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## High performance graphene/AlGa<sub>N</sub>/Ga<sub>N</sub> Schottky junctions for hot electron transistors

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### Abstract

The electronic properties of the graphene (Gr) Schottky junction with an Al<sub>0.22</sub>Ga<sub>0.78</sub>N/GaN heterostructure on silicon have been investigated, both experimentally and using ab-initio DFT calculations. A peculiar high n-type doping ( $1.1 \times 10^{13} \text{ cm}^{-2}$ ), observed for Gr in contact with AlGa<sub>N</sub>, was explained by the combined effect of Fermi level pinning by AlGa<sub>N</sub> surface states and charge transfer. Spatially uniform current injection across the Gr/AlGa<sub>N</sub>/Ga<sub>N</sub> heterojunction was revealed by nanoscale resolution conductive atomic force microscopy (CAFM) analyses. Furthermore, a Gr/AlGa<sub>N</sub>/Ga<sub>N</sub> Schottky diode with excellent rectifying behavior has been demonstrated and used as the key building block for a hot electron transistor (HET) with a 10 nm Al<sub>2</sub>O<sub>3</sub> base-collector barrier. Thanks to the highly efficient hot electron injection from the AlGa<sub>N</sub>/Ga<sub>N</sub> emitter, this transistor exhibits high on-state current density ( $J_{C,ON} \approx 1 \text{ A/cm}^2$ ), high-on state over off-state current density ratio ( $J_{C,ON}/J_{C,OFF} \approx 10^6$ ) and a common-base current gain  $\alpha \approx 0.15$ , solely limited by the high Al<sub>2</sub>O<sub>3</sub> base collector barrier. The excellent performances of the Gr/AlGa<sub>N</sub>/Ga<sub>N</sub> Schottky junction represent an important step towards the development of a HET technology compatible with the state-of-the-art Ga<sub>N</sub> high electron mobility transistors.

**Keywords:** Graphene, Ga<sub>N</sub>, hot electron transistor, conductive atomic force microscopy, heterostructures

## 1. Introduction

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3 One of the main challenges in modern electronics is the development of transistors able to operate at  
4 frequencies in the terahertz (THz) range, i.e., the electromagnetic spectrum range separating  
5 millimeter wave electronics from photonics, which is strategic for application areas like  
6 communications, medical diagnostics and security. Currently, high electron mobility transistors  
7 (HEMTs), based on the field-effect modulation of the lateral current transport in III-V semiconductor  
8 heterostructures, are the main devices for such applications, with operating frequencies exceeding 1  
9 THz for ultra-scaled channel geometry [1,2,3,4,5]. However, further improvements of HEMT's  
10 performances (especially their available output power) will be limited by the technological and  
11 physical issues related to lateral scaling of the channel. In this context, two dimensional (2D)  
12 semiconductors are currently explored as replacement of traditional semiconductors for ultra-scaled  
13 lateral field effect transistors with superior electrostatic gate control [6,7,8].

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15 As an alternative to lateral field effect transistor, vertical devices can represent a solution for high  
16 frequency applications. In this context, the hot electron transistor (HET), based on the transversal  
17 ballistic transport of hot electrons through an ultra-thin base layer, has been proposed from a long  
18 time as potential candidate to operate in the THz frequency range [9,10,11,12]. It is a unipolar  
19 majority carriers vertical device, consisting of three terminals (emitter, base and collector) separated  
20 by an emitter-base and base-collector barriers. Hot electrons (i.e., electrons with energy larger than  
21 the Fermi energy of carriers in the base) are injected from the emitter to the base terminal under  
22 forward base-to-emitter polarization. For a base thickness lower than the electron mean free path,  
23 most of these hot carriers transit through the base without energy loss, and can reach the collector  
24 terminal after overcoming the base-collector filtering barrier modulated by the collector bias.

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26 In spite of its interesting working principle, the practical implementation of this device concept has  
27 been hindered for long time by the difficulty of fabricating a high quality ultra-thin base layer using  
28 conventional growth processes, which typically suffer of increased interface roughness and degraded  
29 transport properties for very thin (<5 nm) conducting films. Recently, the appearance of two-  
30 dimensional (2D) materials provided new solutions for the implementation of high-performance  
31 HETs [13,14]. In particular, graphene (Gr) has been proposed as an ideal base material, as it combines  
32 monoatomic thickness, enabling ballistic electron transit in the transversal direction, with excellent  
33 in-plane transport properties (high mobility, from  $\sim 10^3$  up to  $\sim 10^5$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ , and very low resistivity),  
34 [15,16,17]. Theoretical studies have predicted excellent high-frequency performances, with a cut-off  
35 frequency ( $f_T$ ) up to several terahertz, for Gr base HETs (GBHET) [18,19,20,21,22,23].

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37 Besides the ultra-thin base, an emitter-base barrier allowing efficient hot electrons injection (either  
38 by thermionic emission over the barrier or by tunneling through the barrier) is a key element for the  
39 implementation of the HET device. In the first prototypes of GBHETs, the emitter-base barrier was  
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3 represented by a nanometer-thin SiO<sub>2</sub> tunneling barrier thermally grown on a n<sup>+</sup>-doped Si substrate  
4 (working as the electrons emitter), while the base collector-barrier was obtained with a high-k  
5 insulator (Al<sub>2</sub>O<sub>3</sub> or HfO<sub>2</sub>) deposited on Gr [24,25]. However, these demonstrators suffered of a very  
6 poor injected current density ( $\sim 10^{-4}$ - $10^{-3}$  A/cm<sup>2</sup>) and a high threshold voltage ( $V_{th} \approx 5$  V), mainly due  
7 to the large electron affinity difference between Si and SiO<sub>2</sub>. Significant improvements in the current  
8 injection efficiency have been obtained by a careful choice of the emitter and emitter-base barrier  
9 materials and the improvement of the interfaces quality. As an example, replacing SiO<sub>2</sub> with a higher  
10 electron affinity insulator (such as HfO<sub>2</sub>) grown on Si resulted in a reduced threshold voltage and a  
11 higher injected current, whereas further improvement in the injection efficiency was obtained by  
12 tunnel barrier engineering, e.g., using a TmSiO/TiO<sub>2</sub> bilayer [26].

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21 The early GBHETs demonstrators were developed on a Si substrate, with the aim of integrating  
22 these new devices with conventional CMOS technology. More recently, the possibility of  
23 implementing GBHETs with high on-state current by the integration of Gr with group III- Nitride  
24 semiconductors has been considered [27,28,29]. In particular, thin films of AlN or Al<sub>x</sub>Ga<sub>1-x</sub>N,  
25 epitaxially grown on GaN by MOCVD or MBE, resulted excellent emitter-base barriers, due to their  
26 superior structural quality as compared to oxide layers. Further advantages of these material systems  
27 are the presence of high density ( $10^{13}$  cm<sup>-2</sup>) two dimensional electron gas (2DEG) at the Al<sub>x</sub>Ga<sub>1-x</sub>  
28 N/GaN interface, working as the hot electrons emitter, as well as the possibility of tailoring the  
29 conduction band discontinuity between Al<sub>x</sub>Ga<sub>1-x</sub>N and GaN by the Al content. Very efficient current  
30 injection by Fowler-Nordheim (FN) tunneling mechanism has been recently demonstrated in the case  
31 of Gr junctions with thin barriers of AlN (3 nm) [29] or Al-rich Al<sub>0.65</sub>Ga<sub>0.35</sub>N (4.7 nm) [30] grown on  
32 n<sup>+</sup> doped GaN. High quality bulk GaN substrates with dislocations density  $< 10^5$  cm<sup>-2</sup> have been used  
33 as substrates to grow these very thin barrier layers with a sufficient quality to avoid leakage current  
34 through defects. Actually, the high cost of these substrates will probably limit the widespread  
35 development of the AlN/GaN emitter in the near future.

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46 On the other hand, Al<sub>x</sub>Ga<sub>1-x</sub>N/GaN heterostructures with a thicker ( $\sim 20$  - $25$  nm) AlGa<sub>1-x</sub>N barrier  
47 layer with lower Al content ( $x=0.2$  -  $0.3$ ), typically grown on sapphire, Silicon Carbide (SiC), or  
48 Silicon (Si) are widely employed in the GaN HEMTs technology for radio-frequency (RF)  
49 applications. The development of Gr-base HETs on these heterostructures can be highly interesting,  
50 as it can open the way to the integration of two different high frequency transistor technologies on  
51 the same platform.

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56 To date, only few literature studies [31,32,33] reported on such systems, showing how the vertical  
57 current transport at Gr/Al<sub>x</sub>Ga<sub>1-x</sub>N/GaN interface depends on the composition (i.e., the Al content)

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[33], the microstructure (dislocation density) [31] of the AlGa<sub>N</sub> barrier layer, as well as on Fermi level pinning effects at Gr/AlGa<sub>N</sub> interface [27].

In this work, the electronic properties of the Gr junction with an optimized quality Al<sub>x</sub>Ga<sub>1-x</sub>N/GaN heterostructure (with  $x=0.22$ ,  $t_{\text{AlGa}_N}=21$  nm) on Si(111) have been investigated in details, both experimentally and using ab-initio calculations. A peculiar high n-type doping ( $1.1 \times 10^{13} \text{ cm}^{-2}$ ) was measured for Gr in contact with the AlGa<sub>N</sub>, which was explained at atomistic level by the combined effect of Fermi level pinning by AlGa<sub>N</sub> surface states and charge transfer. Nanoscale resolution conductive atomic force microscopy (CAFM) analyses revealed a highly uniform current injection across the Gr/AlGa<sub>N</sub>/GaN heterojunction. A Gr/AlGa<sub>N</sub>/GaN Schottky diode with excellent rectifying behavior has been demonstrated, where the current injection under forward polarization is ruled by thermionic emission above the AlGa<sub>N</sub> barrier. This diode was used as the key building block for a HET with a 10 nm Al<sub>2</sub>O<sub>3</sub> base-collector barrier. Thanks to the highly efficient hot electron injection from the AlGa<sub>N</sub>/GaN emitter, this transistor exhibits high on-state current density of  $J_{C,ON} \approx 1 \text{ A/cm}^2$  and six decades modulation of  $J_C$  by the base-emitter bias. The common base current gain reached a value of  $\alpha \approx 0.15$ , only limited by the high Al<sub>2</sub>O<sub>3</sub> base collector barrier.

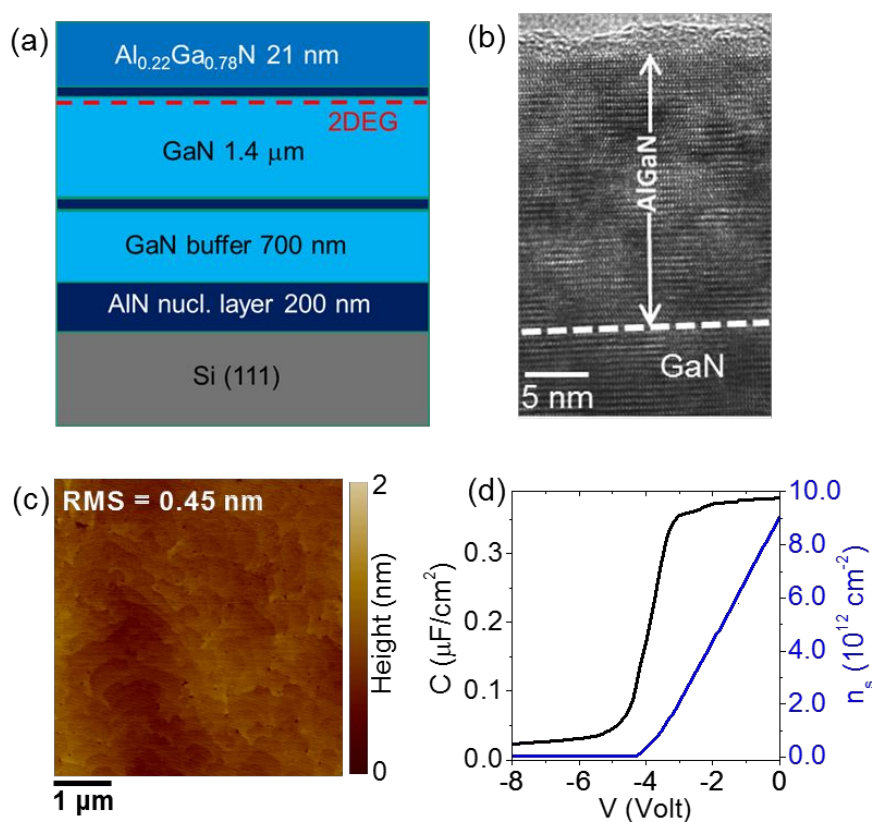
The excellent performances of Gr Schottky junction with the AlGa<sub>N</sub>/GaN heterostructure on Si represent an important step towards the development of a hot electron transistors technology compatible with the state-of-the-art GaN HEMTs production.

