Graphene oxide:
Photochemical reduction and micro-patterning

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Born in Yokohama（横浜）, 1958

1977 Enter into Tokyo Institute of Technology
1981 Graduate from Faculty of Engineering,
Tokyo Institute of Technology
1983 Mater Degree:
Tokyo Institute of Technology,
Department of Chemical Engineering
1983 - 1997 Nikon Co.
1990-1993 Microphotoconversion Project, JRDC
1994 Dr. Eng. Osaka Univ.
1997 - 2003 Associate Professor, Nagoya Univ.
Depatment of Material Processing Engineering
2003 - Present
Professor, Kyoto Univerity,
Department of Materials Science and Engineering

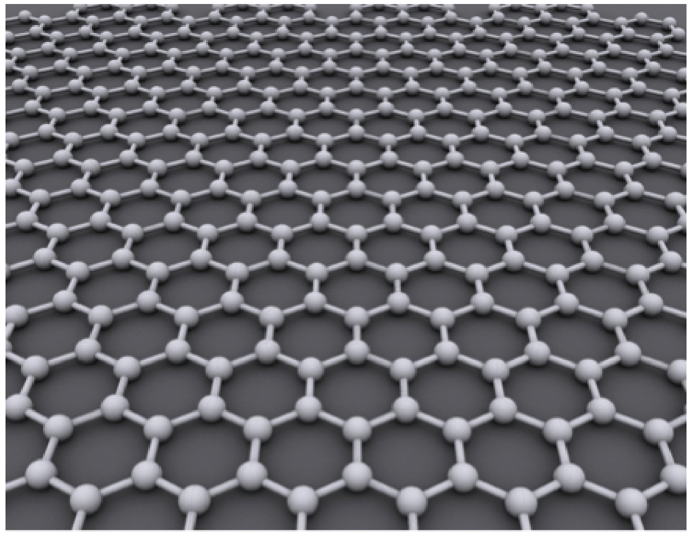

銀閣寺 2014年２月


鴨川 2014年３月

祇園祭 2014年７月

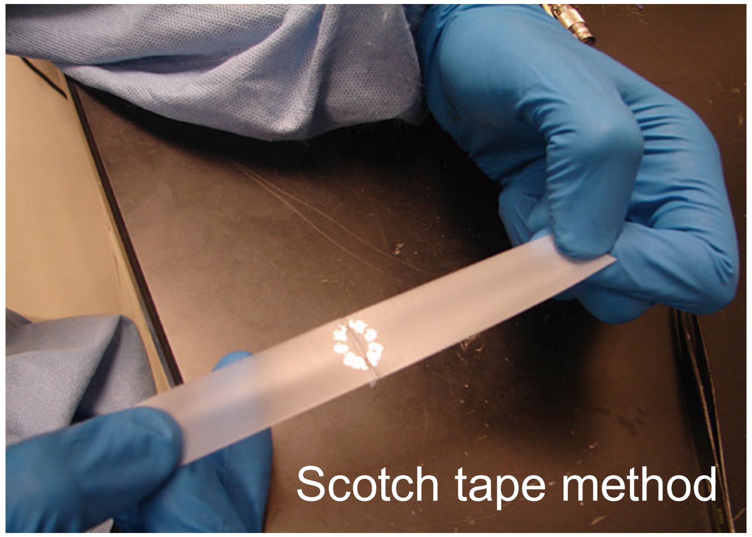

浄住寺 2013年12月

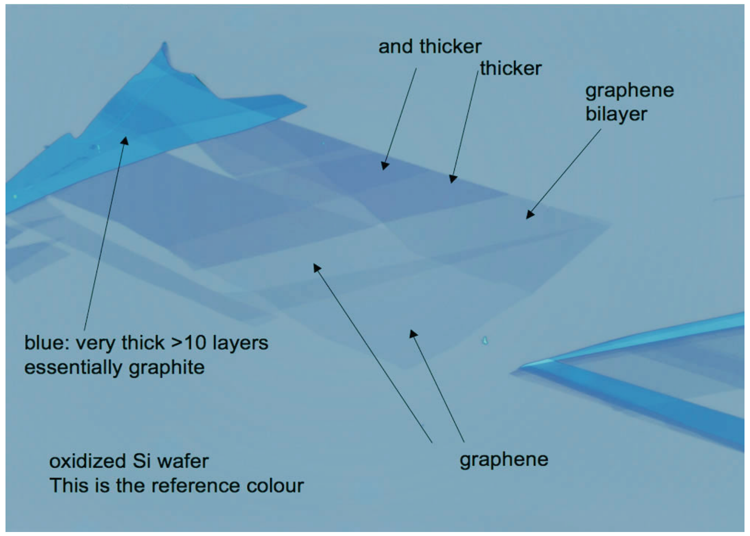
Graphene: *Promising future electronic material*



Graphene molecular structure

Sparks fly over graphene energy device,
Nature News Blog, 15 Mar 2012





Mechanical cleavage: Scotch tape method

JR Minkel, Scientific American, March 20, 2008

Low throughput hinders its industrial application.

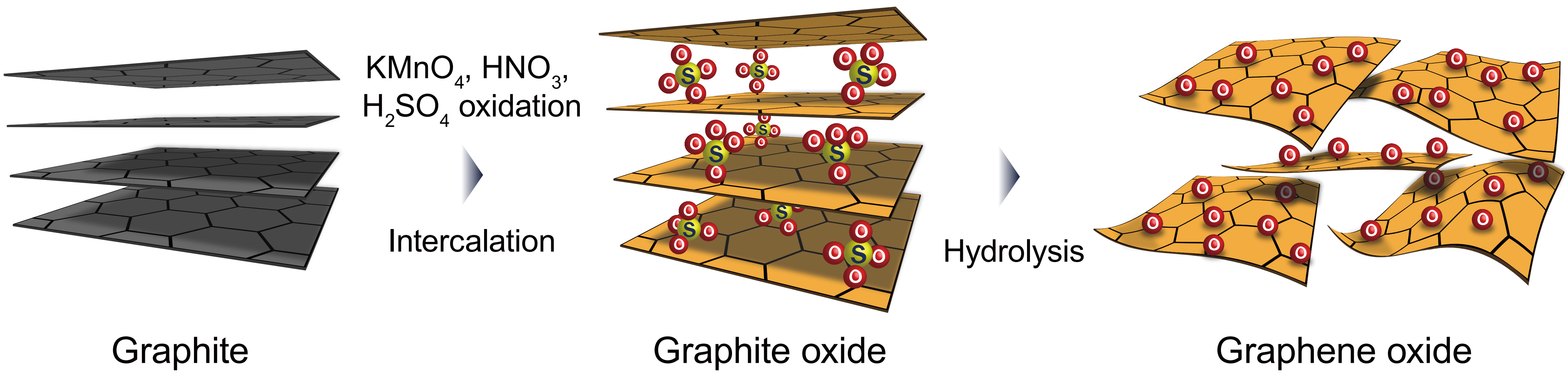
- High carrier mobility
- Quantum Hall effect

Next generation basic electronic material

Need for
1) Mass-production process
2) Fixed on a solid surface

Graphene Oxide: *A derivative of Graphene*

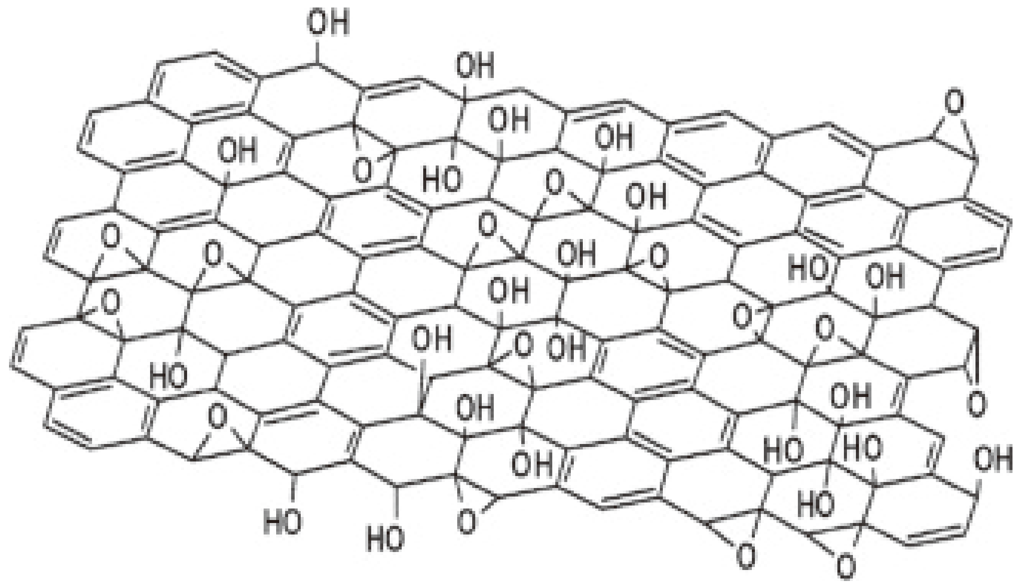
Hummers method: mass-production way

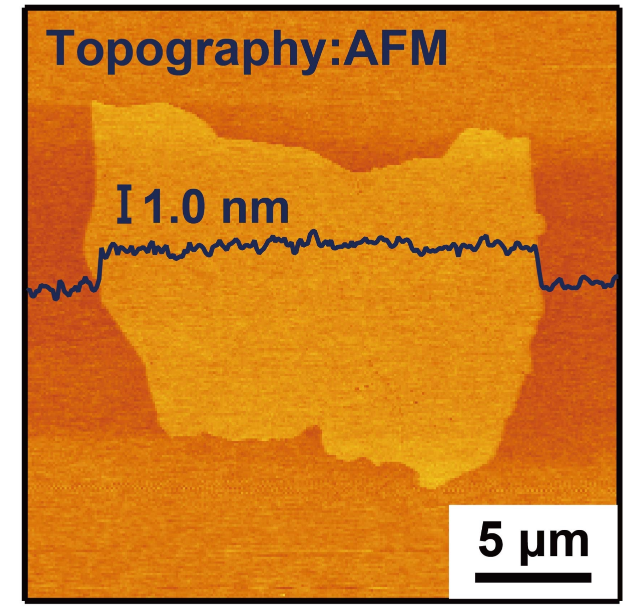


Oxidation $NaNO_3$+$H2SO_4$+$KMnO_4$	**Hydrolysis** Remove oxidants H_2O_2+HCl	**Sonication**	**Centrifuging**

W. S. Hummers and R. E. Offenma, *J. Am. Chem. Soc.* **80** (1958) 1339.
M. Hirata et al., Carbon, 12 (2004) 2929.

GO fabricated by a modified hummers method



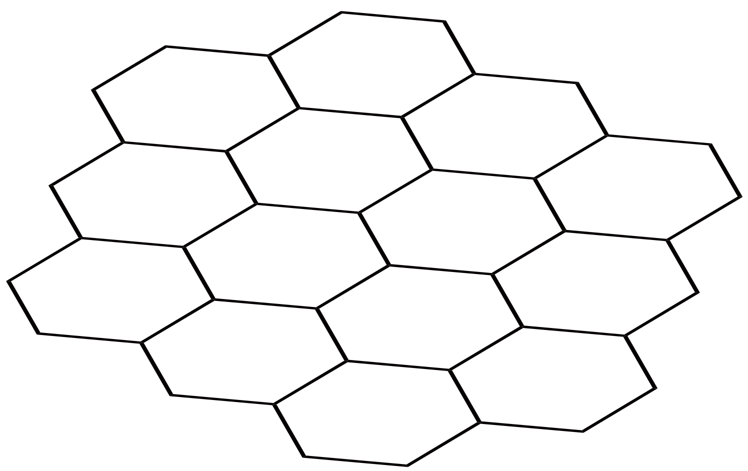


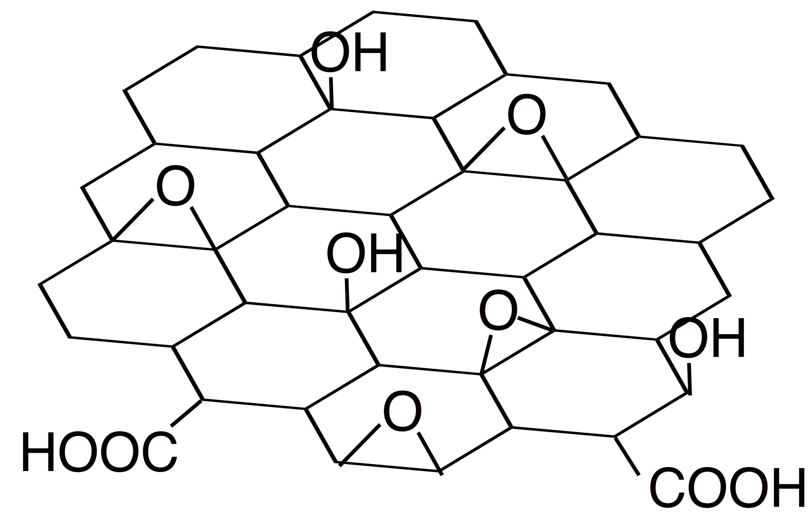
Lerf–Klinowski model of GO
A. Lerf et al., J. Phys. Chem. B 102 (1998) 4477.
H. He et al., Chem. Phys. Lett. 287 (1998) 53.

GO is soluble in water due to its polar functional groups.

GO can be deposited on solid surfaces via casting from the solution.

