Puzzling robust 2D metallic conductivity in undoped β-Ga_2O_3 thin films

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ABSTRACT

Here we report the analogous of an extremely stable *topological-like ultra-wide bandgap insulator,* (a solid that is a pure insulator in its bulk but has a metallic conductive surface), presenting a two-dimensional conductive channel at its surface that challenges our current thinking about semiconductor conductivity engineering. Nominally undoped epitaxial β-Ga_2O_3 thin-films without any detectable defect (after a range of state-of-the-art techniques) showed the unexpectedly low resistivity of (3×10^{-2} Ωcm) which was found to be also resistant to high dose proton irradiation (2MeV, $5x10^{15}cm^{-2}$ dose) and was largely invariant (metallic) over the phenomenal temperature range of 2K up to 850K. The unique resilience and stability of the electrical properties under thermal and highly ionising radiation stressing, combined with the extended transparency range (thanks to the ultra-wide bandgap) and the already known toughness under high electrical field could open up new perspectives for use as expanded spectral range transparent electrodes (e.g. for UV harvesting solar cells or UV LEDs/lasers) as well as robust Ohmic contacts for use in extreme environments/applications and for novel optoelectronic and power device concepts.

1. Introduction

Intriguing metallic surfaces onto otherwise insulating bulk crystals have recently attracted a lot of attention [1,2]. These conductive surfaces also exhibit a number of additional unique properties such as insulator–superconductor–metal transition[3], large magnetoresistance[4], coexisting ferromagnetism and superconductivity [5] and a spin splitting of a few meV [6]. In practice, as the oxide semiconductor bandgap becomes wider, an intrinsic metallic surface is more challenging; it is required more energy to shift the Fermi level from the mid-gap to above the conduction band as the forbidden gap increases.

Beta-gallium oxide (Ga_2O_3) is an ultra-wide band gap (UWBG) semiconductor with a highly distinctive property set compared to other classical correlated oxides such as SrTiO3 [7-8], In2O3 [9-10], CdO[11], or

ZnO[12]. The uniqueness of UWBG Ga_2O_3 lies in the combination of an intrinsically wide large electrical breakdown field [13,14], ability to be efficiently donor doped [15-16], possibility to obtain low resistivity also in amorphous and nano-crystalline states [17-20], a high temperature *p*-type conductivity withought doping[21] and 6-inch crystal low cost fabrication possibility [22] .These features have been key in promoting Ga_2O_3 to the forefront in the quest for the next generation of UVC photodetectors, solar transparent conducting electrodes and high power/speed energy converters/switches.

Recently the authors reported unprecedentedly high conductivity, mobility and carrier concentration in nominally undoped thin films of grown on r-sapphire substrates by pulsed laser deposition (PLD). [23]

This work, presents evidence that the degenerate electrical conduction, in what was expected to be an insulating layer, may be due to two-dimensional like metallic conduction in β-Ga_2O_3. Moreover, the electrical conduction has now proven stable for over two years and shows a remarkable resistance to both thermal and radiation stressing.

The ability to obtain ultra wide band gap undoped Gallium oxide highly transparent and the same time highly conducting makes this material as a very fascinating transparent conducting oxide (TCO), of key enabling materials in increasingly high demand in a variety of new technologies, ranging from thin film coatings, sensors, solar cells, transparent electronics and optoelectronics in telecommunications [24] Additionaly, Analogous of an extremely stable *topological-like ultra-wide bandgap insulator*, presenting a two-dimensional conductive channel at its surface challenges our current thinking about semiconductor conductivity engineering.

2. Intrinsic Ga_2O_3

Nominally undoped β-Ga_2O_3 layers were grown on 2-inch *r*-plane sapphire substrates by PLD as described in Experimental section. The layers (~300 nm thick) were found to be epitaxial with a (201) preferential orientation. The wafers were found to be solar transparent in that they exhibited a large transmittance (> 85%) in the UVA, UVB and visible parts of the optical spectrum. The optical absorption edge gave an estimation of bandgap at about 240 nm (~5.2 eV). The surface and bulk chemical composition of the layers was systematically investigated by several high-resolution techniques (see methods and supplemental materials) including: X-ray photoemission spectroscopy (XPS), energy dispersive X-ray fluorescence spectroscopy (EDS), secondary ion mass spectroscopy (SIMS), and Rutherford backscattering spectrometry (RBS). The depth-resolved CL spectra of the Ga_2O_3 film with identical excitation power, shown in Figure 5(Experimental Section), reveal a symmetrical peak at 3.3 eV. The UV emission band of the film is similar

to those observed for excitons immobilised by a local lattice deformation in a single Ga_2O_3 single crystal .[25] The peak shape and energy position remain unchanged with increasing sampling depth by consequently accelerating voltage, indicating on homogeneity in sample volume. In all cases, no significant density of impurities was detected. Room temperature electron paramagnetic resonance (EPR) [26] was also performed and did not detect any shallow donor related signal. Fig. 1 summarizes the main findings.