## 2 Results and Discussion

### 2.1 Structural and electrical properties the heterojunctions

High quality Al<sub>x</sub>Ga<sub>1-x</sub>N/GaN heterostructures grown by metal organic chemical vapor deposition (MOCVD) on Si(111) wafers were the starting material for the fabrication of the Gr/AlGa<sub>N</sub>/GaN Schottky junctions object of this investigation. Fig.1(a) reports a schematic cross section of the Nitride structure on the Si(111) substrate, including a sequence of different layers (1.4 μm GaN / 20 nm AlN / 700 nm GaN / 200 nm AlN) properly designed to minimize the threading dislocations density reaching the topmost AlGa<sub>N</sub>/GaN heterostructure. A preliminary assessment of the epilayers crystalline quality was obtained by X-ray diffraction patterns, which confirmed the Al mole fraction in the Al<sub>x</sub>Ga<sub>1-x</sub>N barrier ( $x=0.22$ ) and the thickness  $d_{\text{AlGa}_N}=21$  nm. Fig.1(b) shows a high-resolution cross-sectional transmission electron microscopy of the topmost region of the heterostructure, confirming the atomically sharp and high crystalline quality of the AlGa<sub>N</sub>/GaN interface. Fig.1(c) shows a tapping mode atomic force microscopy (AFM) image of the AlGa<sub>N</sub> surface on  $5 \mu\text{m} \times 5 \mu\text{m}$  scan area, which reveals a smooth morphology with a root mean square (RMS) roughness of 0.45 nm. Small pits present on the sample surface can be associated to threading dislocations with a surface

density lower than  $2 \times 10^9/\text{cm}^2$ , in agreement with the full width at half maximum of X-ray diffraction peaks at 620 arcsec for GaN (002) and 1090 arcsec for GaN (302) reflections. Finally, a preliminary electrical characterization of the as-grown AlGaIn/GaN heterostructure was carried out by capacitance-voltage (C-V) measurements with a mercury (Hg) probe. Fig.1(d), left vertical axis, shows a C-V curve acquired at a frequency of 20 kHz by negative biasing the Hg Schottky contact (from 0 to -8V) to deplete the 2DEG at the AlGaIn/GaN interface. The height of the capacitance plateau starting from  $V=0\text{V}$  is related to the AlGaIn thickness  $d_{\text{AlGaIn}}$  according to the relation  $C(0)=\epsilon_0\epsilon_{\text{AlGaIn}}/d_{\text{AlGaIn}}$  (being  $\epsilon_0$  the absolute permittivity and  $\epsilon_{\text{AlGaIn}}=9.39$  the relative permittivity of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  with  $x=0.22$  [34]). The 2DEG pinch-off voltage is  $\approx -4.5\text{V}$ . The blue line (right vertical axis in Fig.1(d)), obtained by integration of the C-V curve, represents the 2DEG charge density  $n_s$  modulated by the applied bias. In particular, a carrier density of about  $9 \times 10^{12}/\text{cm}^2$  at zero bias was estimated. The 2DEG sheet resistance  $R_{\text{sh}}=436 \pm 5 \Omega/\text{sq}$  was obtained by electrical measurements of transmission line model (TLM) test patterns fabricated on the heterostructure. By combining this  $R_{\text{sh}}$  value with the  $n_s$  value from C-V analyses, a carrier mobility  $\mu=(q n_s R_{\text{sh}})^{-1} \approx 1600 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  was estimated for the 2DEG at AlGaIn/GaN interface.

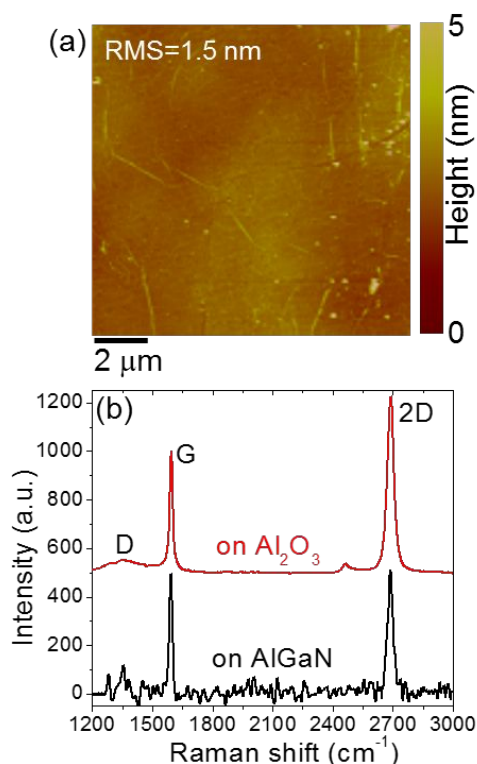


**Fig.1** (a) Schematic cross section of the multilayer structure grown on the Si(111) substrate. (b) High-resolution cross-sectional TEM of the topmost AlGaIn/GaN heterostructure in the multilayer. (c) AFM image of the as-grown AlGaIn surface ( $5 \mu\text{m} \times 5 \mu\text{m}$  scan area). (d) Hg probe C-V measurement

(black line, left vertical axis) of the AlGa<sub>N</sub> acquired at a frequency of 20 kHz by negative biasing the Hg Schottky contact from 0 to -8V. The blue line (right vertical axis) is the 2DEG charge density  $n_s$  modulated by the bias.

Monolayer (1L) graphene (Gr) grown by chemical vapor deposition (CVD) on copper foils was transferred onto the AlGa<sub>N</sub> barrier layer (see the “Materials and Methods” section). A typical AFM image of Gr onto AlGa<sub>N</sub> is reported in Fig. 2(a), showing a uniform coverage of the AlGa<sub>N</sub> surface by the Gr membrane without pinholes and cracks. The higher RMS roughness with respect to bare AlGa<sub>N</sub> (Fig. 1(c)) is mainly related to the presence of wrinkles, i.e., nanometer height corrugations of the Gr membrane. Some of these features are present in Gr starting from the CVD growth [35], whereas part of them are introduced during transfer procedure. The impact of wrinkles on the vertical current injection in the Gr/AlGa<sub>N</sub>/Ga<sub>N</sub> heterostructure will be discussed later on in this paper.

Fig. 2(b) shows two representative Raman spectra of 1L Gr transferred onto the AlGa<sub>N</sub> surface and on a standard insulating substrate (Al<sub>2</sub>O<sub>3</sub> on Si), used as a reference. The two spectra, normalized to the G peak intensity, exhibit a very weak defects-related D peak, indicating a high structural quality of Gr. While Gr onto Al<sub>2</sub>O<sub>3</sub> shows a 2D over G peak intensity ratio  $I_{2D}/I_G \approx 1.3$ , consistent with the typically reported values for 1L Gr with low unintentional p-type doping [36], a significantly lower ratio,  $I_{2D}/I_G \approx 1$ , was found for 1L Gr residing onto AlGa<sub>N</sub>. Such a difference can be ascribed to a higher doping of Gr in contact with this Nitride semiconductor substrate. The type of doping and the carrier density will be further elucidated in the following by electrical measurements on device test structures.





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**Fig. 2** (a) Typical AFM image of monolayer (1L) Gr on the AlGaIn surface, showing a uniform coverage without pinholes and cracks. (b) Representative Raman spectra of 1L Gr onto AlGaIn and on an Al<sub>2</sub>O<sub>3</sub> insulating substrate, used as a reference.

Fig.3(a) and (b) schematically illustrate two top-gated Gr field effect transistors (GFETs) with the Gr channel residing onto the AlGaIn/GaN heterostructure and on the Al<sub>2</sub>O<sub>3</sub>/Si substrate (used as a reference). In both cases, a thin (10 nm) Al<sub>2</sub>O<sub>3</sub> top gate dielectric was deposited on Gr by atomic layer deposition (ALD) [37]. The transfer characteristics ( $I_D$ - $V_G$ ) measured on the two transistors with an applied  $V_{DS}=0.1$  V are reported in Fig.3(c) and (d). A slight positive shift of the neutrality point ( $V_{NP}=0.7$  V) is observed for the Gr FET onto Al<sub>2</sub>O<sub>3</sub>, indicating a small p-type doping of Gr, typically due to resist contaminations or ambient humidity. On the contrary, for the Gr FET onto AlGaIn, a large negative shift of the neutrality point ( $V_{NP}=-2$  V) is found. This indicates a high n-type doping of Gr, which over-compensates the contaminations related unintentional p-type doping. An electron density  $n_{gr}=1.1 \times 10^{13}$  cm<sup>-2</sup> was estimated for Gr onto AlGaIn according to the relation

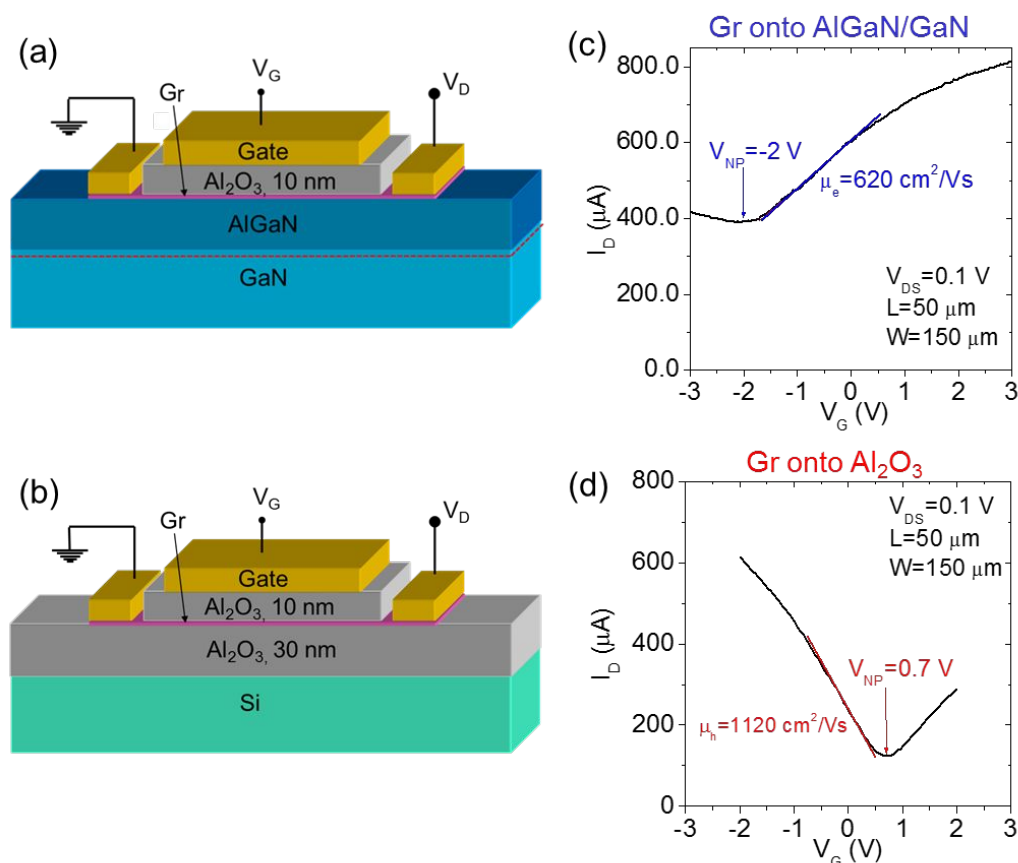
$$n_{gr}=C_{ox}(W_M-W_{gr}-V_{NP})/q, \quad (\text{Eq.1})$$

where  $W_M=5$  eV is the workfunction of the Nickel top-gate metal,  $W_{gr}=4.5$  eV is the theoretical workfunction for charge neutral Gr,  $C_{ox}$  is the top gate oxide capacitance per unit area ( $C_{ox}=\epsilon_0\epsilon_{ox}/t_{ox}$ , with  $\epsilon_{ox}\approx 8$  the Al<sub>2</sub>O<sub>3</sub> relative dielectric constant [37] and  $t_{ox}=10$  nm the oxide thickness). Statistical analysis has been carried out on a set of 10 top-gated Gr FETs onto AlGaIn. From the average value of the neutrality point position ( $\langle V_{NP} \rangle = -2$  V) and its standard deviation ( $\Delta V_{NP}=0.1$  V), the mean carrier density ( $\langle n_{gr} \rangle = 1.1 \times 10^{13}$  cm<sup>-2</sup>) of the n-type doped Gr onto AlGaIn and its variability ( $\Delta n_{gr}=0.4 \times 10^{12}$  cm<sup>-2</sup>) were obtained.

This electrons density corresponds to a positive shift of the Fermi level from the Dirac point  $E_F-E_D \approx 0.39$  eV, evaluated according to the relation:

$$E_{F,gr}-E_D=\hbar v_F(\pi n_{gr})^{1/2}/q \quad (\text{Eq.2}).$$

The field effect mobility values of electrons for Gr onto AlGaIn (and holes for Gr on Al<sub>2</sub>O<sub>3</sub>) was estimated from the slope  $dI_D/dV_G$  of the transfer characteristic, according to the relation  $\mu=L/(WC_{ox}V_{DS})dI_D/dV_G$ , where  $L=50$   $\mu$ m and  $W=150$   $\mu$ m are the channel length and width, respectively, and  $V_{DS}=0.1$  V the drain bias. The lower carrier mobility ( $\mu_e=620$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) for Gr onto AlGaIn with respect to Gr onto Al<sub>2</sub>O<sub>3</sub> ( $\mu_h=1120$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) can be ascribed to the enhanced Coulomb scattering due to the high n-type doping of Gr.

