Li interaction with epitaxial graphene / Ru(0001) islands monitored by LEEM and visible-light PEEM

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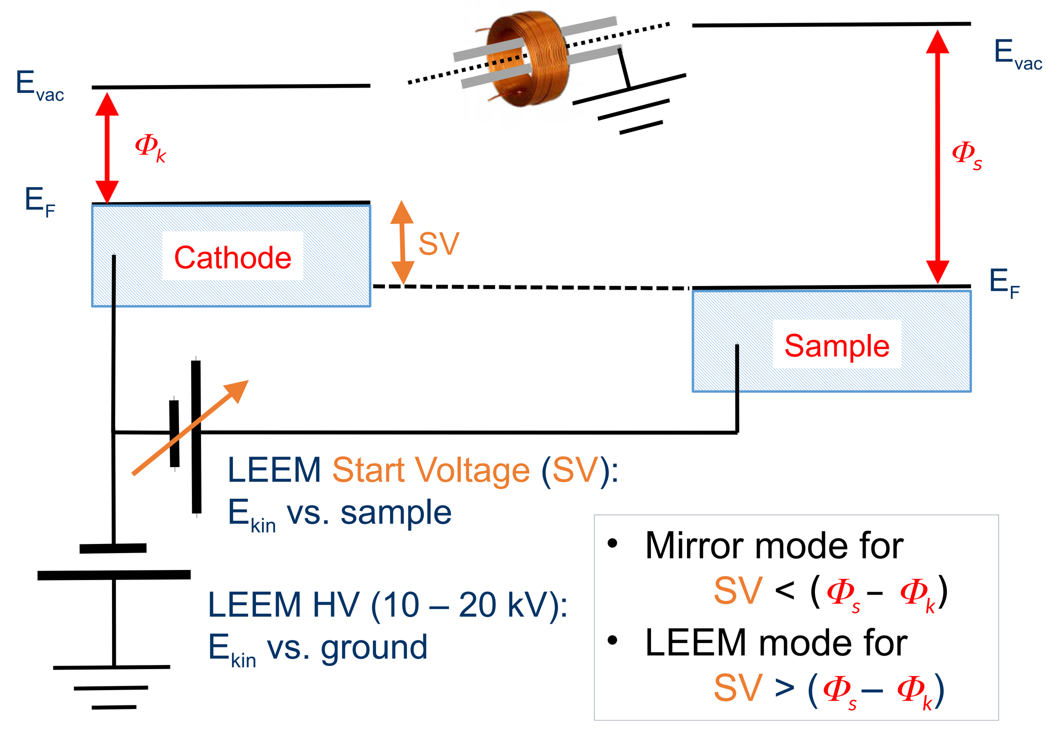
Abstract

Graphene promises many fascinating applications, also in advanced batteries, while the intercalation of Li in graphite has attracted much interest due to its use in anodes of Li-ion batteries. It is therefore of great interest to study the interaction of graphene with Li. In this work [1], we have used LEEM to monitor in-situ and in real time the work function evolution during Li deposition on epitaxial "native" graphene patches on Ru(0001). The system has been studied in real and reciprocal space, comparing the changes taking place on the graphene with those on the bare Ru(0001) surface. It is found that Li deposition decreases the work function of the graphene islands but to a smaller degree than of Ru(0001), as corresponds to its intercalation underneath the graphene overlayer. In this system, the strong reduction of the work function makes it possible to perform photoemission electron microscopy (PEEM) with a visible-light (violet, 3.06 eV) laser. This allowed us to study the diffusion of Li out of the graphene islands upon annealing [1].

Motivation

- Graphene: many promising applications, also in advanced batteries.
- Lithium-intercalated graphite: widely used as anode in Li-ion batteries.
- Lithium interacalation in monolayer graphene: interesting for nanosized, graphene-based batteries.
- We set out to study Li inter- and deintercalation dynamics in epitaxial graphene/Ru(0001) islands by means of LEEM and visible-light PEEM [1].

