed to the Ga atoms bonded with As atoms,[34] whereas, the higher one at 20.5 eV can be due to Ga atoms at the place of Zn sites (Ga_{Zn}).[39] At low annealing temperatures the atomic percentage of diffused Ga is found to be lower than that of As (Fig. 3(b)). From the XPS spectra (Fig. 6), it is found that initially at 600 – 700 °C, Ga on diffusion from SI-GaAs forms bonding with As. On further increase in annealing temperature to 800 °C, Ga substitutes Zn forming a shallow donor complex, Ga_{Zn}. Here, a Ga^{3+} ion substitute a Zn^{2+} ion and release a free electron in the ZnO lattice. Thus Ga_{Zn} forms shallow donor states with an ionization energy of 55 meV at higher annealing temperature.[40,41] In sample C, the atomic percentage of Ga is estimated to be more than that of As (Fig. 3(b)). So, the acceptors as well as the native acceptor defects (V_{Zn}, as is evident from Fig. 4(a)) have been compensated by free electrons donated by ${Ga_{Zn}}^{3+}$ in the crystal lattice.

Here both As and Ga diffuse into the films. Since As is much more volatile than Ga, initially at lower annealing temperatures, the diffusion of As dominates and forms the As related acceptor complex (As_{Zn}–$2V_{Zn}$). This acceptor states will give rise to sufficient number of holes to surplus the electrons already there in the nonstoichiometric ZnO and will show p-type conductivity in it. A proposed mechanism is shown in Figs. 7(a) and 7(b) for samples A and B respectively. At higher annealing temperature (800 °C), Ga diffuses more and form Ga related donor complex (Ga_{Zn}). Since the ionization energy of Ga_{Zn} (55 meV) is lower than that of As_{Zn}–$2V_{Zn}$ (150 meV), the former will give rise to shallow donor states within the ZnO band gap (Table II). Electrons due to this shallow level will compensate the positive charge carriers (holes) already there and will show the n-type conductivity in the sample which was pictorially demonstrated in Fig. 7(c). Thus the anomalous behavior vis-à-vis the carrier type conversion, observed by various authors, is a result of the charge compensation as explained above. For further investigation the diffusion profiles of As and Ga atoms in the ZnO films, as a function of post-growth annealing temperature, has been studied by SIMS measurements.

The SIMS data of samples A, B, and C have been plotted against the depth in Figs. 8(a)–8(c), respectively. The XPS measurements, as mentioned earlier, typically showed a surface properties (particularly chemical states and surface composition), whereas, the SIMS measurements were performed to investigate the diffusion profiles of As and Ga into ZnO. Figure 8(a) shows poor

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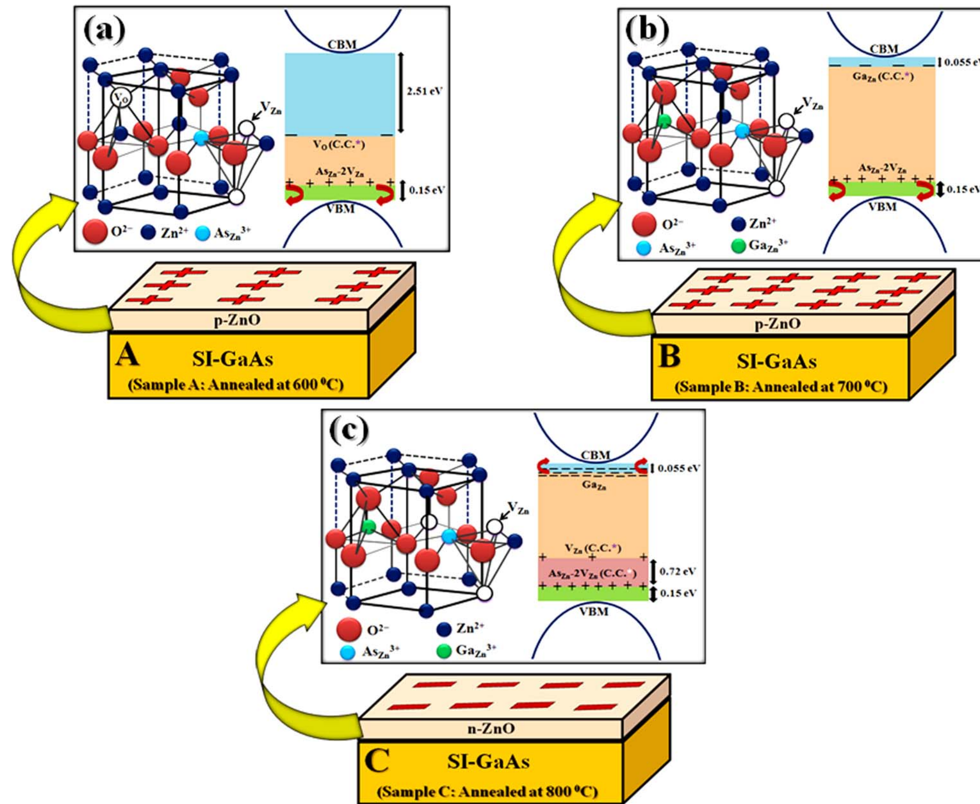

