

Supplementary Information

Low Schottky barrier height and transport mechanism in Gold-Graphene-Silicon (001) heterojunctions

Jules Courtin^a, Sylvain Le Gall^b, Pascal Chrétien^b, Alain Moréac^a, Gabriel Delhaye^a, Bruno Lépine^a,
Sylvain Tricot^a, Pascal Turban^a, Philippe Schieffer^a and Jean-Christophe Le Breton^{a†}

*Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes, France. Département
Matériaux et Nanosciences, Institut de Physique de Rennes, UMR 6251, CNRS-Université de Rennes 1, Campus
de Beaulieu, Bât 11E, 35042 Rennes cedex, France.*

*Group of electrical engineering Paris (GeePs), CNRS, CentraleSupélec, Univ. Paris-Sud, Sorbonne Université, 11
rue Joliot-Curie, 91192 Gif-sur-Yvette CEDEX, France*

S1 - Graphene transfert protocole

Single layer graphene realized by Chemical Vapor Deposition on copper was purchased from Graphenea©. A 200nm Polymethyl methacrylate (PMMA) layer was then deposited on top. After PMMA coating, copper was etched in a FeCl₃ solution until no metallic copper could be seen and the floating PMMA/Graphene was rinsed several times in deionized water. Graphene was then transferred onto a Si substrate. The Si was degrease in acetone and isopropyl alcohol followed by 30 minutes UV/Ozone cleaning leading to the formation of a thin SiO₂ layer of about 1nm. The floating PMMA/Graphene was deposited onto the oxidized silicon and left to dry 30 minutes at 50°C followed by 15 minutes at 135°C. After removal of PMMA in acetone, samples were introduced under Ultra High Vacuum (UHV) where they were annealed at 300°C for 3 hours to remove resist residues. Samples were then taken out of the UHV chamber for a final oxide etch in 2% hydrofluoric acid (HF) before re-introduction under UHV. Au was then sequentially deposited at room temperature by

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molecular beam epitaxy with an effusion cell at a rate of 0.2-0.4 Å/min for submonolayer thicknesses and 1-2 Å/min otherwise.

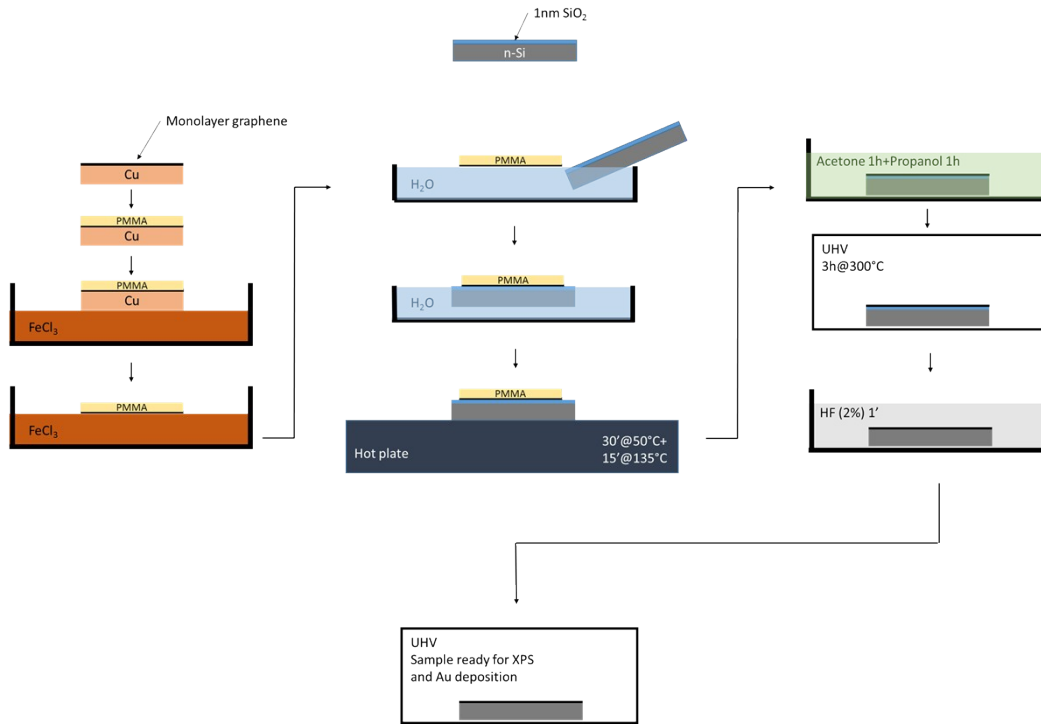


Figure S1: Graphene transfert process

S2 - Schottky Barrier Height XPS determination

In order to determine the Schottky Barrier height (SBH), the analyzer is first calibrated with a thick gold sample. We assume an energy difference of 84.0eV between the Au4f7/2 peak and the Fermi level¹. The SBH ϕ_B is then determined as follows:

$$\phi_B = (\Delta(VB - Si2p) + E_g) - BE(Si2p)$$

Where $\Delta(VB - Si2p)$ is the energy difference between the Si2p core level and the valence band, E_g is the Si bandgap and $BE(Si2p)$ is the measured binding energy of the Si2p core level referenced to the Fermi level. $\Delta(VB - Si2p)$ is set to 98.74eV² and the bandgap to 1.12eV.