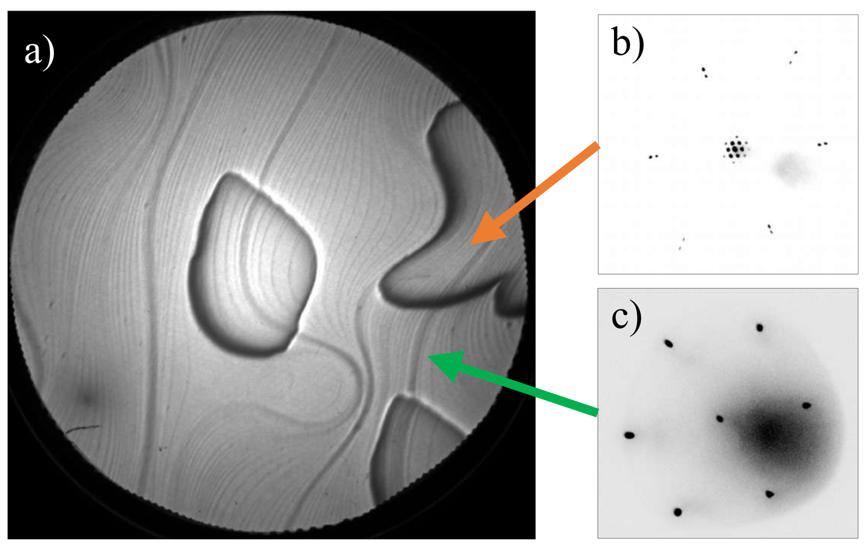
Measuring work functions by LEEM



- Mirror mode for SV < (Φ_s – Φ_k)
- LEEM mode for SV > (Φ_s – Φ_k)

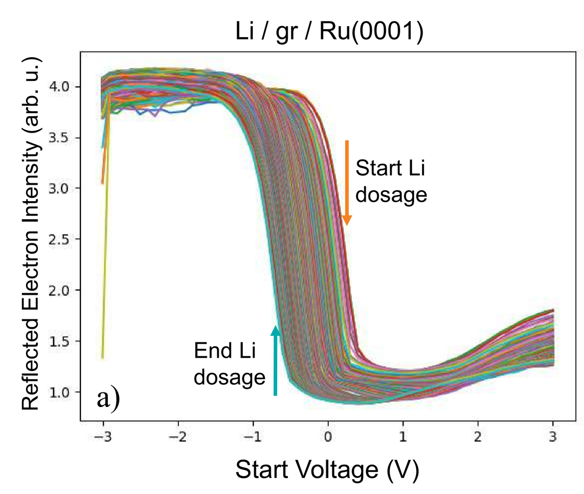
ML – islands on Ru(0001)

- Growth of graphene patches on Ru(0001) by C segregation at ~ 700 ºC



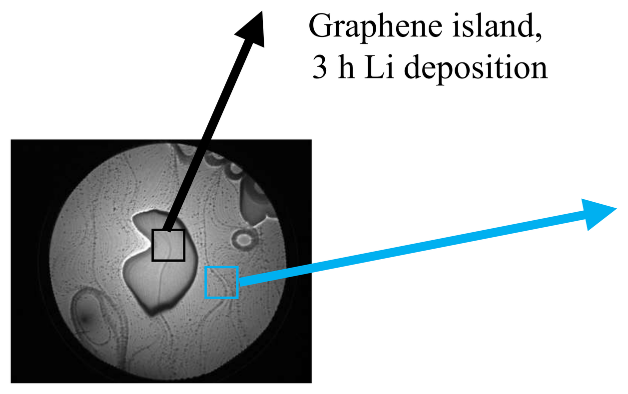
a) LEEM image (10 µm) of graphene / Ru(0001)
b) LEED pattern of graphene
c) LEED pattern of clean Ru(0001)

