

Supplementary information

Scalable, flexible and high resolution patterning of CVD graphene

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1. Ink-jet printing

A solution of 1mg/ml AlCl hexahydrate in Ethanol was prepared. 10ml of this solution was filled in an empty ink-cartridge of a commercial ink-jet printer (Epson Artisan A50). The copper foil was attached to a letter sized paper and patterns were printed.

2. Contact-printing

Molding of grating

PDMS elastomer (Sylgard 184) was prepared by mixing the two components in a ratio of 1:10. The material was then cast onto the exposed pit-structure of a DVD. Bubbles were removed by applying a mild vacuum for 30 minutes. The PDMS was then cured at 100C for 20 minutes.

Patterning

A solution of 1mgAlCl₃ in 1ml Ethanol was prepared. 500ul of this solution was deposited onto a 1x1cm grating. After a brief drying period (1min) the stamp was pressed onto Cu foil. The patterned Cu foil was then subjected to CVD growth.

3. Characterization of passivation layer

The chemical properties of the passivation layer were investigated after annealing by X-ray photoelectron spectroscopy (XPS) and Figure S1 shows an XPS spectrum of the Al 2p peak region. The absence of a peak at 73.7 eV indicates that no metallic aluminum is present. The good fit of the main feature to one symmetric peak indicates that no undercoordinated Aluminum is in the oxide and that the alumina is indeed Al_2O_3 . The small side peak at 77.3 eV is identified as the 3p peak of copper oxide originating from the oxidized substrate.

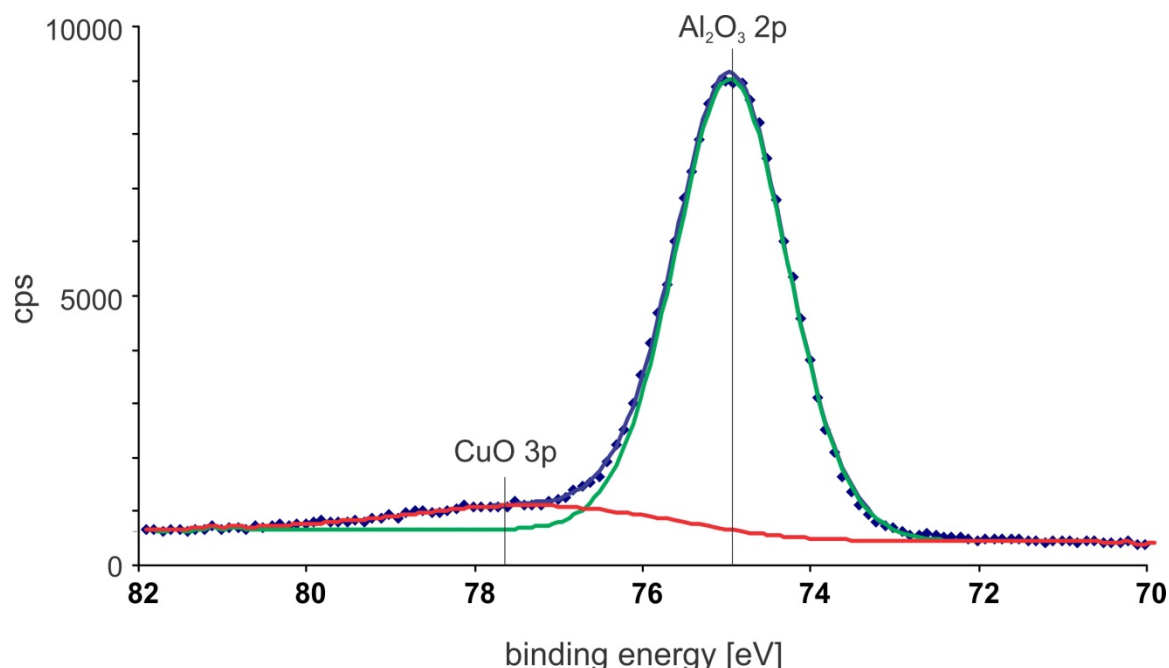


Figure S1. XPS spectrum of the deposited passivation layer after graphene growth with indication of the position of metallic aluminum and identification of the occurring peaks

Based on the above presented process, graphene patterns were generated through lithographical patterning of Al_2O_3 on Cu foil. Wet chemical removal of the alumina passivation layer during transfer proved difficult which was attributed to the transformation of amorphous Al_2O_3 into crystalline corundum under the growth conditions. Variation of the growth process or etching procedure is expected to overcome this issue. The presence of the passivation layer, however, was not detrimental to the experiments but proved useful for alignment of the patterned graphene on the target substrate. **Scenarios** could be conceived where a thin, high quality dielectric layer could prove useful, i.e. as spacers in LCDs. The patterned graphene was then transferred onto a Si/SiO₂ substrate and an optical micrograph is shown in Fig. 2(a). The high resolution of the obtained pattern can be analyzed by atomic

force microscopy (AFM) and clear boundaries between the passivation layer and the surrounding area can be seen in Fig. 2(b).