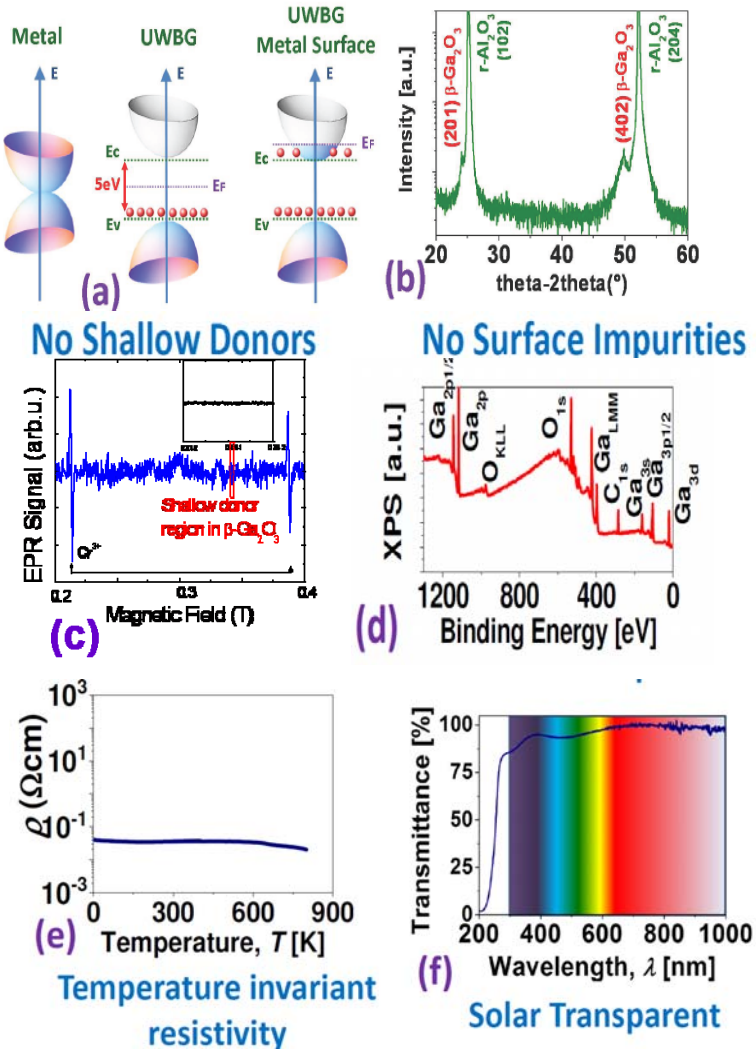

Fig.1 (a). Sketch showing the band structure of the Ga_2O_3 conductive surface. (b) The Ga_2O_3 layers are epitaxial with (201) preferential orientation (XRD). There are no detectable (c) shallow donors (EPR) or (d) surface impurities (XPS). (e) The Ga_2O_3 temperature invariant metallic conductivity. (f) The Ga_2O_3 layers are solar transparent (80% transmittance in whole UVB, UVA and visible ranges).

3. Transport Properties – Low Temperature

The electrical transport properties of the films were studied in a Van der Pauw and "4 aligned point contacts" method configurations. The room temperature resistivity (ρ(300K)) was found to be exceptionally low for an intrinsic UWBG material (ρ(300K) =3×10^{-2} Ω.cm which is, to the best of our knowledge, the lowest reported value for undoped Ga2O3 thin films and about equivalent to that for heavily *n*-type doped Ga_2O_3 (Si or Sn doping in the range of 10^{19}-10^{20} cm^{-3})[23,25-31]. Fig. 2a. Hall effect measurements at room under 1 Tesla revealed an electron carrier concentration as high as $n = 8.0\times10^{18}$ cm^{-3} for a film thickness of 200 nm, and a mobility of μ = 19 cm2/Vs. This value of 8×10^{18} cm^{-3}, corresponds to the hypothesis of a thickness homogeneity of the electron carrier concentration. Such a relatively large free charge carrier concentration indicates that the Ga_2O_3 undergoes a Mott metal-insulating (M-I) transition. In Ga_2O_3, a Mott M-I transition would occur at a dopant critical concentration of $N_{Mot}t = 4\times10^{18}$ cm^{-3}, where $N_{Mott}^{1/3} \times a_B \approx 0.27$ and a_B is the impurity Bohr radius (a_B (Ga_2O_3)= 1.8 nm). [32] We integrate over the film thickness, this corresponds to a surface carrier concentration of 1.6×10^{14} cm^{-2}.