FIG. 7. (a) The location of As in ZnO lattice with a proposed band diagram showing the charge compensation in the samples annealed at 600 °C. Band diagram includes As related acceptor states (As_{Zn}–$2V_{Zn}$) along with native defect states (V_O) observed in the XPS spectra. Positive charges compensate the electrons and thus the p-type conductivity is achieved. (b) Diffusion of both As and Ga took place in ZnO lattice which was annealed at 700 °C. Proposed band diagram shows how the charge compensation converted the samples to p-type. The band diagram shows the energy states generated as a result of As-related complex (As_{Zn}–$2V_{Zn}$) and Ga-related complex (Ga_{Zn}). (c) The proposed band diagram shows the location of both Ga and As which were diffused into ZnO lattice when annealed at 800 °C. Band diagram pictorially depicts different energy states originated due to As and Ga related complexes along with the native defect states (V_{Zn}) found in XPS spectra. In this case electrons compensate holes and thus n-type conductivity is found. *C.C. – Compensated Charge.

diffusion of Ga compared to As (Fig. 3(b)) in sample A. So the As related acceptor complex can easily compensate the native donor defects, specially V_O, as is evident from O 1s XPS spectra of the same (Fig. 4(b)) along with the Ga related donor (Ga_{Zn}). Therefore the p-type conductivity in sample A is consistent with the spectroscopic data. The same trend is observed in sample B as well (Fig. 8(b)). Though there was more diffusion of Ga than As atoms (with a decreased As/Ga ratio, as is shown in Fig. 3(b)) with an increase in annealing temperature to 700 °C, sample B showed p-type conductivity with a higher hole concentration compared to that of Sample A. This is due to the absence of native donor defect, V_O, in sample B. On further increase in annealing temperature to 800 °C, in sample C, surprisingly Ga is found to diffuse more into the films as shown in Fig. 8(c) which is similar in nature with the findings of XPS measurements and shown in Fig. 3(b). As mentioned earlier, the Hall measurements showed n-type conductivity in sample C. Charge compensation has been done by Ga_{Zn} donor defects and other as-grown native donor defects to the As_{Zn}-$2V_{Zn}$ acceptor complex, along with acceptor defect, V_{Zn}, as is evident from the Zn 2p XPS spectrum of sample C (Fig. 4(a)). The hump at the interface of ZnO/SI-GaAs in the Ga profile in Fig. 8(c) was considered as a result of the Ga/Zn interdiffusion.[28] Therefore, the less ionization energy of Ga_{Zn}, and interdiffusion of Ga and Zn in the system ZnO/GaAs triggers up the Ga- diffusion more than As into ZnO from SI-GaAs substrates at higher annealing temperature (800 °C) in sample C though As is more volatile than Ga. Thus the defect states due to As- and