Graphene & Graphene Oxide





Graphene

Good conductor

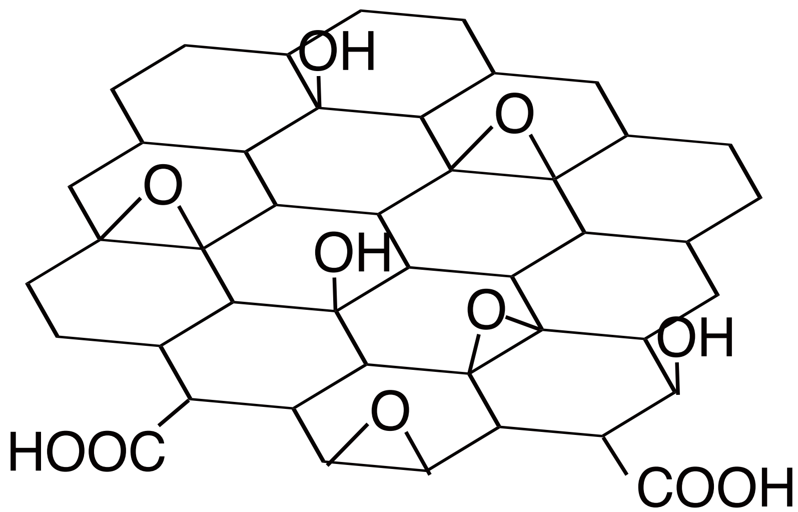
Graphene Oxide

dispersible in varisous solvent

Sp2 domain; conductive
Oxidized domain; insulating

Need for recovering conductivity

Reduced Graphene Oxide : **rGO**

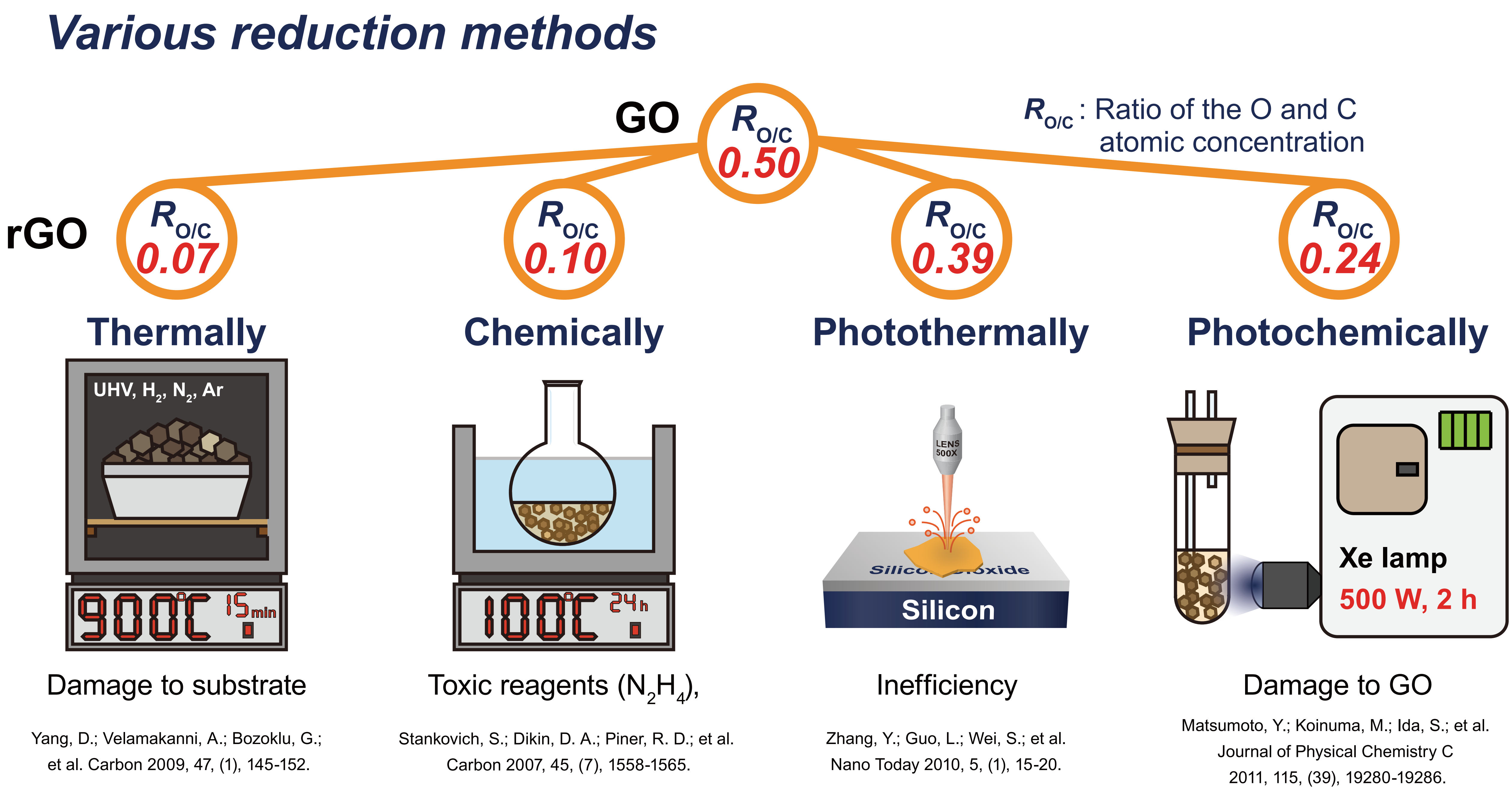


Graphene Oxide: GO

Thermal annealing
Chemical reduction with hydrazine
Photocatalytic reduction - UV illumination

Reduced Graphene Oxide: rGO

Oxygen moieties are partially removed,
Conductivity is improved

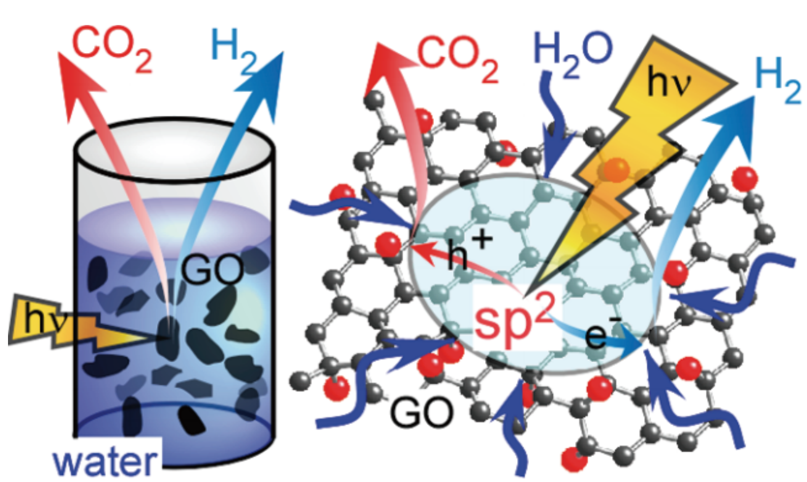

Various reduction methods
GO
$R_{O/C}$ 0.50
$R_{O/C}$: Ratio of the O and C atomic concentration
rGO
$R_{O/C}$ 0.07
$R_{O/C}$ 0.10
$R_{O/C}$ 0.39
$R_{O/C}$ 0.24
Thermally
Chemically
Photothermally
Photochemically
UHV, H_2, N_2, Ar
900°C 15min
100°C 24h
LENS 500X
Silicon Dioxide
Silicon
Xe lamp
500 W, 2 h
Damage to substrate
Toxic reagents (N_2H_4),
Inefficiency
Damage to GO
Yang, D.; Velamakanni, A.; Bozoklu, G.; et al. Carbon 2009, 47, (1), 145-152.
Stankovich, S.; Dikin, D. A.; Piner, R. D.; et al. Carbon 2007, 45, (7), 1558-1565.
Zhang, Y.; Guo, L.; Wei, S.; et al. Nano Today 2010, 5, (1), 15-20.
Matsumoto, Y.; Koinuma, M.; Ida, S.; et al. Journal of Physical Chemistry C 2011, 115, (39), 19280-19286.

UV light Reduction

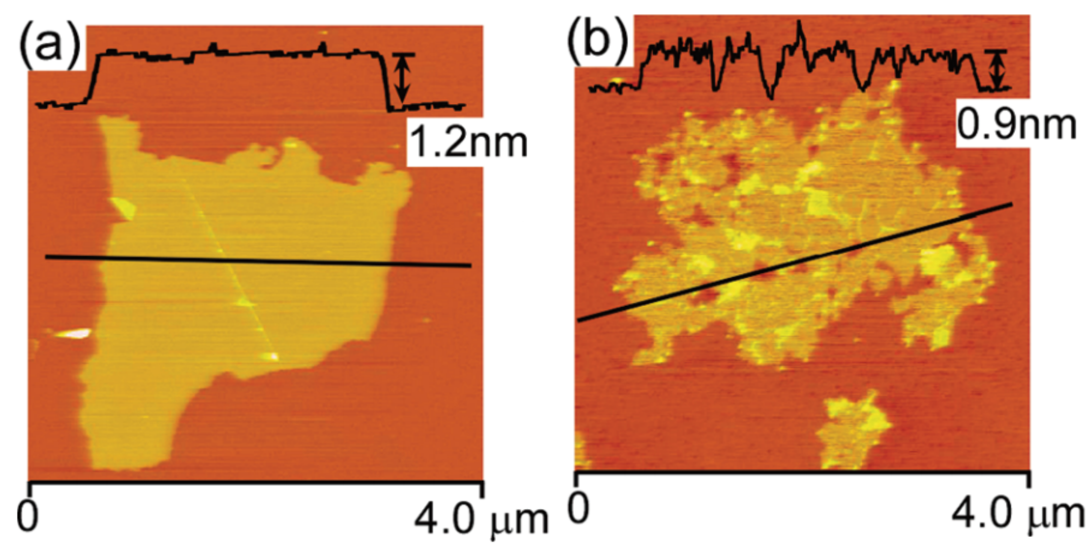
- **Light density:** ***67 mW/cm²*****; Time:** ***2 h*****; Environment:** ***N_2 or H_2***

Matsumoto, Y.; Koinuma, M.; Kim, S. Y.; Watanabe, Y.; Taniguchi, T.; Hatakeyama, K.; Tateishi, H.; Ida, S. Simple Photoreduction of Graphene Oxide Nanosheet under Mild Conditions. Acs Applied Materials & Interfaces 2010, 2, 3461-3466.

- **Light power:** ***500 W*****; Time:** ***8~48 h*****; Environment:** ***H_2O***



Schematic illustration

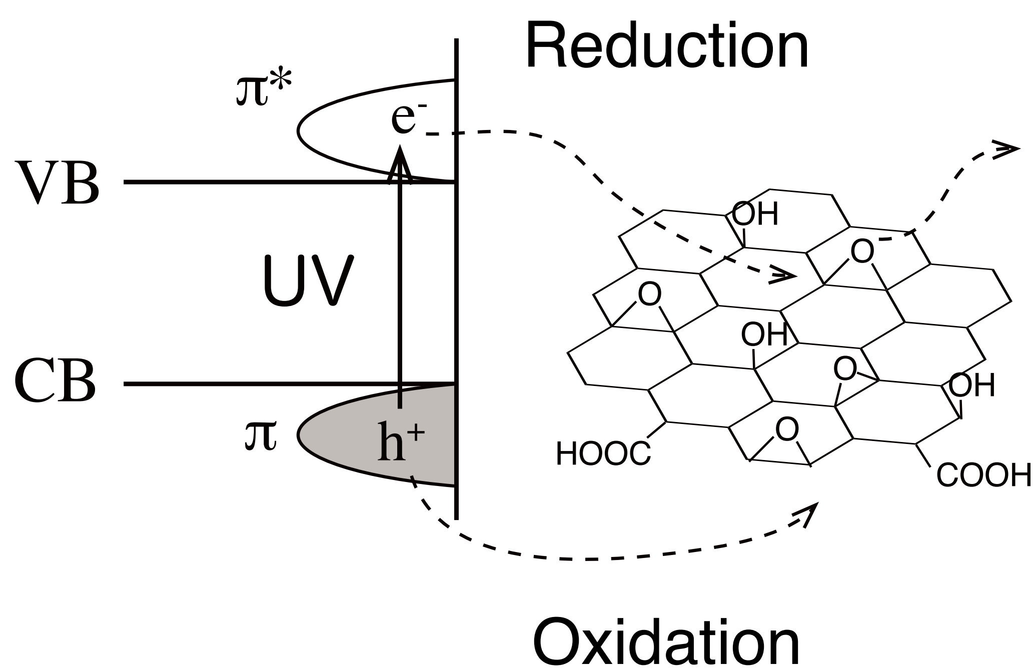


(a) before reduction, (b) after 48 h reduction

Defects formed due to reduction

Matsumoto, Y.; Koinuma, M.; Ida, S.; Hayami, S.; Taniguchi, T.; Hatakeyama, K.; Tateishi, H.; Watanabe, Y.; Amano, S. Photoreaction of Graphene Oxide Nanosheets in Water. Journal of Physical Chemistry C 2011, 115, 19280-19286.

Proposed mechanism of UV reduction



Photocatalytic mechanism

sp2 nano-domins in GO work as semiconucotor

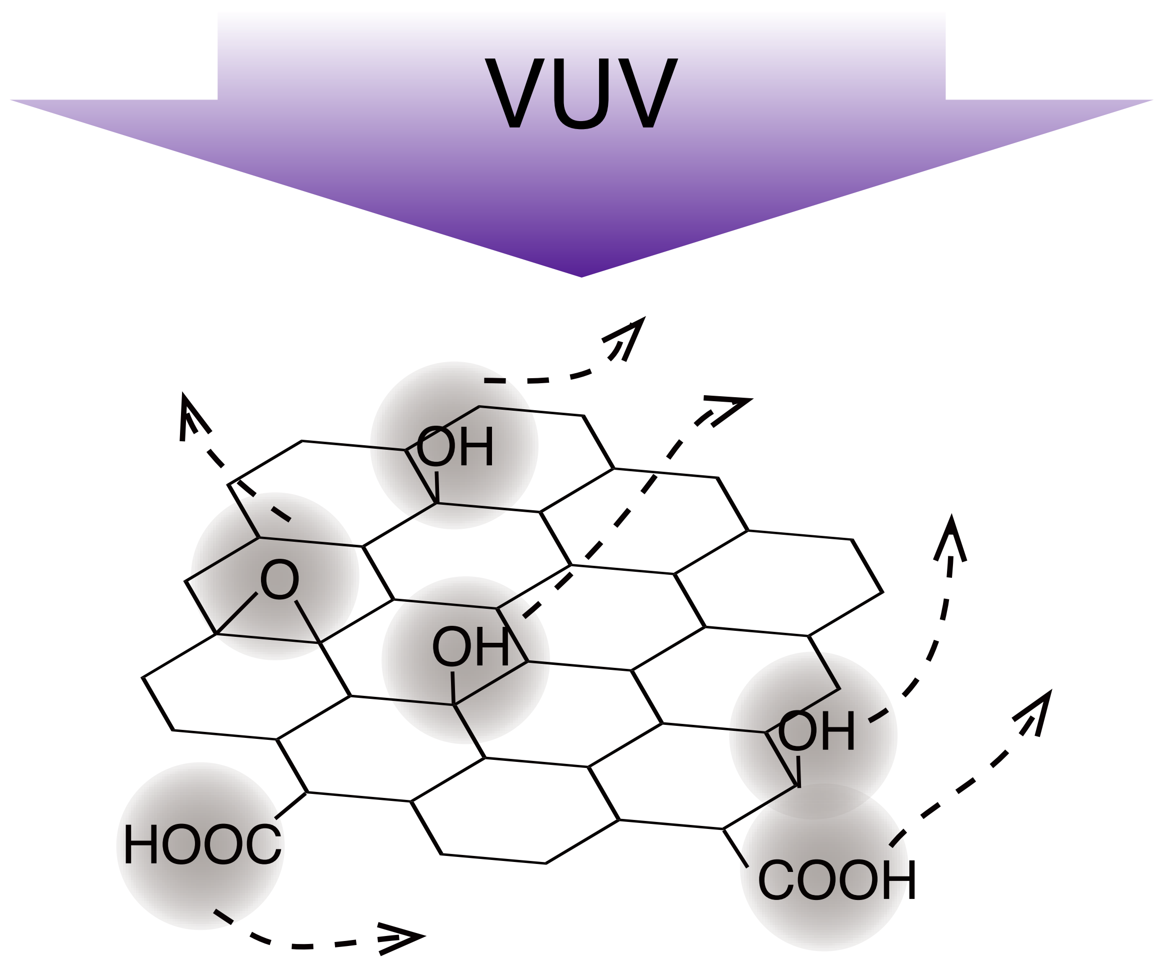
π electrons are excited to VB by UV illumination

