Supplementary Information

Formation of nanocrystalline graphene on germanium

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Content

TGA Analysis

Figure S1 (a) shows the mass loss versus temperature and it's first derivative. A 30 µl drop of S1805 has first been annealed in vacuum at 60°C for 10min to remove the propylene glycol monomethyl ether acetate (PGMEA) solvent, which makes up 80% of the resist S1805 photoresist (see Table S1). TGA measurements have then been carried out under nitrogen flow starting from 30°C. Of the remaining 20% of the original material, the resist loses stepwise over 60% weight upon heating until 800°C. For comparison we have prepared a silicon substrate spin-coated with a thin resist layer and measured the pressure rise during heating in vacuum (Fig. S1 (b)). The data shows the pressure increasing with temperature with a peak around 400°C, likely related to the third step in the TGA data.

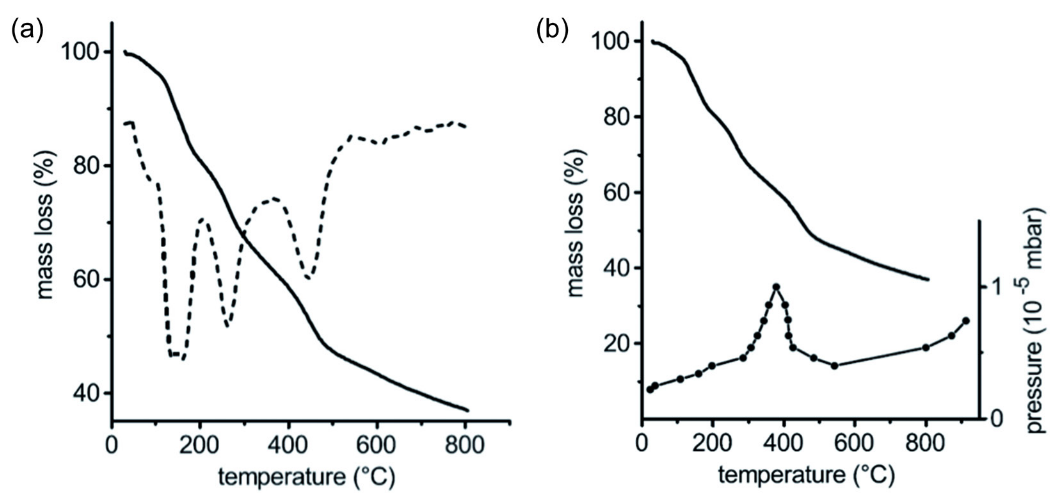

Fig S1 High temperature stability of resist S1805: (a) Mass loss under nitrogen flow (full line). The dashed line is the first derivative. (b) Pressure rise during heating in vacuum (full dots) in comparison with the mass loss under nitrogen flow (full line).

Component Name	Composition (%)
Diazo Photoactive Compound	1.00-10.00
Fluoroaliphatic Polymer Esters	0.01-1.00
Mixed Cresol Novolak Resin	10.00-20.00
Electronic Grade Propylene Glycol Monomethyl Ether Acetate	81.00-86.00
Cresol	0.01-0.99

Table S1 Chemical Composition of the S1805 Photoresist.

NCG crystallite size from Raman analysis

The crystallite size of suspended graphene on germanium wafers of both orientations was derived from the full-width at half maximum (FWHM) of the Raman D and G peaks following the procedure of Riaz *et al.*[27]. In Fig. S2 the data is plotted in four panels for different temperatures and orientations. The calculated crystallite size was found to be in the range of 2-5nm depending on analyzing the D or G mode peak. The results are tabulated in table S2.

