Investigating the quality of CVD-grown graphene on germanium using in-situ surface science methods

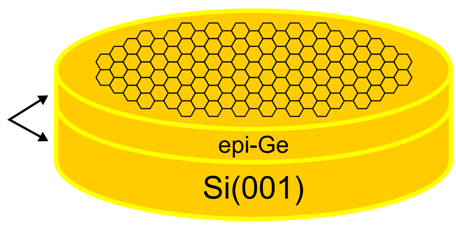
Andreas Becker,* Jarek Dabrowski, Mindaugas Lukosius, Christian Wenger
IHP – Leibniz-Institut für innovative Mikroelektronik, Frankfurt (Oder), Germany
*becker@ihp-microelectronics.com

innovations for high performance microelectronics

Why grow graphene on germanium?

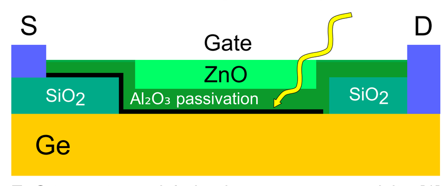
① Germanium grows epitaxially on silicon

This enables wafer-scale graphene growth on Ge/Si using commercial CVD reactors. Graphene forms monolayers on germanium due to the low carbon solubility of the substrate.



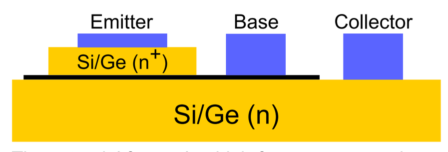
② Graphene/germanium junctions have potential use for devices

Photodetecting Schottky diode



ZnO top gate modulation increases responsivity. [1]

Graphene base heterojunction transistor (GBHT)

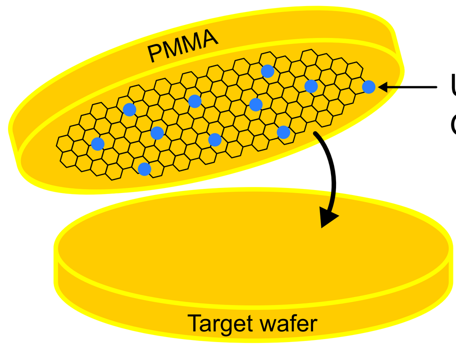


The potential for analog high-frequency operation stems from the short transit time of the thin base. [2]

[1] K. E. Chang et al. (2019): High-Responsivity Near-Infrared Photodetector Using Gate-Modulated Graphene/Germanium Schottky Junction. Advanced Electronic Materials, 5, 1800957.
[2] V. D. Lecce et al. (2015): Graphene base heterojunction transistor: An explorative study on device potential, optimization, and base parasitics. Solid-State Electronics, 114, 23–29.

③ Germanium does not contaminate CMOS processes

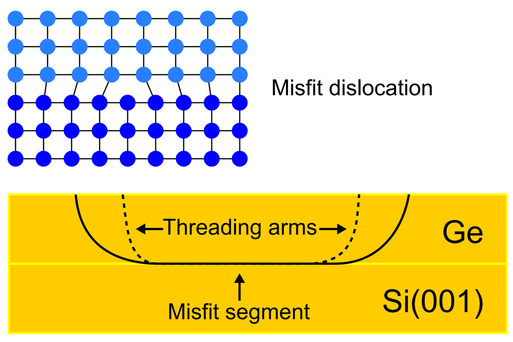
Hence, graphene can be delaminated and transferred to a target wafer.



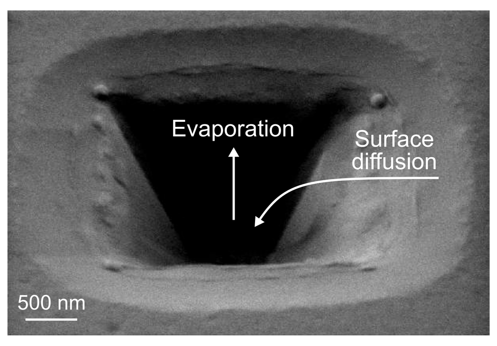
Etch pits form on germanium during annealing if the surface is carbon-contaminated.

During high-temperature annealing, germanium evaporates preferentially near dislocations. If air-borne carbon contamination inhibits surface diffusion, deep etch pits form. On a clean surface, diffusion refills such etch pits until a crosshatch pattern remains, which is the equilibrium morphology.

