UCLA Engineering
Materials Science and Engineering

In situ Microscopy Studies of Mechanical, Chemical, and Thermal Stabilities of Carbides & Oxides

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in situ STM: Prof. Ivan Petrov & Ms. Vania Petrova, UIUC

in situ TEM: Prof. Per Persson, Linköping University, Sweden
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PI: **Suneel Kodambaka** Co-PI: **Jenn-Ming Yang**

Highlights

IN SITU STUDIES OF THERMAL, CHEMICAL, AND MECHANICAL STABILITIES OF REFRACTORY MATERIALS

Grant Number: **FA9550-10-1-0496** (September 2010 ~ August 2013)

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Research Goals

Use *in situ* microscopy tools and develop an atomic-scale understanding of the factors controlling the thermochemical stabilities and mechanical properties of UHTCs.

Status Quo

- Refractory ceramics are often considered brittle with little or no dislocation motion at room temperature.
- Annealing in hydrocarbon ambient is likely to reduce the oxide.
- Carburization and oxidation mechanisms are often derived from *ex situ* post-synthesis and post-processing treatments.
- Diffusion mechanisms governing thermal stability of liquid metal-carbon interfaces are largely unknown.

New Insights

- **Transition-metal carbides exhibit room temperature ductility at small length scales.**
- **Surface oxidation of transition-metal oxides is enhanced in presence of hydrocarbon gases.**
- **Diffusivity of carbon atoms is high in and on the SiC(0001) and graphitization of SiC is limited by the desorption of Si atoms.**
- **Ga droplets undergo Ostwald ripening on carbon surfaces.**

Impact

- **Room-temperature plasticity in refractory ceramics could open up potentially new applications.**
- **Design and development of high-performance transition-metal oxide catalysts and catalyst supports.**
- **Development of better graphite/SiC composite and graphene production technologies.**
- **Ripening kinetics can, *in principle*, help determine surface energies of liquid metals.**

Main Accomplishments

In situ transmission electron microscopy (TEM) coupled with nanomechanical testing was used to discover room-temperature plasticity in ZrC, a high-melting ceramic with high hardness (25 GPa). ZrC(001) pillars exhibit size-dependent yield strength during uniaxial compression.

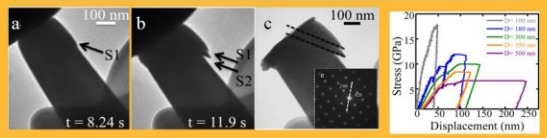


Figure 1. (a-c) *In situ* TEM images acquired during uniaxial compression of a 300-nm-diameter ZrC(001) pillar. Arrows highlight the initiation and propagation of shear planes labeled S1 and S2. Inset in (c) is an electron diffraction pattern from the compressed pillar acquired along [001] zone axis. The dashed lines highlight {110} slip planes. The plots show stress vs displacement for 100-500 nm diameter pillars.

In situ TEM was used to study the thermal stability of liquid Ga droplets on amorphous carbon. Ga droplets undergo Ostwald ripening in the surface diffusion limited regime.

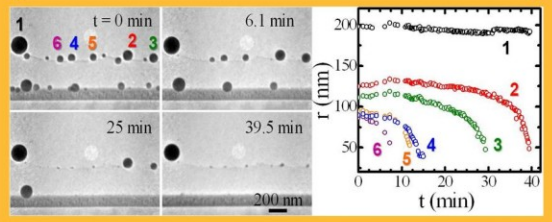


Figure 2. Cross-sectional TEM images acquired from a carbon-covered $ZrB_2/Al_2O_3(0001)$ sample during annealing at 773 K. The nearly spherical features are Ga droplets. Plot of droplet size (r) vs. t showing the coarsening/decay of 6 droplets.

In situ high-temperature (700-1000 K) STM was used to develop atomic-scale insights into the effect of ethylene on the surface structure and composition of rutile-TiO_2(110). The surprising discovery is that ethylene significantly enhances the surface oxidation of TiO_2(110).

Figure 3. *In situ* STM images (150 × 150 nm^2) acquired at 900 K in ethylene (~10^{-7} Torr) + oxygen (3×10^{-9} Torr) mixture at t = 0 and 119 min. The topmost 1×1 terraces and the 2×1 stripes are highlighted by red and green colors, respectively. Associated plot shows temperature-dependent growth rates of TiO_2 on the surface during annealing in C_2H_4+O_2 (red) and O_2 (black).

Direct observation of surface graphitization of single-crystalline SiC(0001), with atomic-scale resolution, using scanning tunneling microscopy (STM) at 1395 K.

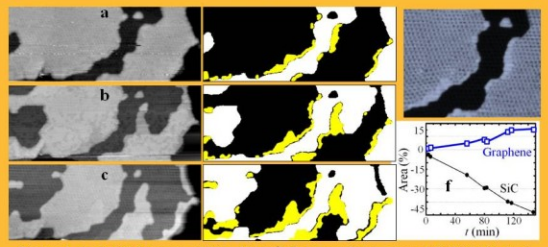


Figure 4. (a-c) STM images (110 × 46 nm^2) from graphene-covered SiC(0001) at: a) 0, b) 62, and c) 147 min during annealing at 1395 K. Color-coded images show the top most 1 ML and 2 ML graphene-covered SiC in black and yellow colors, respectively. High-resolution STM image at 1395 K. Areal coverages of SiC and bilayer graphene plotted vs. time (t).

Publications/Presentations

Publications

1. Y. Murata, V. Petrova, I. Petrov, and S. Kodambaka, *In situ high-temperature scanning tunneling microscopy study of bilayer graphene growth on 6H-SiC(0001)*, **Thin Solid Films** 520, 5289-5293 (2012).
2. Y. Murata, V. Petrova, I. Petrov, C. V. Ciobanu, and S. Kodambaka, *Role of ethylene on surface oxidation of TiO_2(110)*, **Applied Physics Letters** 101, 211601-211605 (2012).
3. S. Kiani, S. Kodambaka, A. M. Minor, and J.-M. Yang, *Size-Dependent Room-Temperature Plasticity in Ceramics*, in preparation.
4. S. Kodambaka, C. Ngo, J. Palisaitis, P. Mayrhofer, and P. O. Å. Persson, *Kinetics of Ostwald Ripening of Ga Droplets on Thin Carbon Films*, in preparation.
5. I. Jouanny, J. Palisaitis, P. Mayrhofer, L. Hultman, P. O. Å. Persson, and S. Kodambaka, *In situ High-Temperature Transmission Electron Microscopy Studies of Pt-Mo Alloy Diffusion in ZrB_2 Thin Films*, in preparation.
6. I. Jouanny and S. Kodambaka, *In situ High-Temperature Transmission Electron Microscopy Studies of Thermal Stability of TiO_2/C Core/Shell Nanoparticles*, in preparation.

Invited Talks

1. "In Situ High-Temperature Scanning Tunneling Microscopy Studies of Graphene Growth on 6H-SiC(0001)," *Intl. Symp. Materials for Enabling Nanodevices (ISMEN)*, UCLA, Los Angeles, CA, August 2012.
2. "In-situ high-temperature STM studies of surface reactions," *ICMCTF 2012*, San Diego, CA, May 2012.
3. "In situ High-Temperature Scanning Tunneling Microscopy Studies of Thermochemical Stabilities of TiO_2(110) and SiC(0001)," *Toyota Technological Institute*, Ichikawa, Japan, October 28, 2011.
4. "In situ High-Temperature STM and LEEM Studies of Graphene Growth," *JAIST*, Kanazawa, Japan, October 26, 2011.
5. (Keynote) "In situ High-Temperature Scanning Tunneling Microscopy Studies of Epitaxial Graphene Growth," Workshop on *Understanding materials using in-situ microscopy*, *University of Göttingen*, Göttingen, Germany, November 2010.

Group Presentations

1. S. Kiani, S. Kodambaka, A. M. Minor, and J-M. Yang, "Insights from In Situ TEM Compression Test of Ceramics," *Gordon Research Conference, Solid State Studies in Ceramics*, Mount Holyoke College, MA, Aug 12-17, 2012.
2. S. Kiani, S. Kodambaka, and J-M. Yang, "Influence of Size on Compression Strength of SiC and ZrC Micro and Nano Pillars," *UCLA Engineering Tech Forum*, Los Angeles, CA, March 13, 2012.
3. S. Kiani, S. Kodambaka, and J-M. Yang, "Size Dependence of Mechanical Properties of Refractory Carbides", *TMS 141th Annual Meeting*, Orlando, FL, March 11-15, 2012.
4. S. Kiani, S. Kodambaka, and J-M. Yang, "Investigation of Compression Strengths of SiC(0001) and ZrC(001) Micropillars", *36th Intl. Conf. and Exposition on Advanced Ceramics and Composites*, Daytona Beach, FL, Jan. 22-27, 2012.
5. Y. Murata, V. Petrova, I Petrov, and S. Kodambaka, "In situ High-Temperature Scanning Tunneling Microscopy Studies of Thermochemical Stabilities of Single-crystalline SiC(0001) and TiO_2(110) Surfaces," *2nd Annual AFOSR Hypersonics Center Review*, Dayton, OH, August 2, 2011.
6. S. Kiani, S. Kodambaka, and J-M. Yang, "Influence of Size on Compression Strengths of Refractory Carbides", *2nd Annual AFOSR Hypersonics Center Review*, Dayton, OH, August 2, 2011.
7. Y. Murata, S. Kodambaka, V. Petrova, and I Petrov, "In situ High-Temperature Scanning Tunneling Microscopy Studies of Epitaxial Graphene Growth on SiC(0001)," *Electronic Materials Conference (EMC)*, Santa Barbara, CA, June 22-24, 2011.
8. Y. Murata, S. Kodambaka, V. Petrova, and I Petrov, "Role of Ethylene on Thermal and Chemical Stability of TiO_2(110)," *EMC*, Santa Barbara, CA, June 22-24, 2011.
9. Y. Murata, V. Petrova, I. Petrov, and S. Kodambaka, "Atomic-scale Understanding of the Thermal Stability of 6H-SiC(0001): An In Situ Scanning Tunneling Microscopy Study," *Intl. Conf. Metallurgical Coatings and Thin Films*, San Diego, CA, May 2011.
10. Y. Murata, V. Petrova, I. Petrov, and S. Kodambaka, "In Situ High-Temperature Scanning Tunneling Microscopy Studies of Ethylene-TiO_2(110) Reactions," *MRS Spring Meeting*, San Francisco, CA, April 2011.
11. Y. Murata, V. Petrova, I Petrov, and S. Kodambaka, "In situ High-Temperature Scanning Tunneling Microscopy Studies of Epitaxial Graphene Growth on SiC(0001)," *MRS Spring Meeting*, San Francisco, CA, April 25 - 29, 2011.