Fig. 2 (b) shows a representative resistance versus temperature curve measured with a colinear four point probe configuration. The resistance was found to be relatively temperature independent (over the full range from 2 K to 400 K) and there was no evidence of carrier freeze-out at lower *T*. Both characteristics are typical signatures of metallic conduction. The slight increase of resistivity observed above 200K is most probably attributable to a decrease in the drift mobility of free carriers. The "hockey stick" shape with a minimum at around T_{min} ~ 190 K is then formed by a slight increase in resistivity at low temperatures, which is most probably due to a weak localization (WL) phenomenon which is related to low dimensional effects [33]. Due to the quantum interference, the electron wave functions diffuse and the backscattering is enhanced which, in turn, increases the resistivity as a function of ln(*T*). As shown in Fig. 2(c), the conductivity at low temperatures increases precisely as ln(*T*) [34]. At higher temperatures, the wave coherence is progressively

lost and the WL effect gives place to metallic behaviour. Similar resistivity vs T dependence has been already reported for confined conductive channels in two-dimensional carbides and oxides such as TiC [35], ZnO [36], LaNiO3, [37] and SrVO3 [38].

The WL effect is sensitive to an applied perpendicular magnetic field (B), which shifts T_{min} towards lower temperatures[39], as shown in Fig 2b. The presence of a strong magnetic field perpendicular to the plane of the conduction channel also leads to a quenching of charge localization contribution and thus produces a negative magnetoresistance. [40] The magnetoresistance (MR) is defined as MR=[$R(B)$-$R(B$=0)]/$R(B$=0), where $R(B)$ is the resistance measured for B perpendicular to the applied current. The MR was found to be always negative at temperatures < 150 K, and the maximum MR value was found to be 2.5 % at B = 9 T (Fig. 2(d).). The field dependence up to a saturation of the negative MR at 2 K, is comparable with that observed for a 2D-like conduction in highly doped semiconductors layers .[40,41] Because of the relatively small value of mobility at low temperature, quantum oscillations would not be observable even at our highest available magnetic field (9T).