Removal of initial carbon contamination requires high-temperature annealing in pure molecular hydrogen and is the prerequisite for subsequent graphene growth. The surface morphology can be an indirect indicator of substrate cleanliness.

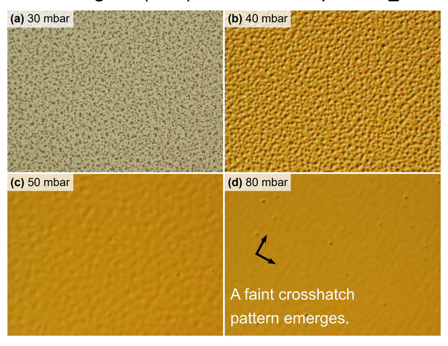


Scratches, mechanical stress and misfit at the Ge/Si interface are sources of dislocations.



SEM image of an etch pit in Ge(001), which formed during high-temperature annealing. Substrate diffusion into the pit is obstructed by step-pinning carbon contamination.

Annealing Ge(001) at 930 °C in pure H_2 for 60 min ...

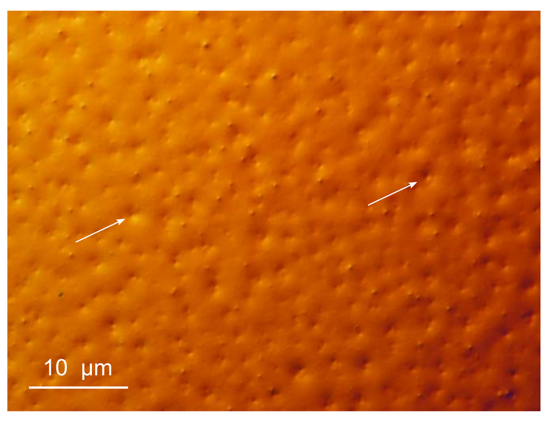


Optical micrographs showing the Ge(001) surface morphology after annealing at 930 °C in pure H_2 for 60 min at different pressures. A cleaner surface is associated with a flatter topography.

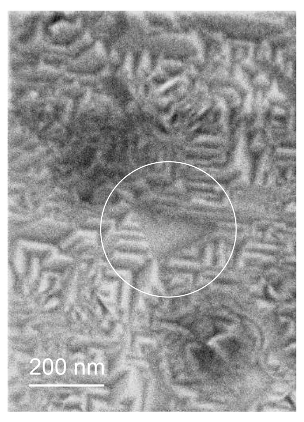
Fast graphene growth is required to prevent etch pit formation at high coverage.

Graphene growth on germanium seems to slow down at high coverage. While substrate can evaporate through small holes in the graphene layer, substrate diffusion is inhibited by Ge-C bonds at the graphene edges. In consequence, etch pits can form before the graphene layer is closed.

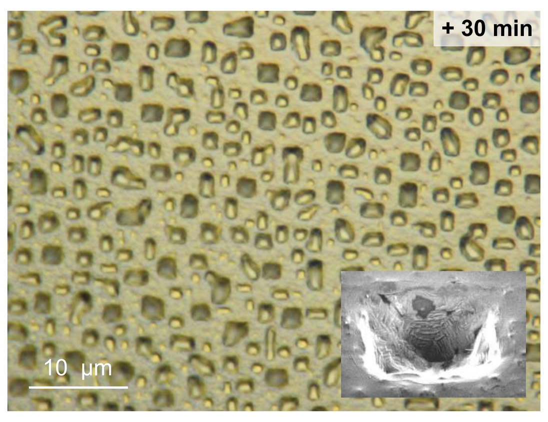
A sufficiently high precursor flow is required to close the graphene layer. Since a high precursor flow results in higher nucleation density, it would make sense to ramp up the precursor partial pressure gradually during the growth process.



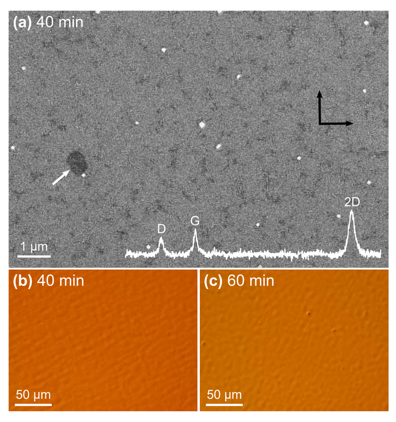
Optical micrograph showing topographic depressions of gr/Ge(001) after 60 min process time.