Outline

* *In situ* TEM studies of SiC(0001), ZrC(001), and ZrC(111) nanomechanics

* *In situ high-temperature* STM (~1400 K) studies of SiC(0001) surface graphitization

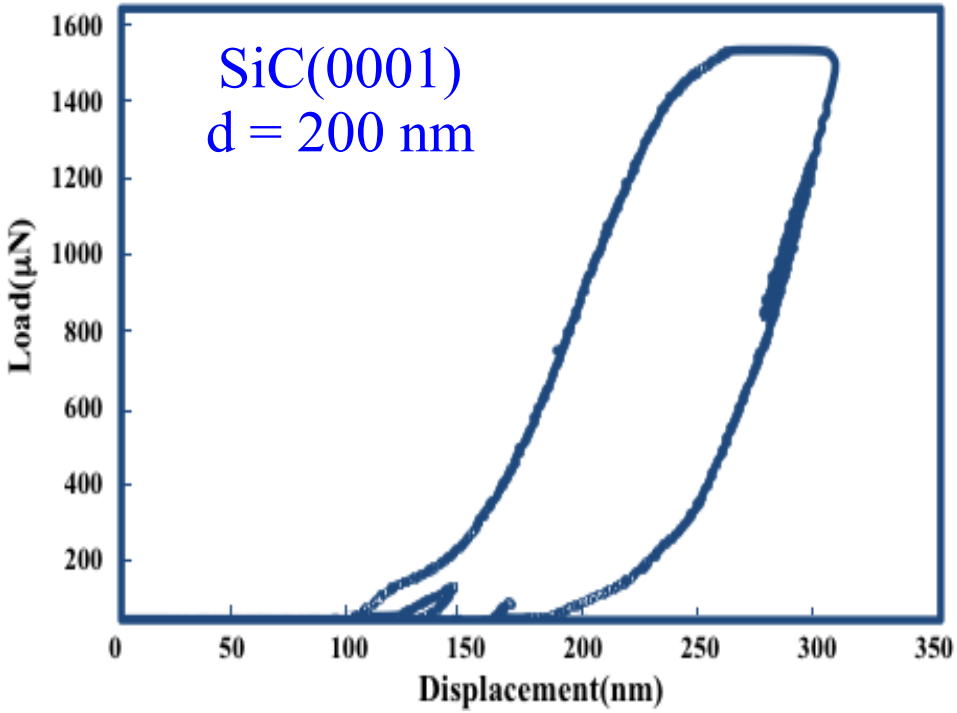
* *In situ* STM studies of $TiO_2(110)/C_2H_4$ reactions

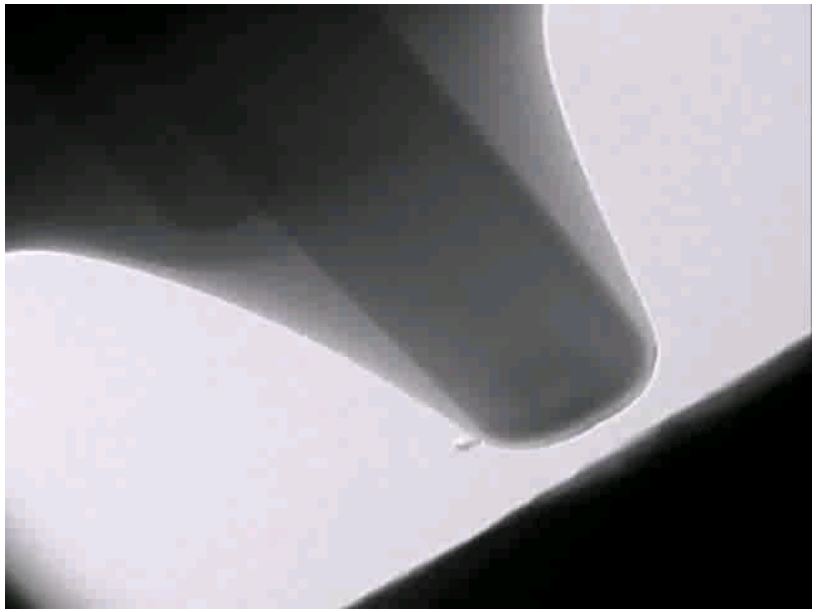
* *In situ* TEM studies of metal/ceramic interface dynamics

Nanomechanics of SiC(0001) single-crystals

Loading sequence:

1) up to 150 nm, 2) up to 200 nm, & 3) 300 nm.



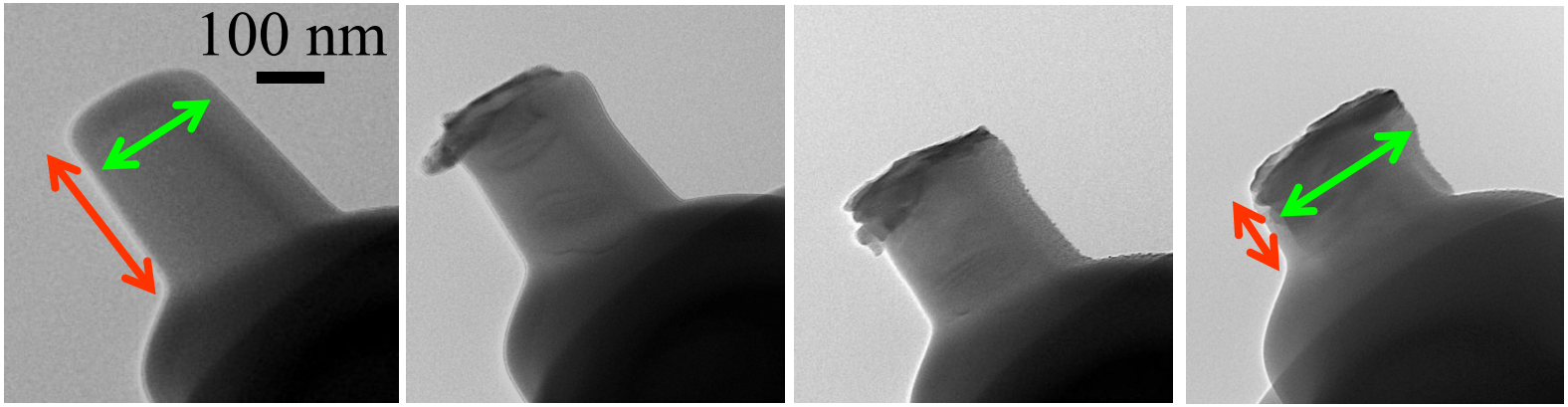


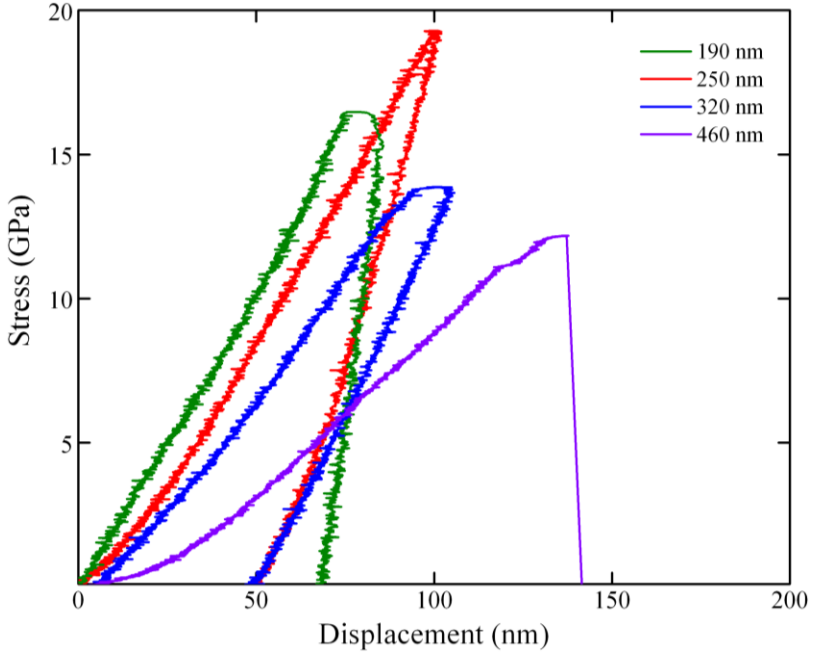
Load vs displacement data were acquired *while* observing microscopic & structural changes during uniaxial compression of the pillars.

Nanomechanics of SiC(0001) single-crystals

Room temperature plastic deformation of SiC(0001) pillars.