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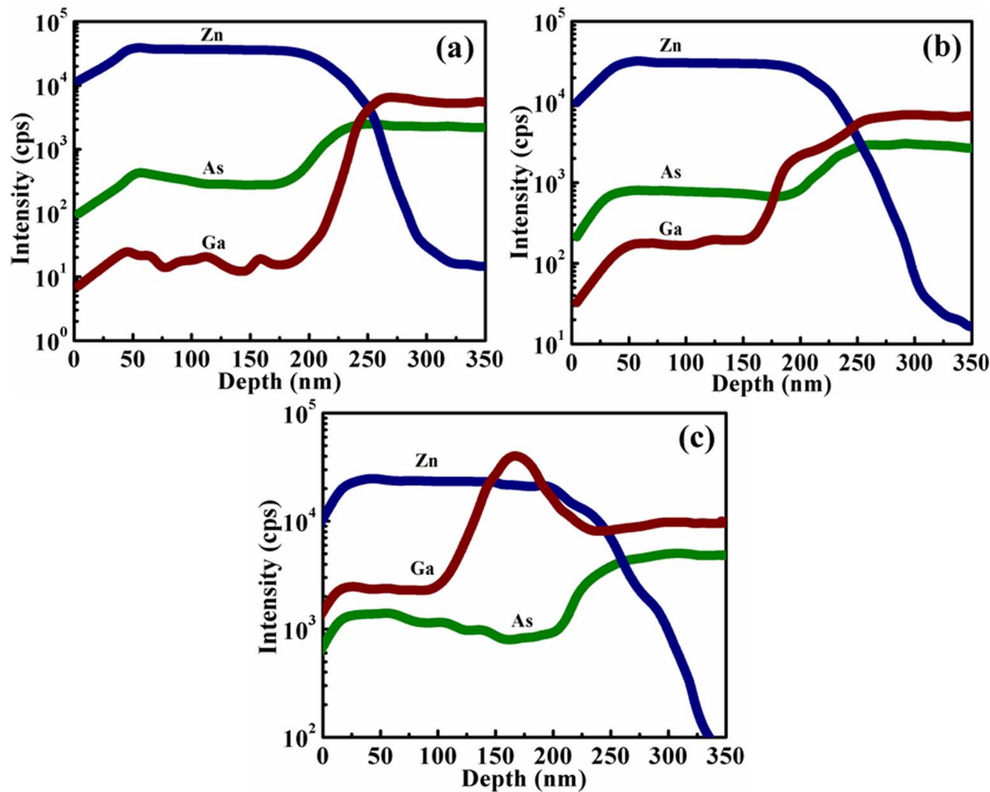

FIG. 8. Depth profile obtained from secondary ion mass spectroscopic measurements in samples annealed at (a) 600 °C; (b) 700 °C; and (c) 800 °C.

Ga-diffusion on thermal annealing from SI-GaAs substrates along with the native defects in ZnO lead to the anomalous conduction behavior which is a result of the charge compensation in ZnO due to competition between Ga and As.

IV. CONCLUSIONS

ZnO thin films, grown on SI-GaAs showed p-type conductivity after post-growth annealing at 600 °C and 700 °C, whereas the conductivity was reverted back to n-type in samples annealed at 800 °C. On the basis of the XPS and SIMS measurements, the following conclusion can be drawn:

(i) Diffusion of As in ZnO films results in As_{Zn}–$2V_{Zn}$ acceptor complex and not As_O. The p-type conductivity is due to shallow acceptor complex with ionization energy of 150 meV. The acceptors surplus the electron concentration in the nonstoichiometric as-grown ZnO.
(ii) The situation remains the same even when the annealing temperature is increased to 700 °C except that the carrier concentration is increased due to less number of oxygen vacancies.
(iii) Diffusion profile of the samples showed that as the annealing temperature is increased to 800 °C, gallium was diffused more than arsenic into ZnO and acted as a donor complex after substituting Zn (Ga_{Zn}) atoms in ZnO lattice. Thus for samples annealed at 800 °C, donor complex exceeds the effect of acceptor complex, it compensates the acceptor charge; and thereby conductivity reverts back to n-type.
(iv) Resistivity of the samples annealed at 800 °C is found to increase significantly due to large number of defect states originating from the simultaneous diffusion of both As and Ga.