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S3 - Raman Characterization

The studies by Micro-Raman Spectroscopy were carried out on a LabRAM HR800 (Horiba Scientific, Jobin-Yvon). The HR800 system is a high-resolution spectrometer fitted with a confocal microscope coupled to different lasers. Our measurements were performed with a 532 nm laser as excitation source. The laser spot size was approximately 1 μm in the focal plane of the x100 objective. An optical density filter was used to decrease the laser power to avoid sample damage at the focus point of the laser on the sample: under the objective, the excitation laser power focused was approximately -100 mW. The spectral dispersion was around 1 cm^{-1} per CCD pixel. These Raman experiments were performed at room temperature.

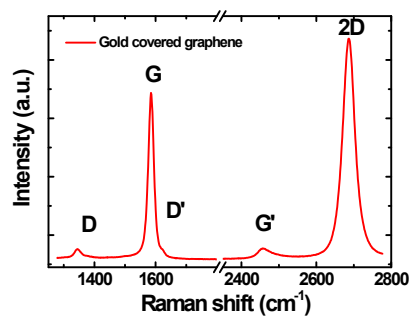


Figure S2: Raman spectrum of gold protected graphene.

The spectrum figure S2 represents a scan of a Au/G/Si junction after UV/Ozone oxidation. The characteristic peaks of graphene monolayers are indicated.

S4 - Optical image, AFM image and resistance histograms of the areas under study

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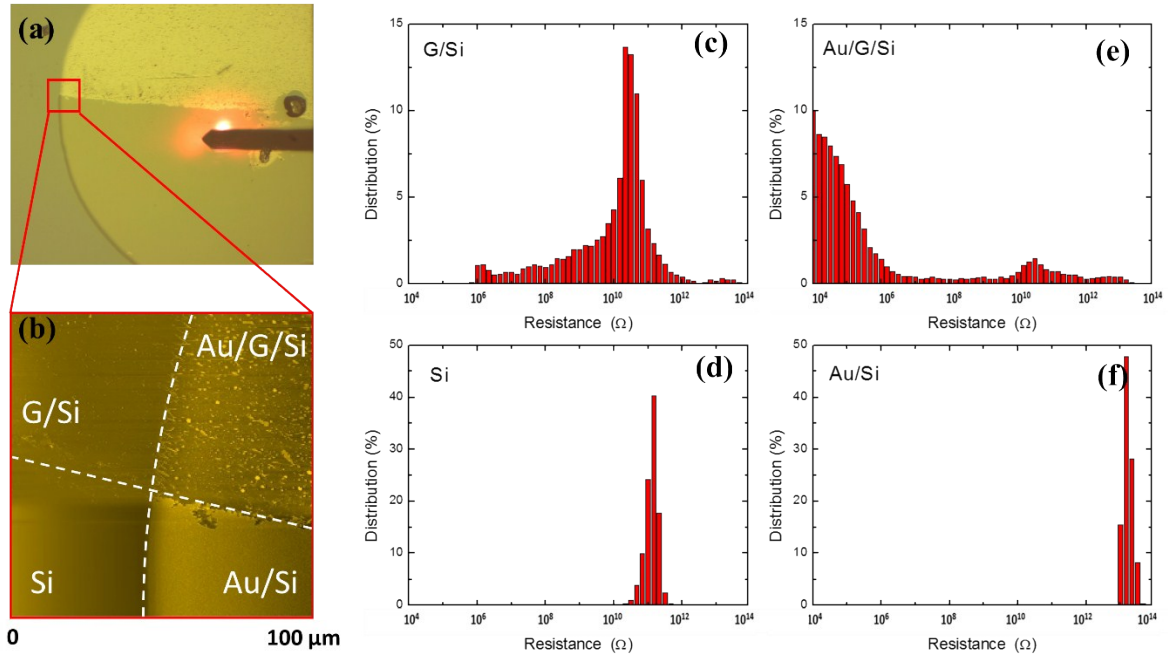


Figure S3: (a) Optical image of the area under study. (b) AFM image corresponding to figure 5a in text and (c-f) resistance histograms of the 4 areas.

- G/Si: the resistance is centered on $5.10^{10} \Omega$ with a broad distribution. Note that this area consists of UV oxidized graphene on silicon. The silicon surface may also be oxidized underneath.
- Au/G/Si: The shape of the resistance distribution for the Au/G/Si is similar to a half Gaussian curve centered on $10^4 \Omega$. Lower resistance values cannot be measured with our apparatus. Higher resistive spots are also observed and related to surface roughness. They are therefore attributed to resist residues.
- Si: this area is covered neither by graphene nor by gold. This surface is therefore exposed to a UV/Ozone oxidation. This measurement corresponds to the resistance of a p++ diamond tip/SiO₂/Si. The work function of the diamond tip (5.21eV) is lower than the work function of gold (5.45eV), we therefore expect a lower SBH over this area. A lower SBH may compensate the additional resistance due to the SiO₂ tunnel barrier³. This might be the reason why the resistance is lower on this area than on the Au/Si area.

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- Au/Si: the large resistance observed here is consistent with the high SBH of Au/Si, although we expect SiO₂ to be present on the surface as observed by XPS.

References

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- (2) Himpsel, F. J.; Hollinger, G.; Pollak, R. A. Determination of the Fermi-Level Pinning Position at Si(111) Surfaces. *Phys. Rev. B* **1983**, *28* (12), 7014–7018.
- (3) Zhou, Y.; Ogawa, M.; Han, X.; Wang, K. L. Alleviation of Fermi-Level Pinning Effect on Metal/Germanium Interface by Insertion of an Ultrathin Aluminum Oxide. *Appl. Phys. Lett.* **2008**, *93* (20), 202105. <https://doi.org/10.1063/1.3028343>.