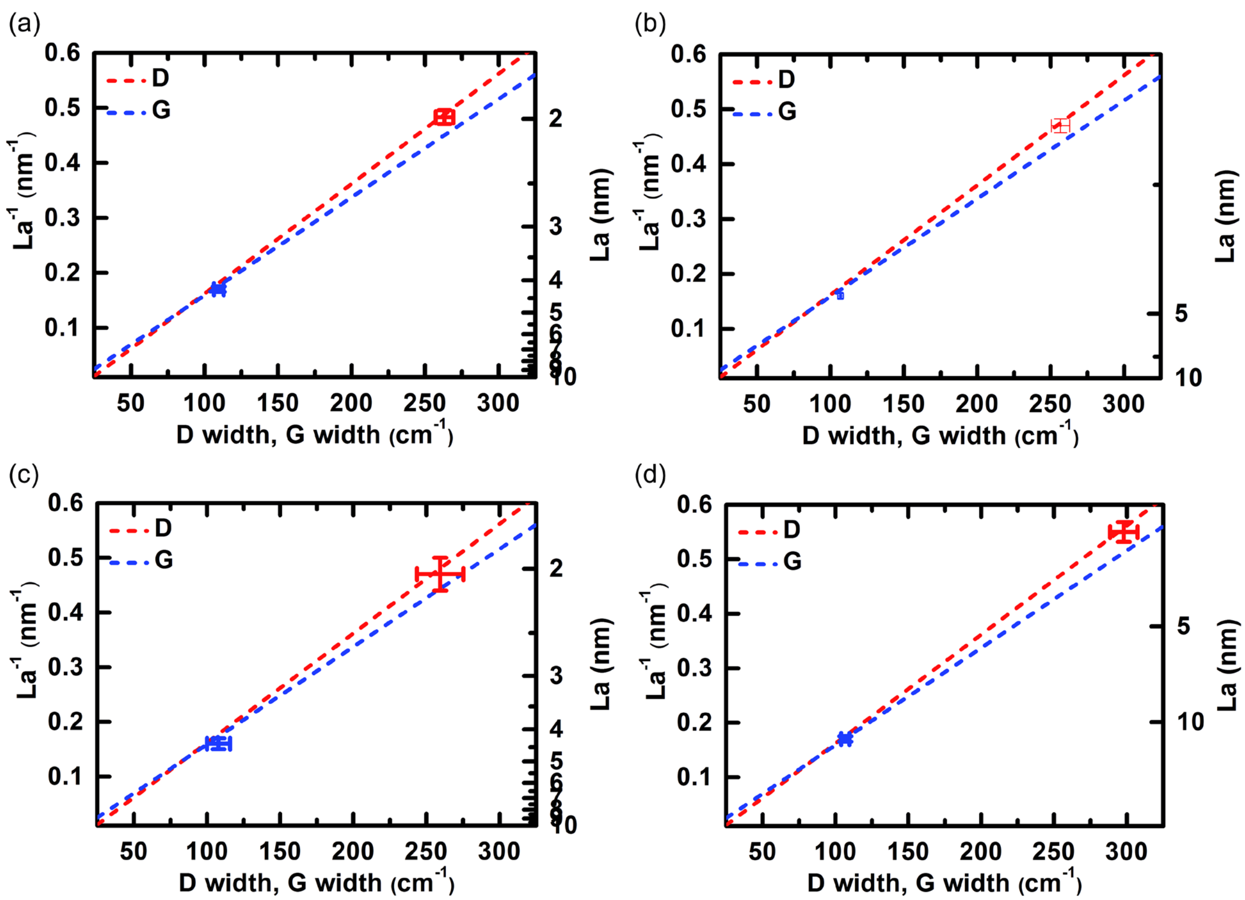

Fig S2 Crystallite size La derived from the with FWHM of the Raman D and G peaks of NCG on (110)-Ge at (a) 927°C, (c) 827°C, and (111)-Ge at (b) 927°C and (d) 827°C, respectively. The dashed lines are extrapolated correlations based on Cançado *et al*., Phys. Rev. B 76 (2007) 064304.

Temperature(°C)	Orientation	G,FWHM (cm^{-1})	D,FWHM (cm^{-1})	La_G (nm)	La_D (nm)
927	(110)	105.98±3.37	251.55±6.01	5.91±0.005	2.17±0.0125
927	(111)	107.67±2.82	245.50±7.04	5.87±0.005	2.12±0.014
827	(110)	106.05±7.88	284.71±15.85	5.91±0.01	1.86±0.03
827	(111)	108.34±2.81	285.88±9.38	5.81±0.05	1.85±0.018

Table S2 Crystallite size La_G and La_D derived from Raman D and G peak analysis, respectively.