$D = 200$ nm

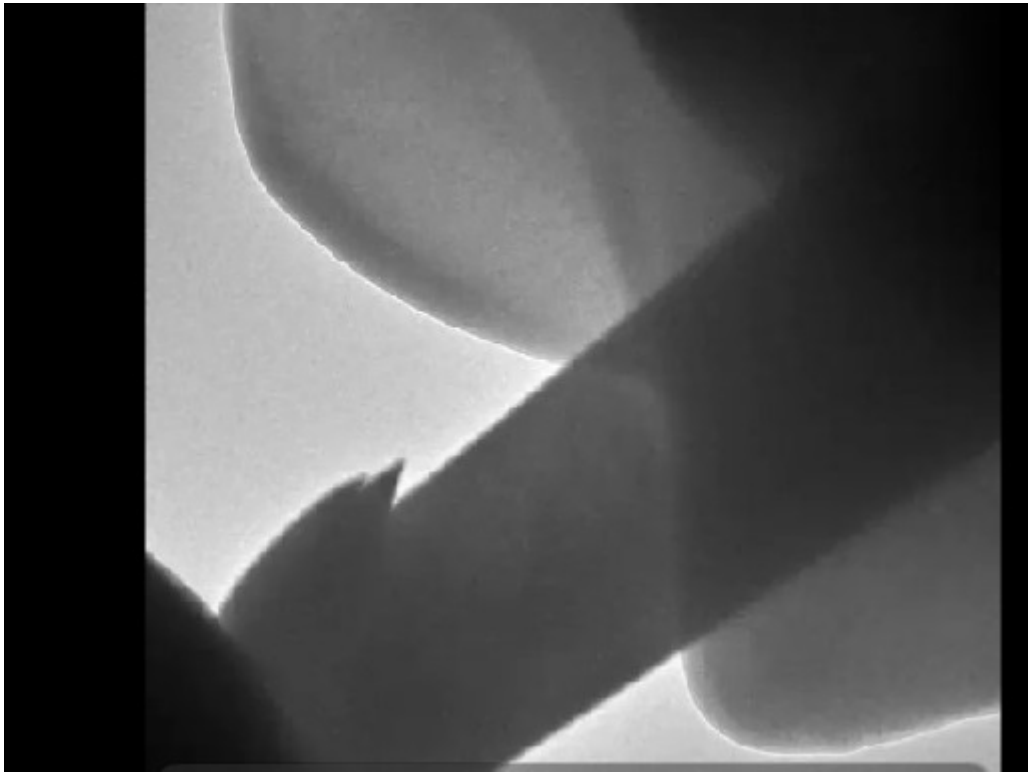


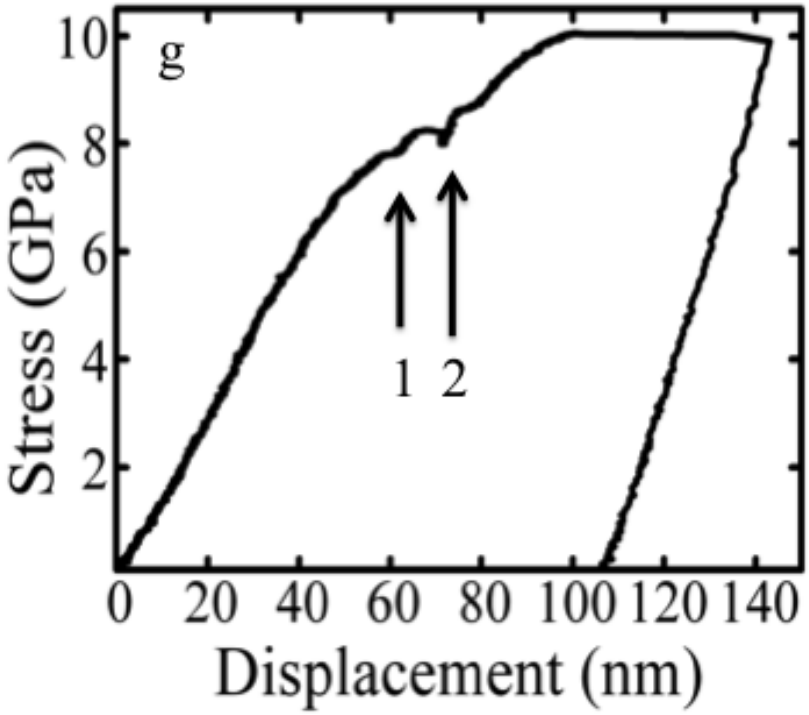


SiC(0001) pillars:
Yield strength increases with decreasing size.

Nanomechanics of ZrC(001) single-crystals

$D = 300$ nm

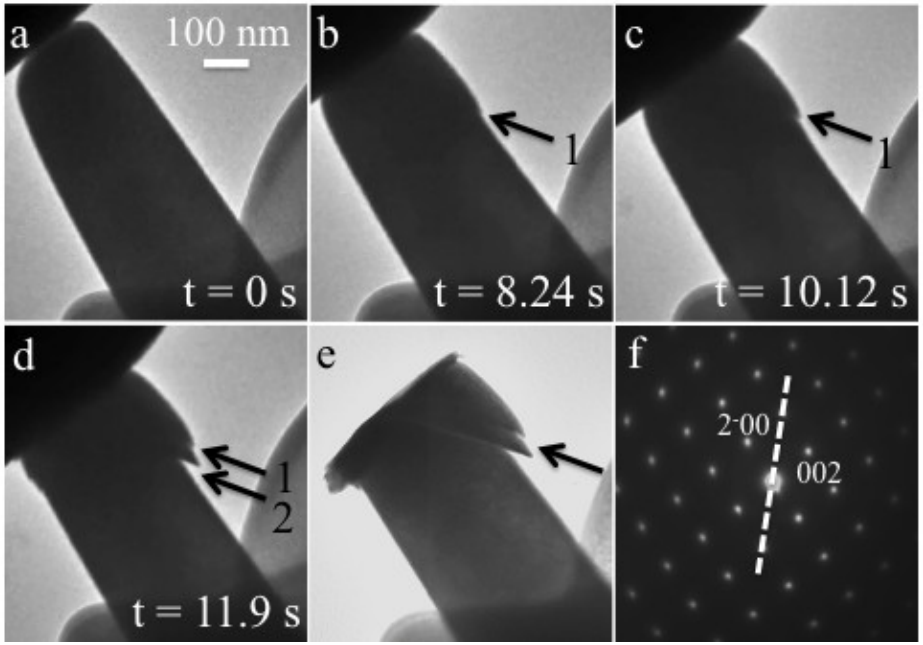




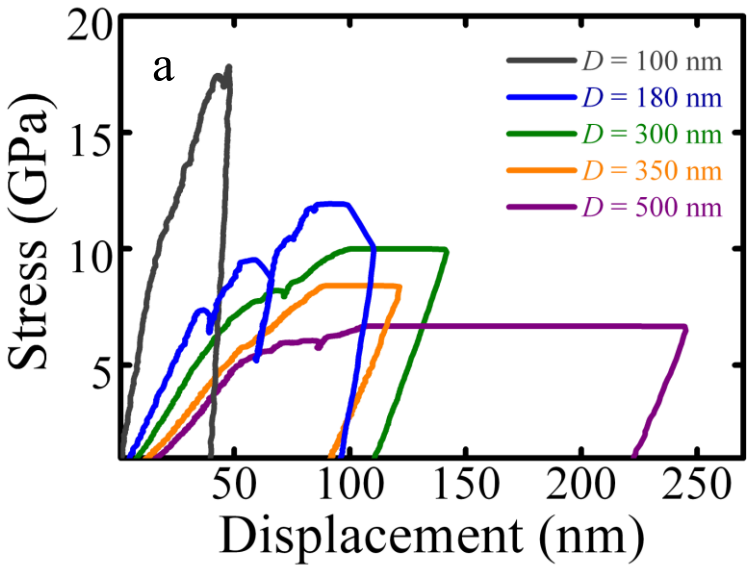
In situ TEM movie showing shear deformation of a ZrC(001) pillar during uniaxial compression at room temperature

Nanomechanics of ZrC(001) single-crystals

D = 300 nm



Arrows highlight the initiation & propagation of shear planes under applied load -- **indicative of plastic deformation *via* shear**

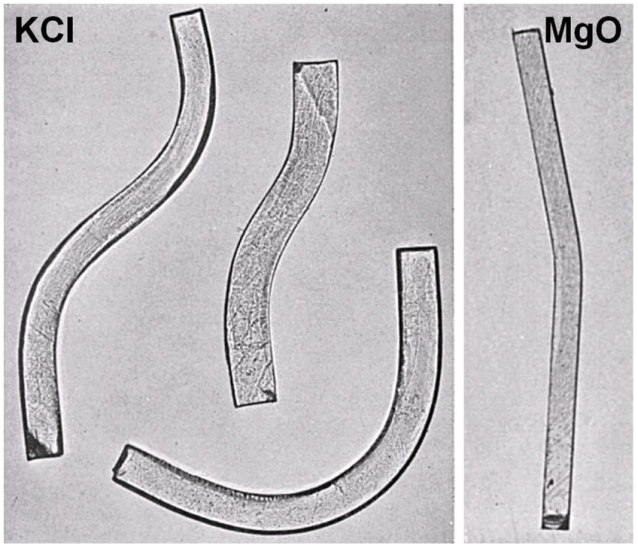


Yield strength increases with decreasing size

Nanomechanics of ZrC(001) single-crystals

direct evidence of dislocation motion in ZrC at room temperture -- origin of plasticity

Room-temperature plasticity in ceramics



- As early as 1950s, bulk ionic crystals (KCl, MgO, etc.) have been shown to deform plastically at room temperature.
  [A. Gorum, E. Parker, and J. Pask, *J. Am. Ceram. Soc.* **41**, 161-164 (1958).]
- Theory predicts that fracture stress increases with decreasing sample size and below a critical size yielding, rather than brittle fracture, is favored.
  [K. Kendall, *Nature* 272, 710-711 (1978).]
- In pure single-crystals, at small sizes, defect density is likely to be low, i.e. the material can withstand higher stresses without fracture -- necessary condition for dislocation motion.
- We expect that this is the case in our experiments.

Nanomechanics: Summary

In situ observations reveal room-temperature plasticity and size-dependent yield strengths in single-crystalline SiC and ZrC samples.

Our results are likely to open up new applications and the design & fabrication of hard-yet-tough ceramics.

In Situ High-T STM Studies of Carburization of SiC(0001)

GOAL:

Determine the atomistics of surface carburization

SiC(0001): Surface Carburization

Annealing SiC(0001) in vacuum leads to desorption of Si & formation of graphene

$$SiC_{(s)} \xrightarrow{\geq 900\,^{\circ}C} graphene + Si_{(g)}$$

A.J. van Bommel, J.E. Crombeen, & A. van Tooren, *Surf. Sci.* **48**, 463 (1975).

Previous studies have shown that:

- Vacuum anneal → nucleation of graphene at SiC step edges
- Presence of Si shifts graphene formation to higher temperatures

J. B. Hannon & R. M. Tromp, *Phys. Rev. B* **77** (2008); R. M. Tromp & J. B. Hannon, *Phys. Rev. Lett.* **102** (2009).
T. Ohta, F. El Gabaly, A. Bostwick, J.L. McChesney, K.V. Emtsev, A.K. Schmid, T. Seyller, K. Horn, & E. Rotenberg, *New J. Physics* **10** (2008).
H. Hibino, S. Mizuno, H. Kageshima, M. Nagase, & H. Yamaguchi, *Phys. Rev. B* **80** (2009).