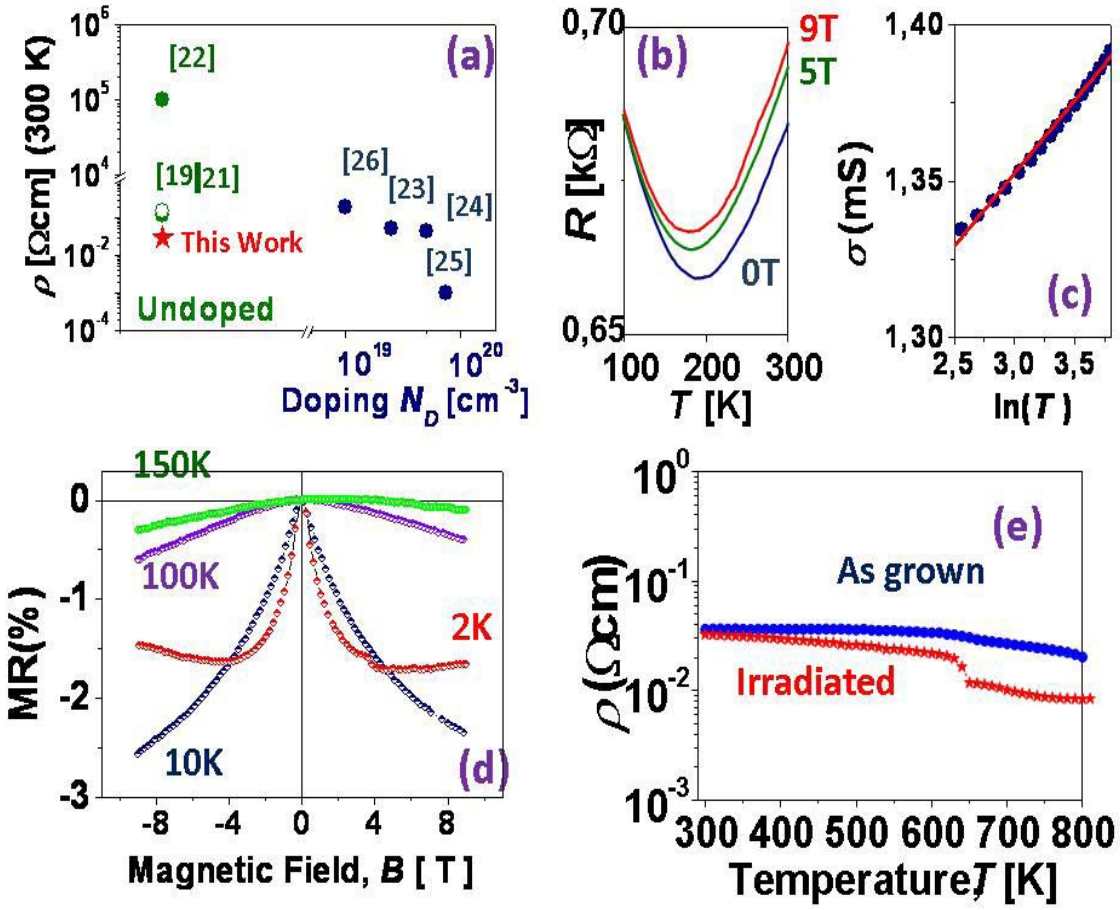

Figure 2. (a) Room temperature resistivity for our undoped Ga_2O_3/r-sapphire sample compared with other undoped and heavily Sn- or Si-doped Ga_2O_3 results from literature[19,22-26]. (b) Zoom Electrical resistance versus temperature at 0T, 5T and 9T applied magnetic fields (c) Sheet conductance σ versus ln(*T*) for up-rise part below the M-I transition temperature (T_{min}) range. The solid line is the linear fit at *zero* magnetic field. (d) Magnetoresistance in perpendicular magnetic field at 2K, 10K, 100K and 150K. Measurement geometry: collinear 4 point probes. e) Electrical resistivity versus temperature (300K-800K) for as grown and proton irradiated (2MeV, $5x10^{15}cm^{-2}$ dose) sample. Measurement configuration was Van der Pauw.

4. High Temperature Electrical Transport Properties

The metallic Ga_2O_3 conduction has been found to be stable and resistant to different stress conditions. Stored on the shelf during two years, it showed no degradation (or drift) after 10 subsequent $R(T)$ characterization cycles. The conductive channel reversibly survived temperatures up to as high as 850 K (limit of the experimental set-up), showing only a small deviation of the resistivity at elevated temperature (ρ(850K) $=1.7\times10^{-2}$ Ωcm). Analogously, the sample was proton irradiated (2MeV, $5x10^{15}cm^{-2}$ dose) (see experimental section) Proton irradiation at these doses and energies would be expected to create oxygen (deep donor) and gallium (deep acceptor) bulk vacancies, thus changing overall conductivity by orders of magnitude [42]. However, as shown in Fig.2(e), the conductivity after irradiation only slightly decreases at high temperatures. As the free carrier concentration is most probably confined in a narrow region close to the surface of the layer, a metallic surface would be more resistant to radiation than bulk conductive samples where random electron-hole pairs would be formed. This high temperature stability is notable when compared with other correlated oxide systems such as confined 2D electrons metallic system (2DES) $LaAlO_3$ and $SrTiO_3$. [43,44] Single-crystal In2O3, ZnO, and TiO2 have been also reported to host a surface 2DES presenting however air-instabilities and practical electrical conduction only at low temperature (i.e., < 100 K). [45]

The resistivity versus temperature quasi invariance stability also ruled out other known non-surface origins of intrinsic Ga_2O_3 conductivity; i.e. the presence of (1) amorphous phases or (2) gallium clusters. Regarding (1) a chemically driven M-I Ga2O3 transition (of seven orders of magnitude) has been previously reported in highly non-stoichiometric, amorphous gallium oxide. [46] As we see from Fig.2 (b), *R(T)* curves showed no significant differences for subsequent heating and cooling cycles. This result excludes the possibility of solid state recrystallization reaction due to amorphous phases being present in the material. Regarding (2), gallium clusters (embedded into the Ga_2O_3 matrix) would also result in resistivity temperature hysteresis due to melting and recrystallization of Ga clusters and a sharp drop of the resistivity at low T (<10

K) (attributed to superconducting state of gallium) [47]. Furthermore, Ga clusters would render the layers non transparent in the visible (coloration due to defects) [48]. Those features were not observed (Fig. 1d,1f) .