Generation of hole-electron pairs

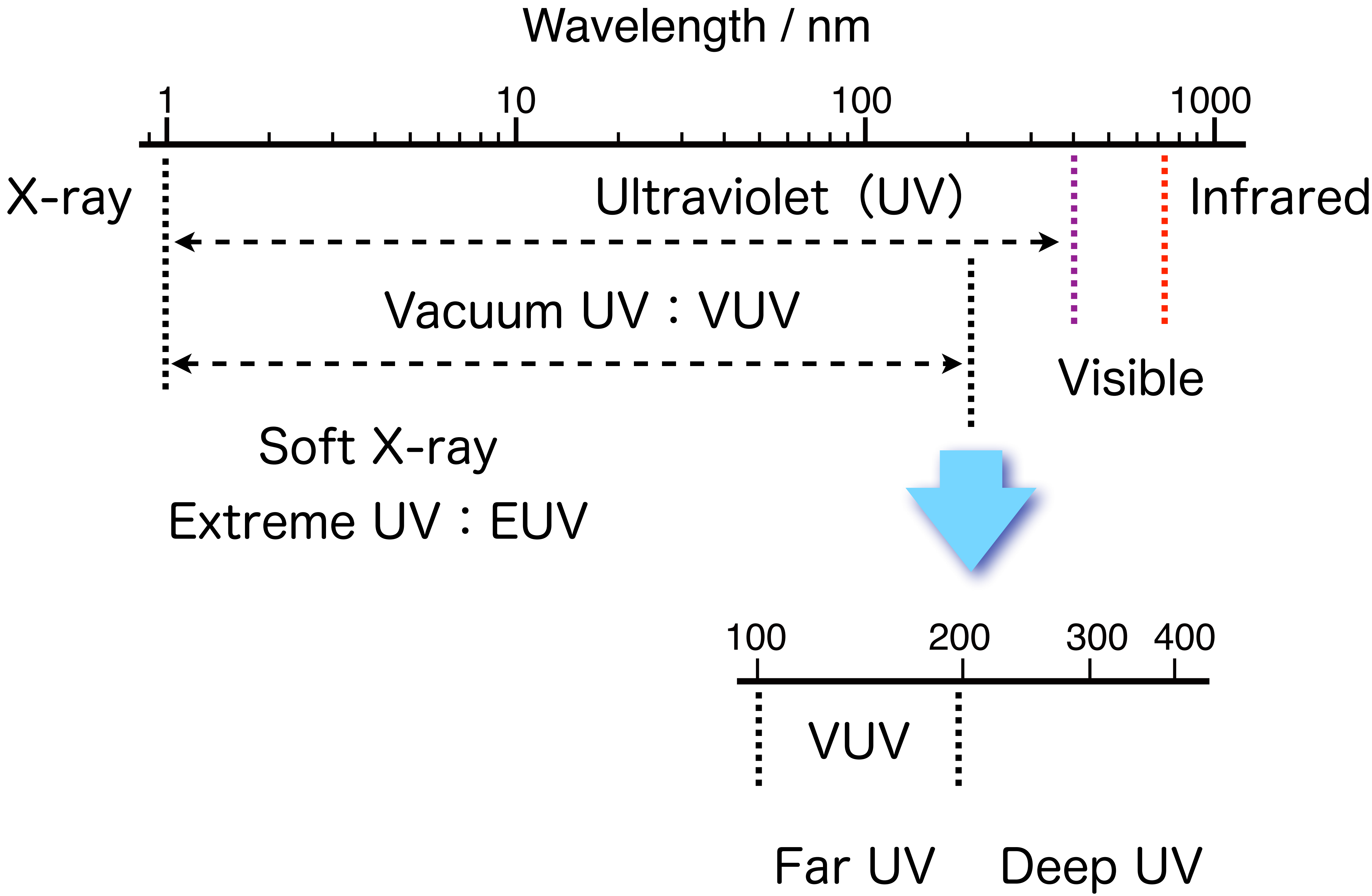
electrons → reduciotion of GO: Oxygen removal
holes → oxidation of GO: Damages to GO