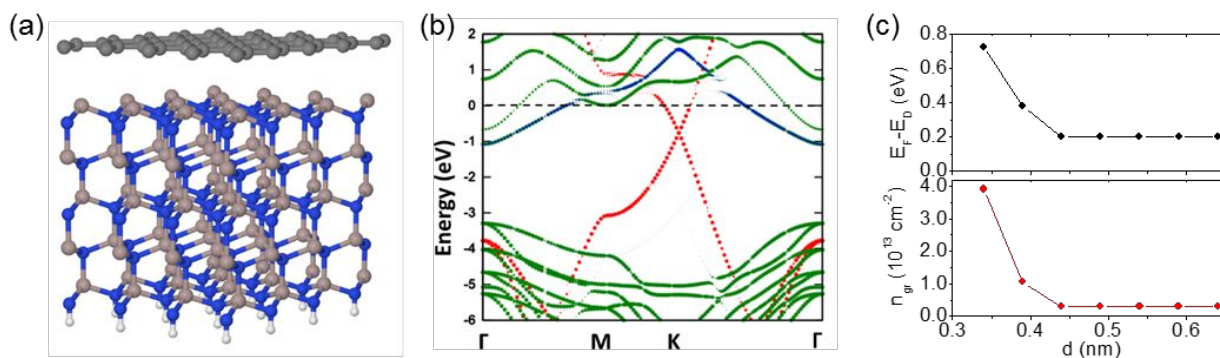


**Fig.3** Schematic illustration of two top gated FETs with Gr residing on the AlGaN/GaN heterostructure (a) and on an Al<sub>2</sub>O<sub>3</sub>/Si substrate (b). Transfer characteristics measured on the Gr FET supported by AlGaN/GaN (c) and Al<sub>2</sub>O<sub>3</sub>/Si (d).

## 2.2 Ab-initio DFT calculations

In the following, ab-initio density functional theory (DFT) calculations of the Gr/Nitride semiconductors interface were carried out, to elucidate the atomistic origin of the high n-type doping of Gr. Due to difficulty of simulating the interface with an Al<sub>x</sub>Ga<sub>1-x</sub>N alloy, AlN was adopted as a model system in our computational analysis [38]. We initially studied the structural and electronic properties of the interface between an ideally Al-terminated AlN(0001) surface and Gr. Fig. 4(a) shows the structural characteristics of this interface upon atomic relaxation. The Gr sheet remains practically flat and maintains a distance of 3.4 Å from the topmost Al atoms on the AlN surface. Such structural decoupling indicates that the heterostructure bonding is intrinsically low. Fig.4(b) shows the calculated band structure of this system, after unfolding the bands of each part of the heterojunction (i.e., Gr and the AlN substrate) to the respective primitive Brillouin zones. The Gr-related bands, reported as red lines, show the unperturbed Dirac cone standing at the K point of the hexagonal Brillouin zone of Gr. The AlN-related bands are indicated as green lines, whereas the blue

lines represent the calculated contribution of the AlN(0001) surface only. The principal characteristic from an electronic viewpoint is the unusually high shift of the Fermi level above the Dirac point ( $E_F - E_D \approx 0.73$  eV), corresponding to an electron density of  $n_{gr} \approx 3.9 \times 10^{13}$  cm<sup>-2</sup>. Furthermore, looking at the positioning of the Fermi level with respect to the AlN, it can be observed that it is “pinned” at the conduction band of the AlN surface (blue line). Besides this Fermi level pinning effect, which is intrinsic of the Al termination of the AlN surface, another possible mechanism contributing to the unusually high n-type doping of Gr can be represented by the charge transfer from the less electronegative Al atoms towards the C atoms of Gr. As a matter of fact, these charge transfer phenomena are expected to depend on the distance between Gr and the AlN(0001) surface. Hence, to evaluate the relative weight of the two mechanisms, we performed single-point energy evaluations by fixing the atomic positions of an ideal Gr/AlN(0001) interface while progressively varying the interface distance from the equilibrium value (3.4 Å) up to 6.4 Å. Fig.4(c) – upper panel illustrates the calculated shift of the Gr Fermi level with respect to the Dirac point ( $E_F - E_D$ ) as a function of the distance and the corresponding changes in the Gr doping (lower panel). It can be observed how the initial high n-type doping rapidly decreases from the value of  $\sim 3.9 \times 10^{13}$  cm<sup>-2</sup> at the equilibrium distance to  $\sim 1 \times 10^{13}$  cm<sup>-2</sup> at 3.9 Å, and it reaches a saturating value of  $\sim 0.3 \times 10^{13}$  cm<sup>-2</sup> for distances above 4.4 Å. While the decreasing doping values are due to charge transfer from the Al atoms, the saturation value can be ascribed to the above discussed Fermi level pinning effect.

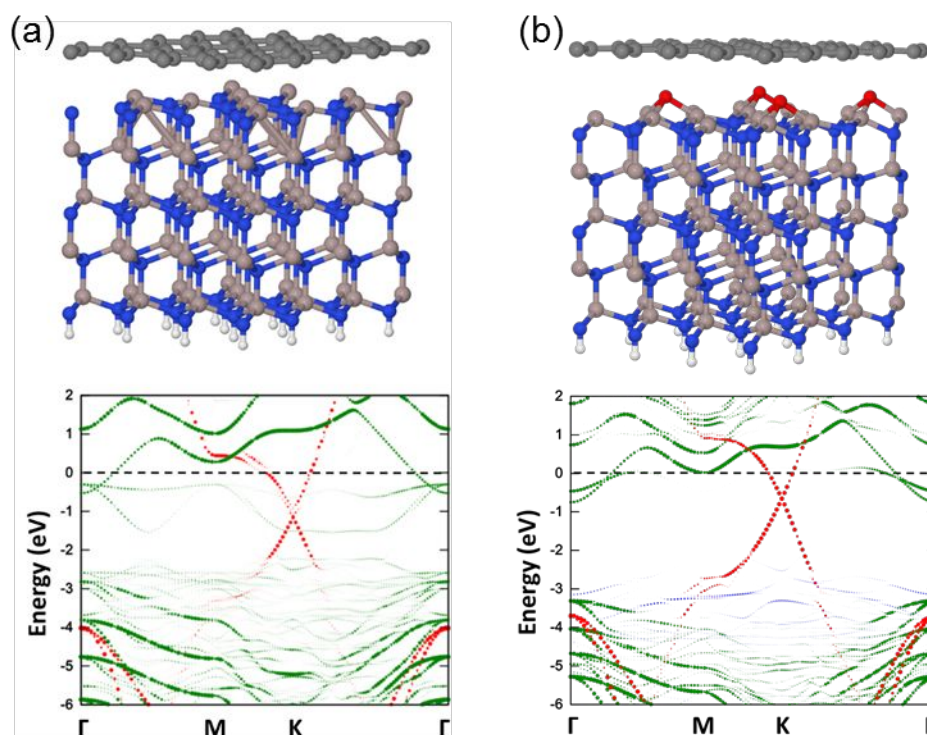


**Fig.4:** (a) Equilibrium structure and (b) energy bands for an ideal AlN(0001)/Gr interface. The bands for the different parts of the heterostructure have been unfolded to the corresponding first Brillouin zones of Gr (red points) and AlN (green points). The contribution of the topmost Al atoms of the AlN surface is shown as blue points. (c) Shift of the Fermi level from the Gr Dirac point ( $E_F - E_D$ ) and corresponding electron density ( $n_{gr}$ ) for a Gr/AlN(0001) interface as a function of the Gr-AlN distance.

These theoretical results, obtained in the case of an ideally Al-terminated AlN surface and Gr, indicate that the high n-type doping of Gr is an intrinsic property of the Gr/AlN interface. We extended the simulations work to consider also some cases of non-ideal AlN surfaces. Fig.5(a)-upper panel, shows

the relaxed configuration of Gr on a Al-poor surface with Al vacancies in a  $(2\times 2)$  surface pattern. In this case, Gr stands closer to the AlN surface (the Al-C distance is just 2.6 Å here) and shows a small corrugation. Both features indicate a stronger interface coupling with respect to the ideal case. Fig. 5(a)-lower panel shows the unfolded band structure of this system. Here, the surface-induced Al band is absent, due to the high concentration of Al defects, whereas numerous defect-states appear inside the band gap. The Gr bands are slightly perturbed near the Dirac point, and an even higher n-type doping is found ( $E_F - E_D \approx 1.15$  eV corresponding to  $n \approx 9.7 \times 10^{13}$ ) due to the closer Al-C distance and the higher charge transfer from the Al atoms towards Gr.

Finally, we also simulated the effect of a partial oxidation of the AlN surface, that can be found experimentally, to understand its effect on the electronic properties of the AlN(0001)/Gr heterostructure. To this purpose, we have considered a model based on O adatoms with a  $(2\times 2)$  pattern over the ideal AlN surface (Fig. 5(b)-upper panel). Even in this case, the high electron doping is found to be extremely robust (Fig. 5(b)-lower panel), excluding that a partial interface oxidation can change the qualitative picture described previously.



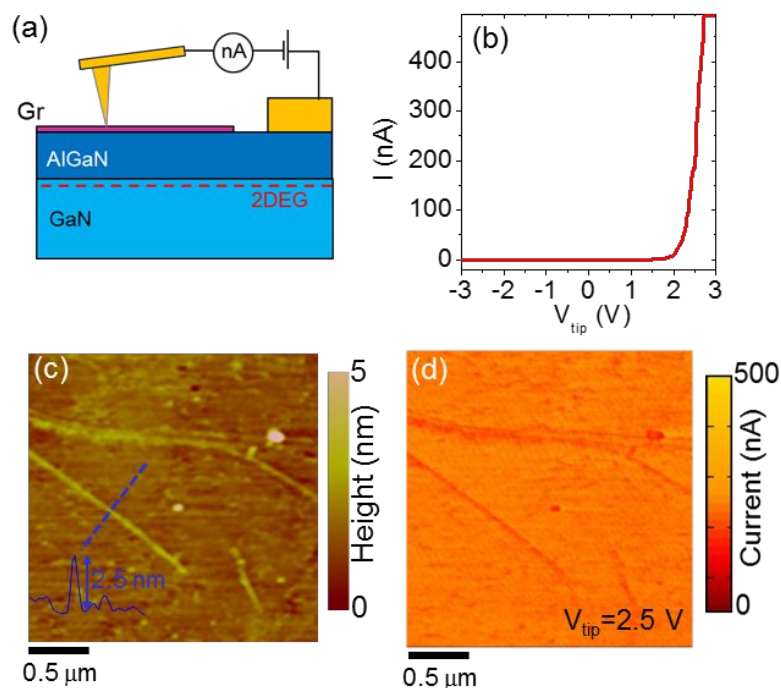
**Fig.5:** Structural and electronic properties for (a) an Al-poor AlN(0001)/Gr interface and for (b) an oxygen-rich AlN(0001)/Gr interface. The respective band structures have been unfolded to the corresponding first Brillouin zones of Gr (red points) and AlN (green points). The contribution of the topmost Al atoms (a) and the oxygen ad-atoms (b) are shown as blue points.

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3 DFT calculations provide a picture of the origin of Fermi level pinning and high n-type doping in Gr  
4 residing on the surface of AlN(0001). These considerations can be extended to the case of Gr onto  
5 the AlGa<sub>N</sub> barrier layer object of this experimental investigation.  
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### 8 9 **2.3 Electrons injection at Gr/AlGa<sub>N</sub> interface**