Relatively little is known concerning the **atomistics** of graphene formation on SiC

SiC(0001): Experimental

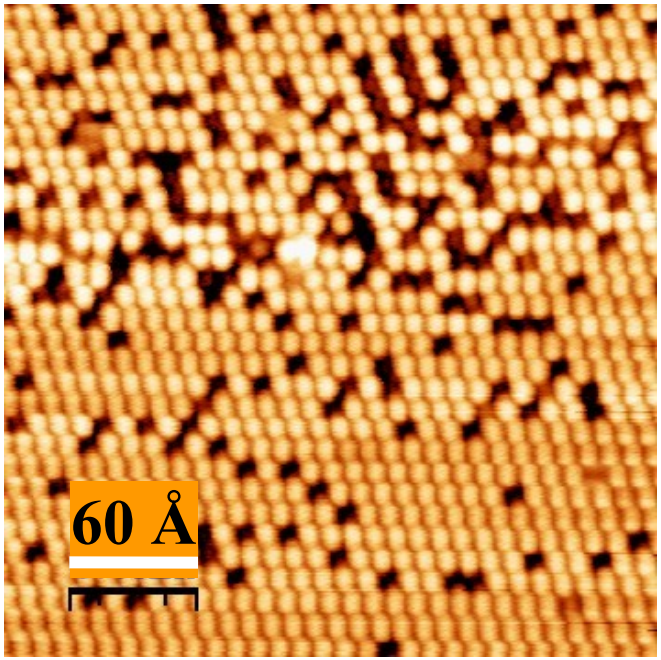
A. Substrate: 6H-SiC(0001)

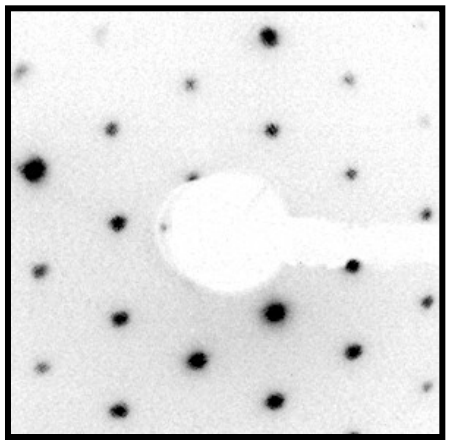
B. Clean in UHV (< 2 10^{-10} Torr)

C. Deposit Si at ~ 900 °C
→ 3 × 3 reconstruction

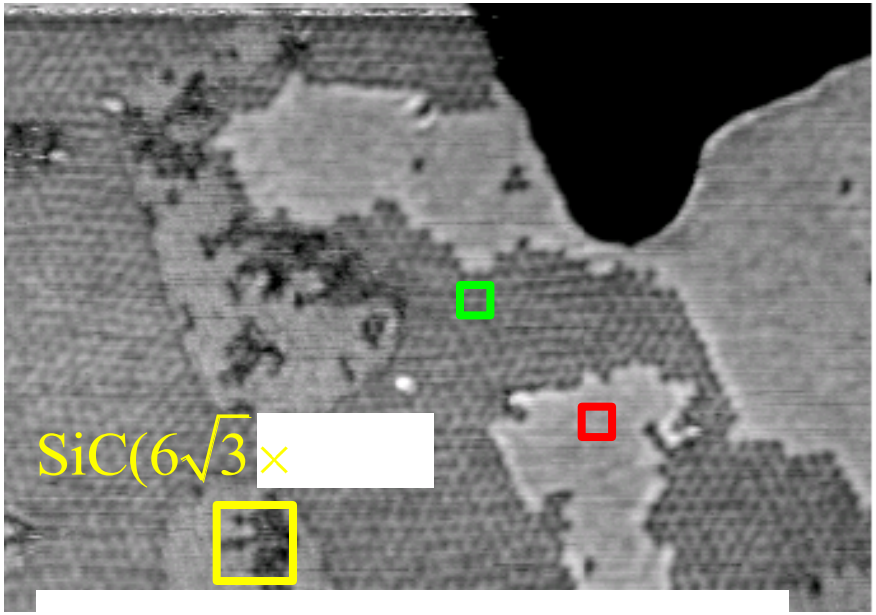
D. Anneal in UHV at T > 1100 °C
→ STM

SiC(0001)-3 × 3

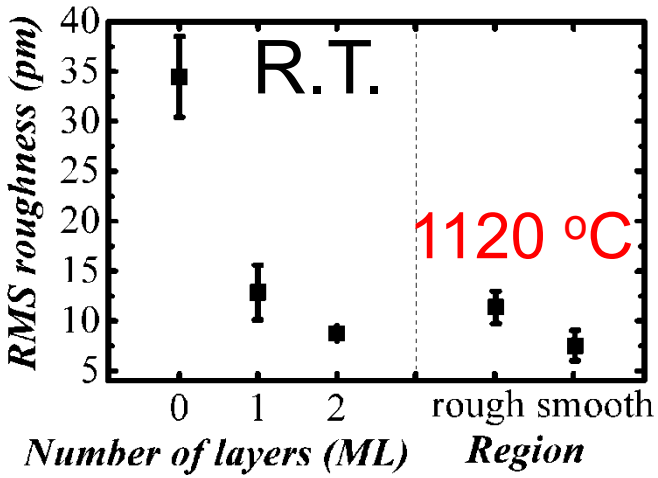


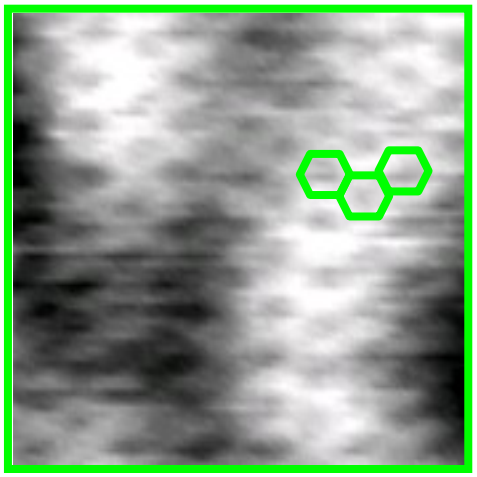


Graphene/SiC(0001)

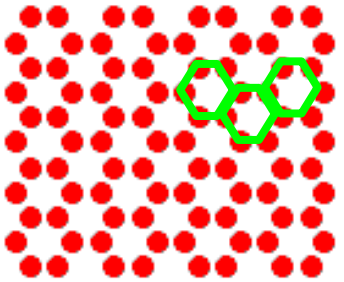


nm²

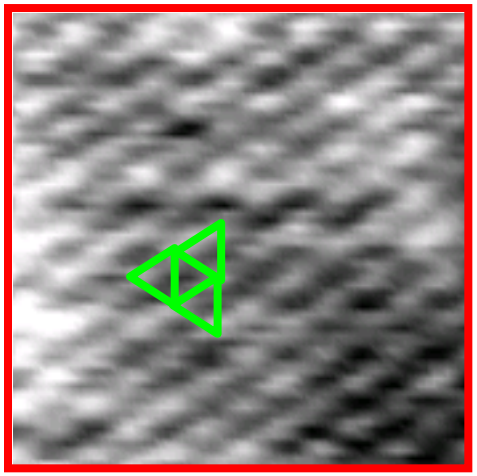




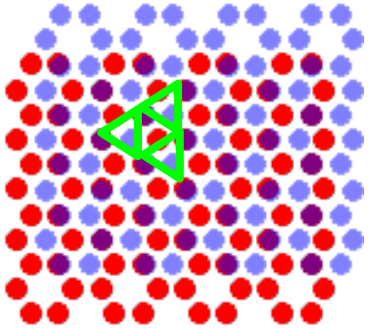
1 ML graphene



hexagon



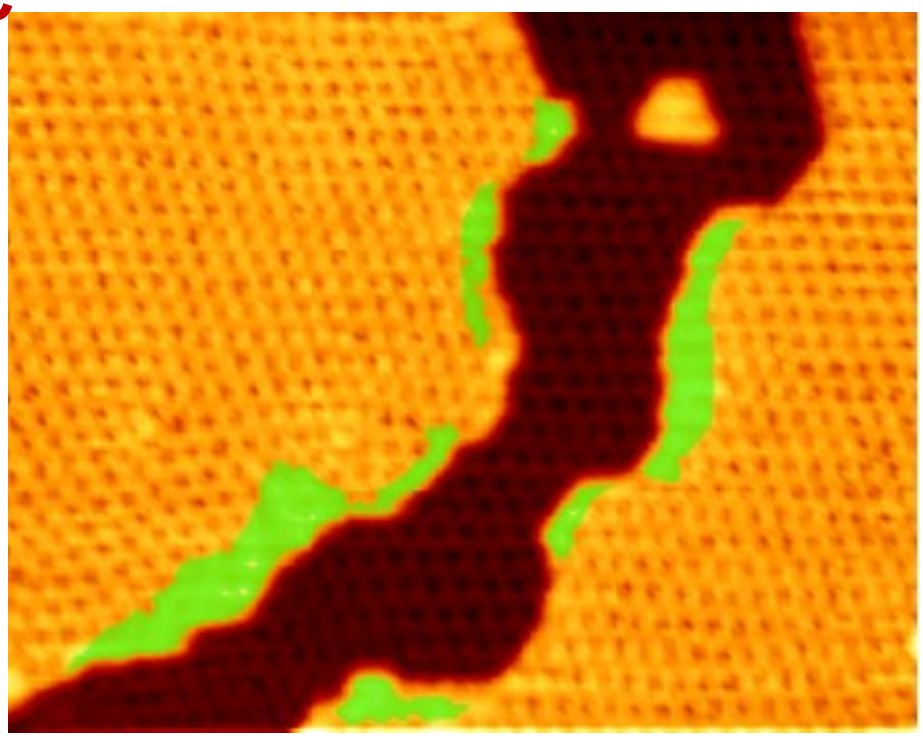
2 ML graphene



triangle

Graphene/SiC(0001)