VUV irradiation to GO in vacuum

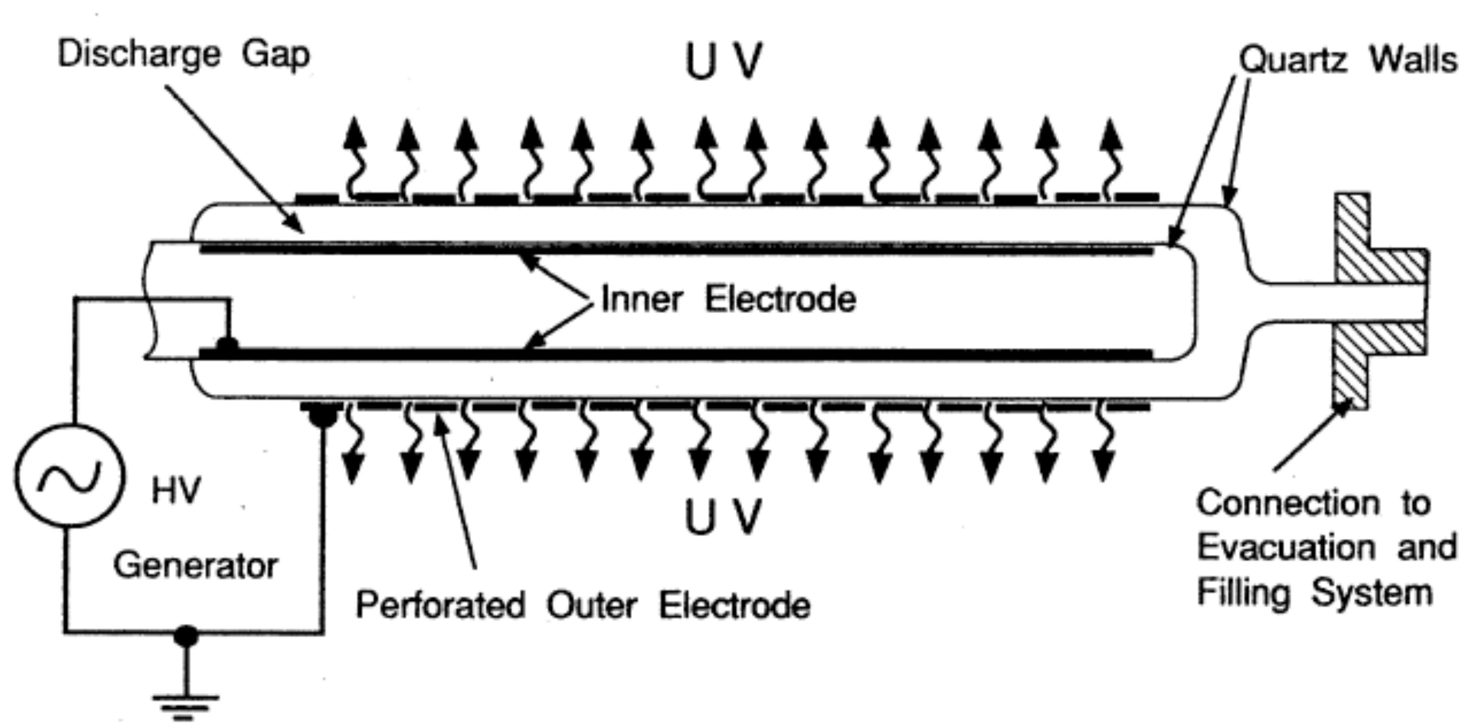
Capability on C-O bond breaking



Wavelength of light



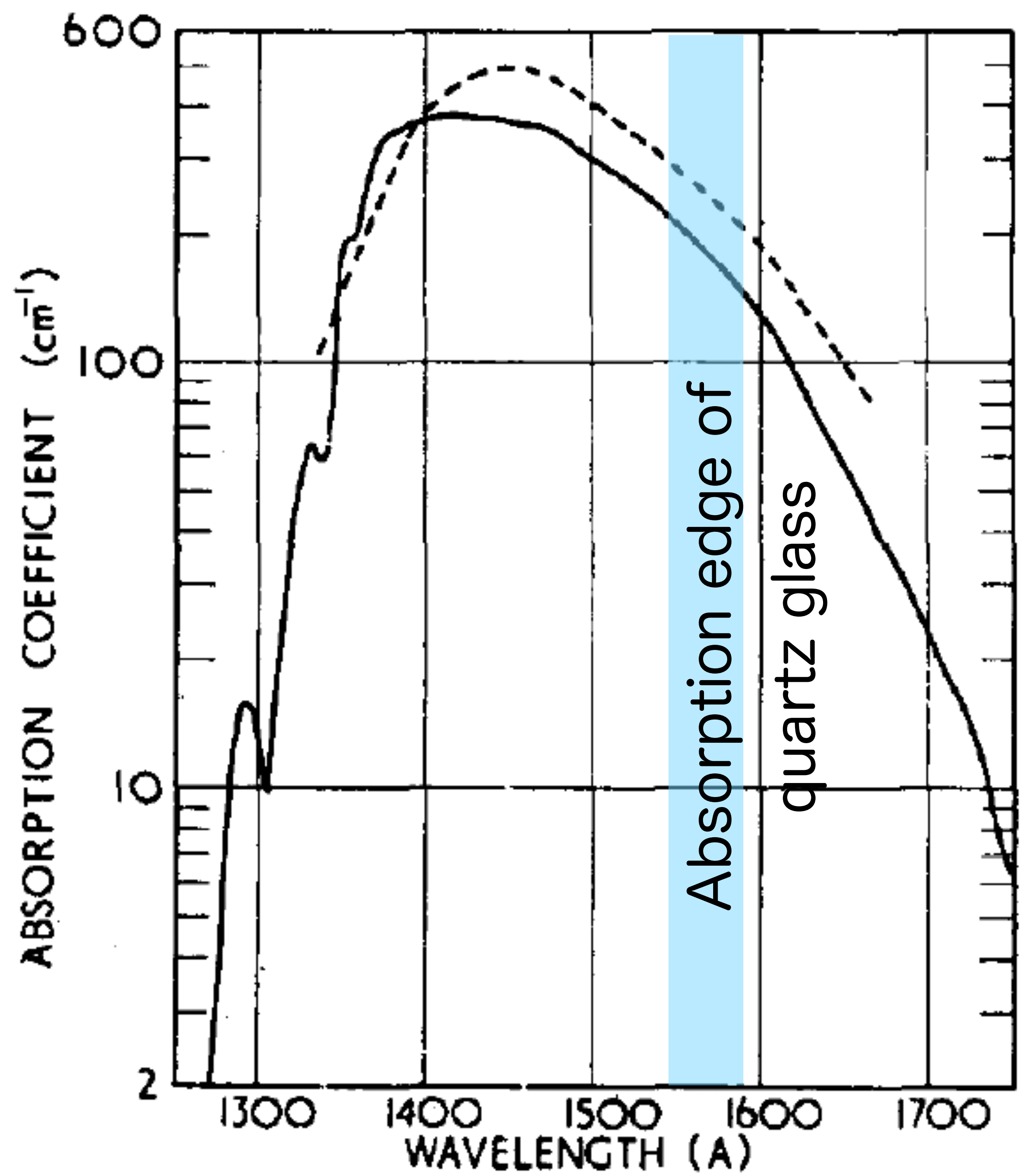
VUV light source: Excimer lamp



U. Kogelschatz, Pure & Appl. Chem. 62, 1667 (1990)

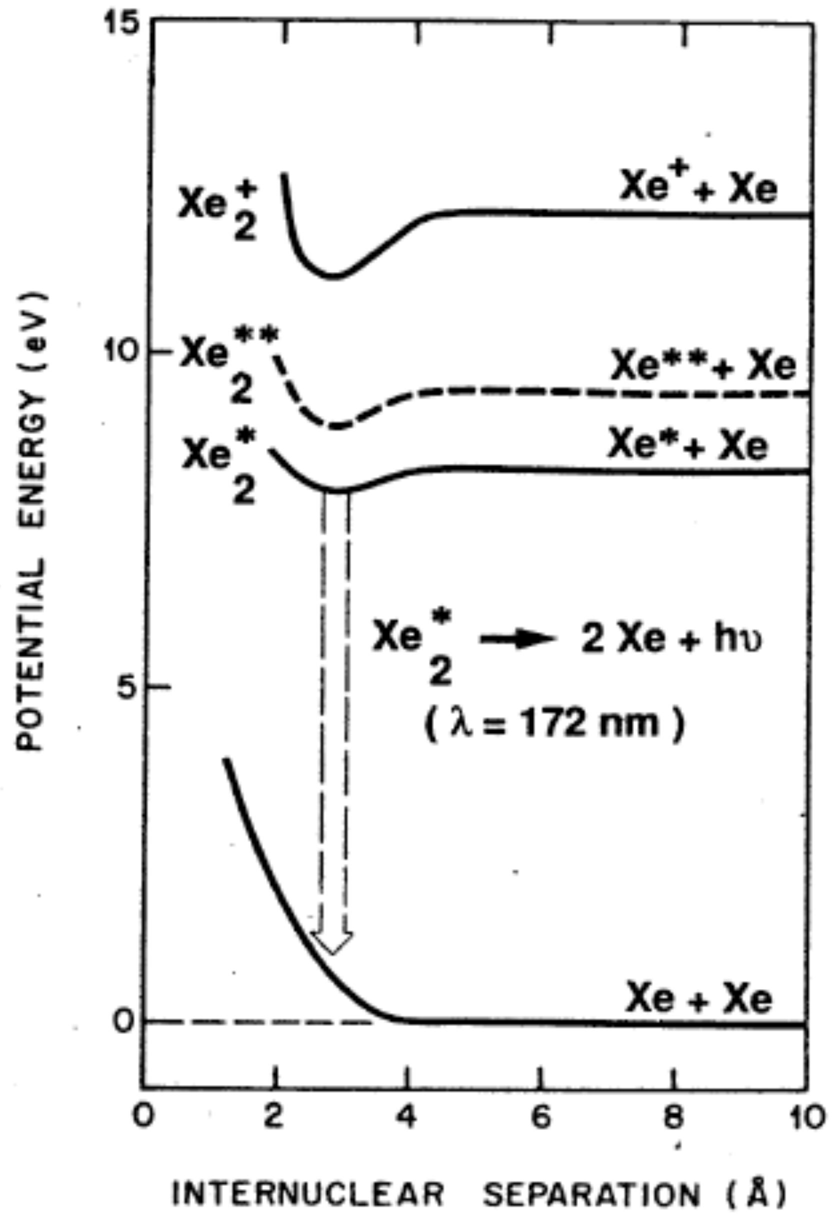
VUV Absorption of Oxygen

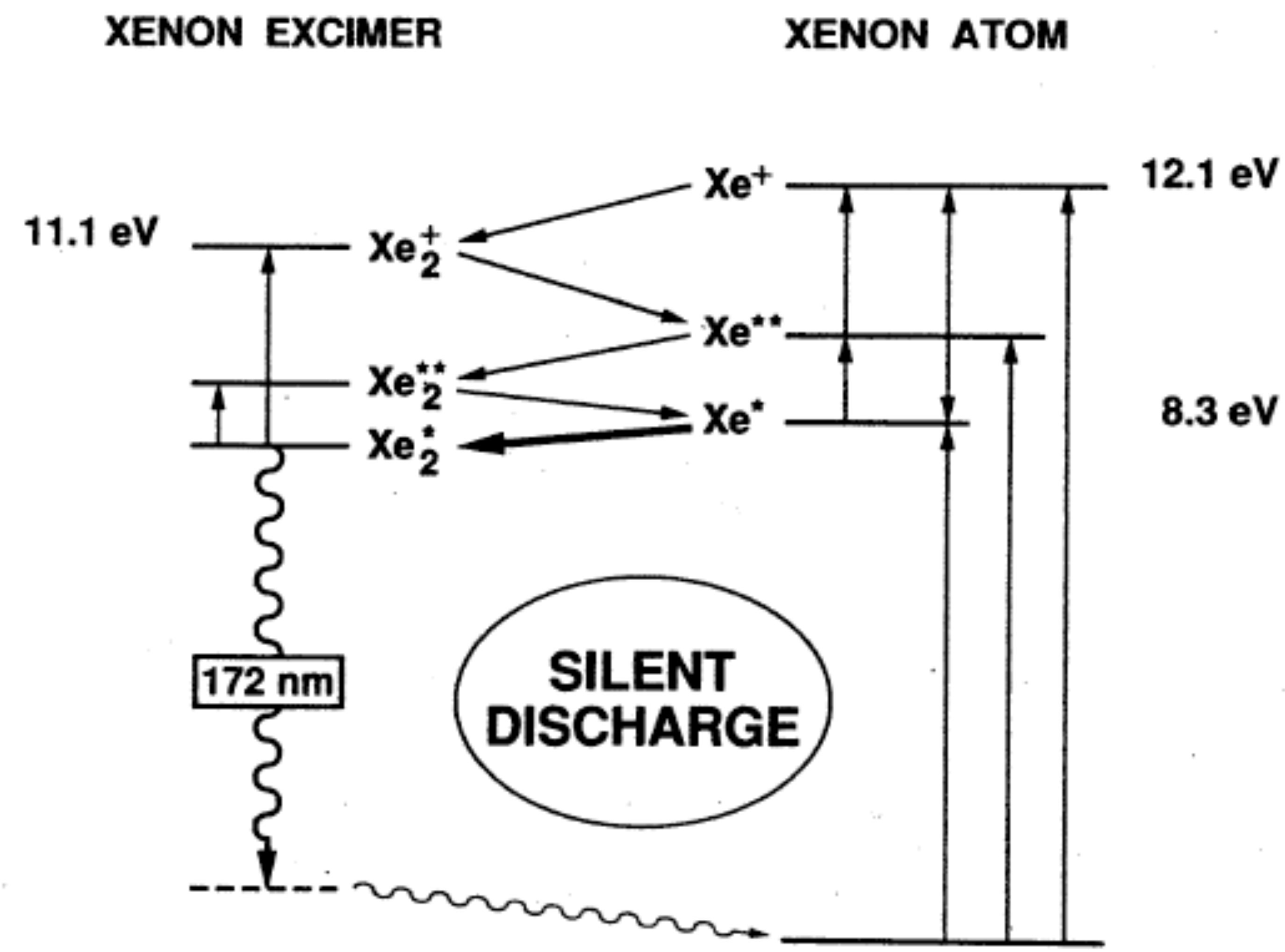
E. C. Y. Inn, Spectrochim. Acta 7, 65 (1955-56)



Ar_2^*	Kr_2^*	F_2^*	Xe_2^*	Hg	ArF^*
126 nm	146 nm	157 nm	172 nm	185 nm	193 nm

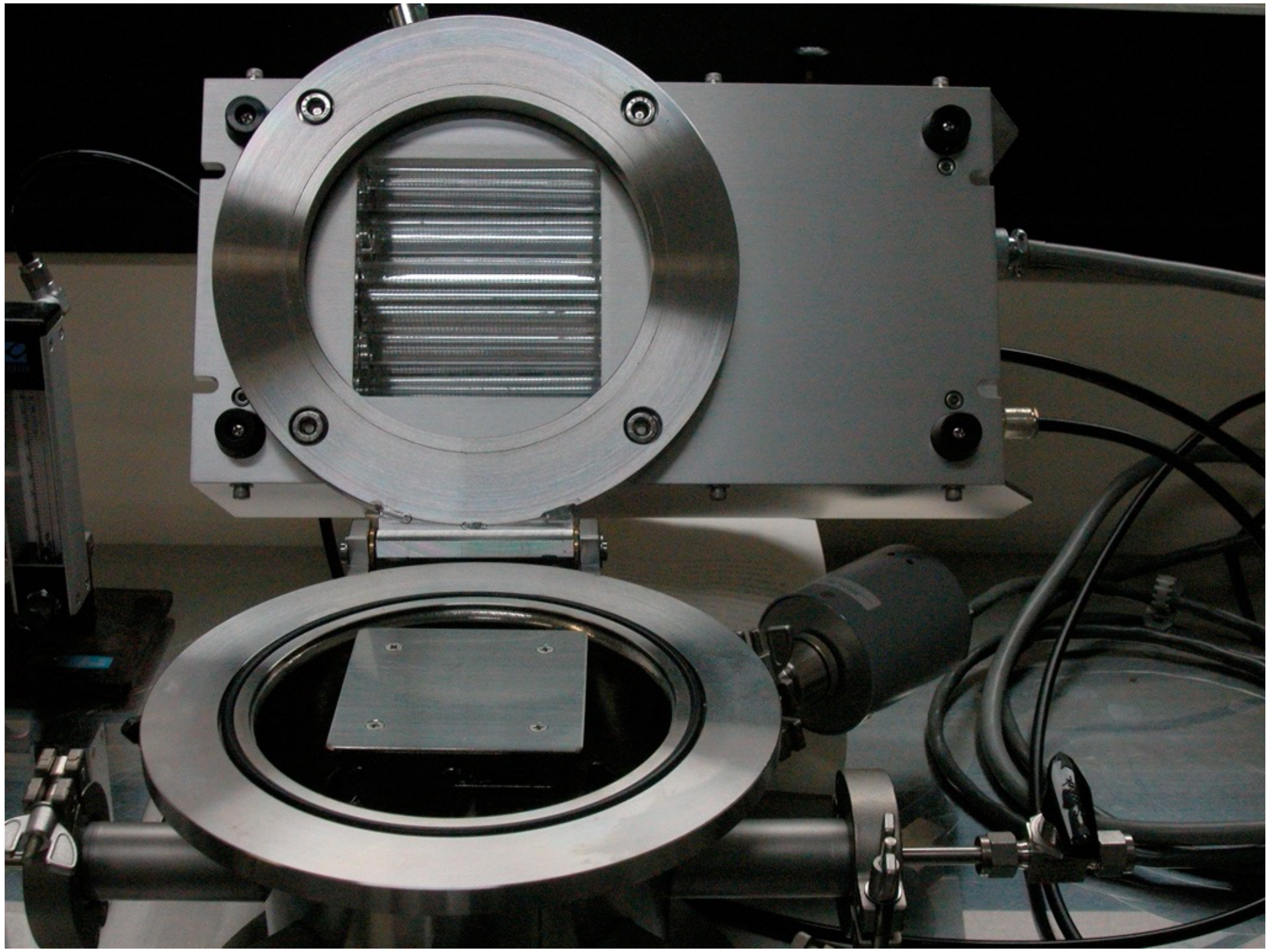
Emissionform Xe_2 Excimer

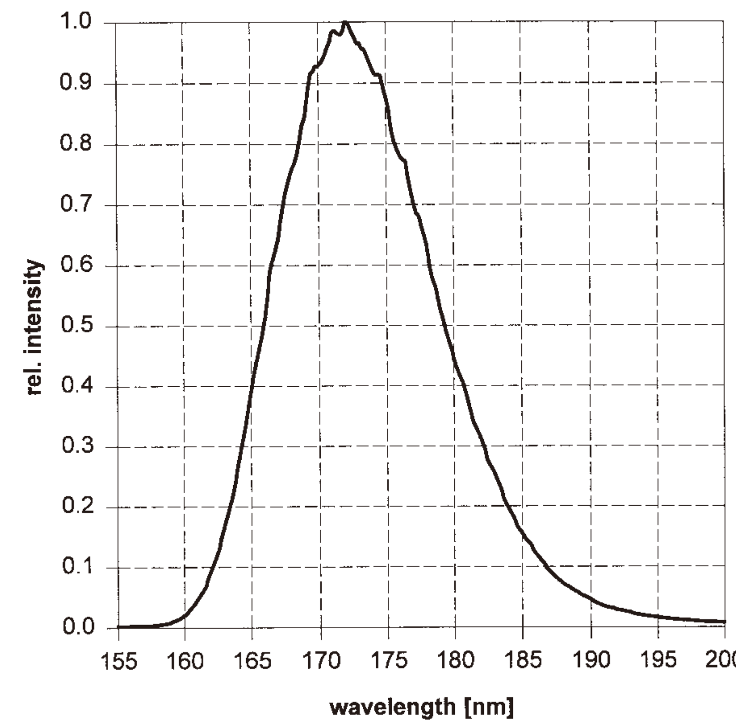




U. Kogelschatz, Pure & Appl. Chem. 62, 1667 (1990) より

Xe_2^* excimer lamp





Excimer lamp

- Wavelength = 172 nm
- FWHM 14 nm
- Intensity 10 mW/cm^2

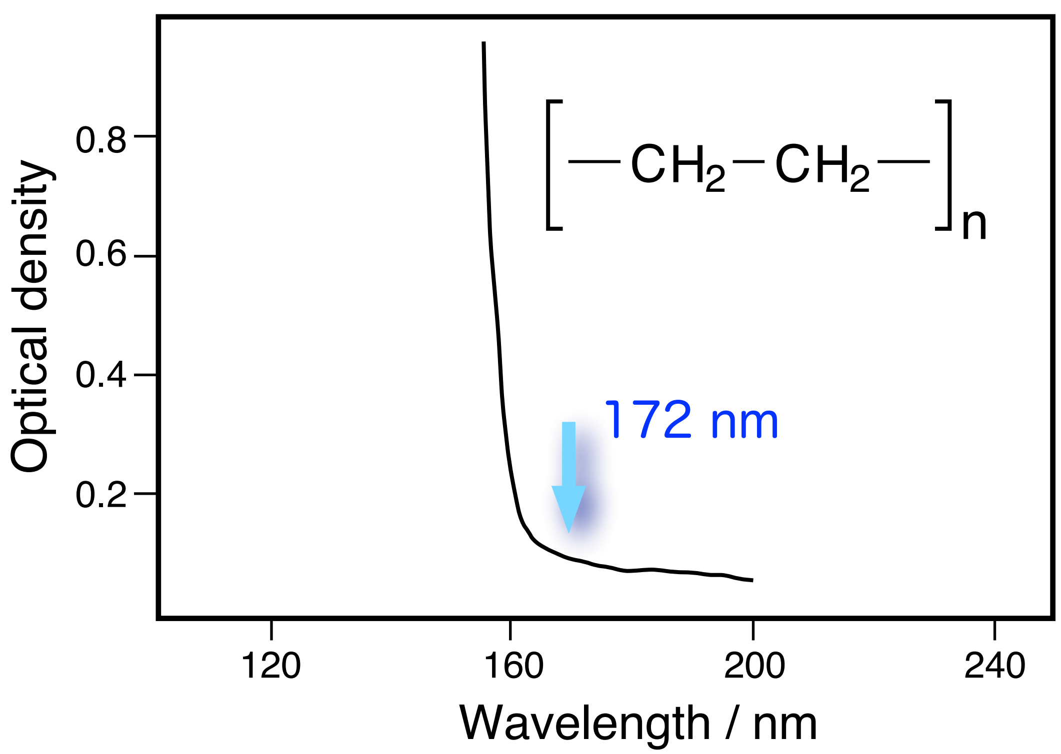
High photon energy

≈7.2 eV

VUV photochemistry

saturated hydrocarbons; polyethylene (PE)

VUV absorption

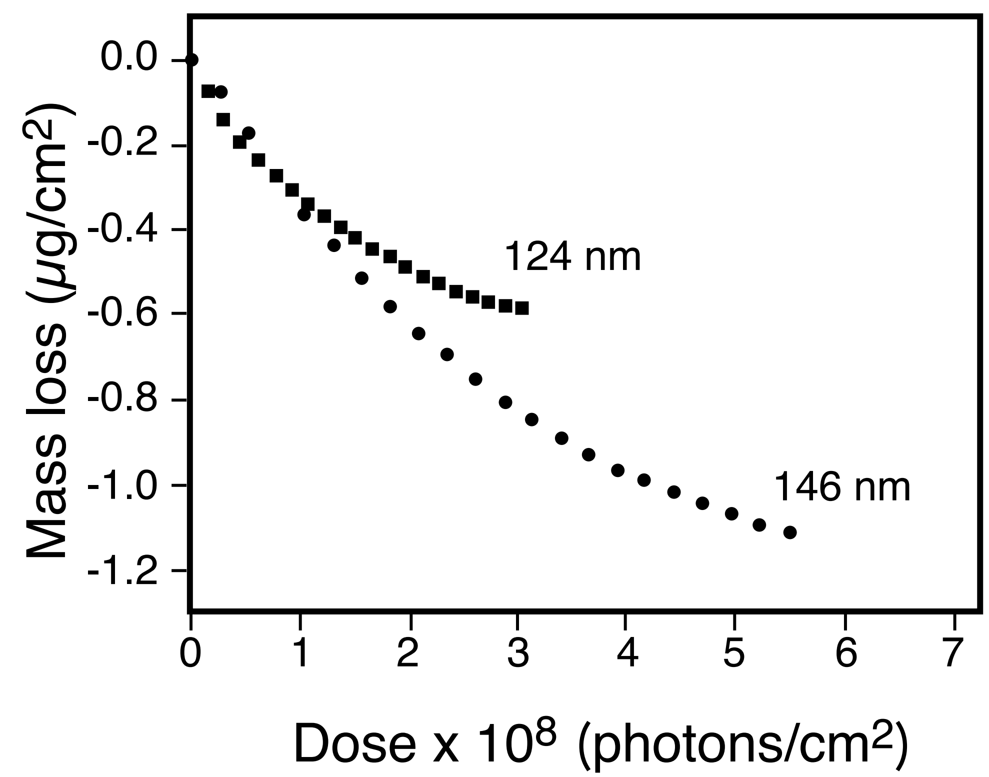


S. Onari, *J. Phys. Soc. Japan* **26** (1969) 500.

VUV light shorter than 160 nm is required to excite C-C and C-H bonds.

