Nanoscale Horizons

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Cite this: *Nanoscale Horiz.*, 2019, 4, 1251

Will surface effects dominate in quasi-two-dimensional gallium oxide for electronic and photonic devices?

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Received 24th April 2019,
Accepted 6th June 2019

DOI: 10.1039/c9nh00273a

rsc.li/nanoscale-horizons

There is currently great interest in ultra-wide bandgap semiconductors for their applicability in power switching electronics with improved efficiency compared to current technologies and also to solar-blind UV detection. One of the most promising materials is Ga_2O_3, available in large area bulk crystals and as exfoliated nano-layers (nanobelts, nanomembranes, and nanosheets). One aspect of this material that has not been widely recognized is the sensitivity of its surface to environment. The goal of this brief focus article is to provide some insight into the mechanisms and defects that underlie this effect and explain inconsistencies in the literature.

Gallium oxide has a number of polymorphs, with the b- and a-variants emerging as next-generation ultra-wide bandgap semiconductors (bandgap 4.6–4.8 eV for b and B5.2 eV for a-polymorphs).[1–3] These have the potential for transformative impact on the energy economy, due to their more efficient power switching capabilities in power control and conversion applications such as in the automotive industry, data center power management, grid control, and industrial and locomotive traction control.[1–4] However, a high density of crystal defects in the bulk of Ga_2O_3 significantly hinders the progress in realizing many of the beneficial attributes of power electronics systems.[4] What is less commonly realized is that surface effects are also very important with Ga_2O_3, a factor that has been overlooked in a previous review of its research challenges.[4]

Despite not being a van der Waals material and having very strong ionic bonding, the more commonly studied b-phase can be mechanically cleaved and exfoliated easily along favorable surfaces.[2,3] The large anisotropy of the lattice constant in this monoclinic phase allows a facile cleavage (a[100] = 12.225 Å, b[010] = 3.039 Å, and c[001] = 5.801 Å) along the (100) and (001) faces. From bond strength calculations, the surface covalent bonds in these planes are up to 6 eV per bond stronger than the perpendicular bonds, which break easily.[5] Thin quasi-2D nanolayers (nanobelts, nanomembranes, and nanosheets) can be exfoliated from bulk crystals, similar to true 2D materials such as graphene or MoS_2,[6,7] and used to fabricate transistor and photodetector structures.[8] In addition, single-crystalline ultra-thin quasi-hexagonal (010) b-Ga_2O_3 nanosheets can be homo-epitaxially grown on nanowire seeds.[9] The fabrication of devices using b-Ga_2O_3 nanobelts has several advantages over conventional bulk single crystals, including the absence of strain and the fact that the heat management problem related to the low thermal conductivity[1–3] of b-Ga_2O_3 can be mitigated by applying it to substrates with high thermal conductivity.

The surface termination, relaxation and surface energies for different faces of b-Ga_2O_3 have been reported by Bermudez[10] and provide insight into the structure of nanosheets. Fig. 1 shows schematics of the ideally terminated (100)-A and (100)-B surfaces. A and B refer to two possible terminations, corresponding to stoichiometric unit cells with non-polar surfaces. A refers to termination in rows of $O_{(II)}$s lying along the [0 1 0] direction with each $O_{(II)}$ back-bonded to two $Ga_{(I)}$s. B refers to termination in nearest-neighbor rows of $Ga_{(II)}$ and $O_{(III)}$ atoms, each singly-unsaturated, with full coordination of $Ga_{(I)}$ and $O_{(I)}$ atoms at the surface. Hartree–Fock calculations show that the (100)-B surface has the lowest surface energy under both the ideal (0.96 J m^{-2}) and relaxed (0.68 J m^{-2}) conditions, while the (010) surface has the highest surface energy under the relaxed condition.[10] Experimental data show that Ga_2O_3 powders have equivalent surface and bulk compositions, without favorable surface stabilization.[11,12] Collins *et al.*[11] reported that H_2 is dissociatively chemisorbed, following reaction pathways involving endothermal dissociation occurring over surface Ga sites at $T \geq 450$ K, producing Ga–$H_{(I)}$ bonds (heat and entropy of this hydrogen adsorption were Dh_I = 155 ± 25 kJ mol^{-1} and Ds_I = 0.27 ± 0.11 kJ mol^{-1} K^{-1}). An additional pathway present at low temperatures involves surface Ga–O–Ga species,