T = 1120 °C



I_T = 0.2 nA, V_T = 0.2 V, 61 × 48 nm^2

Monolayer graphene covered surface
with
bilayer graphene at the step edges

In-situ observation of graphene growth

T = 1120 °C

147 min

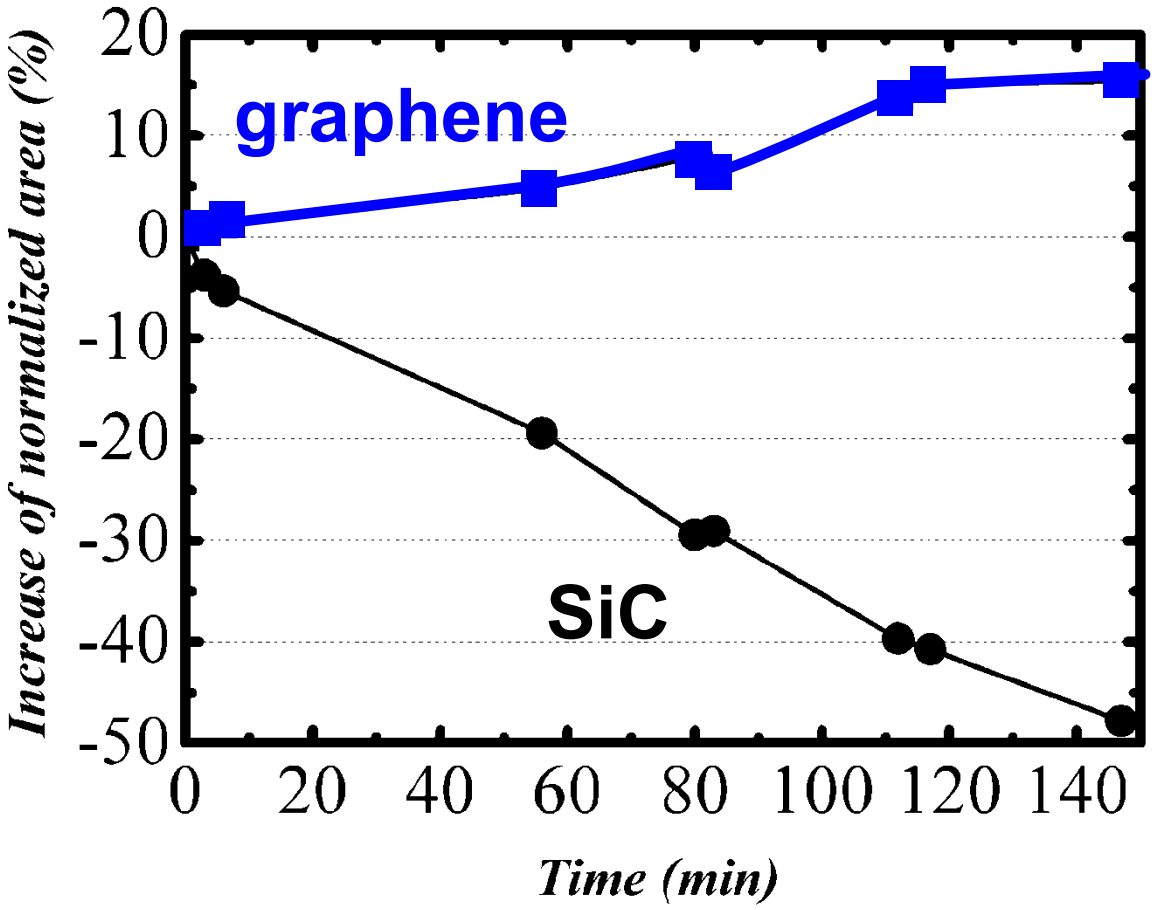
112 × 46 nm²

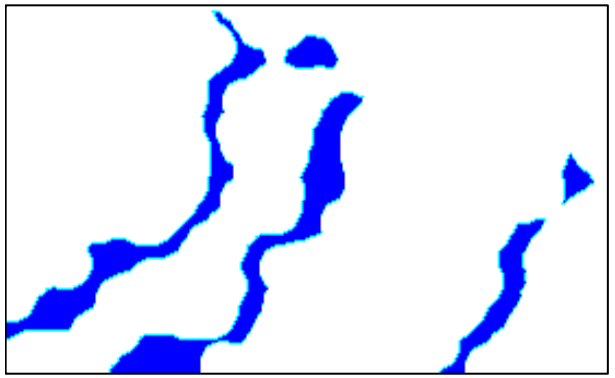
black: SiC island
Yellow : 2nd layer graphene

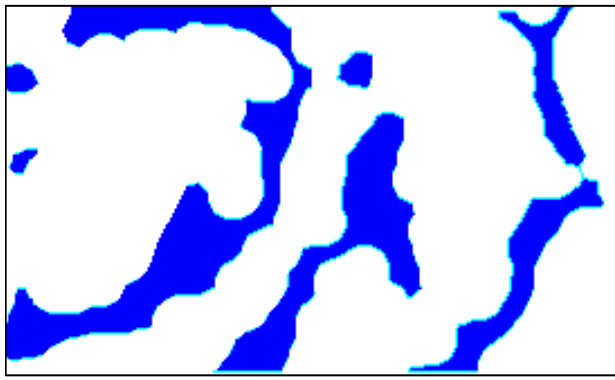
SiC islands shrink, while graphene area increases.

Y. Murata, V. Petrova, I. Petrov, and S. Kodambaka, *Thin Solid Films* **520**, 5289 (2012).

Graphene/SiC(0001): Growth kinetics







Areal change: 2nd layer graphene: **+15%** SiC: **- 47 %**

⇒ 3.15 layers of SiC consumed for each graphene layer

Y. Murata, V. Petrova, I. Petrov, and S. Kodambaka, *Thin Solid Films* **520**, 5289 (2012).

SiC(0001): Summary

- Bilayer graphene growth on 6H-SiC(0001) was investigated by HT- STM.

- We observed three modes of graphene growth:
  1) at graphene-free SiC step,
  2) at graphene-SiC interface and
  3) outward of graphene.

- Identified a possible rate-limiting step for bilayer graphene growth.

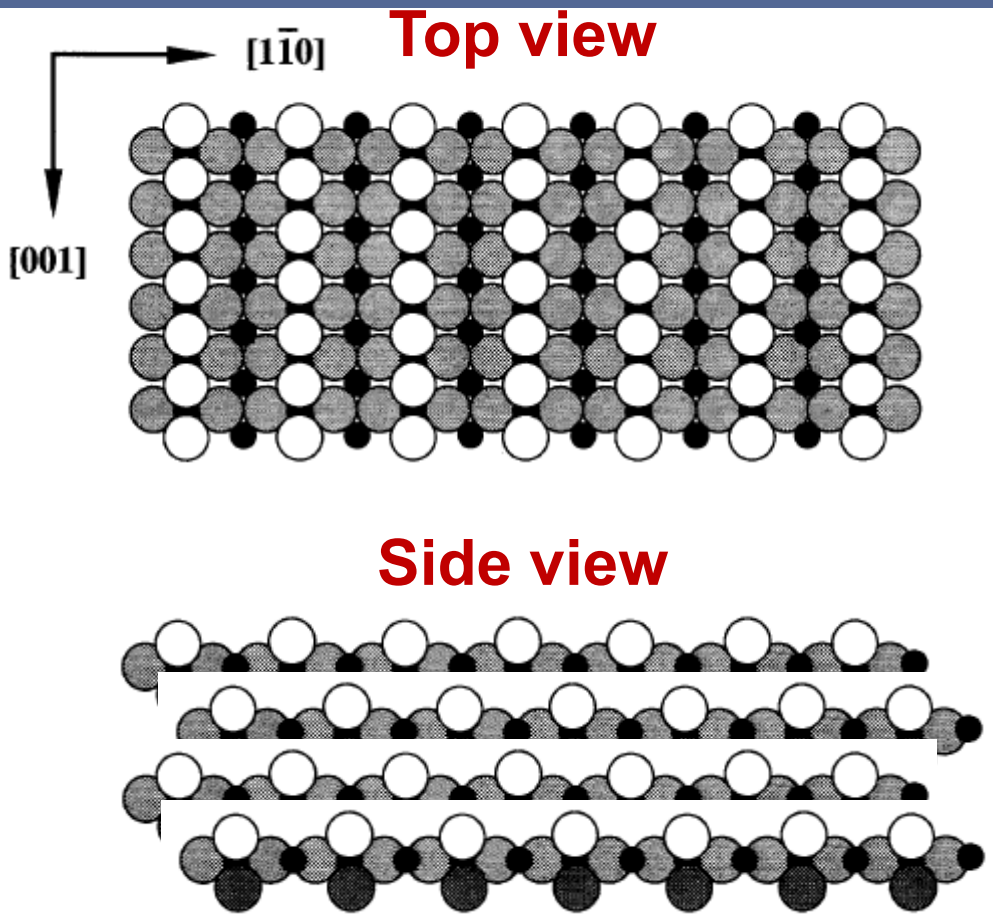
- STM is a powerful *in situ* technique to follow the surface carburization of refractory carbides.

In Situ High-Temperature STM Studies of C_2H_4-TiO_2(110) Reactions

GOAL:

Investigate the effects of gas chemistry (vacuum, O_2, C_2H_4) on surface structure.