XPS

Figure S3 (a) shows the C1s peak of NCG on (110)-Ge graphitized at 927°C, the reference is (110)-Ge only (Fig. S3 (b). The deconvoluted XPS C1s core level spectrum has three components. Peak 1 at 284.64 eV arises from aromatic layers in graphitic sp^2 configurations. Peak 2, at 285.93 eV, is assigned to the carbon atom being directly bonded to the oxygen in hydroxyl/phenolic configurations (C-OH). This corresponds to sp^3-hybridized carbon that is a representative of defective structure[21].The third peak which is located on the tail at 289.64 eV refers to the π-π* level transition[22].The sp^2 carbon fraction in the sample can be calculated by dividing the area underneath the C1s sp^2 peak by that of the entire spectrum[23], which yields 91%. The thickness of the NCG layer of 5.5 nm was determined via the attenuation of the XPS Ge3d signal with respect to the signal of a bare Ge substrate with an attenuation length of 3.6 nm as in Riaz et al., Nanotechnology 26 (2015) 325202.

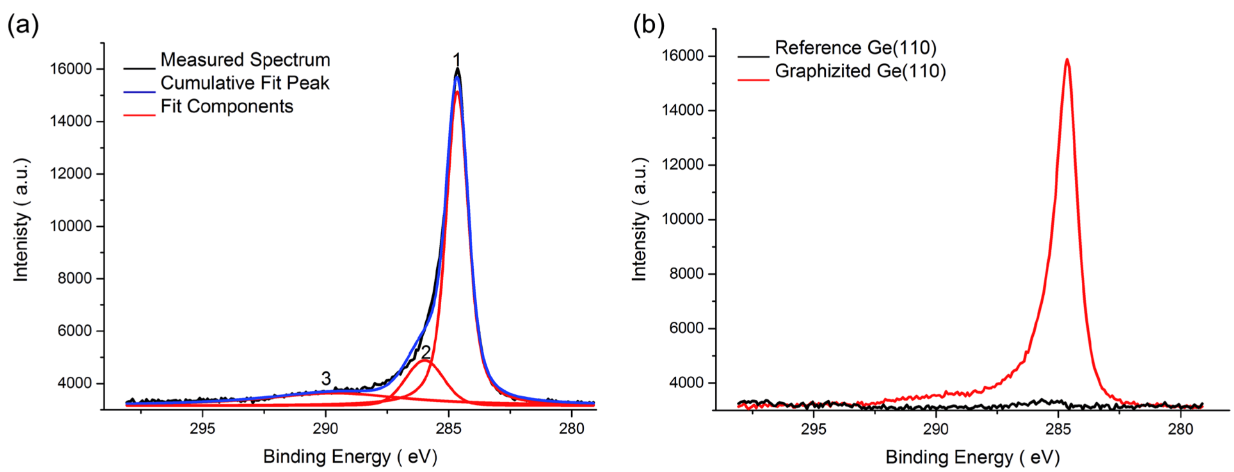

Fig S3 (a) Deconvolution of the XPS spectrum of graphitized (110)-Ge at 927°C. (b) Comparison between the XPS spectrum of a pristine wafer and graphitized (110)-Ge(110) at 927°C.