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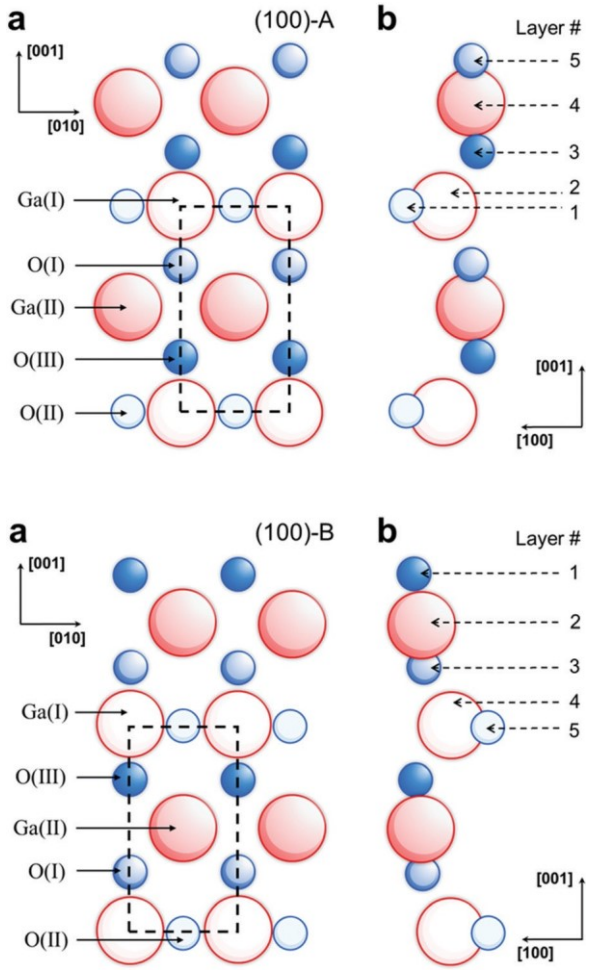

Fig. 1 Schematic representation of ideally terminated (1 0 0)-A (top) and (100)-B surfaces of b-Ga_2O_3. (a) View along surface normal-dashed lines show the surface unit cell; (b) outermost surface layers, viewed along the [0 1 0] direction, with vectors indicating the displacements occurring during relaxation. The displacement vectors are increased by a factor of 4 relative to the interatomic distances. All displacements are in the plane of the page, *i.e.*, the (0 1 0) plane (after Bermudez[9]).

producing GaO–H and Ga–H(II) bonds that are stable after heating under vacuum at $T \sim 650$ K. It has long been established that oxygen vacancies are produced during heating under vacuum,[12] where the relationship between conductivity (s) and O_2 partial pressure (pO_2) is given by $s \propto (pO_2)^{-0.25}$.

While the possible thickness-dependent bandgap and mobility at the nanoscale limit[13] have not been well understood in Ga_2O_3, the nanobelts can also be integrated with other low-dimensional materials, taking advantage of quasi-2D structures, including h-BN, to fabricate metal–insulator–semiconductor field effect transistors.[8,14–17] Zhou *et al.*[16] fabricated nanobelt devices with various thicknesses and found that the threshold voltage (V_T) shifted from negative to positive as the thickness was decreased. Enhancement-mode (E-mode) b-Ga_2O_3 nanobelt FETs demonstrated a breakdown voltage of 185 V with negligible hysteresis and a high on/off ratio, promising for future power devices.[8] There are also extensive studies of solar-blind UV photodetectors fabricated on Ga_2O_3 nanobelts.[8]