SEM reveals small holes in the graphene layer (unfaceted area) through which germanium may evaporate, ...



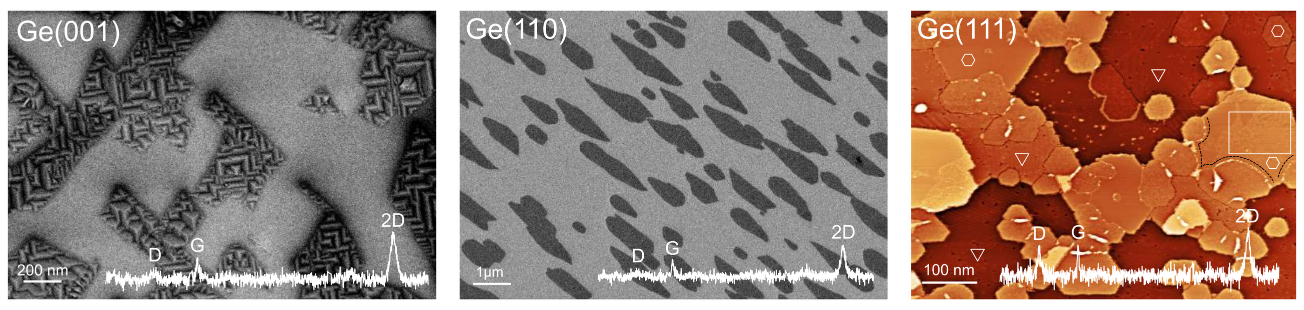
... which eventually leads to deep pyramidal etch pits forming during prolonged growth. Graphene sticks to the substrate and is pulled into the pit.



However, faster growth using a higher precursor flow prevents etch pit formation.

Graphene grain size is largest on Ge(110) and smallest on Ge(111).

Ge(001) forms well-known facets under graphene to minimize surface energy, which may result in low-quality grain boundaries and scattering of charge carriers due to graphene curvature. In contrast, graphene on Ge(111) and Ge(110) is flat. Graphene grains on Ge(110) are µm-sized, whereas the grain size on Ge(111) is the smallest.

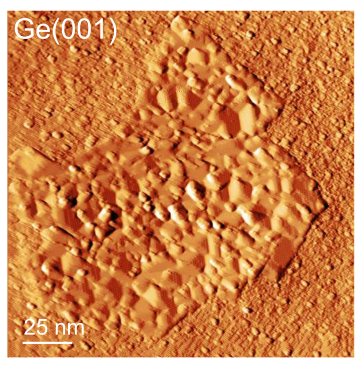


Grown at 930 °C

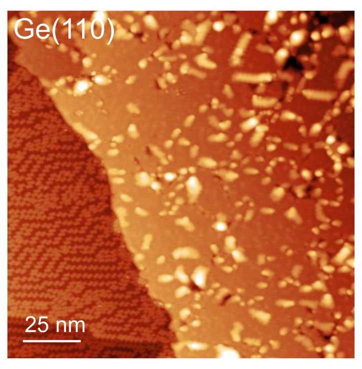
Intragranular defects limit the graphene quality at reduced growth temperature.

At reduced temperature of 850 °C, the graphene quality is limited by intragranular defects and not by grain size. On Ge(111), we observed that holes formed in the graphene layer. These holes seem close incompletely, resulting in point defects that are associated with topographic protrusions.

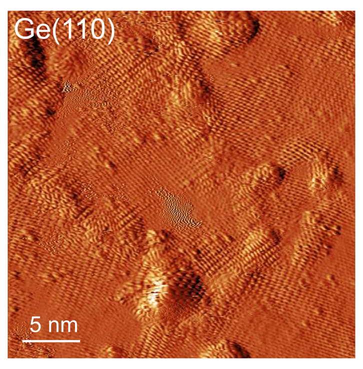
One reason why defects or holes are incorporated into graphene flakes during growth may be insufficient etching of defective carbon structures at the graphene edge. This is in line with the fringy shape of graphene islands.



