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# Germanium arsenide nanosheets applied as two-dimensional field emitters

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**Abstract**. The IV–V groups binary compound germanium arsenide (GeAs) is a semiconductor that can be easily exfoliated in very thin nanosheets and is characterized by a band gap ranging from 0.6 eV (bulk form) up to 2.1 eV (monolayer). We investigate the field emission characteristics of exfoliated multilayer GeAs nanosheets by means of a tip-anode setup, where a nanomanipulated W-tip is positioned in front of the GeAs emitting layer at nanometric distance, all controlled inside a scanning electron microscope. We demonstrate that GeAs multilayers are suitable to develop electron sources, with turn-on field of the order of $10^2$ V$\mu$m$^{-1}$, and field enhancement factor of about 70.

## 1. Introduction

The discovery of graphene [1] has triggered the research activity towards the two-dimensional (2D) materials, including transition metal dichalcogenides (TMDs), which are considered the best candidates for applications in nanoelectronics and optoelectronics [2–5]. For instance, $MoS_2$ is the most investigated TMD monolayer, with a direct band gap of 1.9 eV, already exploited as field effect transistor and photodetector [6–9].

More recently, the research activity is focused on binary compounds of IV and V groups, such as orthorhombic SiP and $GeAs_2$ or monoclinic SiAs, GeP or GeAs. In particular, GeAs is widely investigated because of its high in-plane anisotropy [10]. Moreover an interlayer cohesion energy as small as 0.191 eV atom$^{-1}$ favors easy exfoliation to produce very thin layers. Interestingly, GeAs is a semiconductor with a large direct band gap of 2.1 eV for the monolayer that reduces for multilayers down to a quasi-direct band gap of 0.6 eV for the bulk material.

Profiting of the high aspect ratio due to the sharp edges of thin layers, GeAs can also be exploited for field emission (FE) applications, in order to develop electron sources for vacuum electronics, flat-panel displays, etc. [11,12]. Field emission is a quantum tunneling phenomenon: electrons can escape from a conducting material, either metal or semiconductor, when a strong electric field (of the order of several kV/μm for flat surface) is applied. Electrons are emitted by a cathode (the emitting surface) towards the anode by travelling through the vacuum potential barrier that is made triangular and thin by the strong electric field, favoring the tunneling process.

The advantage of using nanostructures for FE purposes is related to the high aspect ratio of the nanostructures that causes significant enhancement of the applied electric field in proximity of any apex, edge, protrusion of the surface. Consequently, in recent years several nanostructures have been investigated for their potential applicability as field emitters, such as carbon nanotubes[13–17], graphene[18–21], nanoparticles[22,23], nanopillars[24–27], nanowires[28–30], nanoflowers[31], 2D TMDs[32–38].

Here, we report the study of FE properties of GeAs nanosheets obtained from bulk single crystals by mechanical exfoliation. Electrical properties of the material were first characterized in field-effect transistor (FET) configuration by using the silicon substrate as back-gate, and two electrodes contacting the nanosheet as source and drain. Then, by retracting one metallic tip, a high positive voltage is applied to the suspended anode to characterize the FE properties of the GeAs nanosheet.

## 2. Materials and Methods

The crystal structure of the IV–V groups GeAs layered compound belongs to the C2/m(12) space group (centrosymmetric monoclinic): As atoms are coordinated to three Ge atoms; Ge atoms are coordinated to three As atoms and to another Ge atom (see figure 1a).

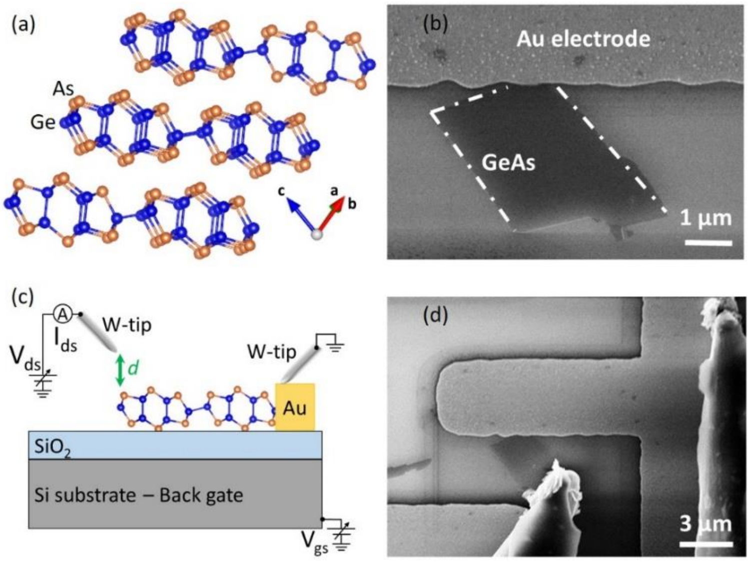


**Figure 1.** (a) Atom arrangement of GeAs. (b) GeAs nanosheet contacted by a metal lead (SEM imaging). (c) Schematic of the measurement setup, with a probe tip landing on the gold electrode and a second probe tip that can be retracted to work as anode in the FE configuration. (d) SEM image of the GeAs nanosheets with the two tungsten tips approached to form the FET configuration.