There are also more speculative potential applications, including resistive-RAM (ReRAM or RRAM), a non-volatile memory gaining attention because it can be utilized to build neuromorphic computing chips.[18] Many metal oxides have been investigated in this regard because the oxygen ions and oxygen vacancies can easily drift under an electric field. The motion of oxygen ions and oxygen vacancies needs to be investigated in b-Ga_2O_3 nano-layers, but memristic behavior has been observed.[19–21] Heterojunction Bipolar Transistors (HBTs) using nano-layer b-Ga_2O_3 as the emitter have great potential because the physical stacking of the exfoliated layers can offer the ideal structure of HBTs without considering the lattice matching.[22] Finally, ultra-thin b-Ga_2O_3 can offer a more robust radiation-hard platform because of the lower chance for damage accumulation. Most high energy particles which commonly cause lethal damage to electronic devices can penetrate through the active area of the nano-scale devices, which is advantageous over the conventional thin-film devices. Monolithic integration of b-Ga_2O_3-based diodes, transistors, gas sensors, solar-blind photodetectors, HBTs, inverters, logic devices, and resistive random access memory (ReRAM) can be demonstrated in b-Ga_2O_3 nanodevices, which will be robust in a harsh environment.[23]

However, it is not widely appreciated that the surface of b-Ga_2O_3 is strongly affected by exposure to gaseous or plasma environments and the influence of changing conductivity and role of surface states in oxidizing or reducing environments are not established. This is despite the fact that gallium oxide diodes are known to be sensitive detectors of hydrogen.[23] Swallow *et al.*[24] reported that as-grown ($\bar{2}01$) single crystals exhibit electron accumulation at the surface, producing downward band bending, ascribed to negatively charged acceptor-type intrinsic surface states. Removal of OH species from the surface shifted the valence band maximum by roughly 0.5 eV and electrons accumulated, causing upward band bending. Other electronic oxides, including ZnO and SnO_2 can also exhibit either surface electron accumulation or depletion and this has been ascribed to the differences in cation/anion size and electronegativity.[25,26]

Photoemission experiments in Ga_2O_3 have typically suggested surface electron accumulation,[27] but the role of cleaning and annealing, processes inherent to actual device processing, indicates a more complex behavior.[24,28] For example, F plasma exposure leads to compensation of near-surface donors by F^- ions and significant changes in Fermi level pinning.[28]

A number of authors have shown that annealing Ga_2O_3 in O_2 *versus* N_2 environments produces a pronounced reduction in near-surface n-type carrier concentration.[3,29] Annealing of undoped Ga_2O_3 in an oxidizing atmosphere at Z1200 1C for extended periods (~20 h) decreases the bulk free electron concentration by about one order of magnitude, while the surface becomes insulating.[3] Moreover, the semiconducting behavior of the surface was recovered by annealing in a H_2-containing reducing atmosphere. The surface conductivity could be reversibly changed by one order of magnitude by only annealing, while the surface of the bulk crystals could be reversibly switched between semiconducting and insulating by annealing in oxidizing and reducing atmospheres.[3,24]

These large swings in near-surface and bulk conductivity will be prohibitive in achieving stable operation of nanobelt devices