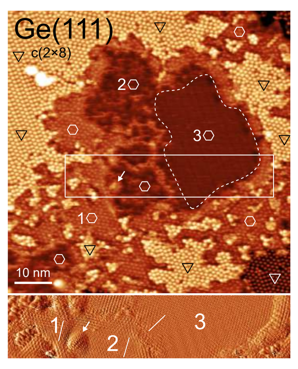
STM image of a graphene island showing disrupted substrate faceting.



Left: Ge(110) reconstruction; right: graphene layer with protrusions.



Defects in graphene on Ge(110), resolved by STM.

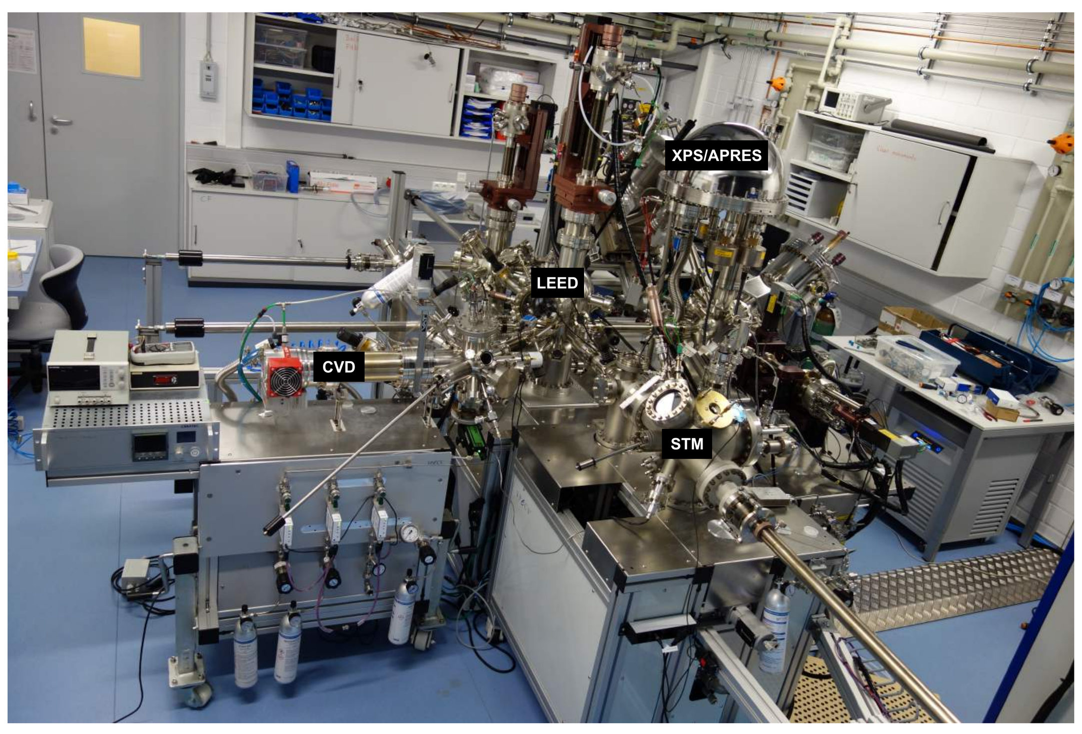


STM showing holes in graphene (⬡) where Ge(111) (▽) features are visible.

Grown at 850 °C

☛ Can the graphene quality be improved by enhanced etching?

Experimental setup



CVD chamber:

- Halogen lamp heats up to 1100 °C.
- Pressure is feedback-controlled up to 100 mbar.
- Base pressure is $2 \cdot 10^{-8}$ mbar.
- In vacuo transfer to UHV cluster tool enables characterization.

Suggested reading

- A. Becker et al. (2019): Control of etch pit formation for epitaxial growth of graphene on germanium. Journal of Applied Physics, 126(8), 85306. https://doi.org/10.1063/1.5108774
- A. Becker et al. (2020): Influence of temperature on growth of graphene on germanium. *(submitted)*
- M. Lukosius et al. (2016): Metal-Free CVD Graphene Synthesis on 200 mm Ge/Si(001) Substrates. ACS Applied Materials & Interfaces, 8(49), 33786–33793, https://doi.org/10.1021/acsami.6b11397
- Jae-Hyun Lee et al. (2014): Wafer-Scale Growth of Single-Crystal Monolayer Graphene on Reusable Hydrogen-Terminated Germanium. Science, 344(6181), 286–289, https://doi.org/10.1126/science.1252268