10  
11 The vertical current injection across the Gr/AlGa<sub>N</sub>/Ga<sub>N</sub> heterojunction was investigated both at  
12 nanoscale, using conductive atomic force microscopy (CAFM) [39,40], and at device level on  
13 Schottky diode structures.  
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16 Fig.6(a) illustrates the setup for CAFM-based vertical current measurements [41,42,31]. In this  
17 configuration, the local current flowing vertically from Gr to the 2DEG at AlGa<sub>N</sub>/Ga<sub>N</sub> interface is  
18 measured by applying a bias between the nanoscale tip scanned onto Gr and a macroscopic ohmic  
19 contact fabricated onto AlGa<sub>N</sub>. A typical current-voltage ( $I-V_{\text{tip}}$ ) characteristic measured in this  
20 configuration is reported in Fig.6(b). It exhibits a rectifying behavior, with negligible current at  
21 negative bias values and current onset at positive ones. Fig.6(c) and (d) show a typical morphology  
22 and the corresponding vertical current map measured with the tip scanned on the Gr membrane.  
23 Uniform current injection can be deduced from Fig.6(d), except for a local reduction of current on  
24 the wrinkles. Such effect can be ascribed to a local reduction of doping induced by the AlGa<sub>N</sub>  
25 substrate in these corrugations of the Gr membrane. This hypothesis is also supported by the results  
26 of DFT calculations for the Gr doping dependence on the distance from the AlN surface (see Fig.4(c)).  
27 Considering that wrinkles locally detach from the substrate by few nm altitude (see line profile in  
28 Fig.6(c)), those calculations indicate that the local doping of Gr can be reduced by more than one  
29 order of magnitude (down to  $\sim 3 \times 10^{12} \text{ cm}^{-2}$ ) in these areas.  
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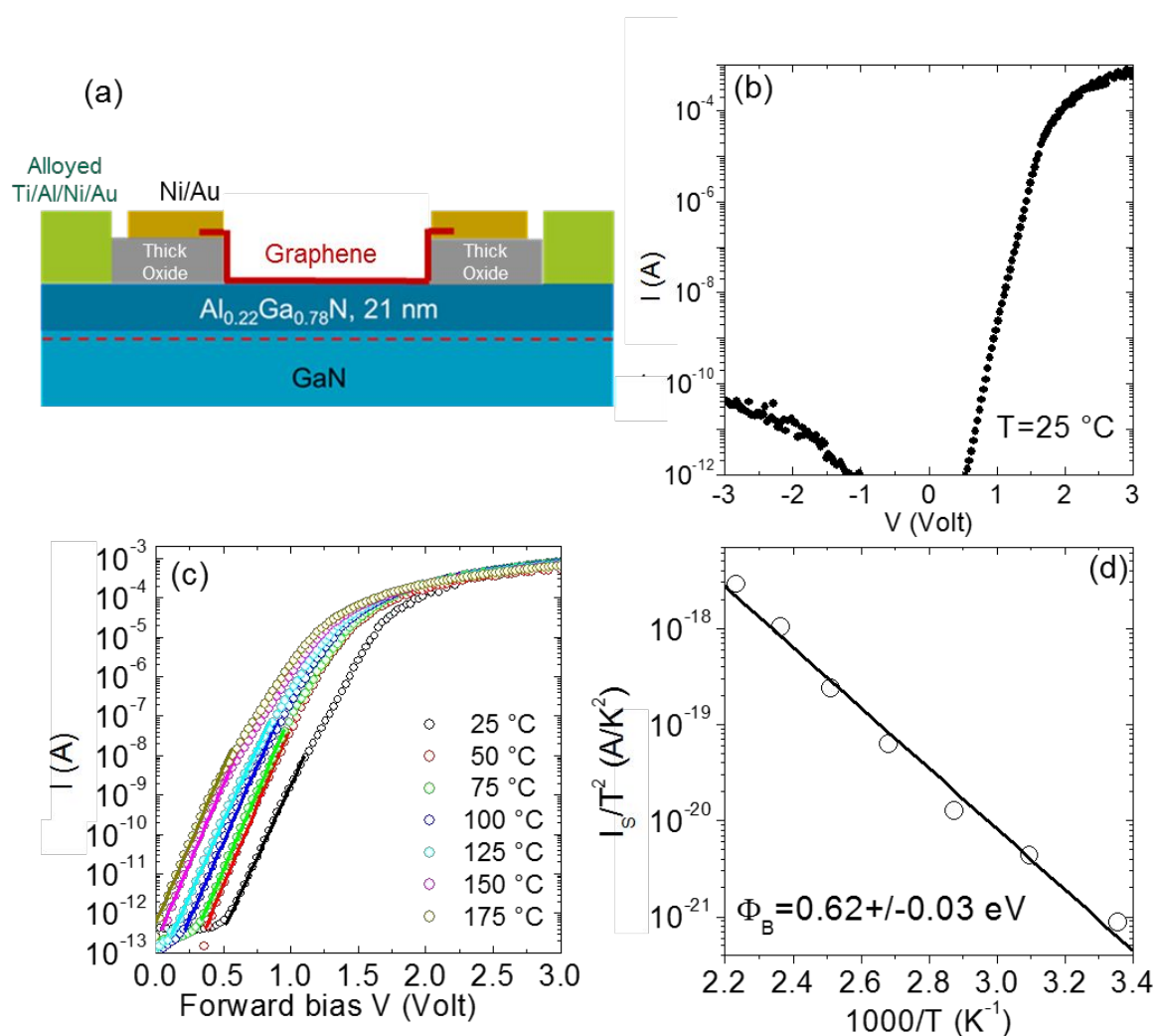


**Fig.6** (a) Schematic illustration of the setup for vertical current measurements with CAFM. (b) Typical current-voltage ( $I$ - $V_{tip}$ ) characteristic measured in the vertical configuration, showing a rectifying behavior, with negligible current at negative bias values and current onset at positive ones. (c) Morphology and (d) vertical current map measured with the tip scanned on the Gr membrane. A linescan showing the height of a Gr wrinkle is shown in the insert of panel (c).

The vertical current injection through the Gr/AlGaN/GaN heterojunction was investigated on properly fabricated diode structures, as discussed in the Materials and Methods section. A schematic cross-section of the diode is illustrated in Fig.7(a), whereas Fig.7(b) shows a typical current-voltage characteristic measured at a temperature  $T=298$  K. This curve exhibits an excellent rectifying behavior, with a very low current under reverse (negative) bias and a linear increase of the current (in the semilog scale) in a range of 8 decades under forward (positive) bias. To further investigate the mechanisms of current injection at this heterojunction, a temperature dependent I-V characterization has been carried out. Fig.7(c) shows a sequence of forward bias I-V curves collected at different temperatures, in the range from 298 to 448 K. A strong dependence of the current on the temperature can be observed, indicating thermionic emission as the main current injection mechanism. In order to evaluate the Schottky barrier height  $\Phi_B$  of the Gr/AlGaN interface, a linear fit of the I-V curves in Fig.7 (c) has been performed in the low bias region. The intercept on the current axis of this fit is the saturation current term  $I_s = AA^*T^2 \exp(-q\Phi_B/kT)$  of the thermionic emission equation  $I = I_s \exp(qV/nkT)$ , where  $A$  is the Schottky diode area,  $A^*$  the Richardson constant,  $k$  the Boltzmann constant,  $q$  the electron charge,  $T$  the temperature and  $n$  the ideality factor. Fig.7(d) shows the semilog-scale plot of

$I_s/T^2$  vs  $1000/T$ . The Gr/AlGa<sub>0.22</sub>N Schottky barrier height value ( $\Phi_B=0.62\pm 0.03$  eV) is obtained as the slope of the linear fit of these data. By statistical analysis of 10 different Gr/AlGa<sub>0.22</sub>N/GaN diodes, a mean Schottky barrier height value  $\langle\Phi_B\rangle=0.64$  eV with a standard deviation of 0.05 eV was estimated.

It is worth noting that this barrier height value is much lower than the one expected according the Schottky-Mott theory for an ideal Gr/AlGa<sub>0.22</sub>N Schottky barrier, i.e.,  $\Phi_B=W_{gr}-\chi_{AlGa_0.22N}=1.9$  eV, being  $W_{gr}=4.5$  eV the workfunction of neutral graphene and  $\chi_{AlGa_0.22N}=2.6$  the electron affinity for Al<sub>0.22</sub>Ga<sub>0.78</sub>N [43]. This large discrepancy can be ascribed to a Fermi level pinning at the interface between Gr and AlGa<sub>0.22</sub>N, consistently with predictions of DFT calculations.



**Fig.7** (a) Schematic cross-section of a Gr/AlGa<sub>0.22</sub>N/GaN diode. (b) Current-voltage ( $I$ - $V$ ) characteristic measured on this diode at a temperature of 25 °C, under forward and reverse polarization. (c) Sequence of forward bias  $I$ - $V$  curves measured at different temperatures, in the range from 25 to 175 °C. For each curve, a linear fit in the low bias region has been carried out to extract the saturation current value  $I_s$ . (d) Semilog-scale plot of  $I_s/T^2$  vs  $1000/T$  and linear fit of the data, from which the Gr/AlGa<sub>0.22</sub>N Schottky barrier height value ( $\Phi_B=0.62\pm 0.03$  eV) is obtained.

The Schottky barrier height at Gr/AlGaN interface is the key parameter ruling current injection in the Gr/AlGaN/GaN heterojunction diode under low forward bias polarization. However, in order to exploit this system as the base-emitter junction for a vertical hot electron transistor, an accurate modeling of the behavior of the injected current with the forward bias is necessary in a wide bias range. Looking in details to a typical I-V characteristic measured on the Gr/AlGaN/GaN diode (see Fig.8(a)), three different conduction regimes can be identified: a low and intermediate current regimes, showing linear  $\ln(I)$ -V behavior with two different slopes (black and red linear fits), followed by a region of current saturation at larger bias. This saturation is due to partial drop of the forward potential on the series resistances (i.e. the contact resistances to AlGaN/GaN and to Gr, and the resistances of the access regions to the device active area) occurring at large current levels. The two linear  $\ln(I)$ -V regions at different slopes are not peculiar of the Gr Schottky contact with AlGaN/GaN, as such behavior has been also observed for common metals on III-V or III-N heterostructures embedding a 2DEG [44]. Recently, Greco et al. [45] observed a similar behavior in the case of Ni/Au Schottky contacts onto AlGaN/GaN heterostructures and described it analytically considering the series combination of two Schottky diodes, the first one (the metal/AlGaN diode) ruling transport at lower bias and the second one (the 2DEG/AlGaN diode) at higher bias.

Hence, this “two-diodes model” was adapted to the specific case of the Gr/AlGaN/GaN heterojunction. Fig.8(b) illustrates the energy band diagrams of the heterojunction at different forward polarization biases. Here,  $\Phi_{B1}$  indicates the Schottky barrier height at the Gr/AlGaN interface (i.e.,  $\Phi_B$  previously evaluated), while  $\Phi_{B2}$  is the barrier of the second-diode between the 2DEG and AlGaN. At  $V=0$  the system is under equilibrium and the Fermi levels of Gr ( $E_{F,gr}$ ) and of the AlGaN/GaN 2DEG ( $E_{F,s}$ ) are aligned. With increasing the forward polarization bias  $V$ , the  $E_{F,s}$  is upward shifted with respect to  $E_{F,gr}$ . This results in a change of the potential  $\Delta V$  across the AlGaN layer, which decreases to zero (at flatband voltage  $V=V_{FB}$ ) and therefore inverts its sign. As illustrated in Fig.8(a), the flatband voltage condition ( $V_{FB}=0.95$  V) can be identified as the intersection point between two linear regions in the semilog scale I-V curves [45]. For  $0 < V < V_{FB}$ , the thermionic emission current at the Gr/AlGaN/GaN junction is ruled by the Schottky barrier  $\Phi_{B1}=0.62$  eV and by the ideality factor  $n_1=2.3$ , according to the equations:

$$I_1 = I_{s1} \exp\left(\frac{qV}{n_1 kT}\right), \quad (\text{Eq.3a})$$

$$I_{s1} = AA^* T^2 \exp\left(-\frac{q\Phi_{B1}}{kT}\right). \quad (\text{Eq.3b})$$

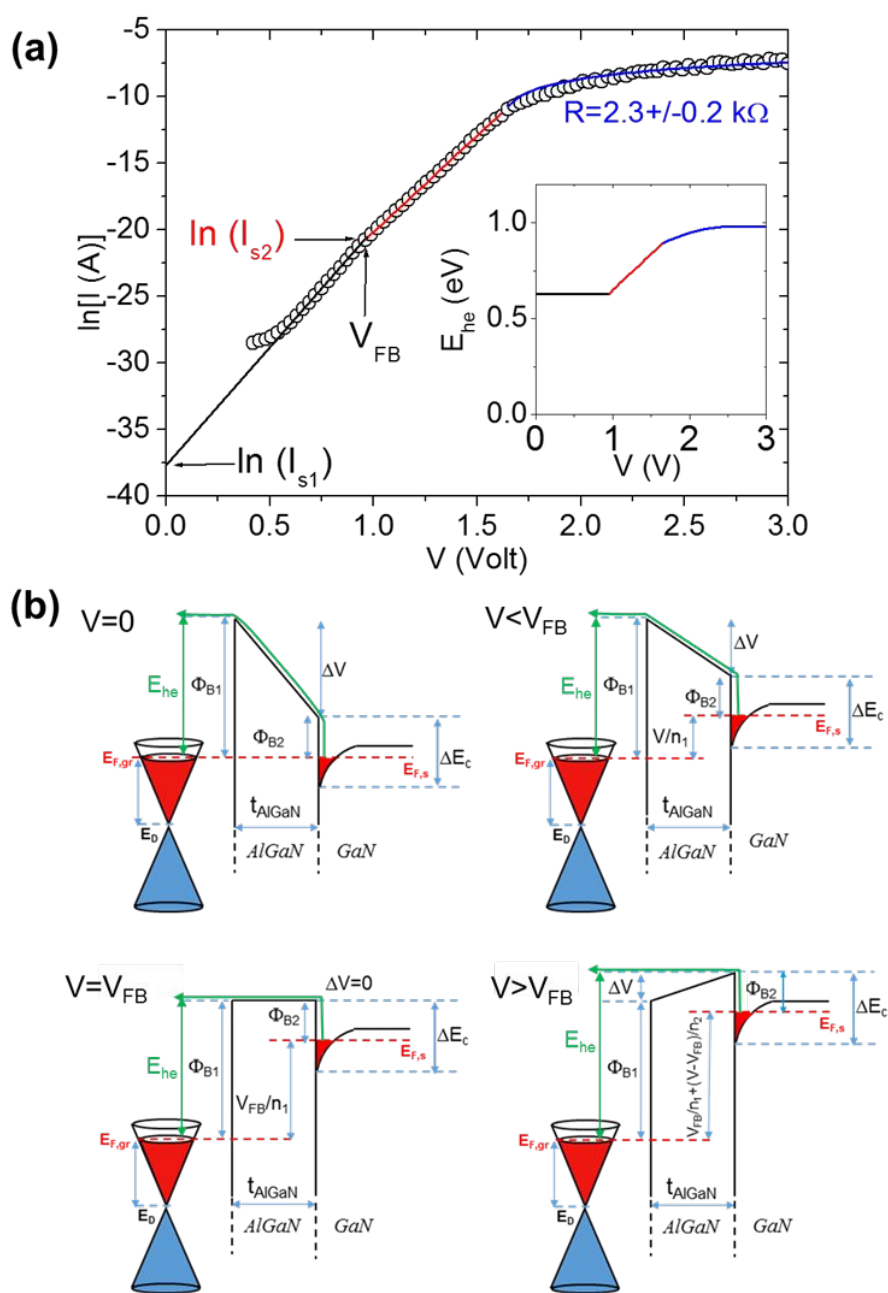
For  $V > V_{FB}$ , the current transport is described by the equations:



$$I_2 = I_{s2} \exp\left[\frac{q(V - V_{FB})}{n_2 kT}\right] \quad (\text{Eq.4a})$$

$$I_{s2} = AA^{**} T^2 \exp\left(-\frac{q\Phi_{B2}}{kT}\right). \quad (\text{Eq.4b})$$

Here,  $A^{**}$  is the Richardson constant for the 2DEG/GaN contact (which can be different from  $A^*$  for the Gr contact onto AlGaN),  $n_2=2.7$  is the ideality factor, and  $\Phi_{B2}$  is the barrier between the 2DEG and AlGaN.