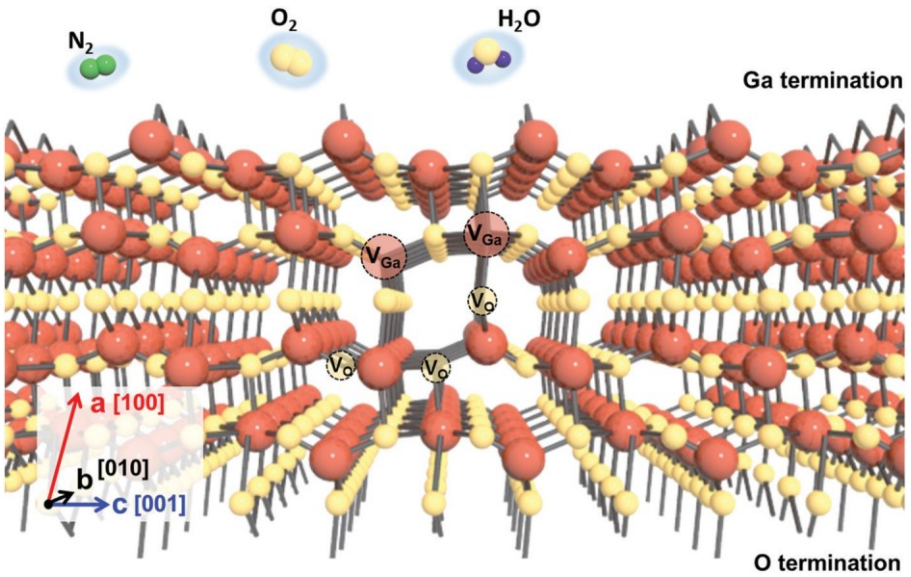

Fig. 2 b-Ga_2O_3 lattice structure showing the presence of O and Ga vacancies and ambient molecules that can affect surface conductivity.

unless the defects responsible are understood and effective passivation schemes are developed. At a minimum, it is already clear that O_2, N_2, H_2 and F_2 exposure can dramatically alter the near-surface conductivity.

Native point defects in b-Ga_2O_3 include Ga vacancies (V_{Ga}) at tetrahedral (Ga1) and octahedral (Ga2) sites, as well as oxygen vacancies at threefold coordinated sites (O1 and O2) and four-fold coordinated sites (O3).[30,31] In most metal oxides, the cation vacancies and oxygen interstitials tend to be acceptors,[6,7] while the oxygen vacancies and cation interstitials are donors. In n-type Ga_2O_3, the gallium vacancy in Ga_2O_3 is a triple acceptor, the oxygen interstitial (Oi) is neutral, and the gallium interstitials (Gai) are in the 3+ charge state.[30,31] The calculated oxygen vacancy (V_O) formation energies of 2.7–3.6 eV suggest that they are deep donors and will be neutral in highly n-type materials and do not directly contribute to the electrical conductivity.[31] Oxygen vacancies occur as neutral (V_O) and double ionized vacancies (V_O^{2-}) with V_O dominating at low oxygen partial pressure.[3] Gallium vacancies (V_{Ga}) form triple acceptors at 3− charge state, between 1.6 and 1.8 eV below the conduction band minimum for V_{Ga1} and V_{Ga2},[30,31] respectively, and are deep acceptors. The V_{Ga} concentration increases with oxygen partial pressure, leading to a conductivity compensation. The influence of environment on the diffusion and complexing of these defects with other defects or impurities in Ga_2O_3 is not currently understood.

Fig. 2 shows a schematic of the b-Ga_2O_3 lattice structure, containing Ga and O vacancies and the typical ambient species present during processes such as annealing during device fabrication.

The configurations of hydrogen in the bulk of b-Ga_2O_3 are now clearer,[32] but the expected donor nature of interstitial hydrogen may be modified in the presence of surface oxygen atoms.[19] All this suggests that variations in the gas atmosphere used during processing by different groups will continue to lead to large variations in reported device performance. Trap spectral measurements show that exfoliated b-Ga_2O_3 inherits the characteristics of the single-crystal b-Ga_2O_3 from which it was separated.[33] Thus the control of defects and impurities in the starting substrate is also key. Optimized passivation layers for b-Ga_2O_3 nanobelts are required to enhance the stability of these devices because the properties are affected by environmental conditions.

In summary, in this Focus Article, we have provided examples of significant changes in the electronic nature of Ga_2O_3 surfaces, and briefly mentioned mechanisms that affect these quantities as well as some techniques to mitigate them. This article should be considered as a short introduction to the vast literature that covers these topics in great depth.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The work at Korea University was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP), with granted financial resource from the Ministry of Trade, Industry and Energy, Korea (No. 20172010104830). The work at UF is partially supported by HDTRA1-17-1-0011 (Jacob Calkins, monitor) and also by NSF DMR 1856662 (Tania Paskova).

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