R. A. George et al., *J. Phys. C* **5** 871 (1972)

VUV etching of PE
in vacuum / 7 x 10^{-4} Pa



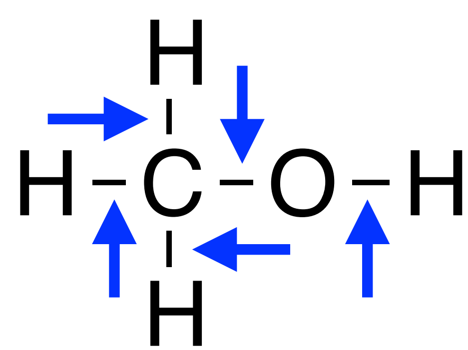
172 nm; negligible
146 nm; etched
124 nm; etched

F. Truica-Marasescu et al., *Macromol. Chem. Phys.* **206** 744 (2005)

VUV photochemistry

Methyl alcohol

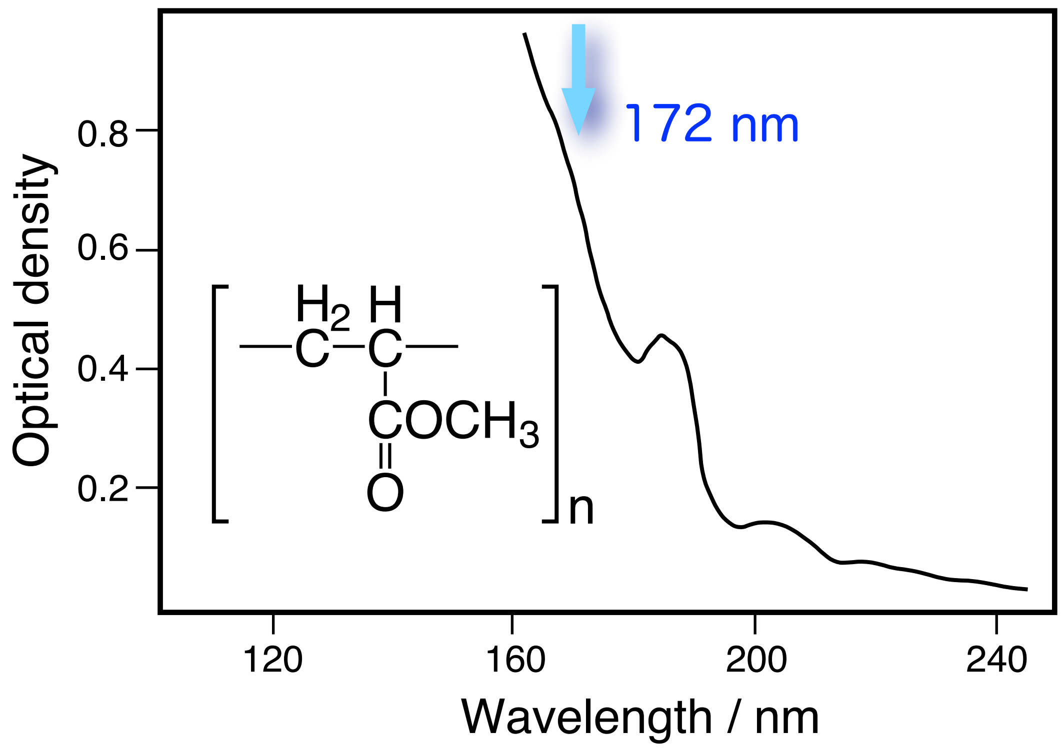
$$CH_3OH \xrightarrow{h\nu} \begin{cases} H^{\bullet} + {}^{\bullet}OCH_3 & \Phi = 0.69 \\ H^{\bullet} + {}^{\bullet}CH_2OH & \Phi = 0.08 \\ CH_2O + H_2 & \Phi = 0.06 \\ HO^{\bullet} + {}^{\bullet}CH_3 & \Phi = 0.05 \end{cases}$$



G. Heit et al. *J. Phys. Chem. A* **102** (1998) 5551.

VUV photochemistry
polymethylmethacrylate (PMMA)

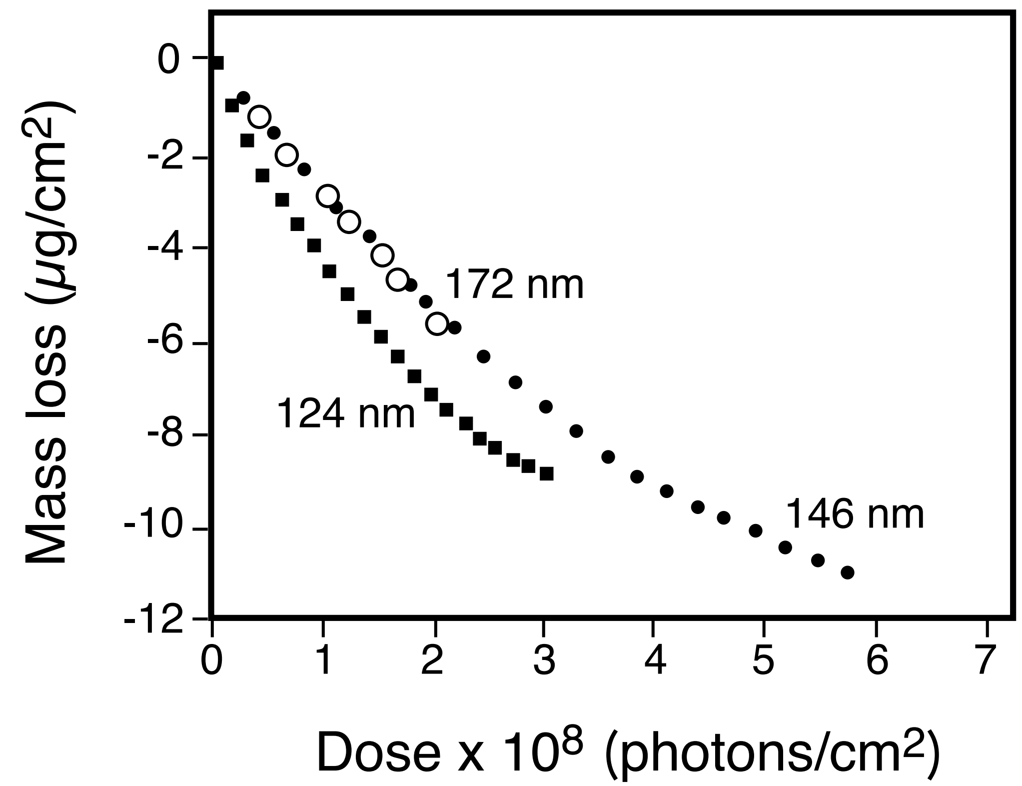
VUV absorption



S. Onari, *J. Phys. Soc. Japan* **26** (1969) 500.

VUV absorption at 172 nm is distinct.

VUV etching of PMMA
in vacuum / 7 x 10^{-4} Pa

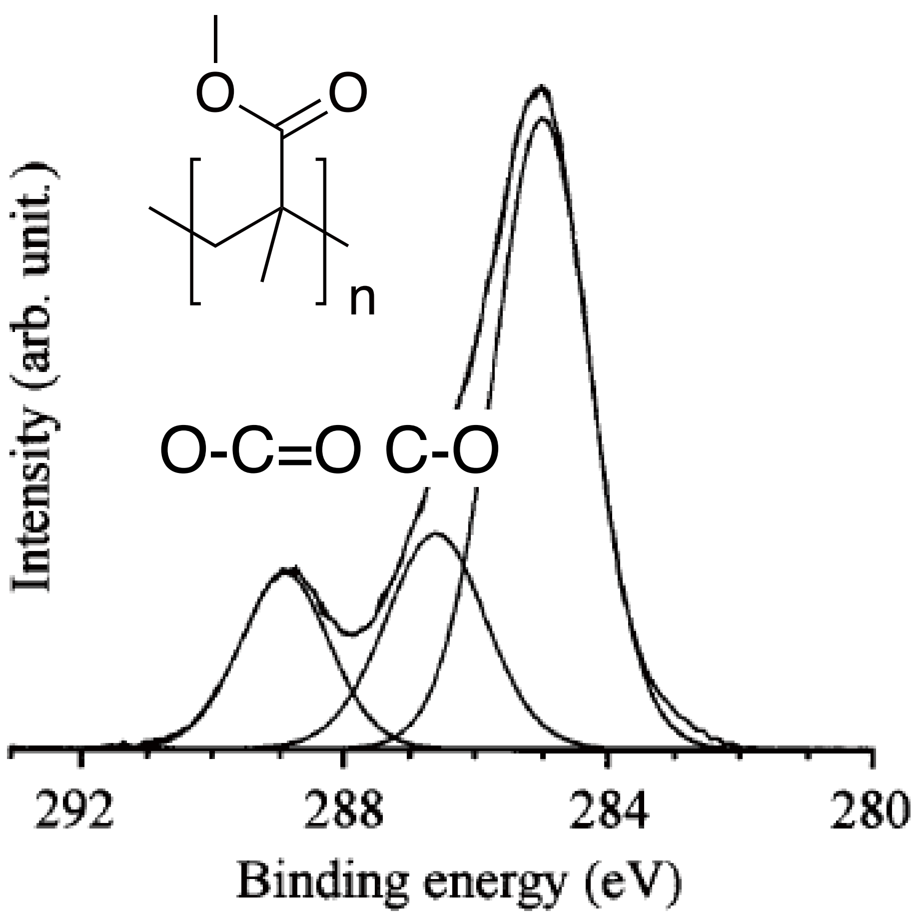


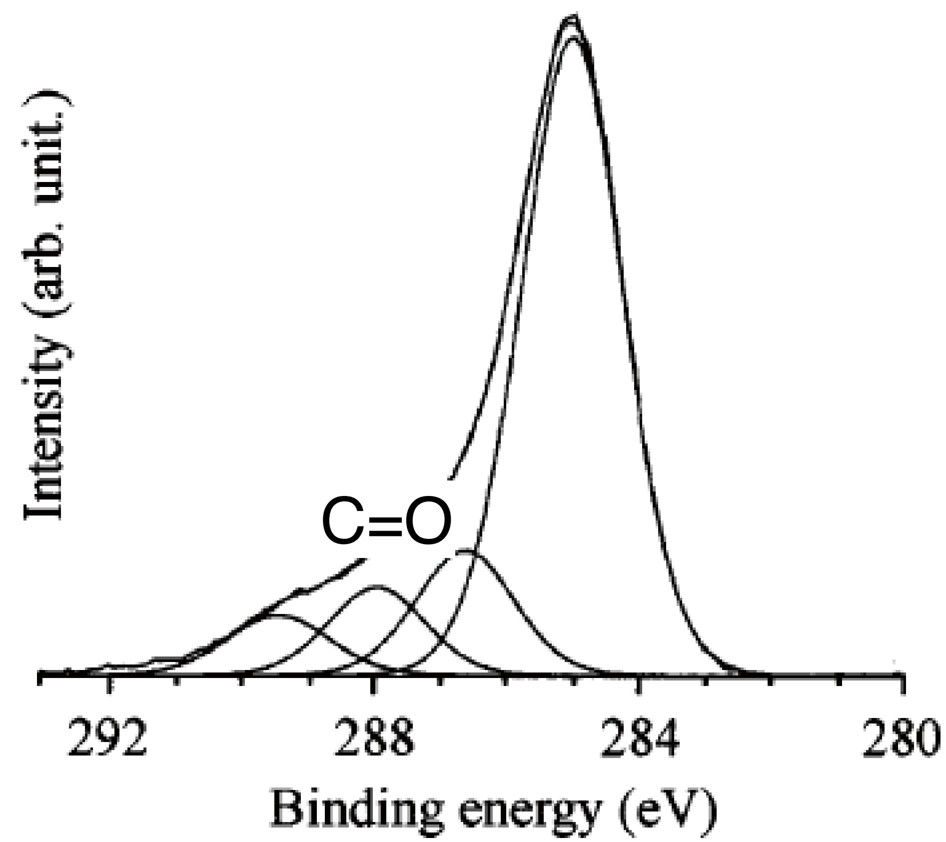
Etching proceeds at 172 nm
Etching at 146 and 124 nm
c.a. 10 times higher than PE

F. Truica-Marasescu et al.,
Macromol. Chem. Phys. **206** 744 (2005)

VUV photolysis of PMMA

VUV irradiation (172 nm) to PMMA in vacuum (10 Pa)

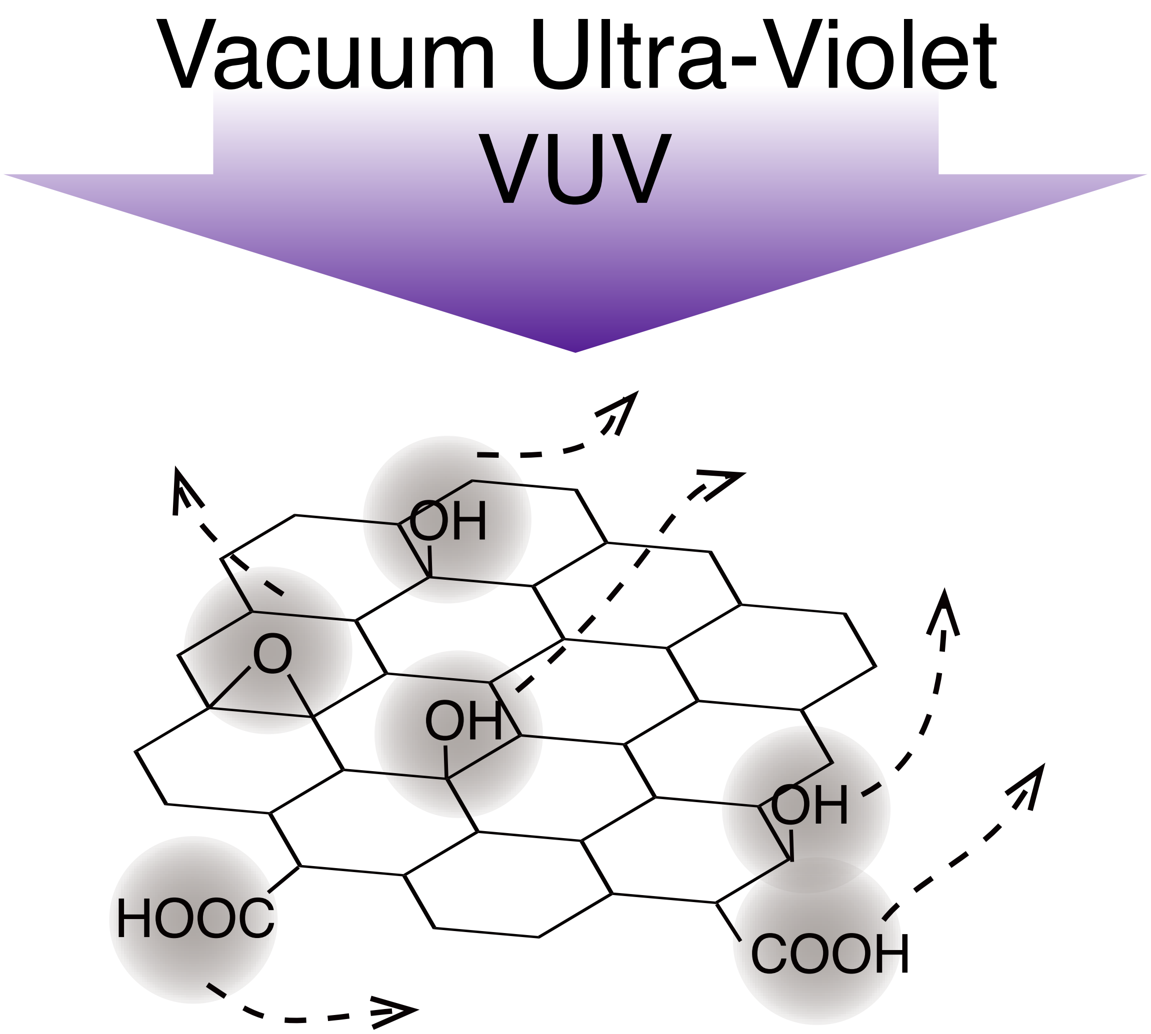




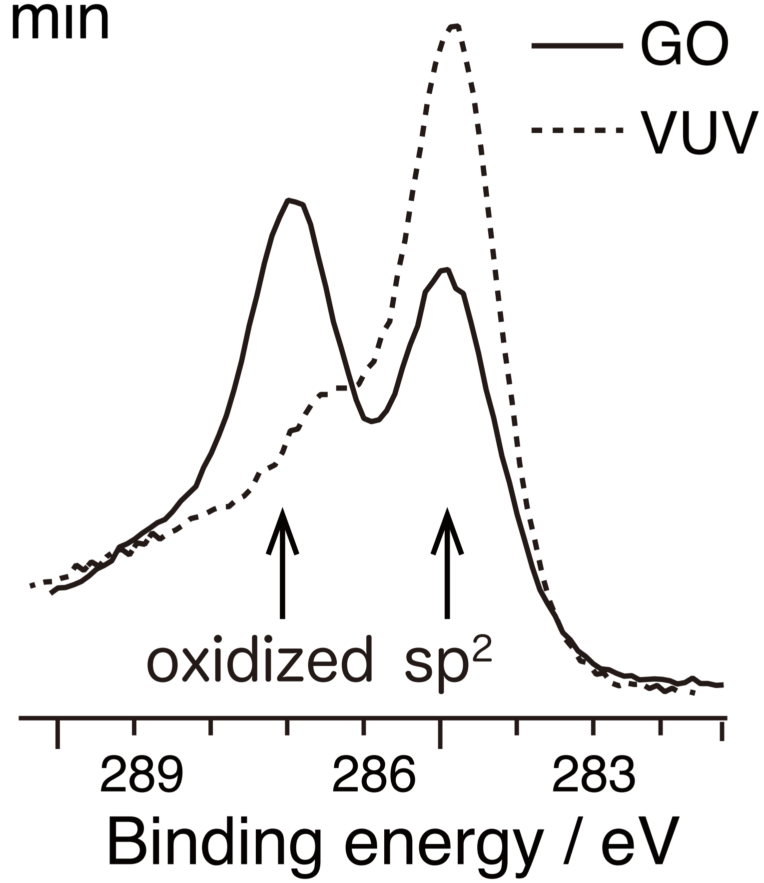
In an oxygen poor environment, oxygen containing parts are trimmed due to VUV irradiation.