**Fig.8** (a) Semilog-scale I-V characteristic of the Gr/AlGaN/GaN Schottky diode under forward bias polarization and (b) energy band diagrams of this system for different bias conditions.

According to Fig.8(a), Eq.3a and Eq.4b give the same current value at  $V=V_{FB}$ . Hence, by equating the second terms of these equations, and from the band diagram in Fig.8(b) for  $V=V_{FB}$ , the following relation can be derived between the barrier heights  $\Phi_{B1}$ ,  $\Phi_{B2}$  and the saturation current values  $I_{s1}$ ,  $I_{s2}$ :

$$\Phi_{B2} - \Phi_{B1} = \frac{kT}{q} [\ln(I_{s2}) - \ln(I_{s1})] \quad (\text{Eq.5})$$

Noteworthy, this equation allows to evaluate  $\Phi_{B2}$  directly from the value of  $\Phi_{B1}$  (obtained from the Richardson plot in Fig.7(d)), and by the experimental values of  $\ln(I_{s1}) \approx -37 \pm 1$  and  $\ln(I_{s2}) \approx -21 \pm 1$ , without the need of knowing the Richardson constant. The obtained value of  $\Phi_{B2} \approx 217 \pm 25$  meV is in good agreement with the expected value ( $\Phi_{B2} \approx 199$  meV) according to the band diagram in Fig.8(b), i.e.:

$$\Phi_{B2} = \Delta E_C - [E_{F,s} - E_{Cmin}], \quad (\text{Eq.6})$$

where  $\Delta E_C = 297$  meV is the calculated conduction band discontinuity at the  $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$  interface for  $x=0.22$  [34] and  $E_{F,s} - E_{Cmin} = 98$  meV is the Fermi level position with respect to the bottom of the quantum well. This was obtained using the expression of  $E_{F,s} - E_{Cmin}$  for a 2DEG of Schrodinger electrons (with parabolic dispersion relation), i.e.,  $E_{F,s} - E_{Cmin} = \pi \hbar^2 n_s / (q m_{eff})$ , being  $\hbar$  the reduced Planck's constant,  $m_{eff} = 0.22 m_e$  the electrons effective mass [34] and  $n_s = 9 \times 10^{12} \text{ cm}^{-2}$  the carrier density (evaluated in Fig.1(c)).

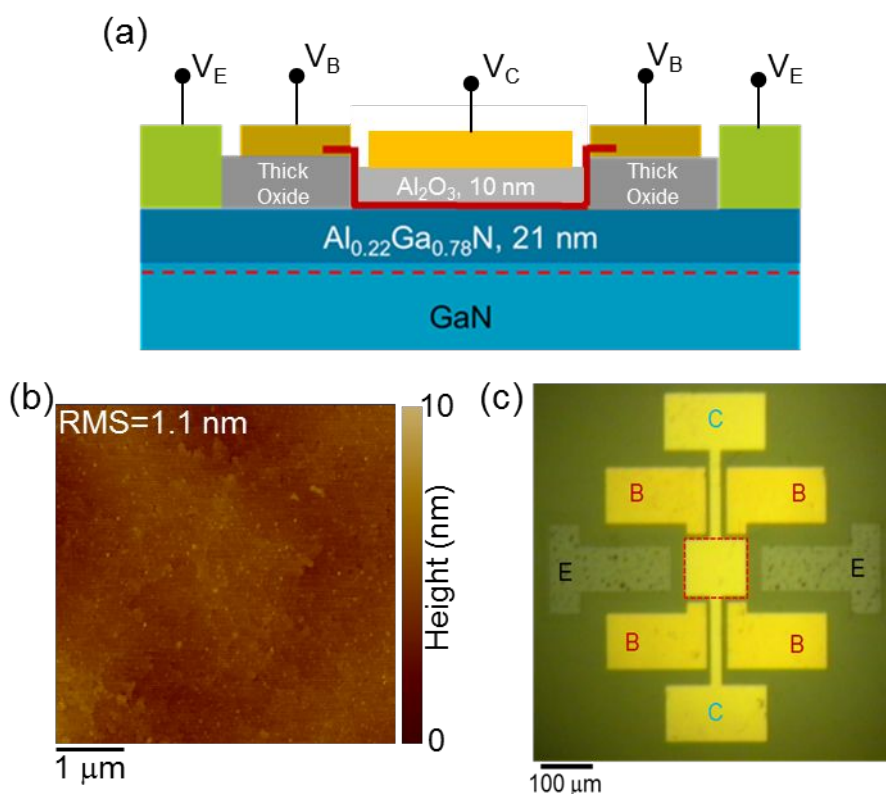
As discussed above, the saturation regime of the  $\ln(I)$ - $V$  characteristics of the Gr/AlGaN/GaN diode at high forward bias is determined by the series resistance contributions associated to the metal/Gr and metal/AlGaN contacts, and to the access regions. A series resistance value of  $R = 2.3 \pm 0.2 \text{ k}\Omega$  was evaluated by fitting this region of the  $I$ - $V$  curve with the function  $I = (V - V_R) / R$ , reported as a blue line Fig.8(a).

Once the key physical parameters describing the Gr/AlGaN/GaN junction have been obtained, these were employed to evaluate the energy of hot electrons ( $E_{he}$ ) injected by thermionic emission over the barrier. As illustrated in the band-diagrams in Fig.8(b), for  $V \leq V_{FB}$ , electrons overcoming the barrier have an energy  $E_{he} = \Phi_{B1}$  (or higher). On the other hand, for  $V > V_{FB}$ , a linear increase of  $E_{he} = \Phi_{B1} + \Delta V$  as a function of the bias  $V$  is expected, followed by a saturation behavior due to the series resistance effect. The behavior of  $E_{he}$  as a function of  $V$  in these three different regimes is reported in the insert of Fig.8(a).

## 2.4 Hot Electrons Transistor

After investigating the basic properties of the Gr/AlGaN interface and modeling the current voltage characteristic of the G/AlGaN/GaN diode in the entire forward bias range, we fabricated a complete hot electron transistor (HET) structure (see the Materials and Methods section). A schematic cross-section of the HET device is illustrated in Fig.9 (a). With respect to the diode structure in Fig.7(a), it includes a thin Al<sub>2</sub>O<sub>3</sub> film, with thickness  $t_{\text{ox}}=10$  nm, working as the base-collector barrier. A typical AFM morphology of the as-deposited Al<sub>2</sub>O<sub>3</sub> on the Gr/AlGaN surface is reported in Fig.9(b), demonstrating the uniform and conformal (i.e. pinholes-free) coverage of Gr by the insulating layer. The Al<sub>2</sub>O<sub>3</sub> deposition was carried out using an optimized two-steps ALD process [37], which consists of a low temperature (100 °C) deposition step for the nucleation of a uniform AlO<sub>x</sub> seed layer on the Gr surface [46], followed by a higher temperature deposition at T=250 °C. This process, initially developed for Gr transferred onto common insulating substrates [37], was demonstrated to result in a very good Al<sub>2</sub>O<sub>3</sub> coverage of the Gr surface. More recent investigations have shown an improved Al<sub>2</sub>O<sub>3</sub> nucleation in the case of highly n-type doped Gr [47], which justifies the very uniform morphology of Al<sub>2</sub>O<sub>3</sub> onto Gr/AlGaN shown in Fig.9(b).

Fig.9(c) reports a top-view optical microscopy of the complete HET device, where the Ni/Au collector contact (C) deposited on the thin Al<sub>2</sub>O<sub>3</sub> film, the Ni/Au pads contacting the Gr base (B) and the alloyed Ti/Al/Ni/Au Ohmic contacts on the AlGaN/GaN emitter (E) are indicated. The device active area (100 μm×100 μm), i.e. the region where the emitter, base and collector are overlapped, is delimited by a red dashed line.



**Fig.9** (a) Schematic cross-section of the hot electron transistor structure. (b) AFM image of the  $\text{Al}_2\text{O}_3$  base-collector barrier deposited on Gr. (c) Top-view optical microscope image of the HET device.

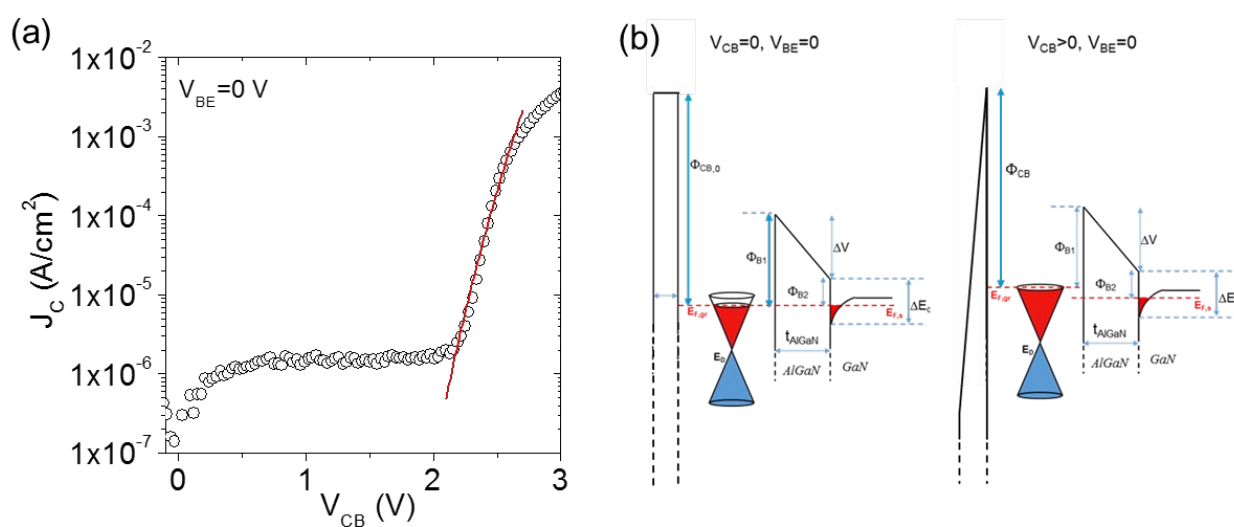
Fig.10(a) shows the collector current density ( $J_C$ ) measured on the base-collector diode by applying a positive bias ramp to the collector terminal ( $V_{CB} = V_C - V_B$  from 0 to 3 V, with the base terminal grounded,  $V_B = 0$ ) and  $V_{BE} = 0$  V at the emitter-base junction. The low current density values  $J_C \approx 1 \mu\text{A}/\text{cm}^2$  measured for  $V_{CB} < 2.2$  V correspond to the leakage current across the base-collector barrier. For  $V_{CB} > 2.2$  V an exponential increase of the  $J_C$  is observed, which was described by a Fowler-Nordheim (FN) tunneling mechanism:

$$J_C = \frac{q^3 m V_{CB}}{8\pi h m_{ox} t_{ox} \Phi_{CB}} \exp \left[ - \frac{8\pi \sqrt{2m_{ox}} \Phi_{CB}^3}{3qh} \left( \frac{t_{ox}}{V_{CB}} \right) \right] \quad (\text{Eq.7})$$

with  $m_{ox}$  the electron tunneling mass for  $\text{Al}_2\text{O}_3$ ,  $m$  the free electron mass,  $h$  the Planck's constant and  $t_{ox} = 10$  nm the  $\text{Al}_2\text{O}_3$  thickness. Fig.10(b) shows the energy band diagrams for the Gr/AlGaIn/GaN system at equilibrium (left panel) and for high enough  $V_{CB}$  allowing tunneling through the triangular barrier (right panel). Noteworthy, the base-collector barrier  $\Phi_{CB}$  depends on the collector bias  $V_{CB}$ , due the field effect modulation of the Gr Fermi level, and it can be expressed as:

$$\Phi_{CB} = \Phi_{CB,0} - \frac{q V_F \left[ \sqrt{\pi \left( n_{gr} + \frac{C_{ox} V_{CB}}{q} \right)} - \sqrt{\pi n_{gr}} \right]}{q}, \quad (\text{Eq.8})$$

where  $\Phi_{CB,0}$  is the base-collector barrier value (at  $V_{CB}=0$ ) and  $n_{gr}=1.1 \times 10^{13} \text{ cm}^{-2}$  is Gr the electrons density, as evaluated from the top-gated GFET characterization in Fig.3(c). By fitting the  $I_C$ - $V_{CB}$  characteristics with Eqs.(7)-(8), a value of  $\Phi_{CB,0}=1.31 \text{ eV}$  was obtained for  $m_{ox}=0.55 m_e$  [48].



**Fig.10** (a) Current-voltage ( $J_C$ - $V_{CB}$ ) characteristic of the base-collector diode (for  $V_{BE}=0 \text{ V}$ ) and fit with Fowler-Nordheim tunneling model. (b) Energy band diagrams for the Gr/AlGaIn/GaN system at equilibrium (left panel) and for high enough  $V_{CB}$  allowing tunneling through the triangular barrier (right panel).