3. Electron accumulation in Ga_2O_3

The origin of the *n*–type intrinsic bulk conductivity for binary metal oxides (i.e., ZnO, In_2O_3, SnO_2 etc) is usually explained with a stoichiometric deviation: an anion (i.e. oxygen) deficiency or metallic cation interstitials. Therefore, intrinsic donors for intrinsic *n*-type conductivity in Ga_2O_3 are the oxygen vacancy, V_O, and gallium interstitial, Ga_i. Hybrid functional calculations predict the V_O to be a deep donor with an ionization energy higher than 1eV in Ga_2O_3. [49] Hence, it is unlikely that bulk oxygen vacancies could be the source of the metallic conductivity observed in our experiment. Interstitial Ga atom Ga_i are relatively shallow donors with an ionization energy of 0.1-0.2 eV. However, Ga_i has very high formation energy [50] which also makes it an unlikely candidate. Because of the breaking of translational symmetry at the surface, an electronic state may exist with significantly different properties and characteristic energies than those in the bulk [51]. A particularly investigated case is In_2O_3 surfaces (indirect bandgap of 2.5 eV and a direct bandgap of 3.6 eV). In_2O_3 surface donors, (rather than bulk defects), are reported to be the source of its downwards band-bending and surface 2DEG. [52] In a similar fashion, surface electron accumulation was also observed on the surfaces of other binary wide bandgap oxides such as CdO (Eg~2.18 eV) and ZnO (Eg~3.37 eV) [53]. In the case of Ga_2O_3, a surface band banding phenomena due to surface defects was already pointed out by Lovejoy *et al.* [54] .Well known quantum Hall Effect in 2D semiconductors and oxides usually can be observed only in high-purity Si or GaAs at very low temperatures and strong magnetic fields and at room temperature only in graphene. [55]

When oxygen vacancies (or other surface donors) are present, surface positive charge causes a downward bend bending; the extra electrons accumulate close to positive charges and create an accumulation layer in the near-surface region; the downward bend bending causes a rigid shift of all peaks in the photoemission spectrum downwards. This shift has been reported to be of 0.2–0.3 eV in the case of reduced titania which is formally associated to the transformation of Ti^{4+} to Ti^{3+}. [56] On the contrary, surface acceptors cause upward bend banding, accumulation of holes close to the surface and shift of the core levels towards lower binding energies (BE). XPS allowed the study of such core levels. The BE shifts in the O1s XPS spectra

result from the difference in the valences of the O2- ions. Lower BE indicates higher electron number at O-ions. The room temperature photoemission spectrum for the Ga2*p*, Ga3*p*, O1*s* and C1*s* core levels is shown in Fig. 3 (a). In this analysis, XPS spectra for our Ga_2O_3 layer surface (labelled *n*-type) are compared with; (1) a control sample of commercial (Novel Crystal Technology, Inc.) nominally *n*-type Si-doped β-Ga_2O_3 (*Nd*-*Na*=1.3×1018 cm-3) epitaxy (500 nm) grown on a single crystal β-Ga_2O_3 (labelled Ref) and (2) a *p*-type Ga_2O_3 surface (containing gallium vacancies) from Nanovation. [21] The BE value of the core level for the Ga2p states at 1119.3 eV (as determined by Michling et al. [57] for cleaved β-Ga_2O_3 single crystals) were used to calibrate the BE positions of the XPS spectra. As shown in Fig. 3(b), the Ga_2O_3 BE shift (Δ*BE*=*BE*-*BE*ref) with respect to the Si-doped Ga_2O_3 Ref correlates well with an *n*-type electron surface accumulation and a *p*-type electron depletion. The *n*-type Ga_2O_3 sample exhibits a shift towards higher BE energy values while the *p*-type sample exhibits a shift towards lower BE values for both anions and cations.

Therefore, as the peaks of all the elements shift the BE in the same direction, it is deduced that the BE shift is dominated by raising/lowering of the chemical potential (i.e. the potential shift due to surface oxygen vacancies or metal interstitials). It is worth mentioning that the XPS for the Ga2p core level spectrum show no appreciable shoulder-like feature for either $Ga2p_{1/2}$ or Ga2p. When the Gai atom occupies an interstitial site, it is surrounded by more oxygen atoms. Therefore, cation shoulder-like features could be treated as direct evidence for the presence of interstitials. The evidence of the BE shift coupled with the absence of shoulder-like features for Ga peaks suggest that the origin of the donors in the *n*-type layers are due to oxygen vacancies.

From valence band photoemission spectra, it is possible to determine the electronic surface properties of the thin-films. The three maxima of the O^{2p} valence band correspond to the three different oxygen sites in βi-Ga_2O_3 (O(1), O(2) and O(3)). The valence band width for the reference sample is ~8 eV, which is in agreement with previous reports. [58] The extrapolation of the first slope (at ~5×102 counts/s) gives Fermi levels of 4.9 eV and 4.4 eV, respectively, for the Ga_2O_3 metallic surface (*n*-type) and the Si-doped control (Ref) samples. Therefore, the Fermi level for the metallic surface was experimentally confirmed to be above the conduction band edge (i.e. degenerately doped electron accumulation) if one assumes the usual bandgap value of 4.8 eV given in the literature. [59] Ultraviolet photoelectron spectroscopy (UPS) also corroborates the degenerately doped Fermi level position at ~4.9 eV as shown in Fig. 3(e).