$TiO_2(110)$-1x1



rutile TiO_2

a = 0.459 nm

c = 0.296 nm

$TiO_2(110)$-1x1

[110] = 0.649 nm

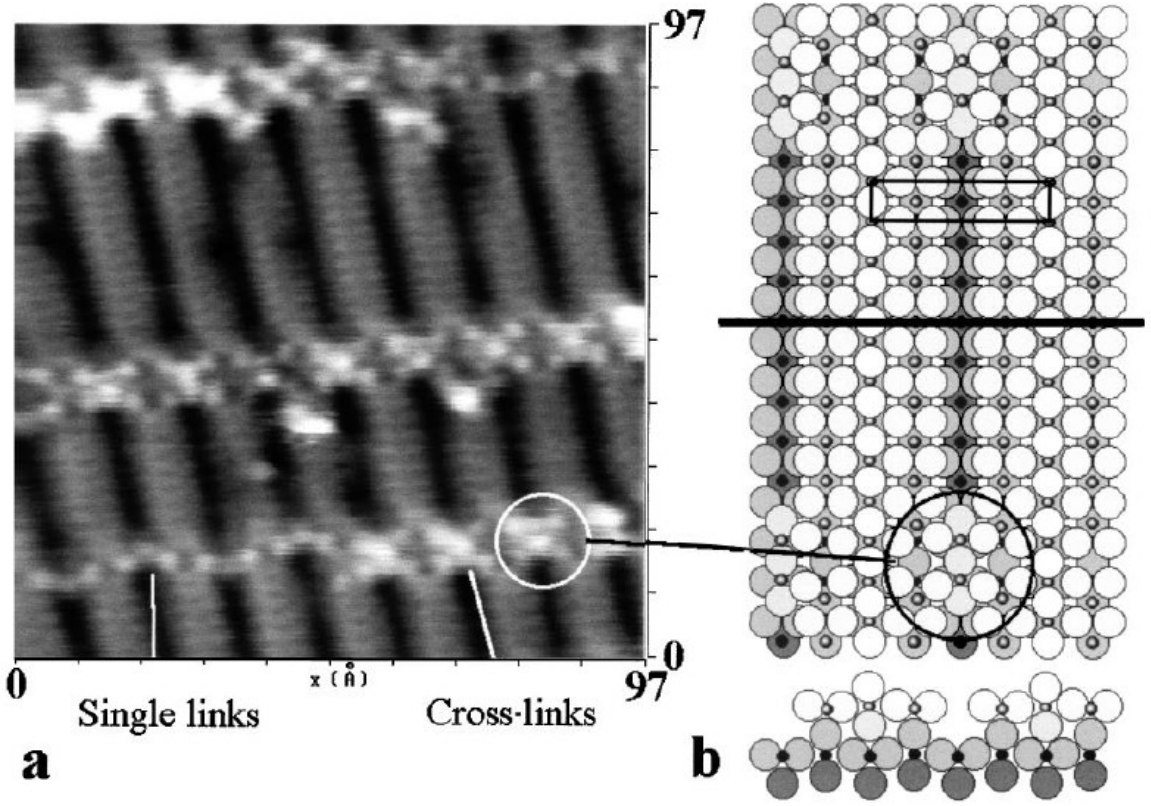
[001] = 0.296 nm

● Ti

○ Oxygen

J. Chem. Soc., Faraday Trans., 1998, **94**(1), 161–166

TiO_2(110)-2x1



rutile TiO_2

a = 0.459 nm

c = 0.296 nm

TiO_2(110)-2x1

[110] = 1.299 nm

[001] = 0.296 nm

● Ti

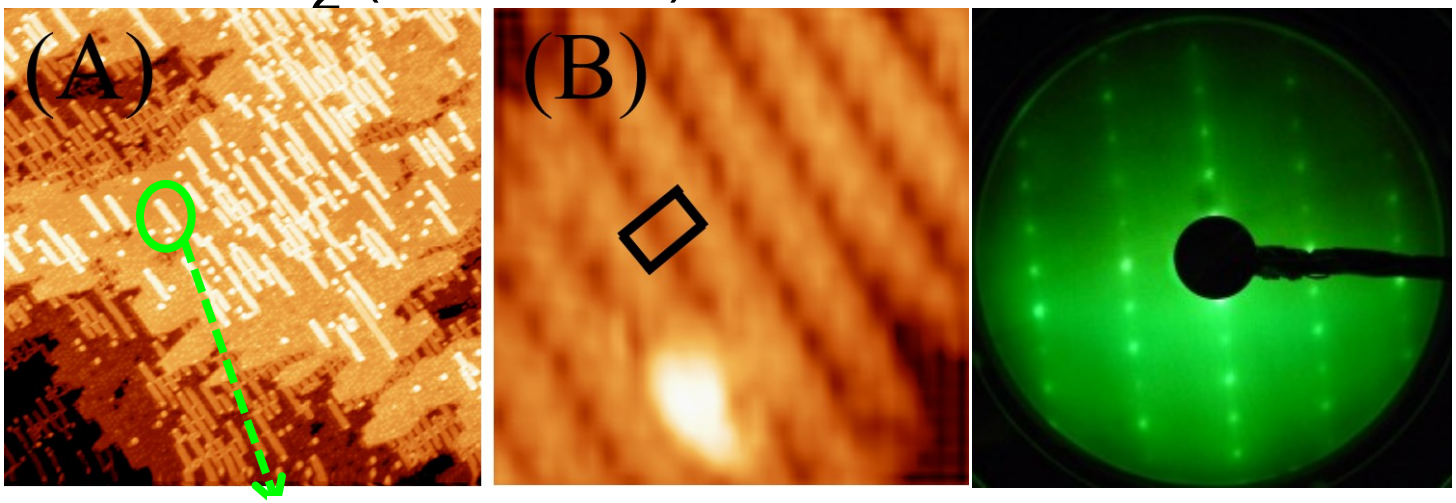
○ Oxygen

R. A. Bennett, P. Stone, N. J. Price, and M. Bowker

Phys. Rev. Lett. **82**, 3831 (1998).

TiO_2(110): Experimental

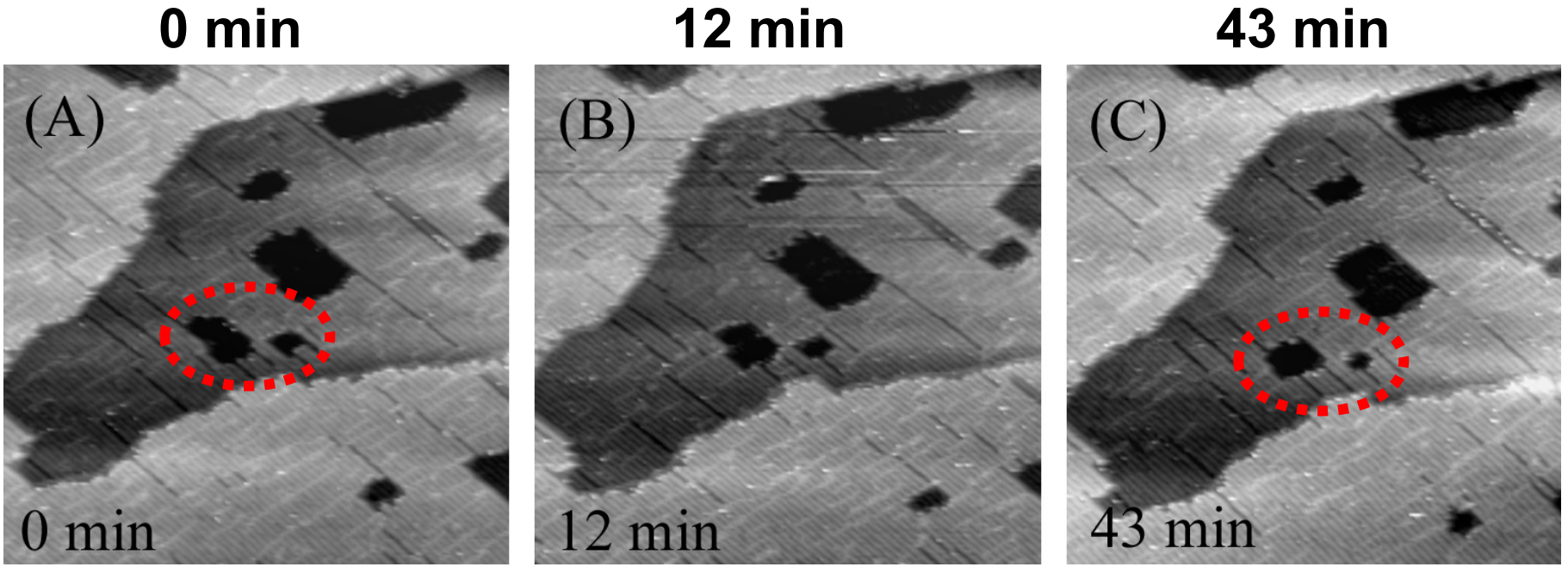
1. Ar^+ sputter, 1 KeV, 30 min
2. Vacuum anneal (~10^{-10} mbar) at 1100 K, 5 min
3. Anneal in O_2 (10^{-7} mbar) at 700 K, 30 min



4. ***In situ* STM, STS**
   - T: 700 – 1000 K (0 – 120 min)
   - P: vacuum, O_2, C_2H_4 (10^{-10} ~ 10^{-7} mbar)