After evaluating the key physical parameters ruling the electron transport across the base-collector barrier, the electrical characterization of the full HET structure has been performed, in order to evaluate the efficiency of hot electrons injection from the AlGaIn/GaN emitter into the Gr base. Fig.11(a) shows the emitter ( $J_E$ ) and collector ( $J_C$ ) current densities measured as a function of the emitter-base bias ( $V_{BE}$  from 0 to 3 V) in the common base configuration ( $V_B=0 \text{ V}$ ) and for a fixed collector bias  $V_{CB}=2 \text{ V}$ . The injected current measured at the emitter terminal ( $J_E$ ) exhibits an exponential dependence on  $V_{BE}$ , consistently with the behavior of the Gr/AlGaIn Schottky diode.

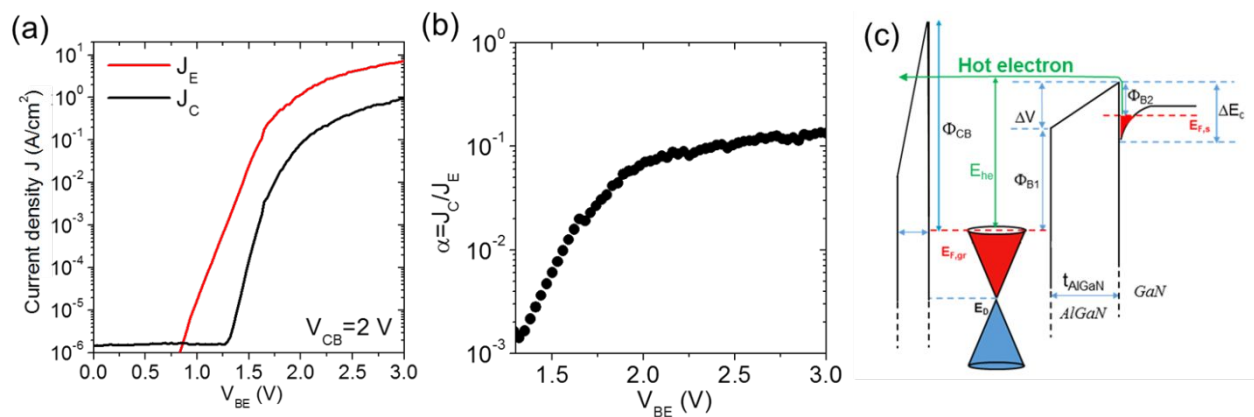
The  $J_C$ - $V_{BE}$  characteristic exhibits a turn-on voltage  $\sim 1.3 \text{ V}$ , with a low off-state current density  $J_{C,OFF} \approx 1 \mu\text{A}/\text{cm}^2$  (for  $V_{BE} < 1.3 \text{ V}$ ) associated to the leakage current of cold electrons through the  $\text{Al}_2\text{O}_3$  barrier. The exponentially increasing  $J_C$  for  $V_{BE} > 1.3 \text{ V}$  is associated to the current of hot electrons

injected from the emitter into the Gr base, that are able to reach the collector. By statistics on 10 different HETs, an average turn-voltage of 1.2 V with a standard deviation of  $\pm 0.1$  V was obtained. Thanks to the efficient hot electrons injection at the Gr/AlGaIn/GaN heterojunction, an ON/OFF current density ratio  $J_{C,ON}/J_{C,OFF} \approx 10^6$  with a  $J_{C,ON} = 1$  A/cm<sup>2</sup> is achieved. Fig.10(b) shows the common base current gain of the transistor, i.e. the ratio  $\alpha = J_C/J_E$ , which reaches values from 0.1 to 0.15 at  $V_{BE} > 2$  V.

Theoretically,  $\alpha$  can be expressed as  $\alpha = \alpha_B \alpha_{BC}$ , where  $\alpha_B = \exp(-t_{Gr}/l)$  is the base efficiency (being  $t_{Gr} \approx 0.35$  nm the monolayer Gr thickness and  $l$  the electron mean free path) and  $\alpha_{BC}$  is base-collector transmission efficiency. For the typical values of  $l$  in substrate-supported Gr [17],  $\alpha_B \approx 1$ . On the other hand, we expect that  $\alpha_{BC}$  is limited by the high  $\Phi_{CB}$  for the used Al<sub>2</sub>O<sub>3</sub> base-collector barrier. According to the band diagram in Fig.11(c),  $\alpha_{BC}$  can be expressed as the probability of hot electrons tunneling across the triangular barrier:

$$\alpha_{BC} = \exp \left[ - \frac{8\pi\sqrt{2m_{ox}}(\Phi_{CB} - E_{he})^3}{3qh} \left( \frac{t_{ox}}{V_{CB}} \right) \right], \quad (\text{Eq.9})$$

where  $\Phi_{BC}$  is the base-collector barrier and the  $E_{he}$  is hot electrons energy. The saturation value  $\alpha \approx 0.15$  of the current gain corresponds to value of  $E_{he} \approx 1$  eV, consistently with the results deduced from the analysis of the Gr/AlGaIn/GaN diode (Fig.8(a), insert).



**Fig.11** (a) Emitter ( $J_E$ ) and collector ( $J_C$ ) current densities measured in the common base configuration ( $V_B = 0$  V) as a function of the emitter-base bias ( $V_{BE}$  from 0 to 3 V) and for a fixed collector bias  $V_{CB} = 2$  V. (b) Common base current gain of the transistor. (c) Band diagram illustrating the hot electron injection and transit in the base and base-collector barrier for the experimental conditions in (a).

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3 This indicates that the on-state current and the gain of our HET is solely limited by the high value  
4  $\Phi_{BC}$  of the used  $\text{Al}_2\text{O}_3$  base-collector barrier. Large space of improvement in the device performances  
5 is expected by the development of alternative base-collector barrier layers on Gr with more favorable  
6 band alignment and suitable structural quality. As an example, further progresses in the van der Waals  
7 epitaxy of thin GaN or InGaN layers on Gr [49,50] should meet these requirements.  
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### 10 11 12 **3 Conclusion**

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14 In conclusion, the Gr Schottky junction with an optimized quality  $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$  heterostructure on  
15 silicon has been investigated as a key building block of hot electron transistors with high on-state  
16 current. The peculiar electronic properties of the Gr/AlGaN interface, such as a high n-type doping  
17  $\sim 1.1 \times 10^{13} \text{ cm}^{-2}$  of Gr and the low Schottky barrier height ( $\Phi_B \approx 0.62 \text{ eV}$ ), were explained by the  
18 combined effect of Fermi level pinning by AlGaN surface states and charge transfer. A  
19 Gr/AlGaN/GaN Schottky diode with excellent rectifying behavior was demonstrated, and used as  
20 building block for a HET with a thin  $\text{Al}_2\text{O}_3$  base-collector barrier. Thanks to the highly efficient hot  
21 electron injection from the AlGaN/GaN emitter, this transistor exhibits high on-state current density  
22 of  $J_{C,ON} \approx 1 \text{ A/cm}^2$  and six decades modulation of  $J_C$  by the base-emitter bias. The common base current  
23 gain,  $\alpha \approx 0.15$ , was limited by the high base-collector barrier of  $\text{Al}_2\text{O}_3$ , and  $\alpha$  approaching the unity  
24 value is expected replacing  $\text{Al}_2\text{O}_3$  with a material with a more favorable band alignment with the  
25 AlGaN/GaN emitter, e.g., a GaN or InGaN base-collector barrier layer.  
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28 The demonstration of highly efficient hot electrons injection in Gr/AlGaN/GaN Schottky junctions  
29 on silicon represents an important step towards the development a hot electron transistors technology  
30 compatible with the state-of-the-art GaN HEMTs.  
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### 35 36 37 38 39 40 41 42 **Acknowledgements**

43  
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## Materials and methods

**Growth of AlGaIn/GaN heterostructures on silicon.** The heterostructures were grown by MOCVD on 50 mm Si (111) wafers in a closed coupled showerhead system. After an in situ deoxidation in H<sub>2</sub> atmosphere, a 20 nm AlN seed layer was first grown at 900°C followed by 180 nm of AlN grown at 1150°C and a 700 nm GaN film grown at around 1000°C. Then, a thin AlN layer (20 nm) is grown strain relaxed in order to allow the growth of a compressively strained GaN layer on top. The mismatch strain between GaN and AlN is 2.5% and progressively relaxes in the 1.4 μm thick GaN by bending of dislocations which favors the defect filtering and avoids layer cracking upon sample cooling. Finally, the active layers consist of a thin (2nm) AlN spacer layer grown on the GaN and a 21 nm AlGaIn barrier with an Al molar fraction  $x=22\%$ .

**Transfer of Gr onto AlGaIn/GaN.** Monolayer Gr samples, grown by CVD on Cu foils using CH<sub>4</sub>/H<sub>2</sub> as precursors, were purchased by the Graphenea company. Spin coated PMMA onto Gr/Cu was used as protective layer for the Gr membrane during manipulation. Furthermore, a thermal release tape (TRT) laminated onto PMMA worked as carrier layer to allow PMMA/Gr handling after detachment from Cu. The Cu substrate was completely etched by overnight immersion in an ammonium persulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> water solution. After cleaning in de-ionized water, the TRT/PMMA/Gr stack was transferred to the target substrate by thermo-compression printing, with the TRT released during the heating ramp of this process. Finally, the PMMA carrier layer was removed in acetone. A subsequent annealing at 400 °C in Ar ambient for 10 min was performed to eliminate the nanometric polymer residues which remained on the Gr surface even after solvent cleaning. The Ar ambient was chosen to avoid oxidation of the AlGaIn surface, as this can be detrimental also for the electrical properties of the AlGaIn/GaN 2DEG. The used thermal budget did not significantly affect the electrical properties of the AlGaIn/GaN heterostructure, as confirmed by electrical characterization of an HEMT control structure fabricated by depositing a Ni/Au gate Schottky contact in a sample region where Gr was not transferred.

**Fabrication of the Gr/AlGaIn GaN Schottky diode and hot electron transistor.** After lateral isolation of the AlGaIn/GaN active area by plasma etching, ohmic contacts onto AlGaIn/GaN were fabricated by deposition of a Ti/Al/Ni/Au multilayer followed by rapid thermal annealing at 800 °C for 1 min in Ar. A thick (~40 nm) Al<sub>2</sub>O<sub>3</sub> film was subsequently deposited by ALD onto AlGaIn and the diode active area was defined by opening in this insulating layer. Finally Gr transfer was carried out, followed by lateral isolation with O<sub>2</sub> plasma and the deposition of base contacts (Ni/Au).

The full HET structure was obtained by atomic layer deposition (ALD) of 10 nm Al<sub>2</sub>O<sub>3</sub> onto, followed by the deposition of the Ni/Au collector contact. The ALD growth was carried out using Trimethylaluminum (TMA) and H<sub>2</sub>O as the aluminum and oxygen precursors, respectively. The