A. Hozumi, T. Masuda, K. Hayashi, H. Sugimura, O. Takai, and T. Kameyama, Langmuir 18 (2001) 9022-9027

VUV irradiation to GO in vacuum

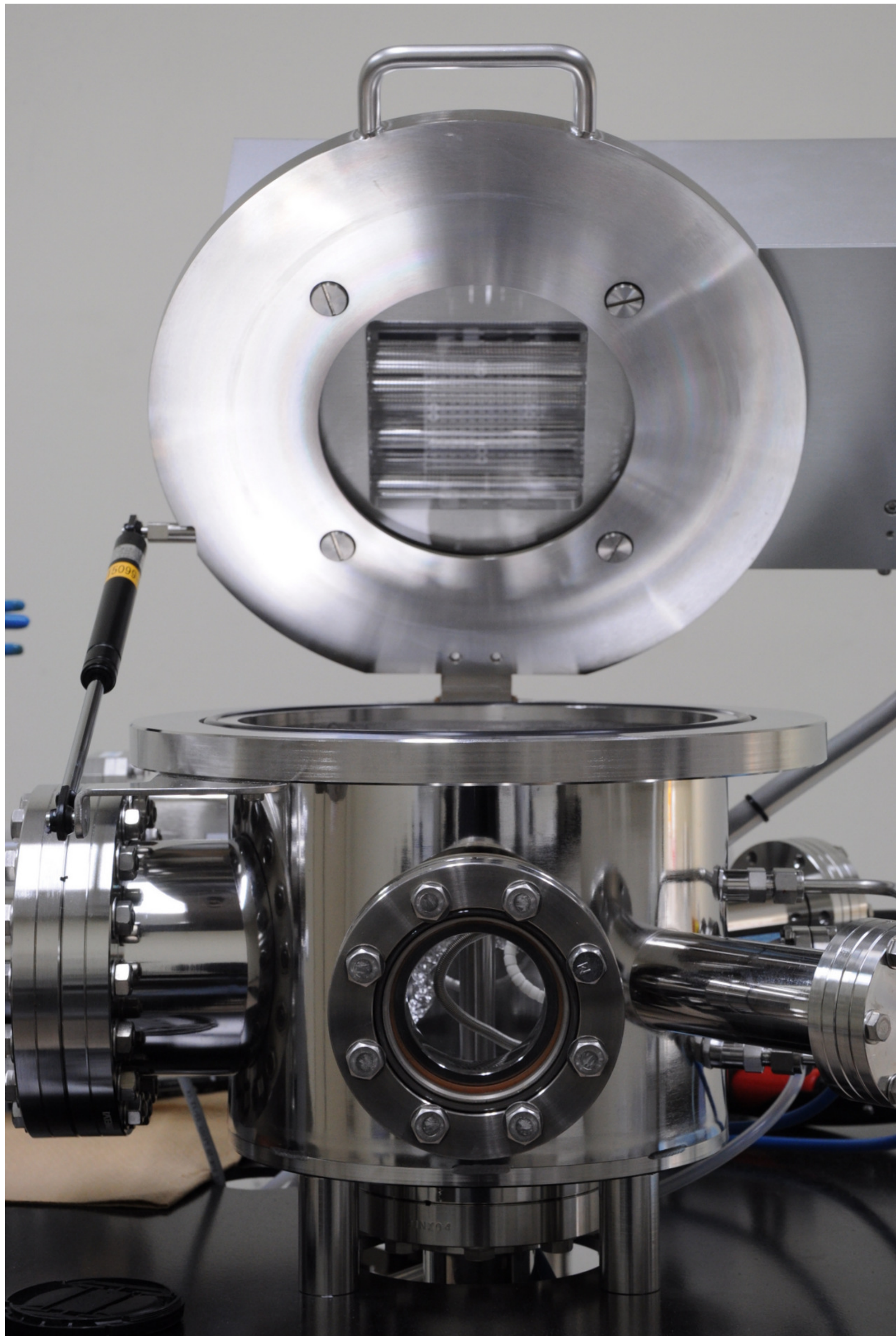


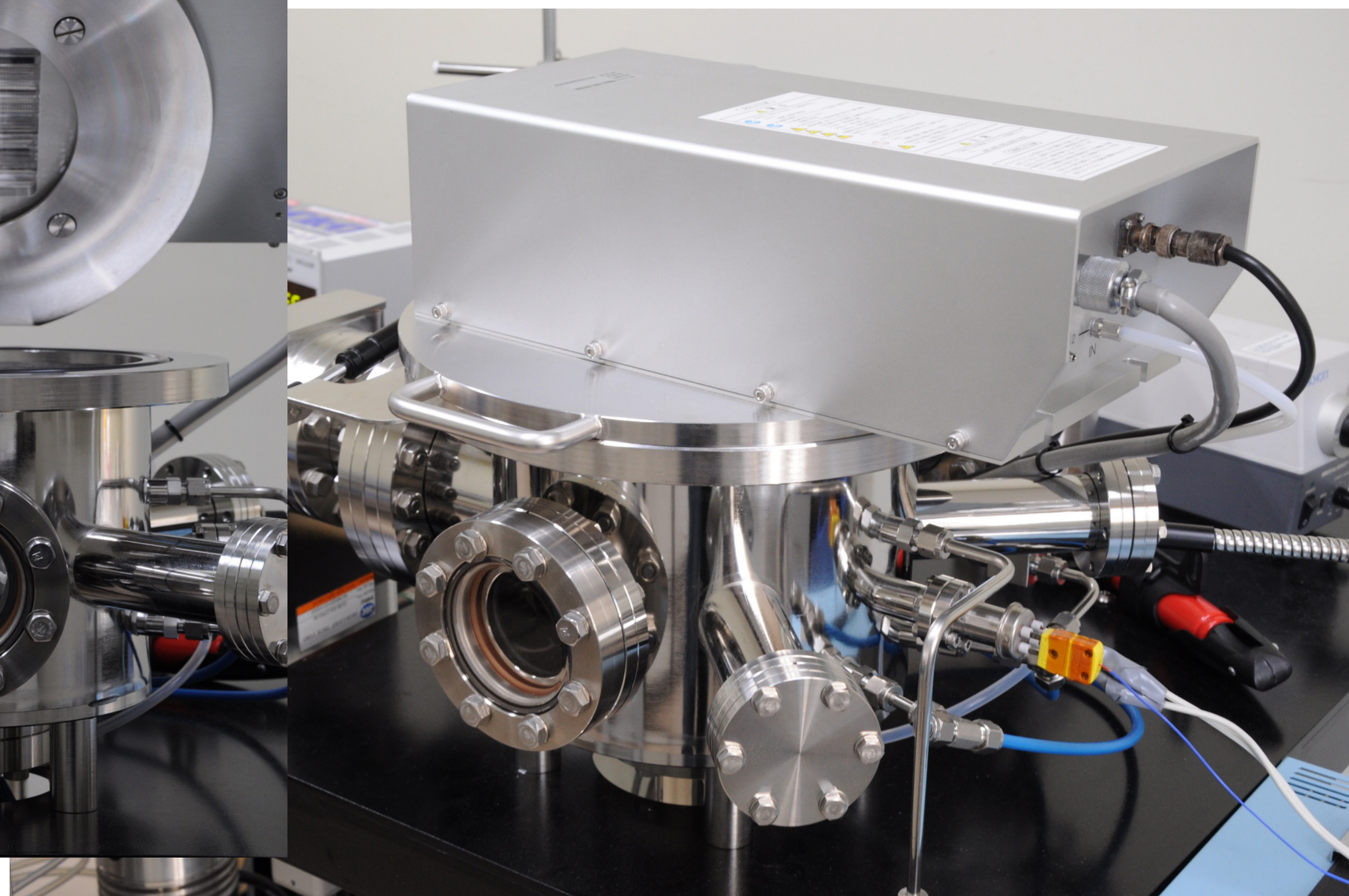
in vacuum < 10^{-3} Pa
10 $mWcm^{-2}$,
15 min