$TiO_2(110)$: vacuum anneal

T = 1000 K, UHV: 1.0×10^{-10} mbar



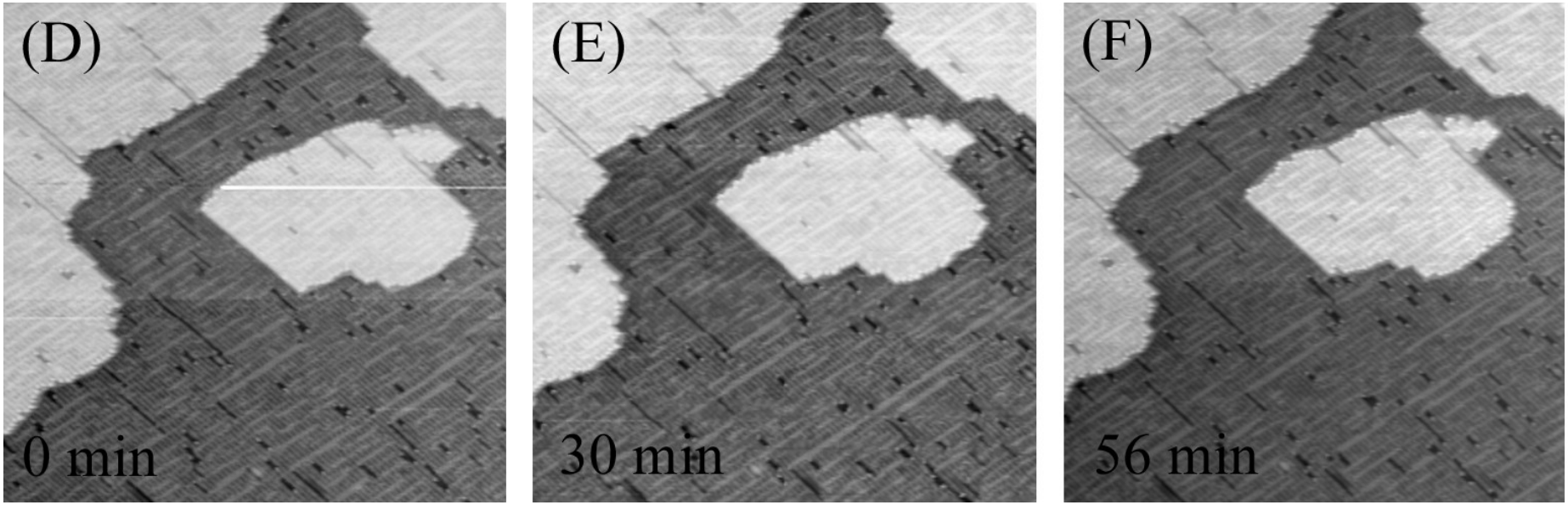
111 × 111 nm²

Annealing in vacuum → decrease in TiO_x coverage,
i.e. O-deficient surfaces form

$TiO_2(110)$: Effect of O_2

T = 1000 K, O_2: 5.0×10^{-9} mbar

0 min **30 min** **56 min**

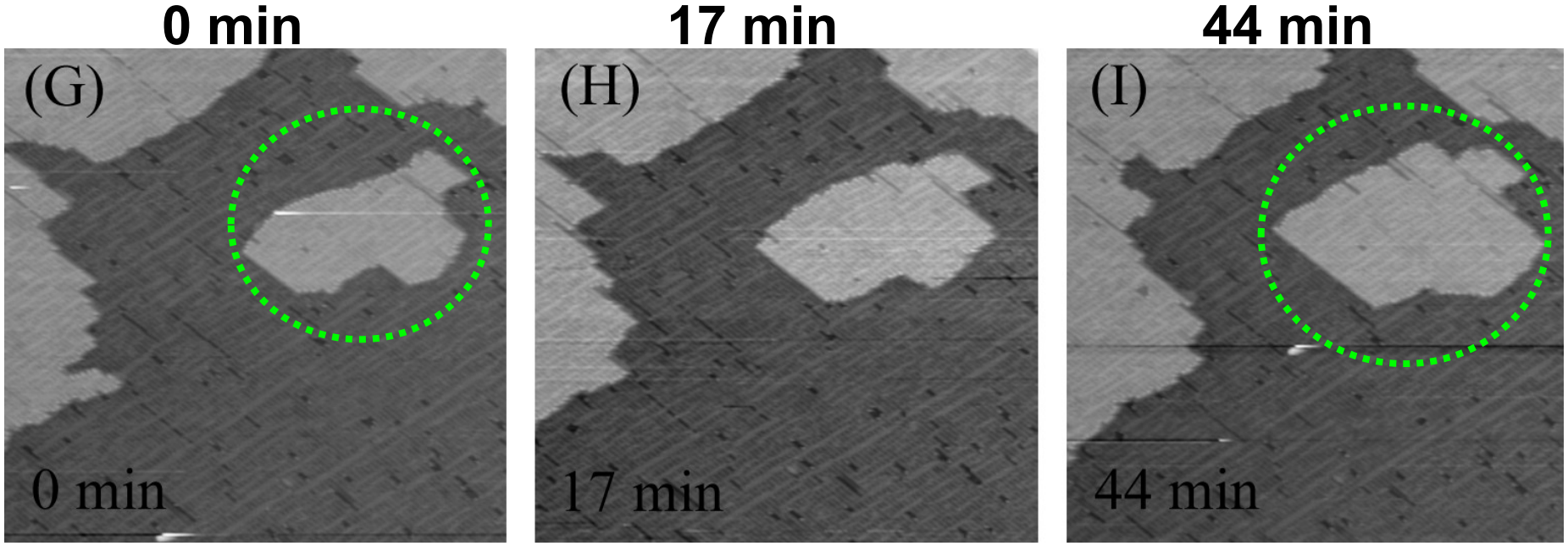


150 × 150 nm²

Annealing in O_2 → restores stoichiometric surface.

$TiO_2(110)$: Effect of C_2H_4

T = 1000 K, C_2H_4: 1.3×10^{-7} mbar



150 × 150 nm²

Surface island area increases with time

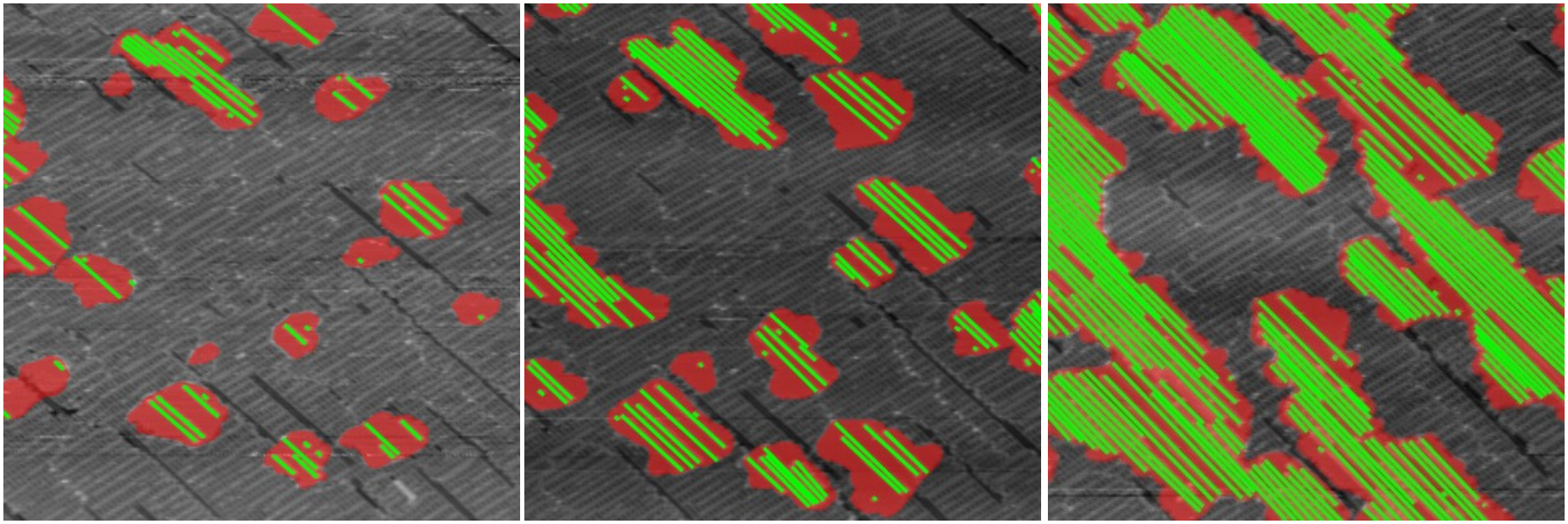
⇒ **growth of TiO_x!!**

Y. Murata, V. Petrova, I. Petrov, C. V. Ciobanu, & S. Kodambaka, *Appl. Phys. Lett.* **101**, 211601 (2012).

$TiO_2(110)$: Effect of C_2H_4

T = 900 K, C_2H_4: 1.3×10^{-7} mbar

0 min | 30 min | 119 min



150 × 150 nm²

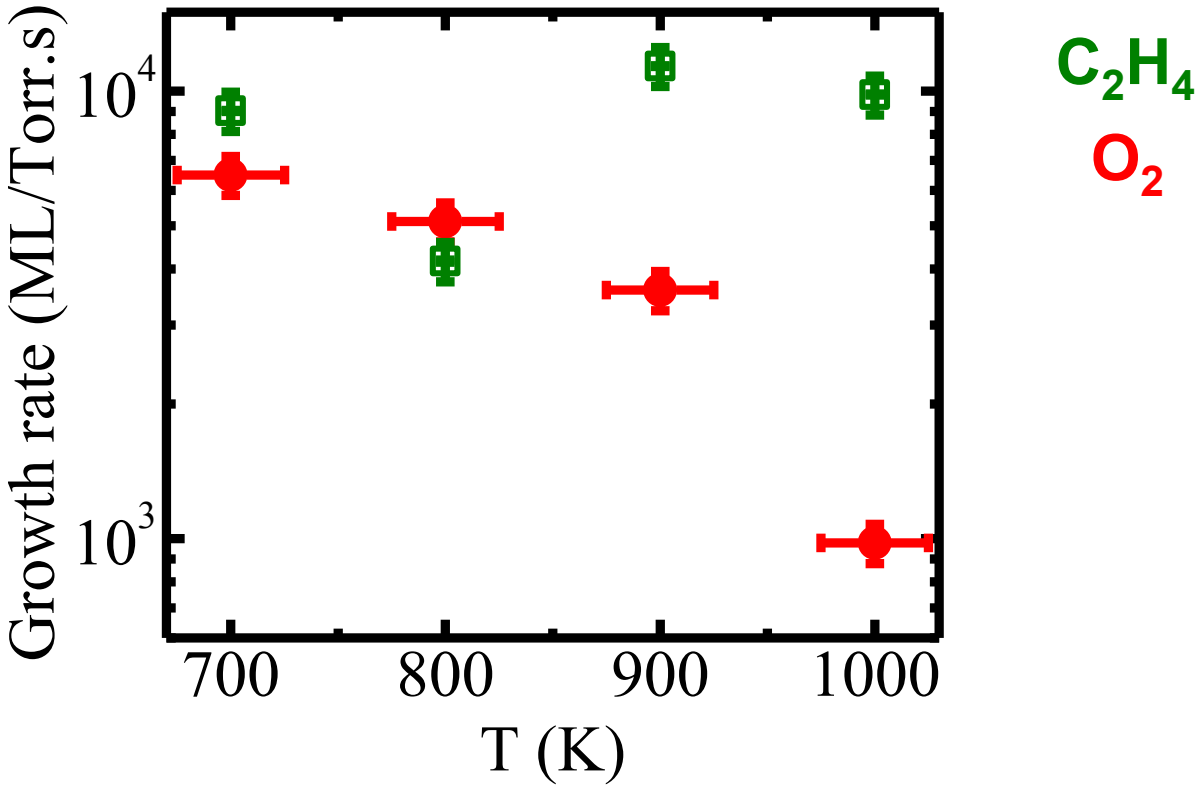
gray & green: 2×1

Red: 1×1

TiO_x coverage increases with time

Y. Murata, V. Petrova, I. Petrov, C. V. Ciobanu, & S. Kodambaka, *Appl. Phys. Lett.* **101**, 211601 (2012).

TiO_2(110): Effect of C_2H_4 vs. O_2



C_2H_4 promotes growth of TiO_x on the surface

Y. Murata, V. Petrova, I. Petrov, C. V. Ciobanu, & S. Kodambaka, *Appl. Phys. Lett.* **101**, 211601 (2012).

$TiO_2(110)$: Summary

- *In situ* HT-STM used to investigate the effect of reducing gas on the surface structure of $TiO_2(110)$.