Scanning electron micrograph of annealed germanium without NCG

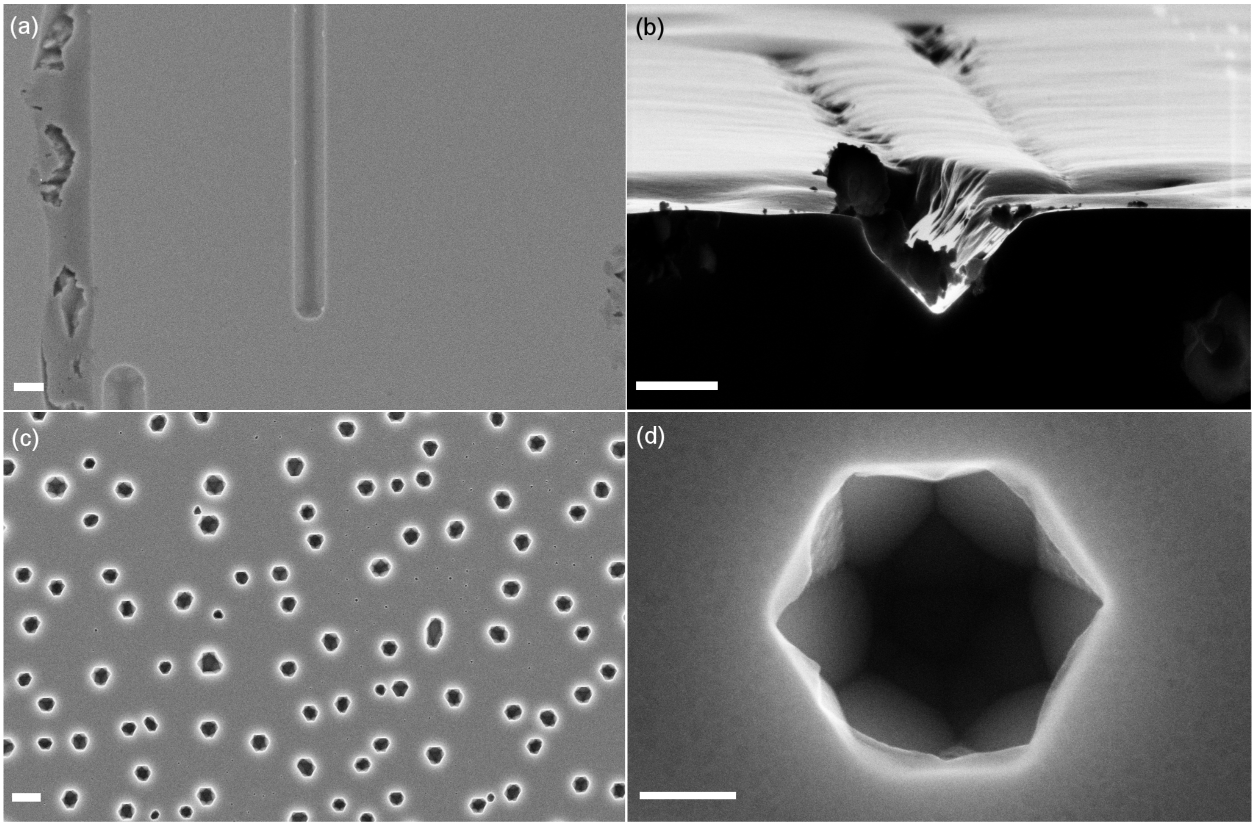

Fig S4 Scanning electron micrographs of cavities in (a) (110)-Ge and (c) (111)-Ge. (b) and (d) are corresponding higher resolution images. The cavities were formed during vacuum annealing of germanium without resist layer (no graphitization). Scale bars, 2 µm.

Additional Raman intensity map

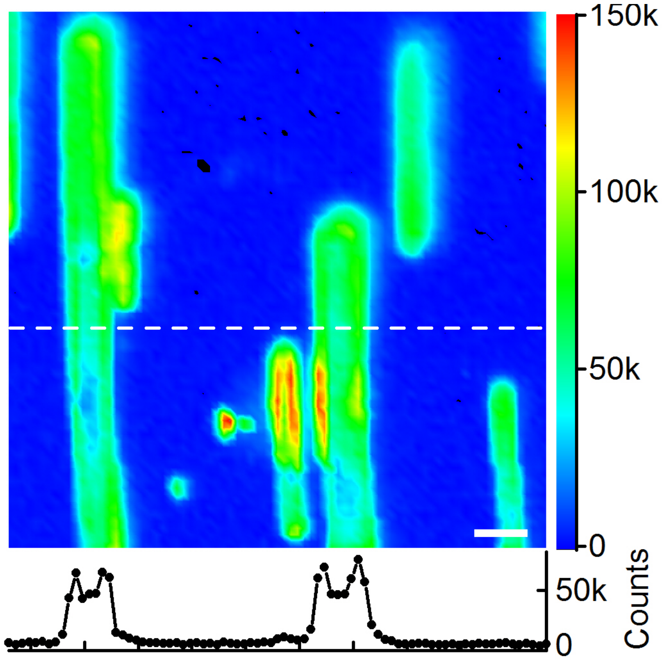

Fig S5 Raman intensity map of NCG on (110)-Ge. Regions of high intensity correlate with trenches in Ge. Plotted is the Raman signal integrated from 800-2000 cm^{-1}. The intensity profile cuts through the map along the dashed line. Scale bar, 2µm. The trenches appear bent at the bottom due to drift while scanning.

References

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