4. Electrical Transport across passivation barrier

A graphene/Al₂O₃/graphene device was fabricated with a barrier length of 1mm and a channel width of 5mm. The measured current is in the sub-nA range which indicates the high quality of the dielectric barrier.

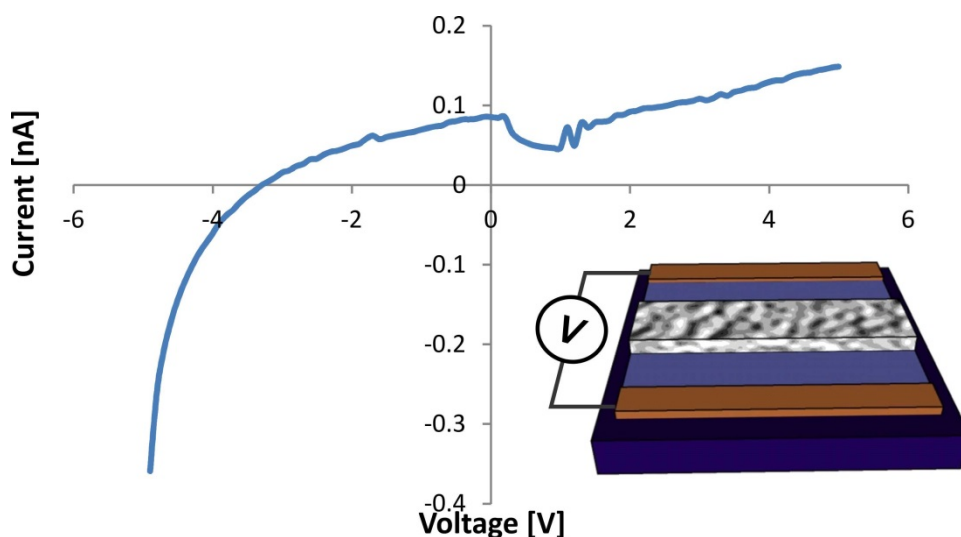


Figure S2. Current-Voltage plot across aluminum oxide barrier, (inset) schematic of device

5. Characterization of graphene

The presence and quality of graphene was analyzed by Raman spectroscopy. A map was obtained by taking one Raman spectrum every 100x100nm and Fig. S3(c) shows the spatial variation of the G'-band peak intensity in a region where graphene surrounds a passivated area. The G'-band feature is enhanced in graphene because of a double resonance process and can be considered a characteristic feature of graphene¹¹. The passivation layer pattern is clearly distinguishable by the absence of a G'-band feature as well as other Raman peaks that occur for graphitic materials (Fig. S3(d)). The background in the Al₂O₃ Raman spectrum is assumed to originate from defect-induced photoluminescence of the material¹².

The high quality of the graphene grown in the unpassivated areas can be inferred from the sharp Raman peaks and the low defect induced D-band Raman feature. The D-band intensity was found to increase during a transfer related annealing step and thus does not only reflect the intrinsic defect density.

Macroscopic Hall measurements in van-der-Pauw geometry were performed to characterize the electronic properties of the graphene films. A sheet resistance of $1000\Omega/\square$ and a macroscopic Hall mobility of $650\text{cm}^2/\text{Vs}$ were obtained that is comparable to other CVD graphene films grown with the same CVD procedure.