GeAs nanosheets, used in this study, were obtained by standard scotch-tape mechanical exfoliation from a GeAs single crystal and then they were transferred on a p-Si/$SiO_2$ substrate (300 nm thick oxide). Nanosheets were identified and characterized by means of optical microscopy, Raman spectroscopy and atomic force microscopy. Selected nanosheets (thickness ~12 nm, i.e., 20 layers) were then contacted by metal leads (Ni-5nm/Au-50nm) fabricated by electron beam lithography. In figure 1b we report the scanning electron microscope (SEM) image of a GeAs nanosheet that is contacted by one metal lead. This configuration is suitable for FE measurements because the metal pad allows a good ohmic contact to the emitting layer (cathode) while the anode is realized by a tungsten tip (see figure 1c). The image in figure 1d shows the tungsten tips position.

The experimental setup used for electrical measurements is realized by a Zeiss LEO 1430 SEM working at $10^{-6}$ torr and room temperature, with two piezo-nanomanipulators for precise positioning of metallic tips, electrically connected to a Keithley 4200 semiconductor characterization system. When both electrodes are in contact with the GeAs nanosheet, the FET configuration is realized.

## 3. Results

We first characterized the FET device by approaching both tips (one on the gold pad and one directly on the GeAs flake), working as source and drain, and by using the silicon substrate as back-gate (see the inset of figure 2a for a schematic of the FET device). In figure 2a we show the $I_d - V_{ds}$ characteristics measured in the gate voltage range between -80V and +80V using a $V_{gs}$ step of 10 V. We notice a slight non-linearity probably due to asymmetric contacts [39,40] and a hole conduction behavior since the device current increases for negative gate voltages. In figure 2b we also show the $I_d - V_{gs}$ characteristic, measured at fixed $V_{ds}$, that confirms hole conduction and current modulation. Moreover, the hysteresis is due to charge traps[41]. From figure 2b we estimated the mobility as $\mu = 0.6\ cm^2V^{-1}s^{-1}$.

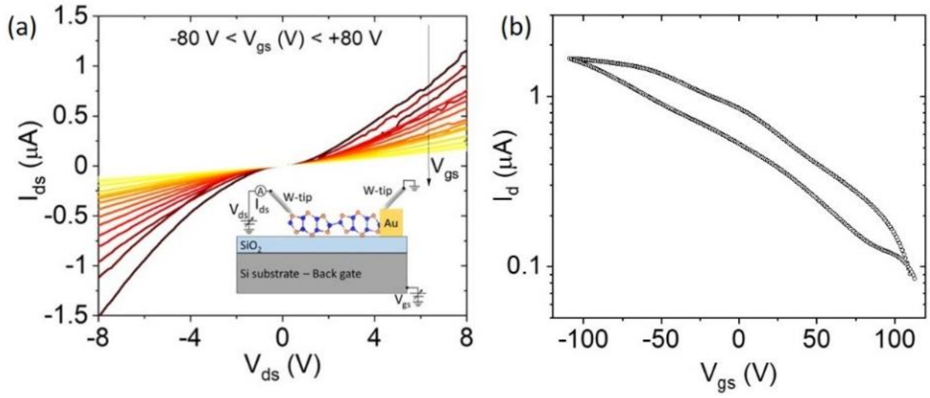


**Figure 2.** Electrical characterization of GeAs nanosheet in FET configuration. (a) $I_{ds} - V_{ds}$ curves for various back-gate voltage voltages $V_{gs}$. In the inset, schematic of FET configuration with both tips contacting the GeAs nanosheet. (b) Transfer characteristic $I_{ds} - V_{gs}$ measured in a complete voltage sweep loop evidencing current modulation and hysteresis.

To perform FE characterization of the GeAs we then retracted the tungsten tip that was directly contacting the nanosheet. By profiting of the precise piezo-driven nanomanipulator, we positioned the (anode) tip 400 nm above the GeAs edge. Then, by applying positive voltage sweep up to 110V on the suspended anode, we succeeded in extracting electrons from the GeAs nanosheet. Indeed, in figure 3a we observe (on linear scale) that the current starts to raise exponentially at certain turn-on voltage. To better identify such value, we plot in figure 3b the I-V characteristic in log-scale. We notice that the FE phenomenon starts at about 50 V and the current grows exponentially for three orders of magnitude up to few nA. Below 50 V, the measured current corresponds to the floor noise of our experimental setup and it is of the order of pA.