- Observed $TiO_2(110)$-1×1 ⇔ 2×1 as a function of T & ambient chemistry.

- $TiO_2(110)$-1×1 area ↑ as O_2 ↑
  & as T ↓

- **C_2H_4 promotes the growth of TiO_2.**

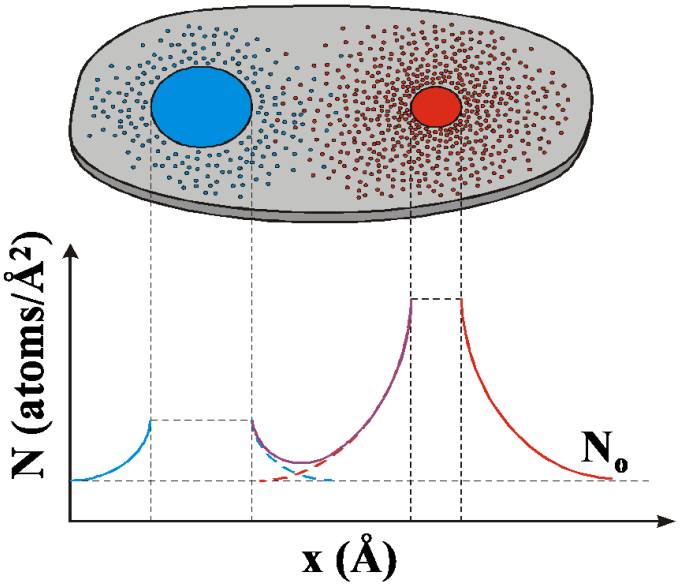
Liquid-metal/Solid Interface Dynamics: Ostwald ripening of Ga droplets on carbon

GOAL: To understand the mass transport mechanisms controlling thermal stability

Ostwald ripening

- Curvature-driven process
- Large clusters grow at the expense of small clusters
- Governed by Gibbs-Thomson relation

Ostwald ripening



Mean-Field Theory

- uniform surface adatom concentration
- large droplet sizes

$$\exp\left(\frac{2\gamma\Omega}{rkT}\right) \approx 1 + \frac{2\gamma\Omega}{rkT}$$

Gibbs-Thomson relation

$$\frac{N(r)}{N_o} = \exp\left(\frac{2\gamma\Omega}{rkT}\right)$$

- N : atoms/Å²
- Ω : volume/atom (Å³)
- γ : surface tension (eV/Å²)

Atomic processes

1. **Detachment** from small droplets
2. **Diffusion** on the surface
3. **Attachment** at larger droplets.

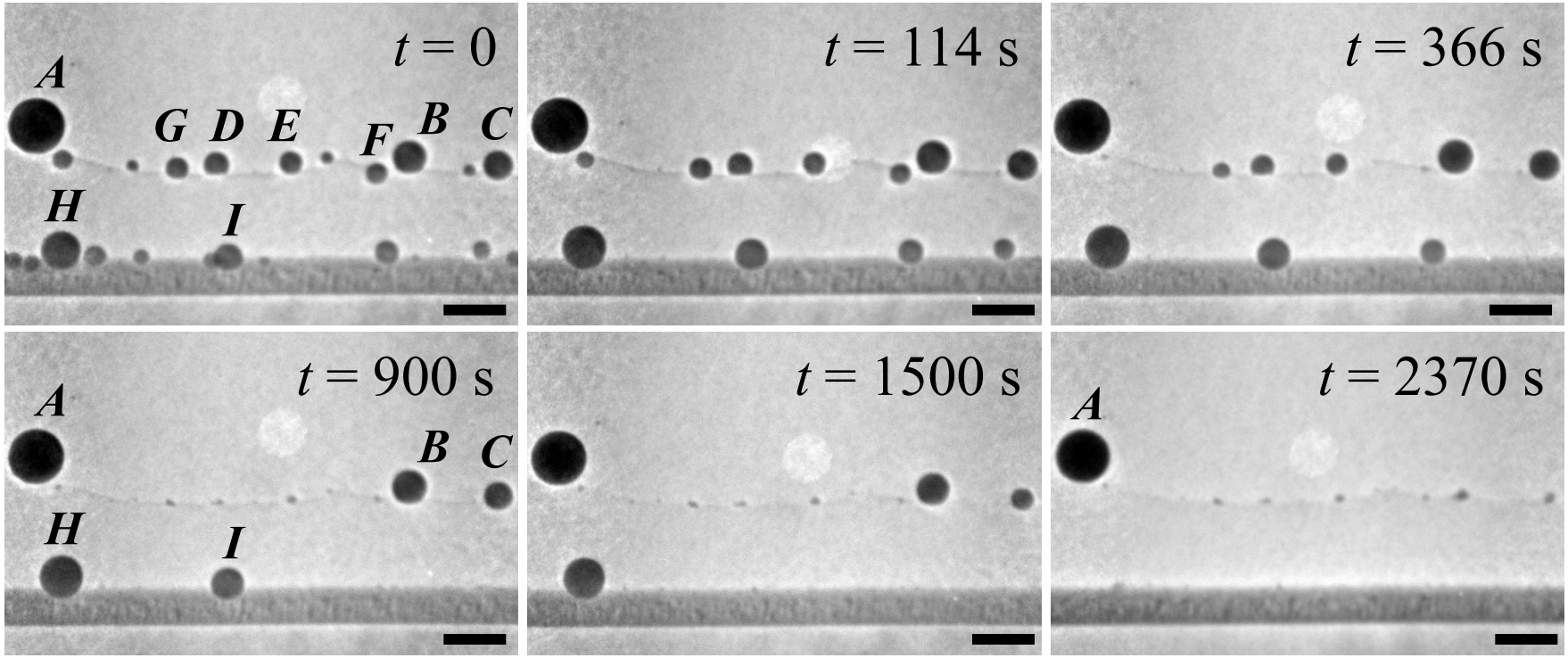
$$V \propto (t^*-t)^n$$

- n = 1 ⇒ detachment-limited
- n = 3/4 ⇒ diffusion-limited

I.M. Lifshitz & V.V. Slyozov, *J. Phys. Chem. Solids* **19**, 35 (1961).

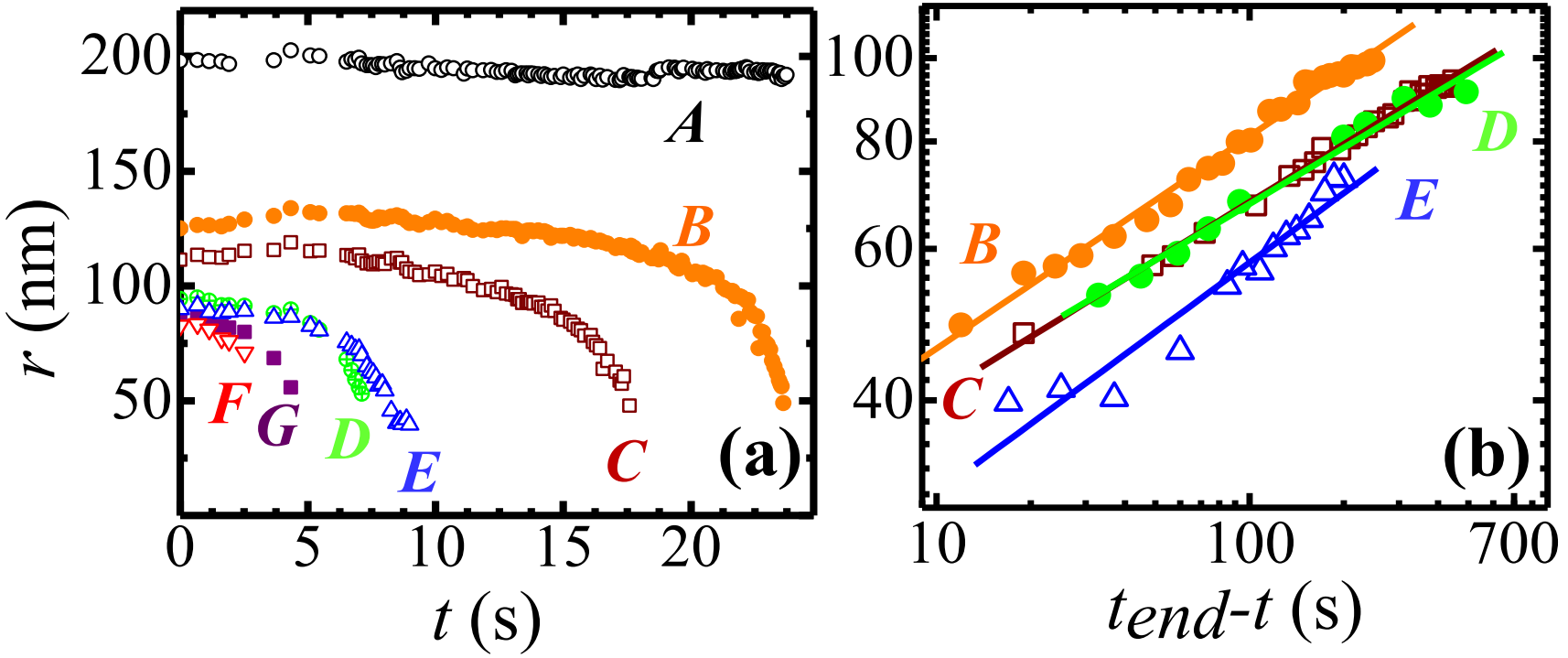
Ostwald ripening of Ga droplets

T = 500 ºC



Scale bar: 200 nm

Ostwald ripening of Ga droplets



Droplet decay rates are consistent with surface-diffusion-limited kinetics

In situ TEM: Summary

In situ high-temperature TEM studies are useful in determining the mass transport mechanisms controlling the thermal stability of interfaces.

Our ongoing studies are focused on extending these approaches to the investigation of ceramic-ceramic interfaces.