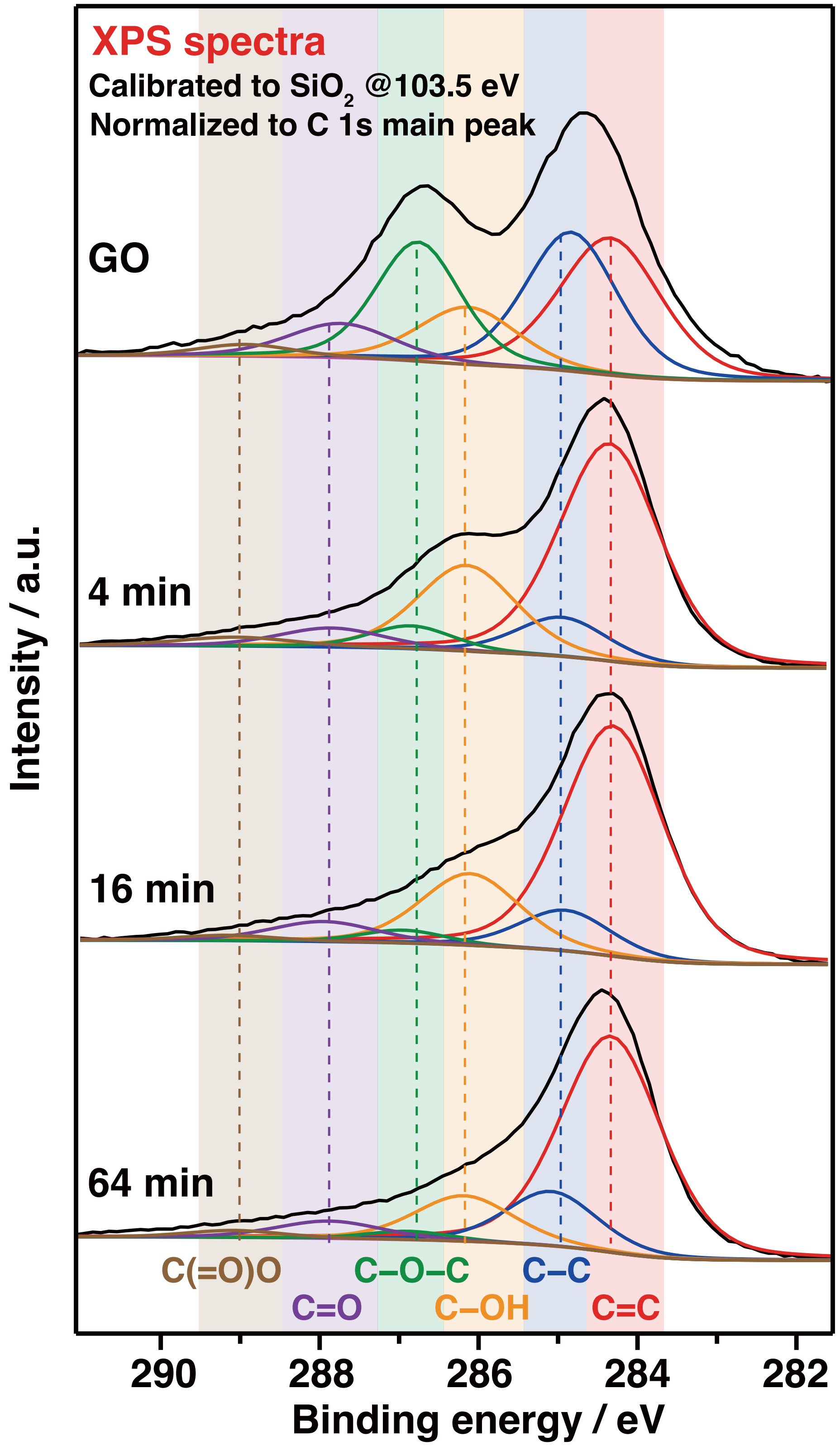
C1s-XPS

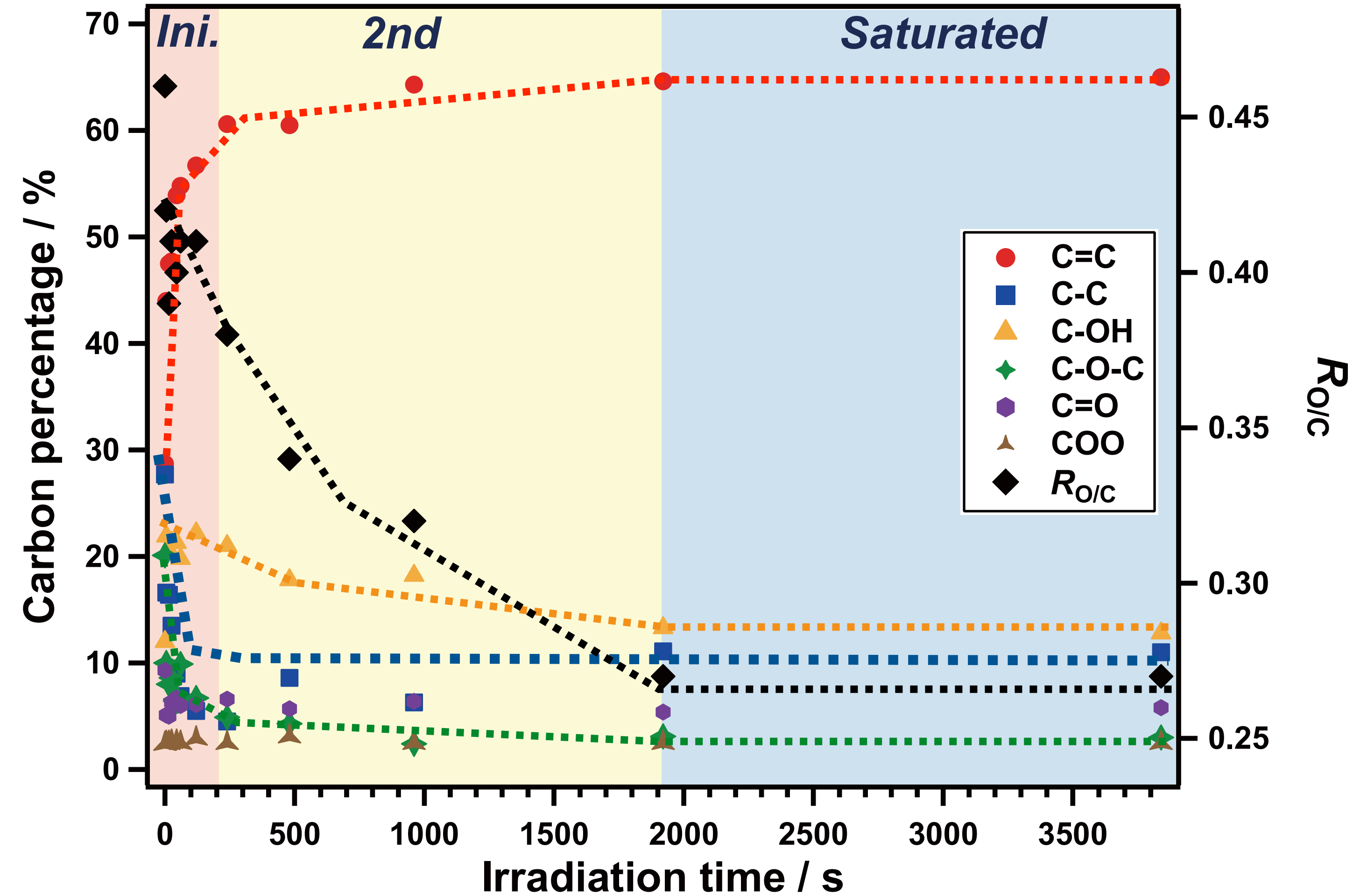
High Vacuum VUV System

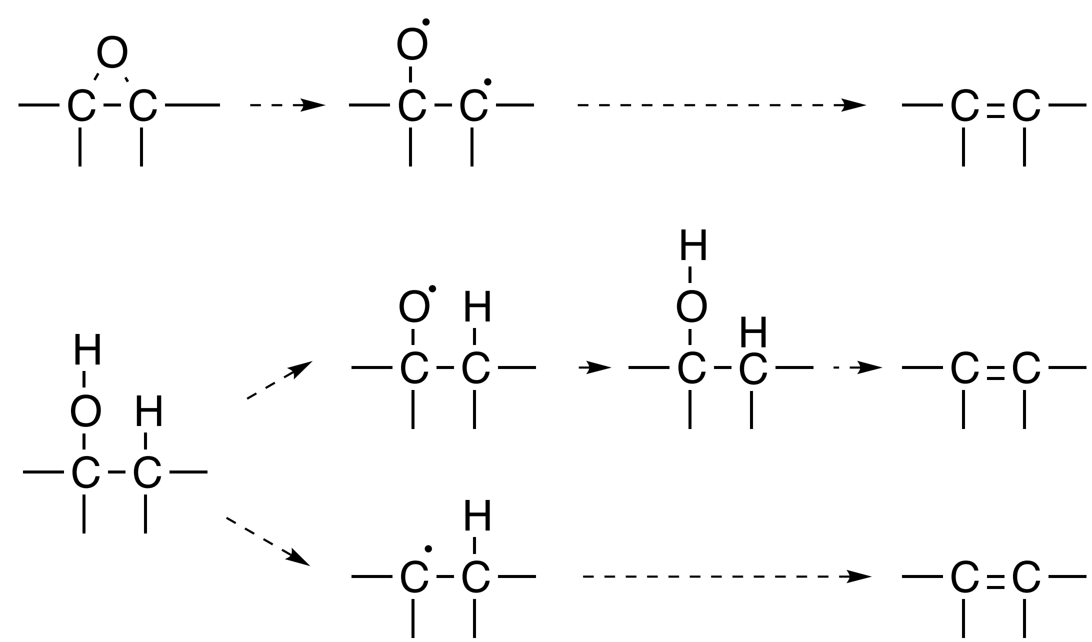




C1s-XPS of VUV-rGO

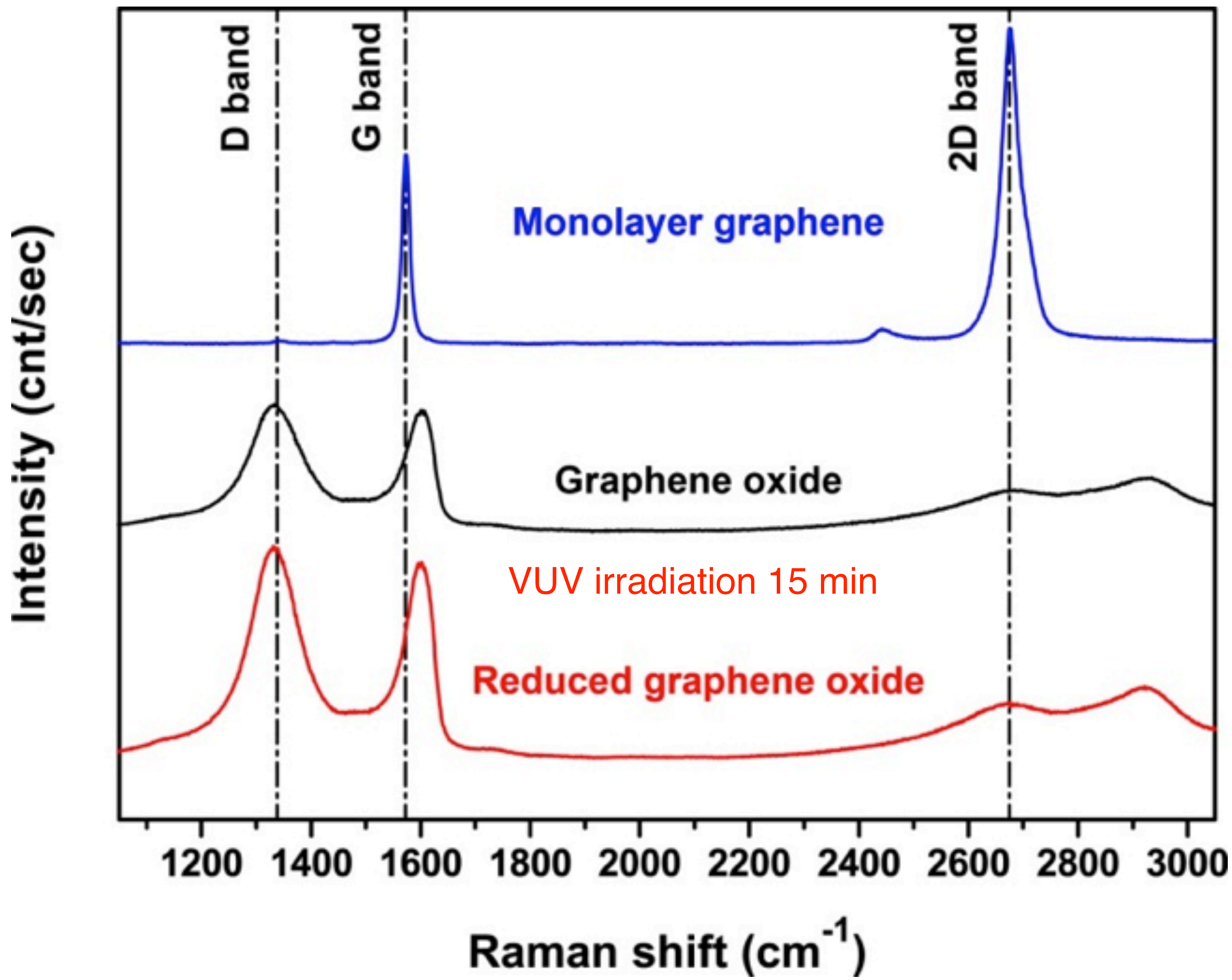






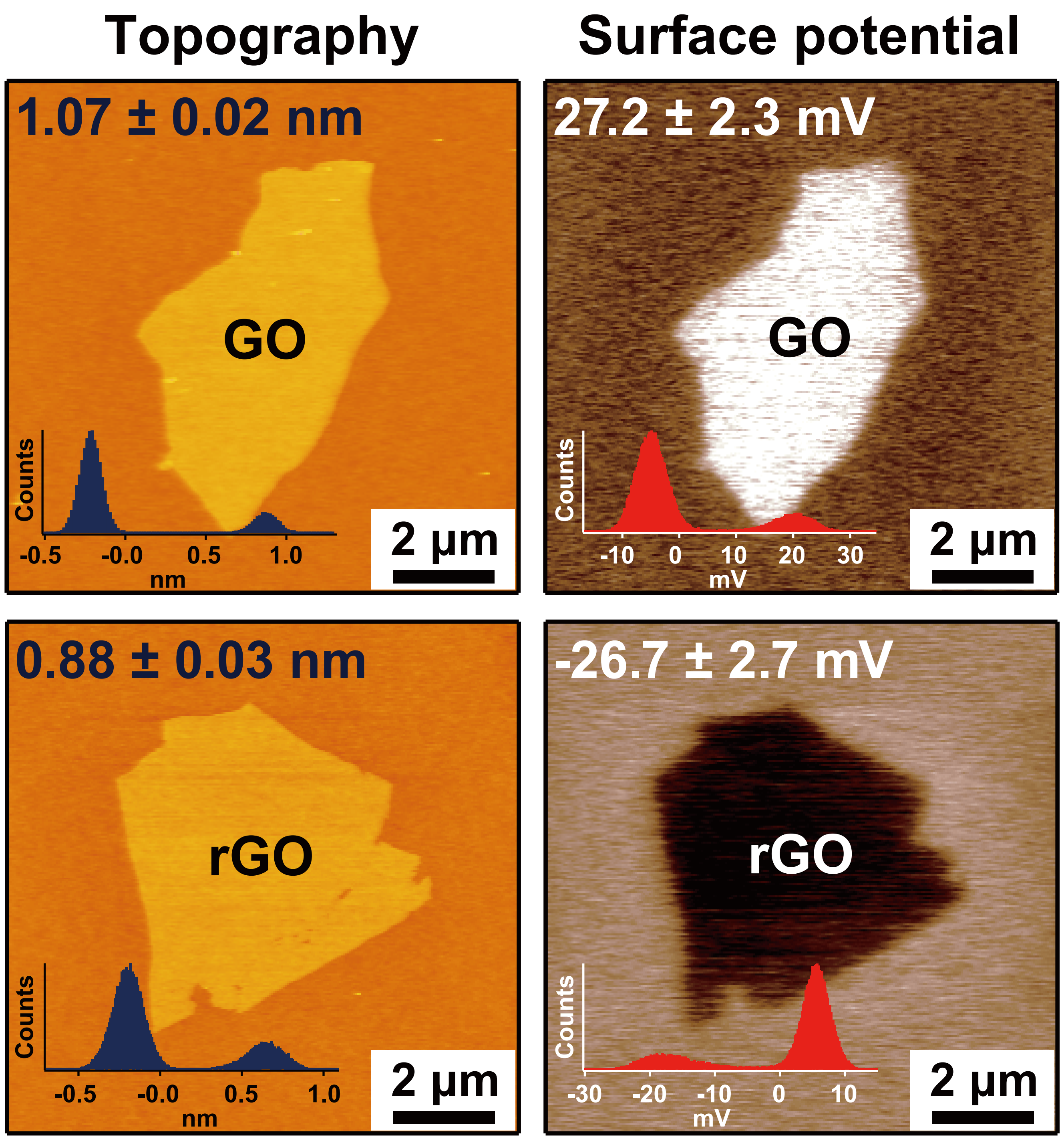
Plausible chemical routes

Raman spectroscopy



Increase in Raman intensity → Increase in sp2 domain
G peak position and D/G ratio: NOT CHANGED → sp2 domain size: UNCHANGED

Scanning probe microscopy



VUV irradiation for 16 min

Acquired by
Kelvin-probe force microscopy
(KFM)

After irradiation,

- Sheet thickness decreased:
  O atoms were removed from the GO surface
- Surface potential (compared to the SiO_2 substrate) decreased:
  Difficult to explain the mechanism and apply theoretical calculation.
  Possibly induced by the change of electrical properties (e.g. dipole)

Applicable for observing GO/rGO patterns

Y. Tu, T. Ichii, O. P. Khatri, H. Sugimura.
Appl. Phys. Express **2014**, 7, 075101

Kelvin probe force microscopy

M. Nonnenmacher, M. P. O'Boyle, and H. K. Wickramasinghe
T. J. Watson Research Center, IBM, Yorktown Heights, New York 10598

(Received 21 March 1991; accepted for publication 27 April 1991)

Measurements of the contact potential difference between different materials have been performed for the first time using scanning force microscopy. The instrument has a high resolution for both the contact potential difference (better than 0.1 mV) and the lateral dimension (<50 nm) and allows the simultaneous imaging of topography and contact potential difference. Images of gold, platinum, and palladium surfaces, taken in air, show a large contrast in the contact potential difference and demonstrate the basic concept.