So, conclusively it is established that the p-type behavior in As doped ZnO is due to shallow acceptor complex As_{Zn}–$2V_{Zn}$ found in samples annealed at temperatures, 600 and 700 °C, in the present investigation whereas Ga_{Zn} acted as the shallow donor complex in samples annealed at higher

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temperature, say, 800 °C. XPS and SIMS data showed consistency on the diffusion behavior of As and Ga from SI-GaAs substrates into ZnO films. Possibly less ionization energy of Ga_{Zn} and the interdiffusion between Zn and Ga at the interface of ZnO/GaAs resulted in the avalanche diffusion of Ga into the ZnO films reverting it to n-type on compensation of the holes.

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[1] A. Janotti and C. G. Van de Walle, Rep. Prog. Phys. **72**, 126501 (2009).
[2] S.-M. Peng, Y.-K. Su, L.-W. Ji, C.-Z. Wu, W.-B. Cheng, and W.-C. Chao, J. Phys. Chem. C **114**, 3204 (2010).
[3] P. Sudhagar, T. Song, D. H. Lee, I. Mora-Seró, J. Bisquert, M. Laudenslager, M. S. Wolfgang, W. I. Park, U. Paik, and Y. S. Kang, J. Phys. Chem. Lett. **2**, 2011 (1984).
[4] E. S. Kumar, J. Chatterjee, N. Rama, N. DasGupta, and M. S. R. Rao, ACS Appl. Mater. Interfaces **3**, 1974 (2011).
[5] H. He, S. Lin, G. Yuan, L. Zhang, W. Zhang, L. Luo, Y. Cao, Z. Ye, and S. T. Lee, J. Phys. Chem. C **115**, 19018 (2011).
[6] M. A. Thomas and J. B. Cui, J. Phys. Chem. Lett. **1**, 1090 (2010).
[7] J.-F. Chien, C.-H. Chen, J.-J. Shyue, and M.-J. Chen, ACS Appl. Mater. Interfaces **4**, 3471 (2012).
[8] Y.-S. Choi, J.-W. Kang, D.-K. Hwang, and S.-J. Park, IEEE Trans. Electron Devices **57**, 26 (2010).
[9] S. Limpijumnong, S. B. Zhang, S.-H. Wei, and C. H. Park, Phys. Rev. Lett. **92**, 155504 (2004).
[10] B. Puchala and D. Morgan, Phys. Rev. B **85**, 064106 (2012).
[11] Y. J. Chen, H.-W. Jen, M.-S. Wong, C.-H. Ho, J.-H. Liang, J.-T. Liu, and J.-H. Pang, J. Cryst. Growth **362**, 193 (2013).
[12] V. Vaithianathan, B. T. Lee, C. H. Chang, K. Asokan, and S. S. Kim, Appl. Phys. Lett. **88**, 112103 (2006).
[13] Z. Shi, Y. Zhang, B. Wu, X. Cai, J. Zhang, X. Xia, H. Wang, X. Dong, H. Liang, B. Zhang, and G. Du, Appl. Phys. Lett. **102**, 161101 (2013).
[14] G. Du, Y. Cui, X. Xiaochuan, X. Li, H. Zhu, B. Zhang, Y. Zhang, and Y. Ma, Appl. Phys. Lett. **90**, 243504 (2007).
[15] Y. Ma, Q. Gao, G. G. Wu, W. C. Li, F. B. Gao, J. Z. Yin, B. L. Zhang, and G. T. Du, Mater. Res. Bull. **48**, 1239 (2013).
[16] H. Guan, X. Xia, Y. Zhang, F. Gao, W. Li, G. Wu, X. Li, and G. Du, J. Phys.: Condens. Matter. **20**, 292202 (2008).
[17] Y.-C. Cheng, Y.-S. Kuo, Y.-H. Li, J.-J. Shyue, and M.-J. Chen, Thin Solid Films **519**, 5558 (2011).
