

## Transition Metal Catalyzed Graphene

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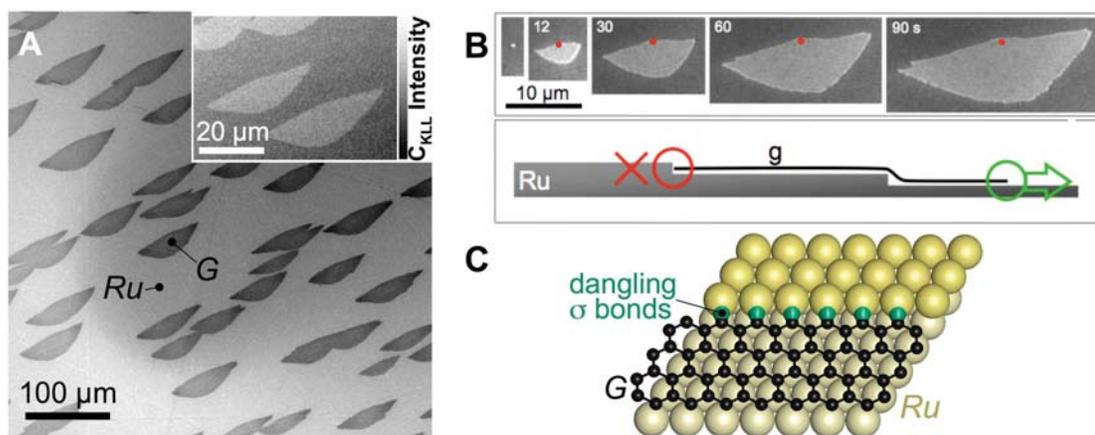
### Scientific Thrust Area

This research program is based in the CFN's scientific thrust on *Interface Science and Catalysis* (P.S., J.S.), and involves collaborators in *Electron Microscopy* (E.S.) and *Theory* (M.H.).

### Research Achievement

Graphene, a two-dimensional honeycomb lattice of  $sp^2$  bonded carbon, shows great promise for applications ranging from post-Moore's law electronics to transparent solar cell contacts. Assuming a continuation of "top-down" processing similar to today's microelectronics, the bottleneck to realizing this potential clearly lies in synthesizing the required starting material: structurally perfect, macroscopically large graphene sheets with uniform thickness, into which active device structures can be carved. Graphene growth on transition metals may provide a viable route toward large-scale graphene synthesis.

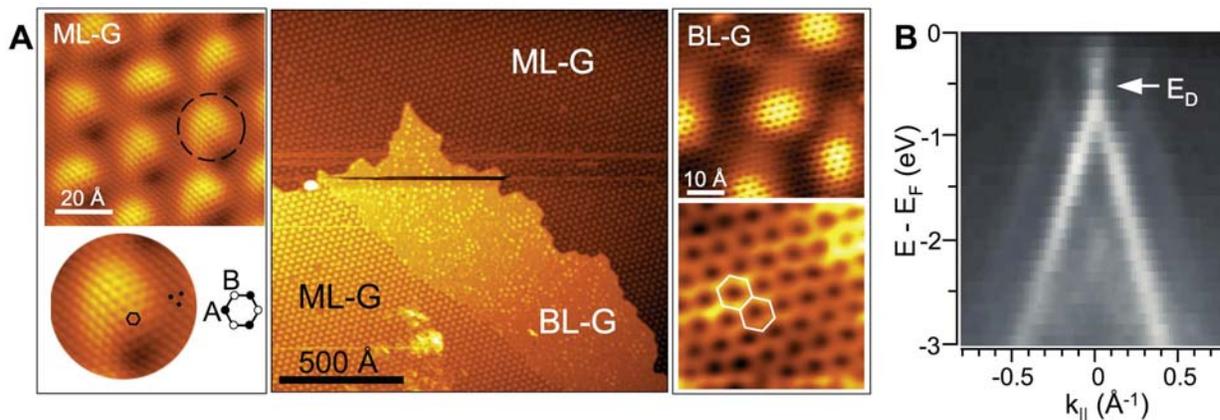
We have used *in-situ* experiments by low-energy electron microscopy (LEEM), synchrotron photoelectron microscopy, and scanning tunneling microscopy (STM), complemented by *ex-situ* measurements and density functional theory to study the growth and electronic structure of epitaxial graphene on Ru(0001). *In-situ* growth studies by LEEM have shown that epitaxy on Ru produces macroscopic single-crystalline graphene domains (fig. 1 A) with very low defect density in a controlled layer-by-layer mode.<sup>1</sup>