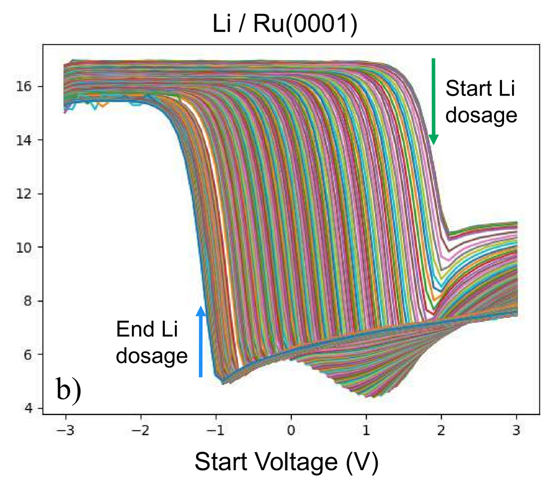
Real time monitoring of Li deposition



- Continuous measurement of electron reflectivity $R(V)$ in (-3.0 – 3.0 eV) range inside a user-defined window during Li deposition
- ⇒ In situ, spatially resolved, real time monitoring of work function (WF) evolution.
- Mirror Mode (MM) – LEEM imaging transition shifts to lower Start Voltages ⇒ WF reduction

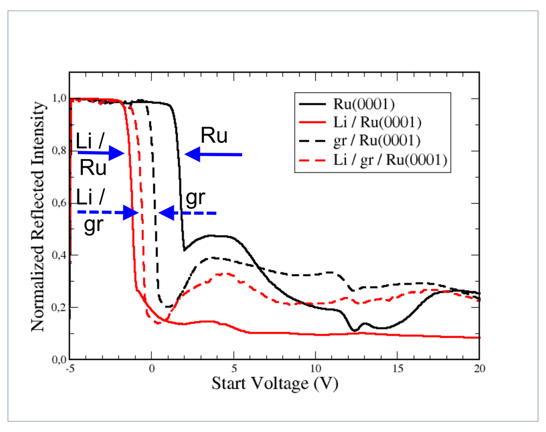
Graphene island, 3 h Li deposition

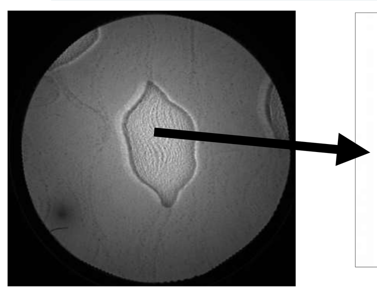


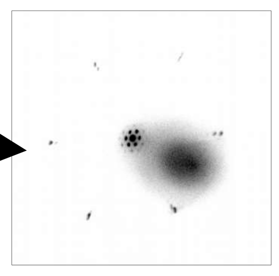


Ru substrate, 1 h 45 min Li deposition

Li / gr / Ru(0001) and Li / Ru(0001)







FoV: 20 µm;
SV = - 0.46 V

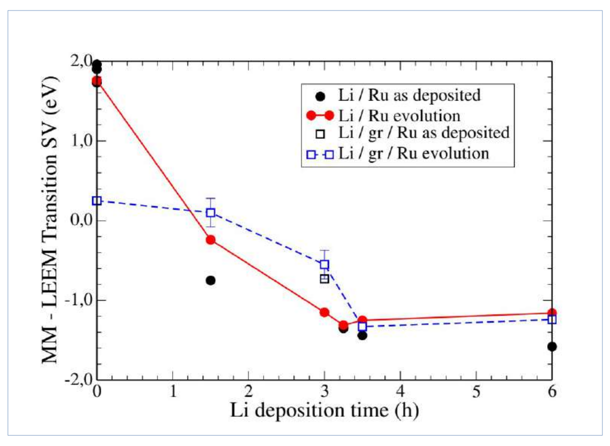
LEED pattern;
45 eV

- Reflectivity curves after Li deposition: Li / Ru(0001) and Li / gr / Ru(0001)
- Here: Li deposition close to maximum reduction of WF:

Δφ (gr/Ru) = – 0.8 eV; Δφ (Ru) = – 3.3 eV

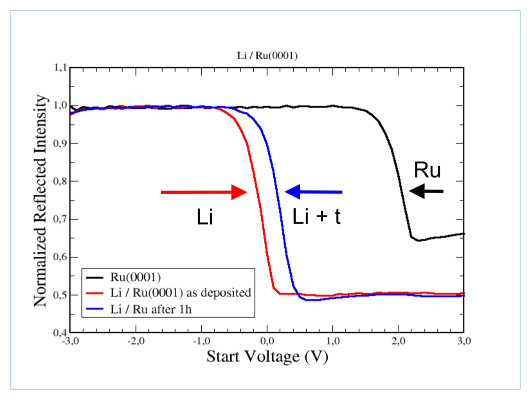
- Reduction of WF for Li / gr / Ru(0001) but smaller than for Li / Ru(0001)
- Li-covered graphene islands: granular structure
- LEED pattern of Li-covererd graphene island: Moiré pattern, very similar to gr / Ru(0001) with higher background intensity: no new superstructure.

Evolution with Li coverage



- Li / Ru: Expected behavior:
- Strong initial decrease of WF with Li coverage ($\Delta\varphi_{max}$ ≈ – 3.3 eV); Minimum for a coverage ~ 0.3 – 0.5 ML [2].
- Subsequent slight increase of WF due to depolarizing field of other dipoles (Topping model) + reduction of polarizability.
- Li / gr / Ru: similar trend, but reduced effect (factor ~ 1/2): $\Delta\varphi_{max}$ ≈ – 1.5 eV; initially slower decrease, up to coverage of max. reduction in Li / Ru)

Time evolution at RT



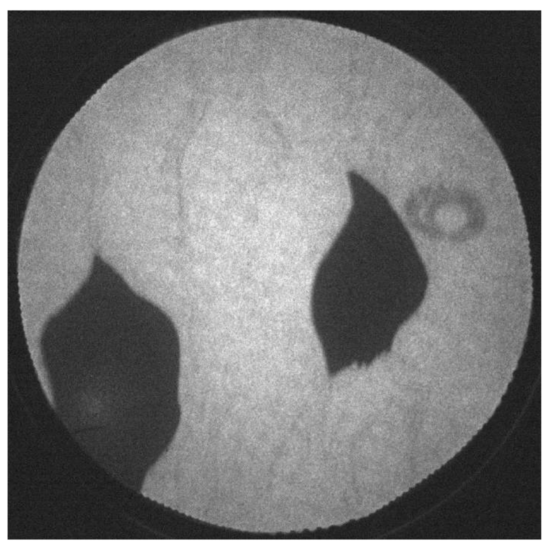
- Kinetics: WF increase after deposition ⇒ Li mobile at RT !
- Possible rearrangement of Li atoms into compact islands: large-patch-regime (patch field effect [3])

Discussion

- Li / gr / Ru: higher WF reduction than Li / Ru in spite of higher EN difference (Li-C: 6.8 eV; Li-Ru: 5.4 (Mulliken)
- Electron transfer for gr / Ru: Δφ (gr/Ru) = 1.6 eV ⇒ p-doped (gr-Ru: strong interaction, high corrugation)
- Higher reduction of WF for Li / gr / Ru than for Li /Ru expected if Li were to reside on gr surface, but opposite is found! ⇒ Li atoms intercalation!
- Consistent with calculations: Li unstable on defect-free graphene [4,5].
- WF evolution: Li intercalation intensifies for coverages 0.3 – 0.5 ML: consistent with picture of Li falling on islands, diffusing to edges and into the islands and onto Ru terraces following concentration gradient.
- Higher background in LEED pattern: compatible with increased electron confinement due to decoupling [6].