[18] M. Ding, B. Yao, D. Zhao, F. Fang, D. Shen, and Z. Zhang, Thin Solid Films **518**, 4390 (2010).
[19] S. B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. B **63**, 075205 (2001).
[20] Y. R. Ryu, S. Zhu, D. C. Look, J. M. Wrobel, H. M. Jeong, and H. W. White, J. Cryst. Growth **216**, 330 (2000).
[21] W. Lee, D.-K. Hwang, M.-C. Jeong, M. Lee, M.-S. Oh, W.-K. Choi, and J.-M. Myoung, Appl. Surf. Sci. **221**, 32 (2004).
[22] W. Lee, M.-C. Jeong, and J.-M. Myoung, Appl. Phys. Lett. **85**, 6167 (2004).
[23] J. H. Liang, Y. J. Chen, and Y. C. Wang, Surf. Coat. Technol. **231**, 243 (2013).
[24] P. Wang, N. Chen, Z. Yin, F. Yang, C. Peng, R. Dai, and Y. Bai, J. Appl. Phys. **100**, 043704 (2006).
[25] See supplementary material at http://dx.doi.org/10.1063/1.4876236 for detail literature review on p-type As doped ZnO.
[26] J. Sun, H. Liang, J. Zhao, Q. Feng, J. Bian, Z. Zhao, H. Zhang, Y. Luo, L. Hu, and G. Du, Appl. Surf. Sci. **254**, 7482 (2008).
[27] H. F. Liu, S. J. Chua, G. X. Hu, H. Gong, and N. Xiang, J. Appl. Phys. **102**, 063507 (2007).
[28] M. K. Ryu, S. H. Lee, M. S. Jang, G. N. Panin, and T. W. Kang, J. Appl. Phys. **92**, 154 (2002).
[29] M. Mapa, K. S. Thushara, B. Saha, P. Chakraborty, C. M. Janet, R. P. Viswanath, C. M. Nair, K. V. G. K. Murty, and C. S. Gopinath, Chem. Mater. **21**, 2973 (2009).
[30] http://www.casaxps.com/release/release2312_/CasaXPS.HLP/Quantification/quantification_of_xps_spcetra.htm.
[31] Y. Y. Tay, S. Li, C. Q. Sun, and P. Chen, Appl. Phys. Lett. **88**, 173118 (2006).
[32] H. Li, L. K. Schirra, J. Shim, H. Cheun, B. Kippelen, O. L. A. Monti, and J.-L. Bredas, Chem. Mater. **24**, 3044 (2012).
[33] S. U. Awan, S. K. Hasanain, M. F. Bertino, and G. H. Jaffari, J. Phys.: Condens. Matter **25**, 156005 (2013).
[34] R. Contreras-Guerrero, J. P. Veazey, J. Levy, and R. Droopad, Appl. Phys. Lett. **102**, 012907 (2013).
[35] *Handbook of X-ray Photoelectron Spectroscopy*, edited by G. E. Muilenberg (Perkin Elmer, Eden Prairie, MN, 1979).
[36] N. Xu, Y. Xu, L. Li, Y. Shen, T. Zhang, J. Wu, J. Sun, and Z. Ying, J. Vac. Sci. Technol. A **24**, 517 (2006).
[37] U. Wahl, E. Rita, J. G. Correia, A. C. Marques, E. Alves, and J. C. Soares, Phys. Rev. Lett. **95**, 215503 (2005).
[38] A. Janotti and C. G. Van de Walle, Phys. Rev. B **76**, 165202 (2007).
[39] V. Avrutin, D. J. Silversmith, and H. Morkoç, Proc. IEEE **98**, 1269 (2010).
[40] G. Hollinger, R. Skheyta-Kabbani, and M. Gendry, Phys. Rev. B **49**, 11159 (1994).
[41] Z. Yang and J. L. Liu, J. Vac. Sci. Technol. B **28**, C3D6 (2010).

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