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3 process was initiated by six H<sub>2</sub>O pretreatment cycles, followed by 60 H<sub>2</sub>O–TMA cycles at low  
4 temperature (100 °C) for the formation of an AlO<sub>x</sub> seed layer on Gr [37]. Afterwards, 80 H<sub>2</sub>O–TMA  
5 cycles at higher temperature (250 °C) were carried out to achieve the 10 nm Al<sub>2</sub>O<sub>3</sub> film thickness.  
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8 **Atomic force microscopy (AFM) and conductive AFM (CAFM) analyses.** AFM measurements  
9 were carried out employing a D3100 microscope with Nanoscope V controller, using Si tips with 5  
10 nm curvature radius. The vertical current transport across the Gr/AlGaN/GaN heterostructure was  
11 investigated by CAFM, using the same system equipped with the current measurement module, and  
12 ultra-sharp Pt coated Si tips as probes.  
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16 **Theoretical calculations.** Density functional theory calculations were performed using the SIESTA  
17 code [51]. We built commensurate graphene/AlN supercells [52] comprising of a (4×4) AlN surface  
18 and a (5×5) graphene sheet, reducing in this way the fictitious interface strain below 0.4%. The study  
19 took place within the local density approximation (LDA) [53]. The wave functions were expanded  
20 on a basis set of double- $\zeta$  polarized orbitals, while Troulier-Martins pseudopotentials [54] were  
21 employed for the ionic cores. Convergence was achieved by sampling the hexagonal Brillouin zone  
22 with a (4×4×1) Monkhorst-Pack grid. The mesh cutoff energy was set to 400 Ry and all atoms were  
23 allowed to relax until forces were less than 0.04 eV/Å. The Gr/AlN interfaces were modeled as slabs  
24 containing five bilayers of the substrate and a single layer of Gr. The lower termination of the AlN  
25 slab was passivated with hydrogen. Band structures were unfolded to the primitive Brillouin zones of  
26 Gr and AlN according to the methodology described in Ref. [55].  
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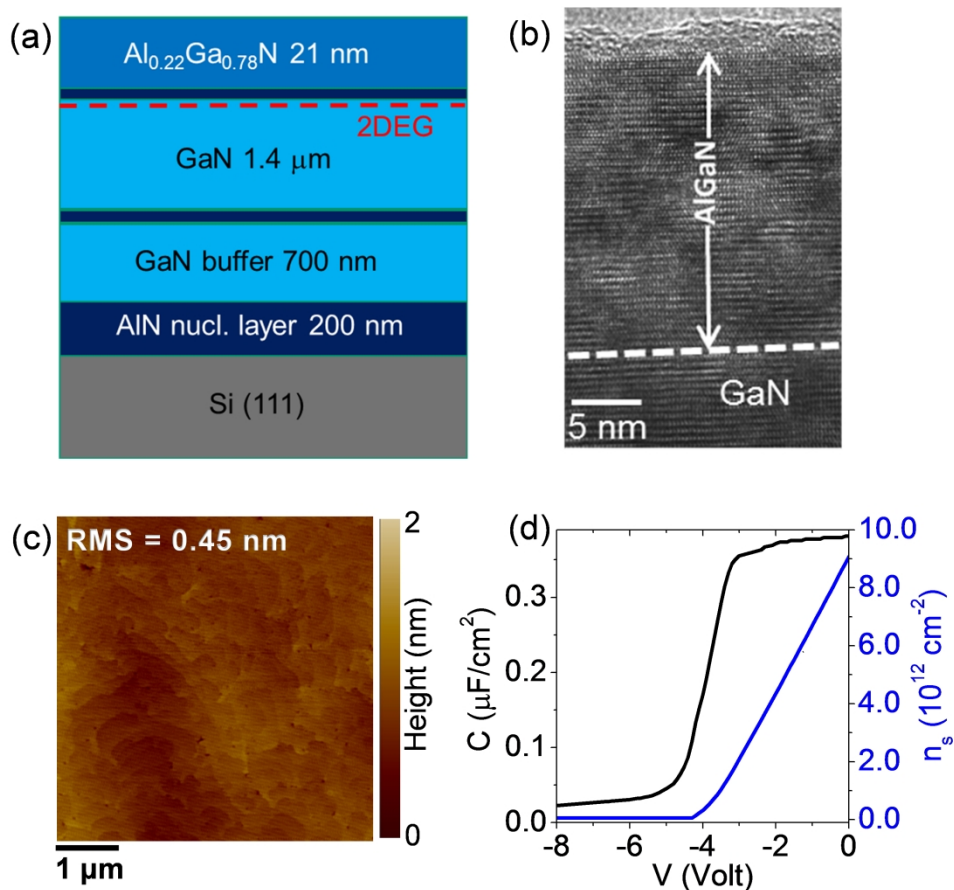
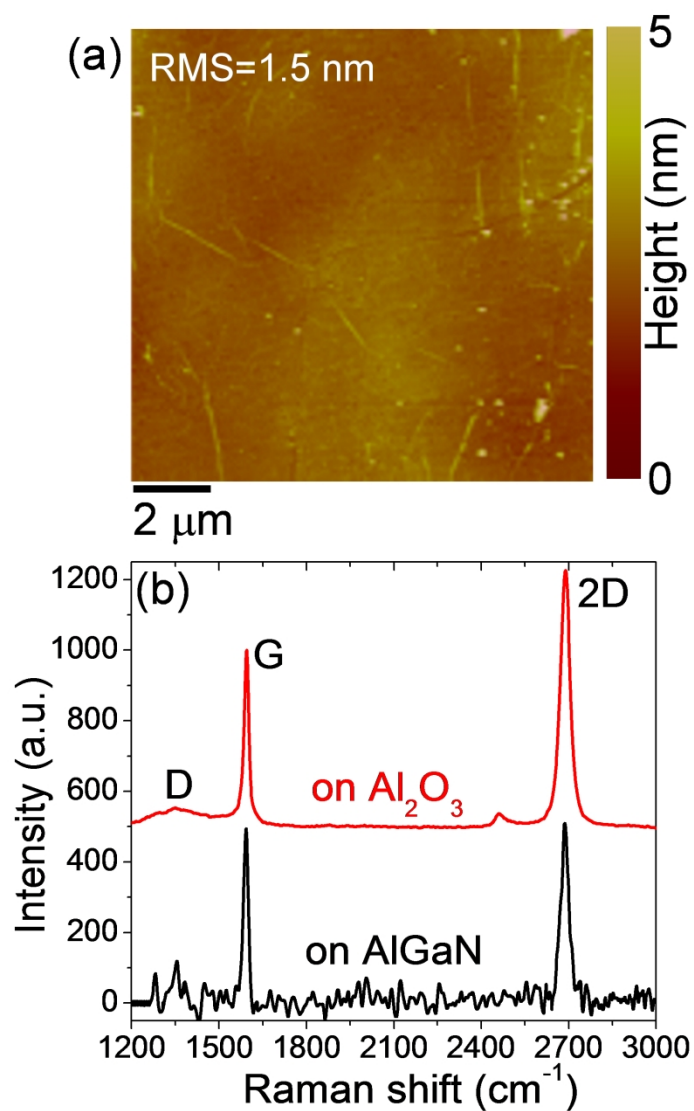


Fig.1 (a) Schematic cross section of the multilayer structure grown on the Si(111) substrate. (b) High-resolution cross-sectional TEM of the topmost AlGaIn/GaN heterostructure in the multilayer. (c) AFM image of the as-grown AlGaIn surface ( $5 \mu\text{m} \times 5 \mu\text{m}$  scan area). (d) Hg probe C-V measurement (black line, left vertical axis) of the AlGaIn acquired at a frequency of 20 kHz by negative biasing the Hg Schottky contact from 0 to -8V. The blue line (right vertical axis) is the 2DEG charge density  $n_s$  modulated by the bias.

712x660mm (120 x 120 DPI)



45 Fig. 2 (a) Typical AFM image of monolayer (1L) Gr on the AlGaN surface, showing a uniform coverage  
46 without pinholes and cracks. (b) Representative Raman spectra of 1L Gr onto AlGaN and on an  $\text{Al}_2\text{O}_3$   
47 insulating substrate, used as a reference.

48 464x658mm (120 x 120 DPI)



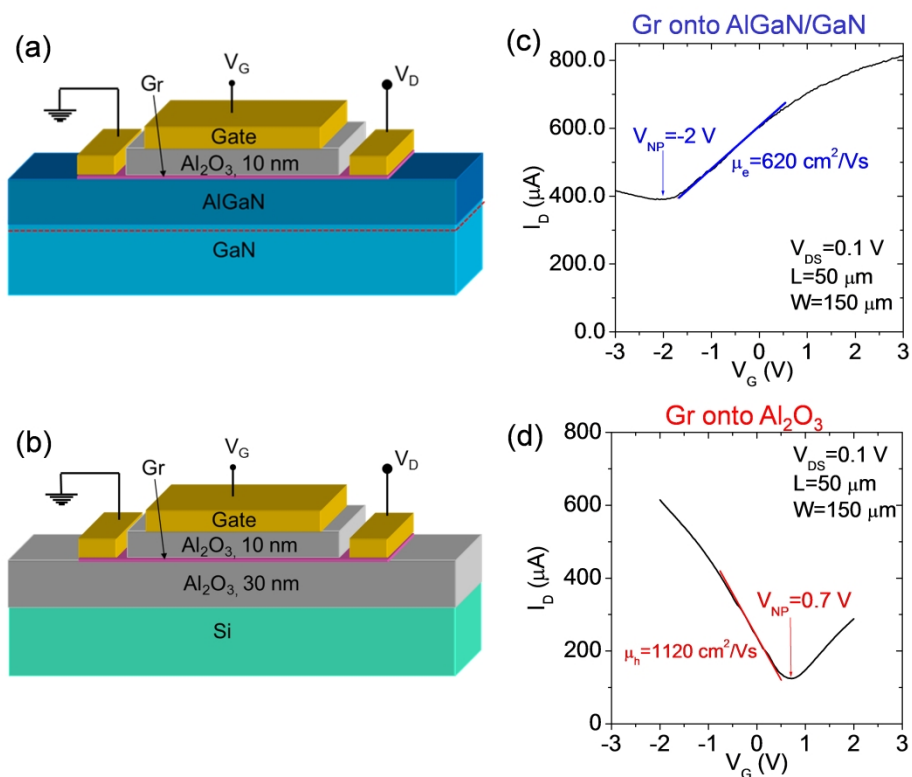


Fig.3 Schematic illustration of two top gated FETs with Gr residing on the AlGaN/GaN heterostructure (a) and on an Al<sub>2</sub>O<sub>3</sub>/Si substrate (b). Transfer characteristics measured on the Gr FET supported by AlGaN/GaN (c) and Al<sub>2</sub>O<sub>3</sub>/Si (d).

928x786mm (120 x 120 DPI)

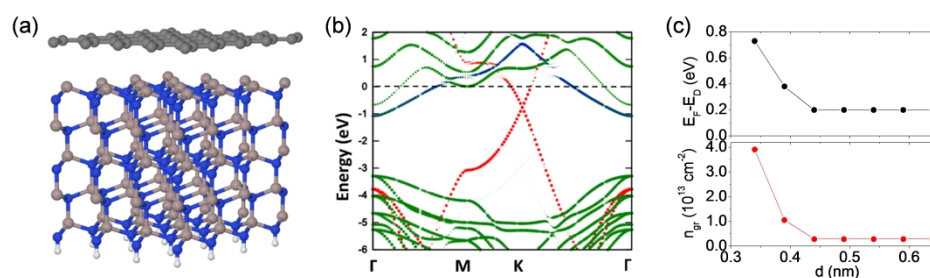


Fig.4: (a) Equilibrium structure and (b) energy bands for an ideal AlN(0001)/Gr interface. The bands for the different parts of the heterostructure have been unfolded to the corresponding first Brillouin zones of Gr (red points) and AlN (green points). The contribution of the topmost Al atoms of the AlN surface is shown as blue points. (c) Shift of the Fermi level from the Gr Dirac point ( $E_F - E_D$ ) and corresponding electron density ( $n_{gr}$ ) for a Gr/AlN(0001) interface as a function of the Gr-AlN distance.

942x295mm (120 x 120 DPI)

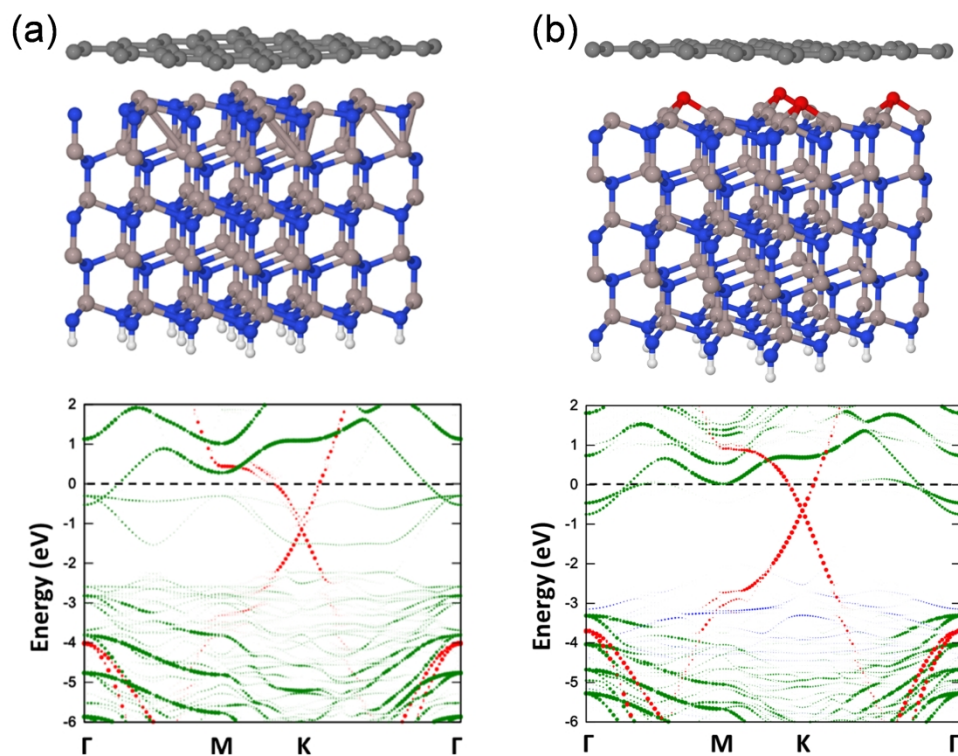


Fig.5: Structural and electronic properties for (a) an Al-poor AlN(0001)/Gr interface and for (b) an oxygen-rich AlN(0001)/Gr interface. The respective band structures have been unfolded to the corresponding first Brillouin zones of Gr (red points) and AlN (green points). The contribution of the topmost Al atoms (a) and the oxygen ad-atoms (b) are shown as blue points.

644x505mm (120 x 120 DPI)

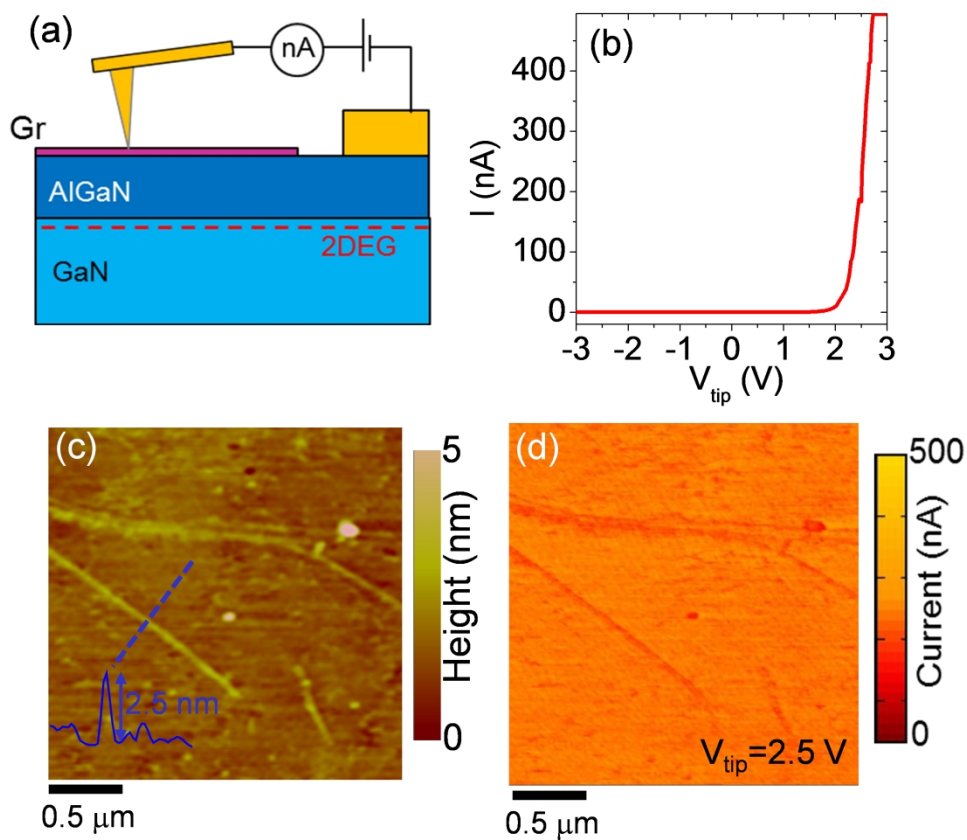


Fig.6 (a) Schematic illustration of the setup for vertical current measurements with CAFM. (b) Typical current-voltage ( $I$ - $V_{tip}$ ) characteristic measured in the vertical configuration, showing a rectifying behavior, with negligible current at negative bias values and current onset at positive ones. (c) Morphology and (d) vertical current map measured with the tip scanned on the Gr membrane. A linescan showing the height of a Gr wrinkle is shown in the insert of panel (c).