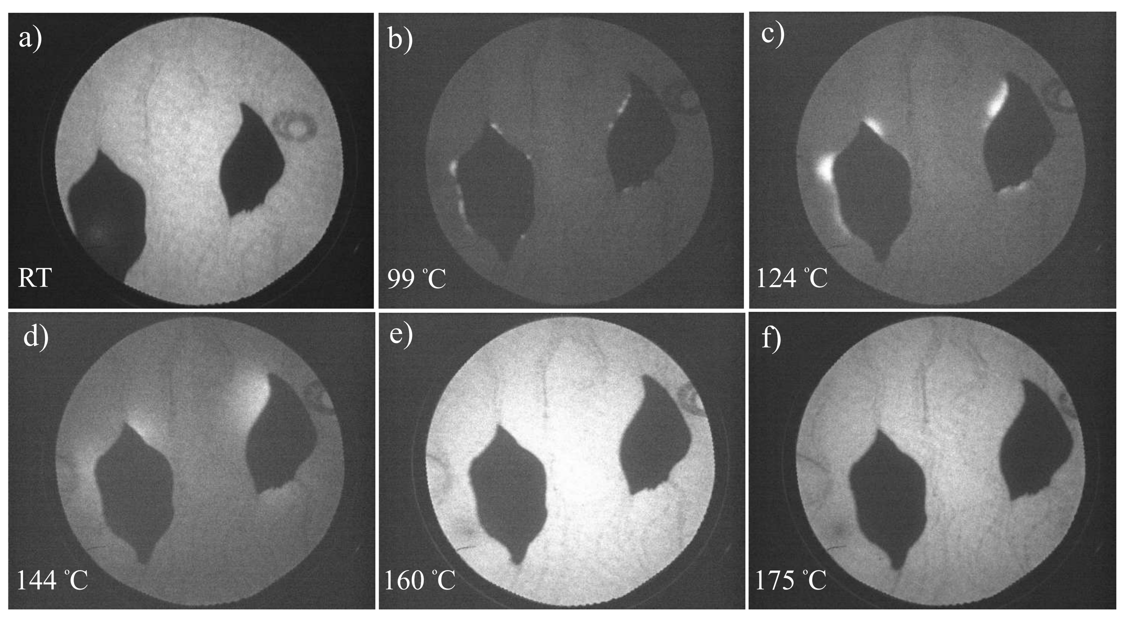
Strong WF reduction !

- Maximum WF reduction for Ru(0001): Δφ ≈ 3.3 eV. Final $\Delta\phi_{Li/Ru}$ ≈ 2.3 eV ⇒ possible to produce photoelectrons with visible-light
- PEEM imaging with a **visible-light** laser (violet, hν = 3.06 eV):



Graphene islands on Ru(0001) covered by Li. FoV: 20 µm

Real-time monitoring of Li diffusion by *visible-light* PEEM



- Real-time, visible (violet)–light PEEM imaging (20 µm) as T is raised.
- Bright regions develop at edges (corners) of islands, grow and spread onto Ru(0001) terraces ⇒ T promotes Li diffusion out of the islands at corners.
- Further support of Li being intercalated below islands.
- Diffusion activation at ~ 100 ºC ⇒ barrier for Li diffusion ~ 40 meV explains RT kinetics and is compatible with Na diffusion on Ru(0001) (46 meV [7]).

References

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Summary and Conclusions

- Growth of submonolayer islands of epitaxial graphene on Ru(0001)
- Monitoring of morphology, structure and electronic properties (work function) by means of LEEM in real time during Li deposition
- Comparison with the case of Li deposition on the clean Ru(0001) surface.
- Li reduces the work function of graphene/Ru(0001) by as much as 1.5 eV, significantly less than 3.3 eV for Ru(0001).
- Our results suggest that intercalation takes place at RT following Li deposition without forming any new superstructure.
- WF of the system is low enough to allow visible-light PEEM.
- Real-time monitoring of Li diffusion by visible-light PEEM.
- Increasing T to ~ 100 ºC promotes the diffusion of Li atoms out of the graphene islands preferentially at their corners and their expansion onto the Ru(0001) terraces.

Acknowledgments

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