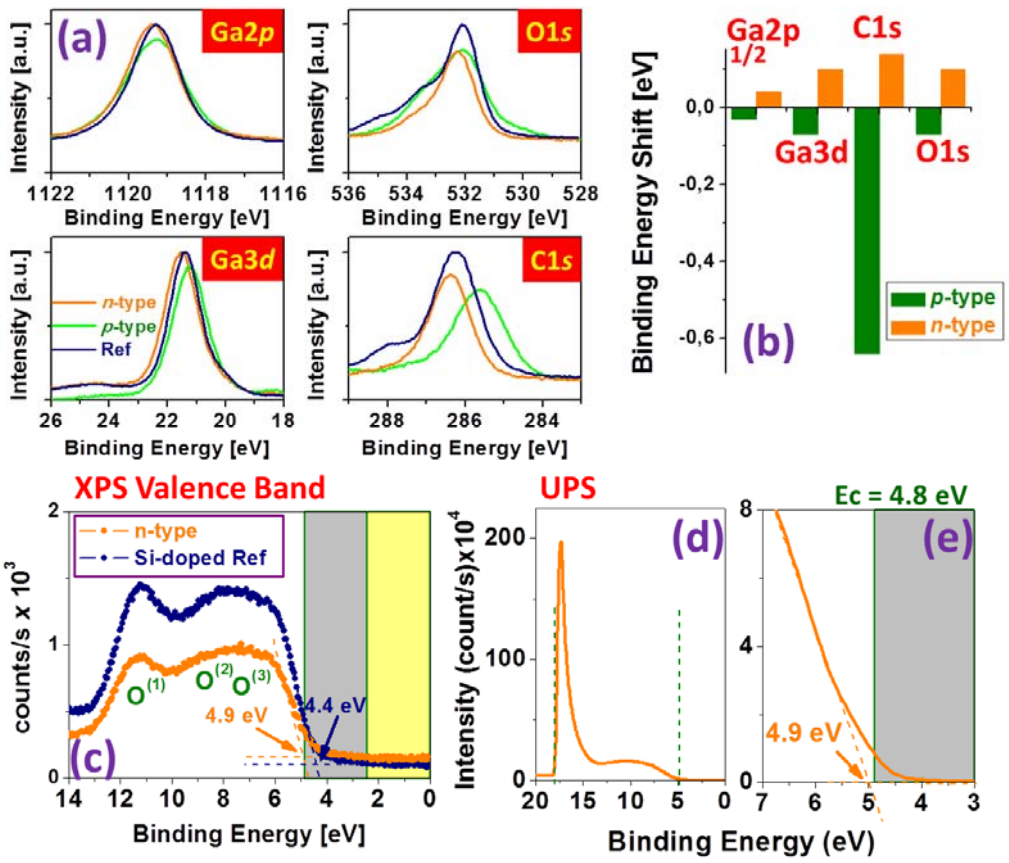

Figure 3. (a) XPS photoemission spectra for the Ga2p, Ga3p, O1s and C1s core levels for n-type studied sample, *p*-type [21] and Si doped reference . (b) *n*-type and *p*-type binding energy shift ($\Delta BE=BE-BE_{ref}$) with respect to the control Si-doped Ga_2O_3. (c) Valence band photoemission spectra for *n*-type and Ref showing that our sample surface is degenerately conductive. (d) UPS spectra of the surface of the undoped conductive surface. e) Zoom at conduction band edge.

Theoretical estimation of carrier accumulation

The 2DEG free electron concentration density profile can be estimated by the Thomas-Fermi approximation for a 2D system (see supplementary information).[60] It is possible to find a relationship between the surface Fermi level (measured from the band edge) and the bulk three-dimensional electron density using:

$$E_F = \left(3\pi^2\right)^{2/3} \frac{\hbar^2}{2m_e*} n^{2/3} \quad (2)$$

where E_F is the average difference between the Fermi energy and the band gap potential $V(z)$, which changes along the z-axis (the z-axis being perpendicular to the sample surface). Therefore,

$$E_F - V(z) = \left(3\pi^2\right)^{2/3} \frac{\hbar^2}{2m_e*} n(z)^{2/3} \quad (3)$$