568x516mm (120 x 120 DPI)

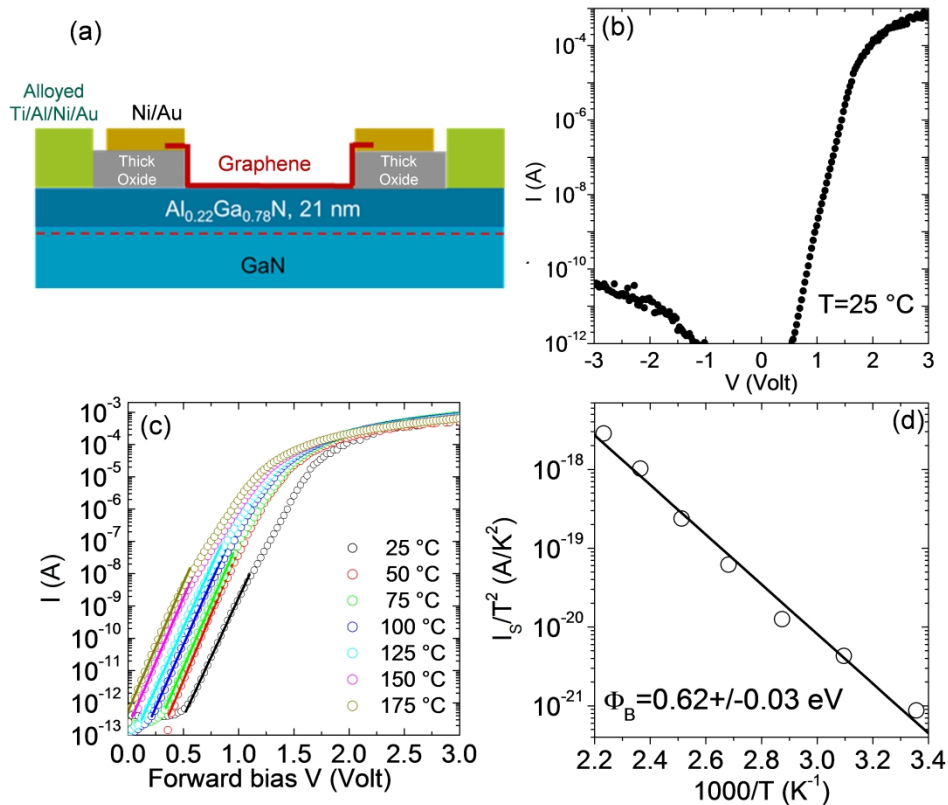


Fig.7 (a) Schematic cross-section of a Gr/AlGaN/GaN diode. (b) Current-voltage (I-V) characteristic measured on this diode at a temperature of 25 °C, under forward and reverse polarization. (c) Sequence of forward bias I-V curves measured at different temperatures, in the range from 25 to 175 °C. For each curve, a linear fit in the low bias region has been carried out to extract the saturation current value  $I_s$ . (d) Semilog-scale plot of  $I_s/T^2$  vs  $1000/T$  and linear fit of the data, from which the Gr/AlGaN Schottky barrier height value ( $\Phi_B = 0.62 \pm 0.03\text{ eV}$ ) is obtained.

928x843mm (120 x 120 DPI)

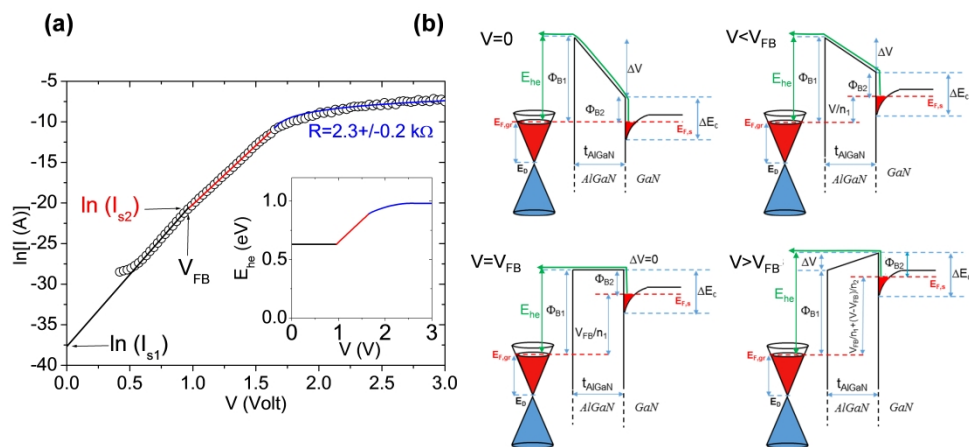


Fig.8 (a) Semilog-scale I-V characteristic of the Gr/AlGaN/GaN Schottky diode under forward bias polarization and (b) energy band diagrams of this system for different bias conditions.

1755x787mm (120 x 120 DPI)

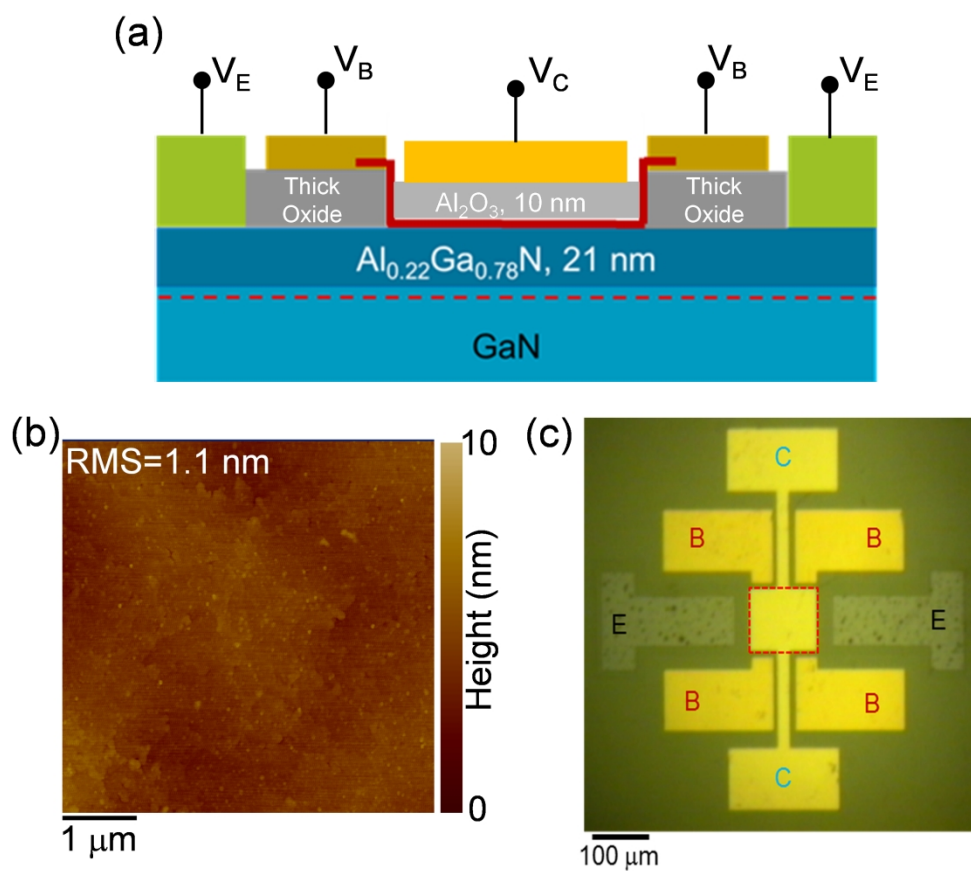


Fig.9 (a) Schematic cross-section of the hot electron transistor structure. (b) AFM image of the  $\text{Al}_2\text{O}_3$  base-collector barrier deposited on Gr. (c) Top-view optical microscope image of the HET device.

603x541mm (120 x 120 DPI)

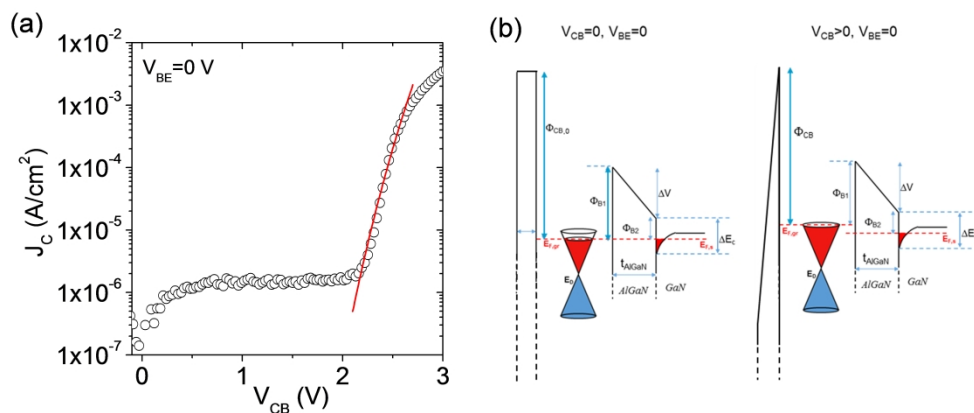


Fig.10 (a) Current-voltage ( $J_C$ - $V_{CB}$ ) characteristic of the base-collector diode (for  $V_{BE}=0$  V) and fit with Fowler-Nordheim tunneling model. (b) Energy band diagrams for the Gr/AlGaIn/GaN system at equilibrium (left panel) and for high enough  $V_{CB}$  allowing tunneling through the triangular barrier (right panel).

1026x503mm (120 x 120 DPI)



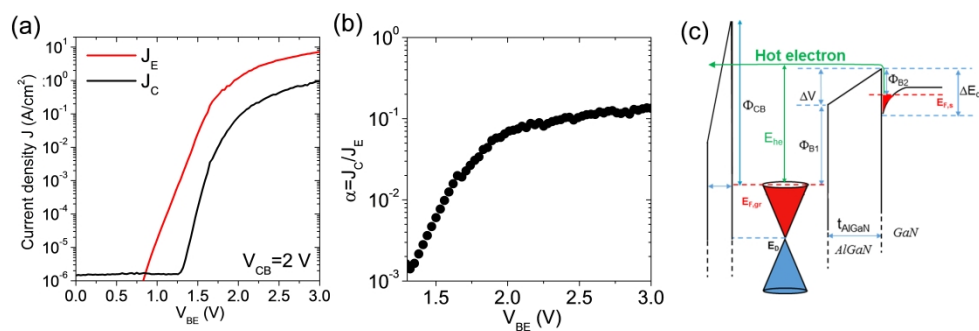


Fig.11 (a) Emitter ( $J_E$ ) and collector ( $J_C$ ) current densities measured in the common base configuration ( $V_B=0$  V) as a function of the emitter-base bias ( $V_{BE}$  from 0 to 3 V) and for a fixed collector bias  $V_{CB}=2$  V. (b) Common base current gain of the transistor. (c) Band diagram illustrating the hot electron injection and transit in the base and base-collector barrier for the experimental conditions in (a).

1722x666mm (120 x 120 DPI)

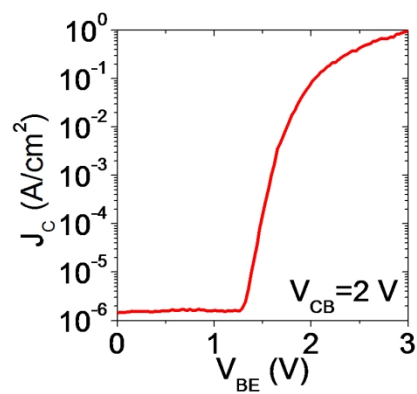
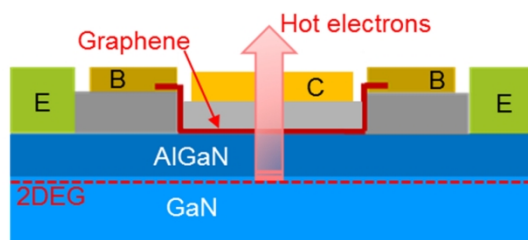


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