To analyze the experimental data, we can consider the Fowler-Nordheim theoretical framework that considers the simple system of a planar metal cathode at 0 K temperature. The system is described as one-dimensional free electron model and the tunneling probability is obtained in the Wentzel-Kramers-Brillouin approximation [42]. Despite its simplicity, FN theory has been demonstrated to be useful in first approximation to correctly identify the FE parameters also for nanostructures, and the current is

$$I = S \cdot A\phi^{-1}(F)^2 exp\left[-B\, \phi^{3/2}(F)^{-1}\right] \quad (1)$$

where $S$ is the surface, $\phi$ = 4.0 eV is the work function, $A = 15.4 \cdot 10^{-7} eVAV^{-2}$ and $B = 6.83\ eV^{-3/2}nm^{-1}V$ are constants, $\beta V/kd = F$ is the local electric field depending on $\beta$ (field enhancement factor), $V$ is the applied voltage, $d$=400 nm is the anode-cathode distance and $k \sim 1.6$ is a geometrical factor due to the tip-shaped anode.

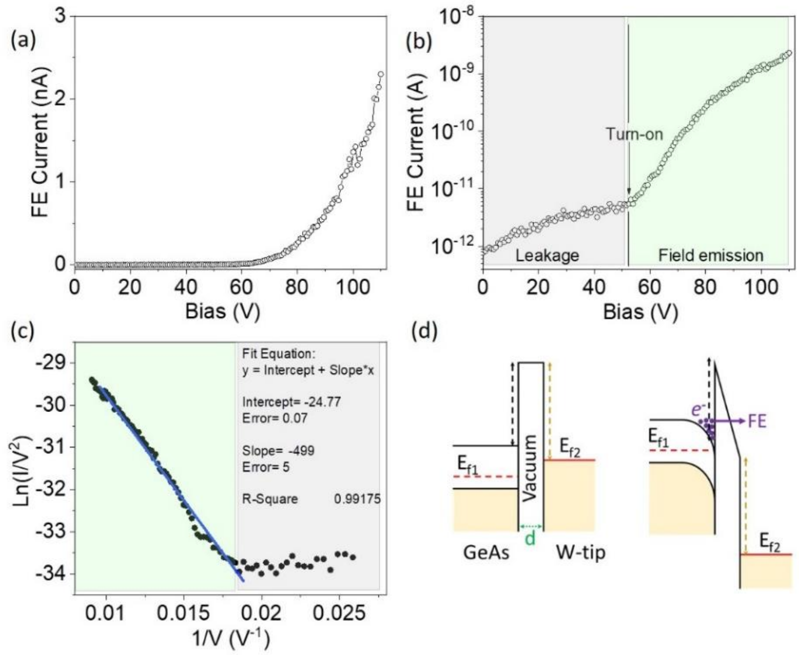


**Figure 3.** (a) FE current-voltage (I-V) curve (linear scale) measured with the anode tip positioned 400 nm above the GeAs surface. (b) The I-V curve is shown on semi-log scale to evidence the turn-on voltage at which the FE current starts to rise exponentially. (c) Fowler-Nordheim plot with linear fit (solid blue line) to demonstrate the FE nature of the measured current. (d) Band diagram for the system GeAs/vacuum/W-Tip before and after the application of a (positive) bias on the tungsten anode-tip.

According to the current equation obtained within the FN theory, we expect that the so-called FN-plot, i.e. $\ln(I/V^2)$ versus $V^{-1}$, has a linear dependence, and this test is typically performed to confirm that the measured current is originated by FE phenomenon. Consequently, in figure 3c we show the FN plot for the data reported in figure 3a and 3b. We notice that the FN plot is linear, the solid line representing the best fit. Moreover, from the slope m of the FN plot we can calculate the field enhancement factor as $\beta = -Bkd\phi^{3/2}m^{-1} \approx 70$. We notice that the turn-on field is of the order of $10^2$ $V\mu m^{-1}$, thus comparable to the values reported for other two-dimensional TMD materials. We need also to consider that GeAs is p-doped as demonstrated by the transistor characterization. Consequently, in order to extract electrons, it is necessary to apply a field high enough to cause band bending and inversion (see figure 3d), in order to increase the number of available electrons.

## 4. Conclusions.

We performed experimental investigation of electrical and FE properties of exfoliated GeAs nanosheets on $Si/SiO_2$ substrate. The field effect transistor configuration evidenced a p-doping of GeAs, with 0.6 $cm^2V^{-1}s^{-1}$ carrier mobility and a small hysteresis in the transfer characteristics due to charge trapping/detrapping. We then demonstrate that by applying a high electric field, a relevant band bending can cause the inversion providing excess electrons for the field emission. We also report relevant FE parameters as turn-on field of the order of about 100 V/μm and field enhancement factor of about 70. These experimental results confirm the suitability of GeAs nanosheets as field emitters.

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