Setting the energy to zero at E_F, Poisson's equation for near surface potential energy is (neglecting fixed charges):

$$\frac{d^2V}{dz^2} = \frac{1}{3\pi^2}\left(\frac{e^2}{\varepsilon_r\varepsilon_0}\right)\left(\frac{2m_e*}{\hbar^2}\right)^{3/2}(-V)^{3/2} \quad (4)$$

for which solutions are,

$$V(z) = -\frac{b}{(z+z_0)^4}, \quad b = \left(\frac{60\pi^2\varepsilon_r\varepsilon_0}{e^2}\right)^2\left(\frac{\hbar^2}{2m_e*}\right)^3 \quad (5)$$

$$n(z) = \frac{a}{(z+z_0)^6}, \quad a = \left(\frac{2m_e*b}{\hbar^2}\right)^{3/2} \quad (6)$$

$$n(z) = \frac{a}{(z+z_0)^6}, \quad a = \left(\frac{2m_e*b}{\hbar^2}\right)^{3/2} \quad (6)$$

In Eq. (5-6) z_0 is defined by the boundary condition value of $V(0)$. Band bending at the surface BB was used for determining it. For BB :

$$BB = E_{v-F}^{S} - E_{v-F}^{B} = E_{v-F}^{S} - \left(E_g - E_{c-F}^{B}\right) \quad (7)$$

Where E_{v-F}^{S} and E_{v-F}^{B} are the top of valence band to Fermi energy distance at the surface and in the bulk respectively. The latter can be expressed as the sum of bulk band gap, E_g, and the distance between the Fermi energy and the bottom of conduction band in the bulk material. In Ref. 55 temperature narrowing of the bandgap in Ga_2O_3 is studied and a 4.65 eV room temperature bandgap is reported; our electron concentration corresponds to E_{c-F}^{B} =0.05 eV.

As the zero of energy is at E_{c-F}^{B}

$$V(0) = -(BB + E_{c-F}^{B}) = -(E_{v-F}^{S} - E_g) \quad (8)$$

In our case

$$V(0) = -0.25eV, \; BB = 0.2eV.$$

Taking into account the experimental XPS and UPS Fermi level of 4.9 eV, an estimation of the characteristic depth profile for the bandgap potential ($V(z)$) and 2DEG density ($n(z)$) may be determined as shown in Fig. 4 (a,b). The calculated concentration of surface electrons $n(0) = 10^{21}$ cm^{-3}, with an average concentration n_{av} ~ 10^{19}cm^{-3} matches well with the free electron concentration estimated in the Hall effect. The calculated electron concentration drops to ~10^{19} cm^{-3} at a depth of z = 5 nm, which represents roughly two Ga_2O_3 unit cells (Fig. 4(c)). Under this approximation, the sheet charge concentration of the 2DEG is $ns \sim 2\times10^{14}$cm^{-2}. Such a high value of sheet charge density induces a large diffusion of carriers and, consequently, a low value of mobility. This is the reason why no quantum oscillations are seen as a function of temperature and magnetic field in the available ranges. This may be further investigated. Nevertheless, the robust metallic

conduction, appears to be connected with surface band bending, as already observed in other oxide semiconductor surfaces.

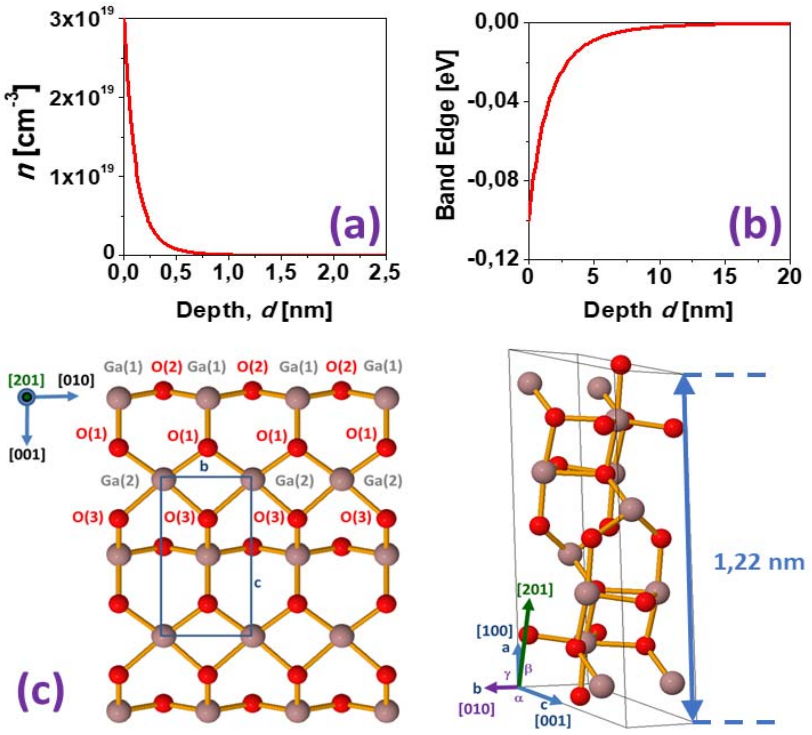

Figure 4. (a), (b) Simulated two-dimensional channel profile using the Thomas-Fermi approximation. (c) Sketch of the (201) plane and the Ga_2O_3 unit cell.