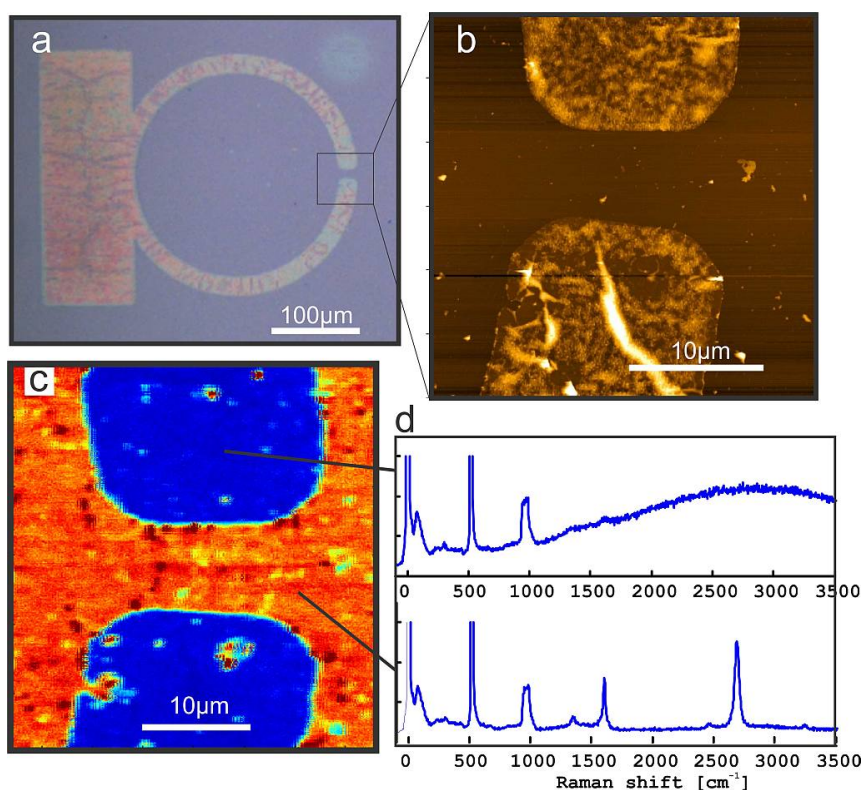


Figure S3. a) Optical micrograph of patterned structure, b) magnified AFM image of structure, c) Raman map of the 2D band of the same region, d) representative Raman spectra of passivated region (top) and exposed region (bottom)

The transition region between the passivation layer and the graphene was investigated by Raman spectroscopy (Fig. S4). It was found that the sharpness of the transition exceeded the resolution of the measurement system and the finite slope observed was caused by the Gaussian beam shape of the micro-Raman tool.

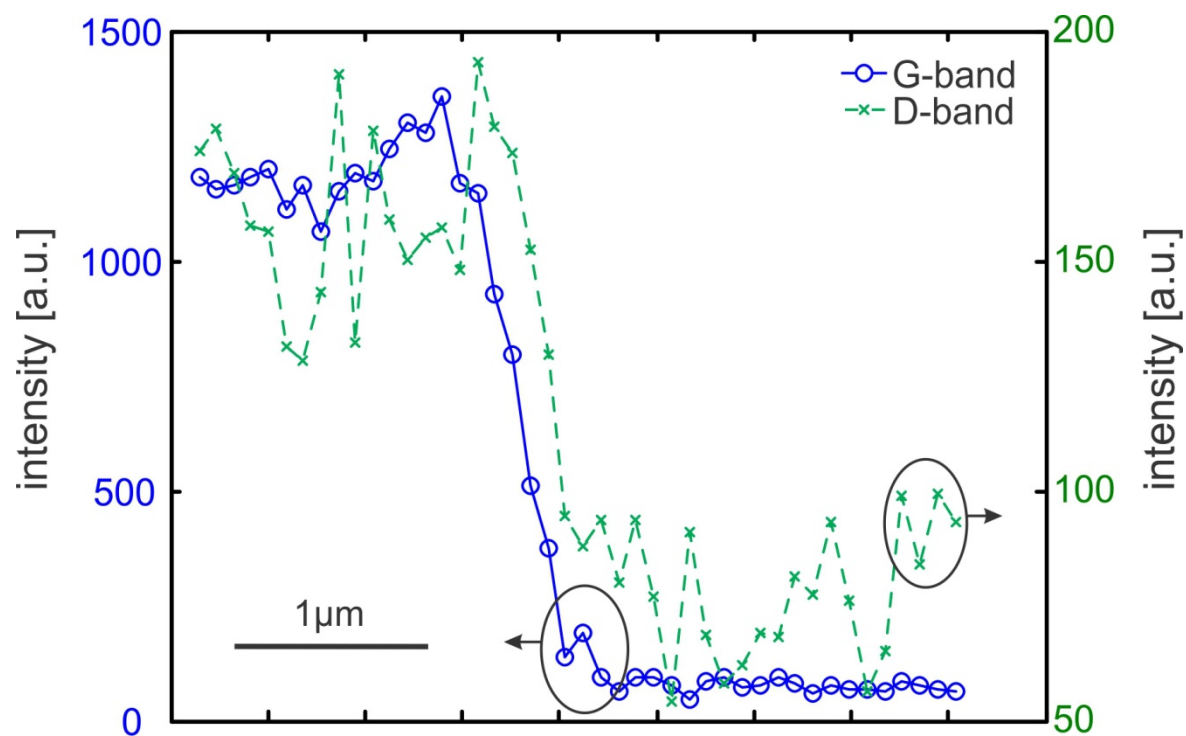


Figure S4 Raman G-band (o) and D-band (x) peak intensities of transition region between graphene (right) and passivation layer (left)

The absence of an increased Raman D-band intensity in the transition region (Figure S4) suggests that higher quality edges are formed compared to those formed with traditional lithographical approaches⁹³. This property would be promising for improving the electrical performance of nanoribbon-based devices.