**FIGURE 1: Macroscopic graphene growth on Ru(0001).** A – Ultrahigh-vacuum scanning electron micrograph of ML graphene domains (G) on Ru. Inset:  $C_{KLL}$  scanning Auger map. B – Time-lapse LEEM sequence showing the nucleation and growth of a ML graphene domain on Ru at 850°C. Numbers indicate elapsed time in seconds following nucleation. Substrate steps, visible as faint dark lines, are aligned from lower left to upper right. Red dots mark the position of the nucleation site. C – Schematic sketch of the interaction of a zigzag graphene edge with an "uphill" Ru step.

The interaction with Ru substrate steps is key to the growth of monolayer (ML) graphene domains with size much larger than the step spacing. At high temperatures epitaxial graphene domains on Ru(0001) nucleate very sparsely and rapidly expand by carbon incorporation into graphene edge sites. *In-situ* microscopy during growth (fig. 1 B) shows a fast expansion of growing graphene domains parallel to substrate steps and across steps in the "downhill" direction, but an almost complete suppression of the crossing of "uphill" steps. Given that a graphene sheet projects a zigzag

edge with dangling  $\sigma$  bonds onto Ru steps (fig. 1 C), a boundary encountering an “uphill” step maximizes the orbital overlap and becomes immobilized at the step edge. Conversely, a graphene sheet growing in the “downhill” direction shows minimal overlap and can flow uninhibited in a carpet-like fashion across substrate steps.



**FIGURE 2: Structure and electronic properties of ML and BL graphene on Ru(0001).** **A** – Scanning tunneling microscopy of epitaxial ML and BL graphene on Ru. Moiré structure of ML graphene; honeycomb structure with equivalent carbon sublattices on BL graphene. **B** – Micro-ARPES intensity map for BL graphene on Ru near the K-point of the two-dimensional Brillouin zone.

If sufficient carbon is supplied, ML graphene domains grow and ultimately coalesce to a complete layer. Additional growth can be used to produce bilayer (BL) or thicker few-layer graphene in a controlled layer-by-layer fashion. Measurements by Raman spectroscopy,<sup>1</sup> and more recently by STM and selected-area angle-resolved photoemission (micro-ARPES) in LEEM<sup>2</sup> have been used to determine how the proximity of the metal substrate affects the electronic structure of epitaxial graphene. For ML graphene, the coupling to Ru d-states strongly affects the graphene  $\pi$ -states near the Fermi energy. This strong coupling persists over almost the entire moiré unit cell of the ML graphene (fig. 2 A). The situation changes dramatically with the addition of one more layer. The top sheet of BL graphene is largely unperturbed by residual substrate interactions. Screened from the metal substrate by the interfacial graphene sheet, it shows the hallmarks of free-standing ML graphene: a honeycomb structure with equivalent carbon sublattices imaged in STM (fig. 2 A), and a linear dispersion of  $\pi$ -bands near the Dirac point (fig 2 B). These findings are relevant to graphene growth, and apply more generally to interfaces between graphene and transition metals, e.g., in device contacts.

### Future Work

- Exploration of the chemical reactivity of epitaxial graphene on transition metals. Epitaxial graphene as a template for size-selected metal nanocluster catalysts.
- Isolation of epitaxial graphene from a transition metal substrate.

### Publications

1. P. Sutter, J.I. Flege, and E. Sutter, “Epitaxial graphene on ruthenium”, *Nature Materials* **7**, 406 (2008).
2. E. Sutter, D.P. Acharya, J.T. Sadowski, and P. Sutter, “Scanning tunneling microscopy on epitaxial bilayer graphene on ruthenium (0001)”, *Applied Physics Letters* **94**, 133101 (2009).
3. P. Sutter “Epitaxial graphene: How silicon leaves the scene”, *Nature Materials* **8**, 171 (2009).
4. BSA 08-37, “Monolayer or/and few-layer graphene on metals or metal-decorated semiconductors”, patent pending.