CONCLUSIONS

In this work, temperature dependent electrical transport measurements revealed that than nominally undoped β-Ga_2O_3 thin films exhibited degenerate metallic conduction with a room temperature Hall *n* of 8×10^{18} cm^{-3} and Hall μ of 19 cm^2/Vs. A number of high resolution techniques did not reveal any bulk or shallow donor signatures that could explain the conductivity in terms of conventional impurity or defect doping. The conductivity *vs* temperature was found to be unprecedentedly stable over the range from a few K to 850 K (limit of the measurement set-up), both, in air and nitrogen ambient and insensitive to high dose of proton irradiation (2MeV, $5x10^{15}cm^{-2}$ dose). These suggested that the electrical conduction was mainly confined to the layer close to the surface. Photoelectron spectroscopy and *hockey stick-like* behavior in low temperature magnetoresistance studies were also coherent with a 2D like conduction. The origin of a such exceptionally robust conduction merits to be investigated more deeply, since this exceptional result challenges our current understanding and methods to achieve, solar transparent conducting electrodes, Ohmic contacts and potential transistor conductive channels in a wide bandgap insulator which is now considered to be a key enabler of a sustainable and greener future.

Experimental section

Fabrication Details

Ga_2O_3 Epilayer. Nominally undoped β-Ga_2O_3 layers were grown on 2-inch diameter *r*-plane sapphire substrates from a commercial sintered 4N Ga_2O_3 target using a Coherent LPX KrF (λ = 248nm) laser by pulsed laser deposition (PLD). Uniform 2-inch diameter wafer coverage was obtained using optical rastering of the incident laser beam. Substrate temperature during growth was measured with a thermocouple to be ~550°C and the ambient during growth was 10^{-4} torr of molecular oxygen. Ga_2O_3 layers were epitaxial, showing (201) preferential orientation [23]. The relative low temperature (i.e. T=500-550°C) is enough for Ga_2O_3 complete crystallization as reported previously by several groups [61-64]. However the crystallization temperature may vary from one set-up to another as other authors has reported that larger temperatures are required to avoid amorphous phase. [65-66]

Characterization Methods

X-ray diffraction (XRD). The crystallographic structure of the films was analysed with a Siemens D-5000 diffractometer using Cu-K_α radiation (λ = 1.54 Å).

Interferometry. The thickness of the gallium oxide layers was around 300 nm, estimated using optical reflection interferometry with an Ocean Optics Nanocalc system. The layer thickness was further corroborated with cross-sectional ***scanning electronic microscopy*** **(SEM)** FEI Quanta 650F Environmental SEM equipped with ***energy dispersive X-ray spectroscopy*** **(EDX)** for point analysis and chemical maps.

Electron Spin Resonance (ESR) measurements have been performed with a Bruker X-band spectrometer under standard conditions: 100 kHz field modulation and low (μW) microwave power to avoid nuclear polarization effects. Only 2 transitions corresponding to a Cr contamination of the Al_2O_3 substrate were observed.

Secondary-ion mass spectrometry (SIMS) was carried out with the aid of using a Cameca IMS 4f tool equipment.

X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were performed with a Phoibos 150 analyzer (SPECS GmbH, Berlin, Germany)) in ultra-high vacuum conditions (base pressure 3×10^{-10} mbar). XPS measurements were performed with a monochromatic Al K_α X-ray source (1486.74 eV). UPS measurements were realized with a monochromatic HeI UV source (21.2 eV). Optical transmission spectra were measured in 200-2000 nm spectral range with a Perklin Elmer 9 spectrophotometer.

Transport measurements. Electrical contacts were made by soldering indium. As verified by I-V measurements, all contacts showed Ohmic I/V characteristics. DC-resistivity and magnetoresistance were studied using a commercial "DC-resistivity" configuration in a 9T-PPMS (Quantum Design Inc.) environment, while for high temperature (T>300K) measurements a home-designed high impedance measurement set-up was used. Magnetoresistance measurements were made with a magnetic field, $B=\mu_0 H$, applied perpendicular to the film plane. Hall effect measurements were performed in the Van der Pauw configuration for perpendicular magnetic fields of up to 1.6 T.

Proton Irradiation. Proton irradiation was performed with a Van de Graaff 2.5MV accelerator. A proton energy of 2MV was chosen in order to generate a homogeneous defect profile over the entire film and put the end of range in the sapphire substrate. The total fluence was $1x10^{16}$ cm^{-2}. The current was 1 microA/cm^2 , a value for which the film is expected to stay close to room temperature.

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