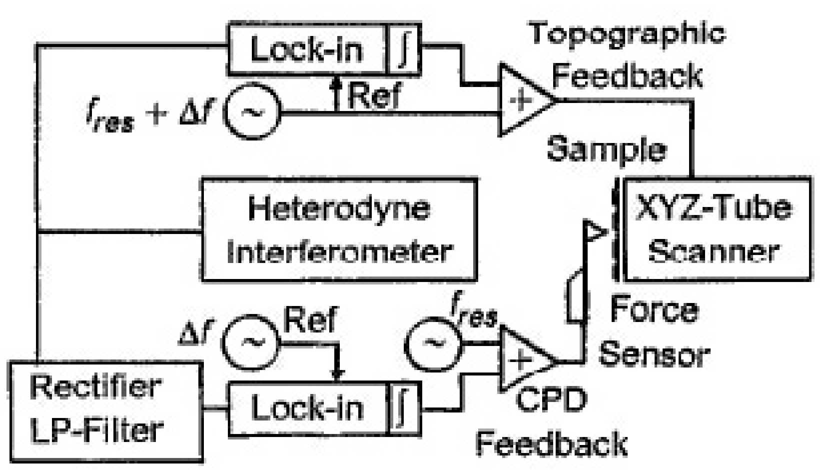
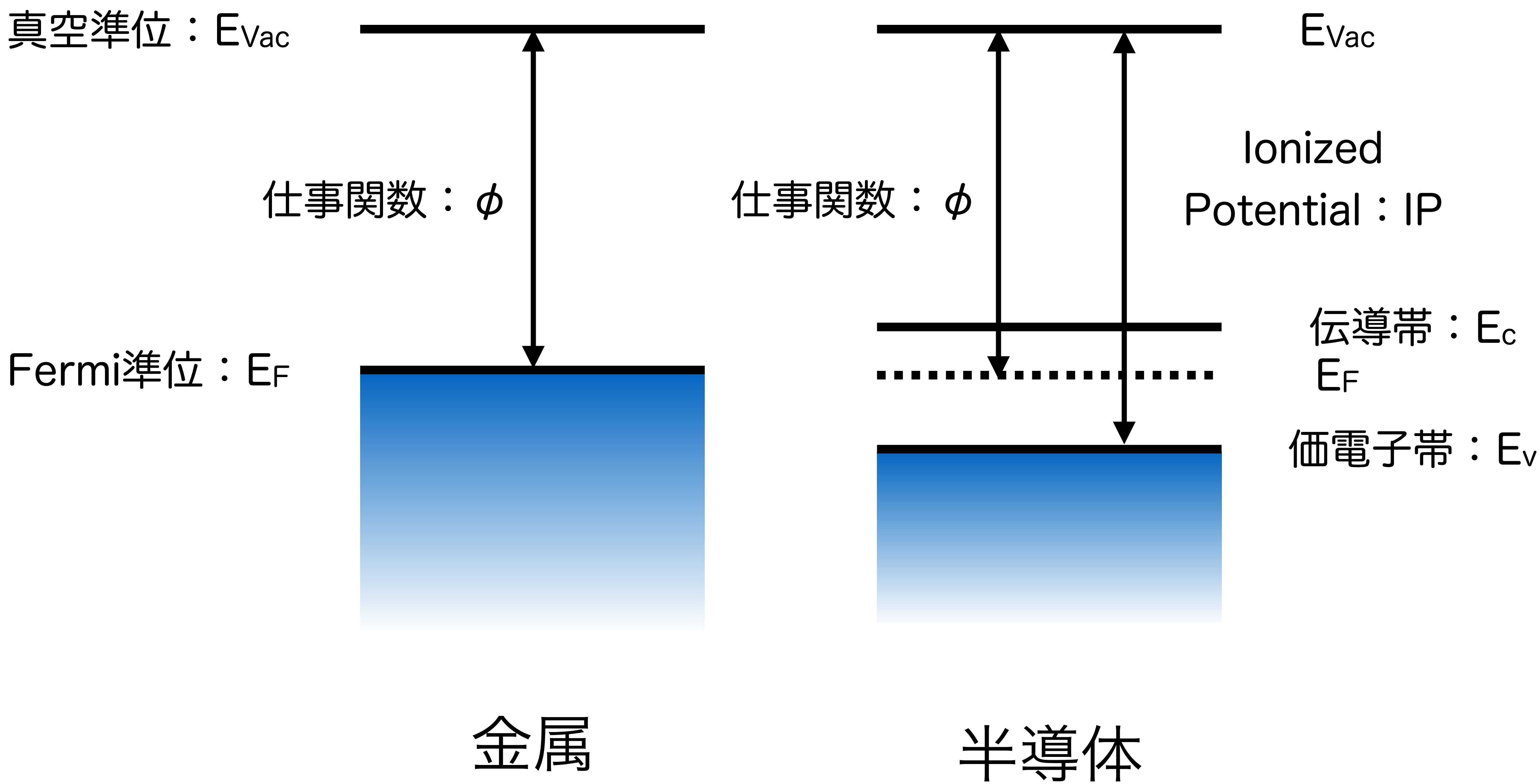


FIG. 1. Schematic diagram of the setup for simultaneous topographic and CPD measurements.

The contact potential difference (CPD) between two materials depends on a variety of parameters such as the work function, adsorption layers, oxide layers, dopant concentration in semiconductors, or temperature changes on the sample.[7,8] The measurement of the CPD can be used in principle to obtain information concerning these parameters. A common method to measure the contact potential difference is the vibrating capacitor method or Kelvin method.[8] In the Kelvin method two conductors are arranged as a parallel plate capacitor with a small spacing. In a simple model the contact potential between the two materials is $V_{CPD} = 1/e(\Phi_2 - \Phi_1)$, where ϕ_1 and ϕ_2 are the work functions of the conductors including changes due to adsorption layers on the surface.[8,9] A periodic vibration of the distance between the two plates at ω results in a current $i(t)$ given by

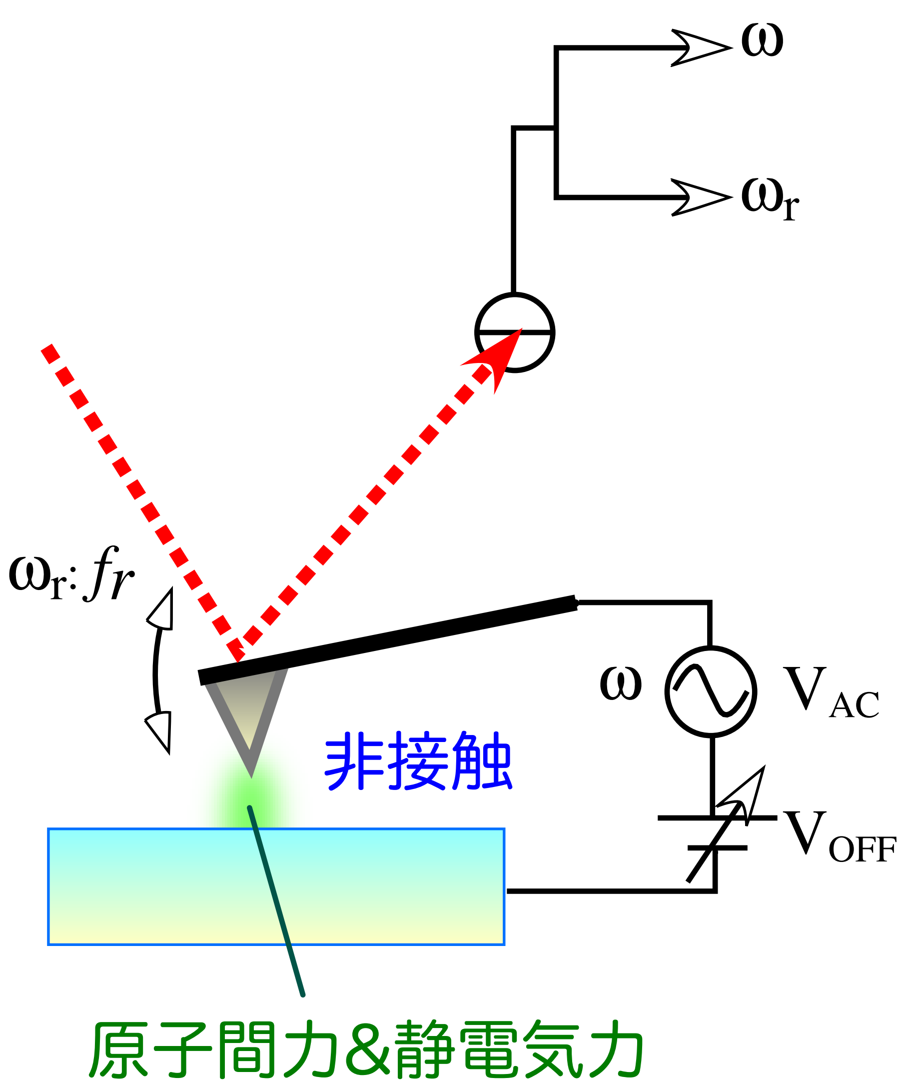
Appl. Phys. Lett., 58(25) (1991) 2921-2923.

Principle of KFM

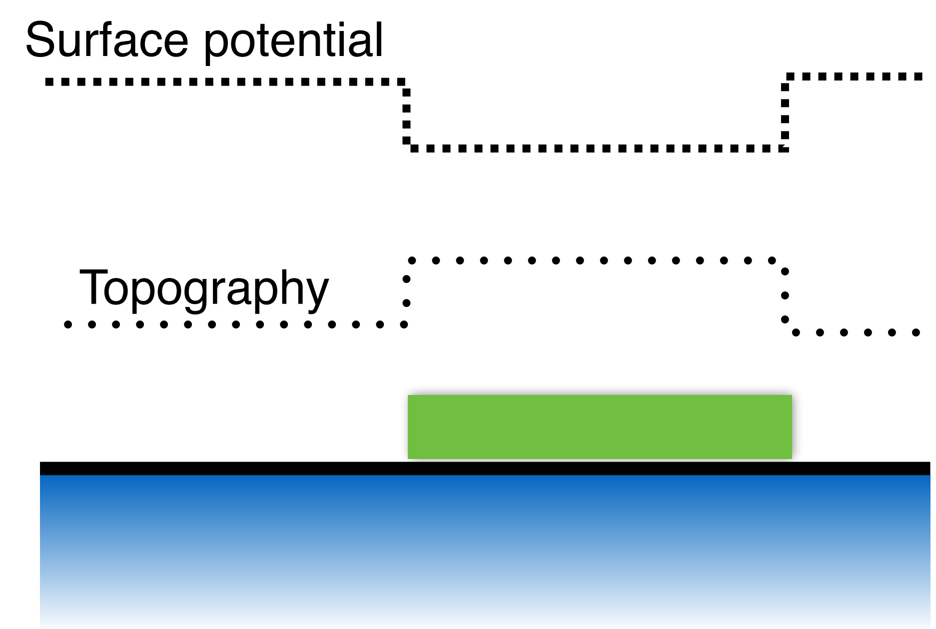


KFM: Imaging surface potential contrasts

KFM is one of SPM based on the electrostatic force detection.



Electrostatic force is
governed by surface potential

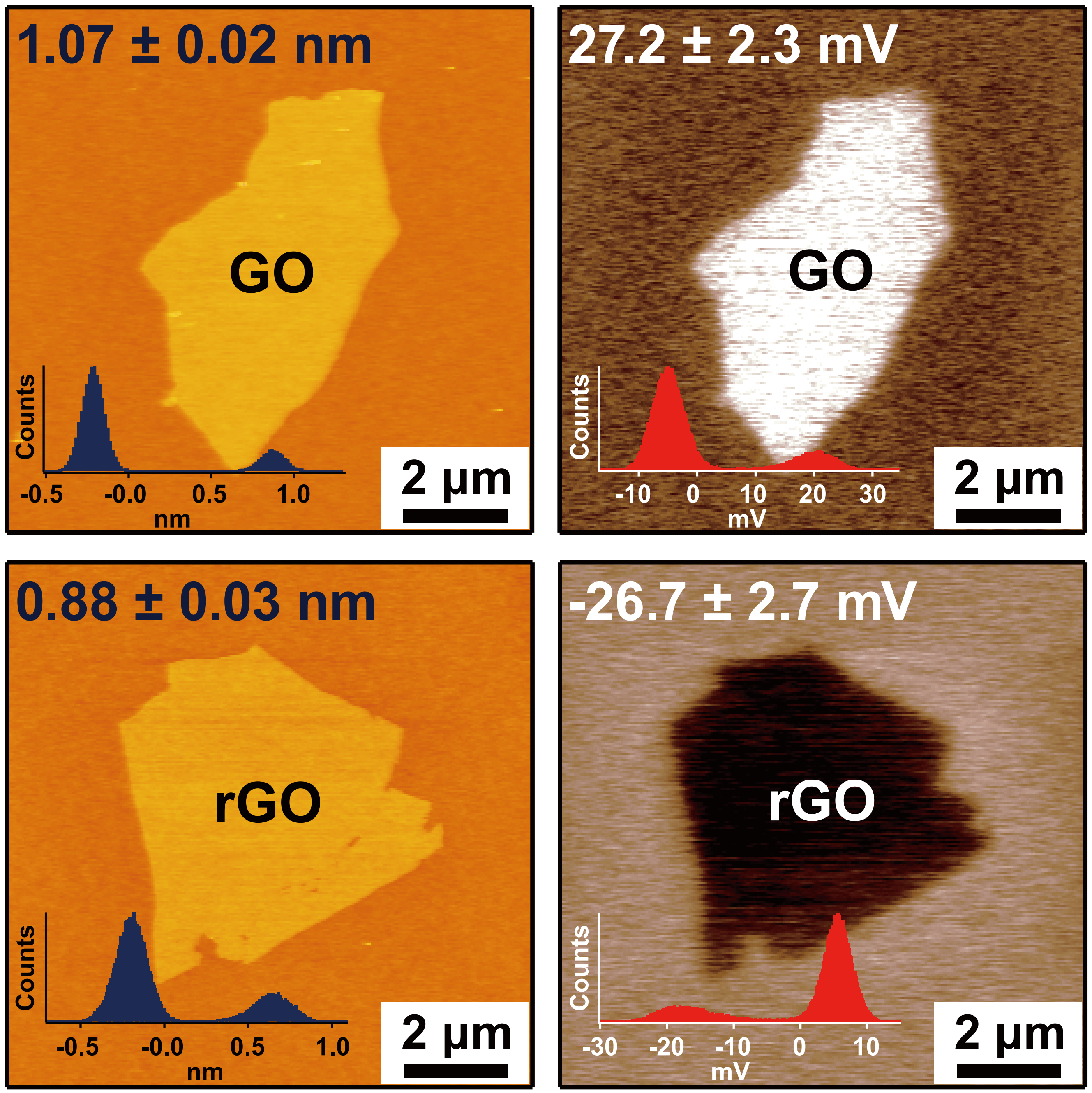


Difference

Material
↓
Work function
↓
Surface potential
↓
Electrostatic force

Scanning probe microscopy

Topography **Surface potential**



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Applicable for observing GO/rGO patterns

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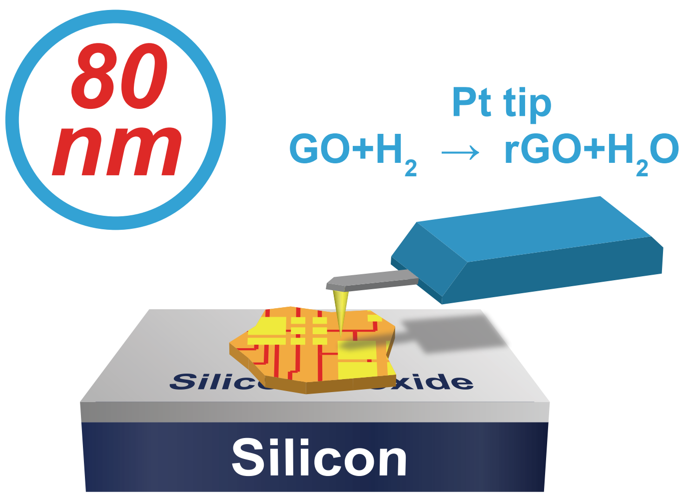
Appl. Phys. Express **2014**, 7, 075101

Micropatterning of Graphene

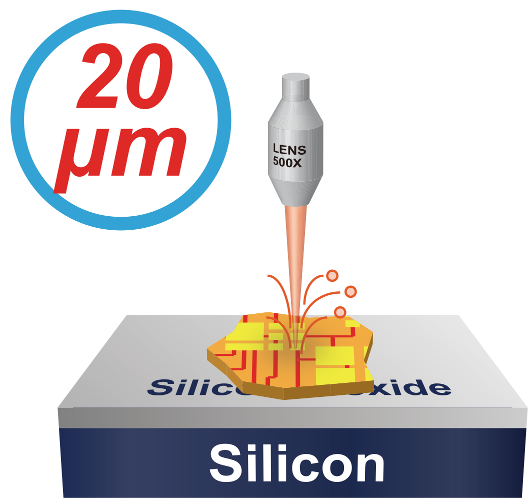
Scanning probe lithography



High cost,
Low throughput

Zhang, K. et al. Nat. Commun. 2012, 3, 1194.

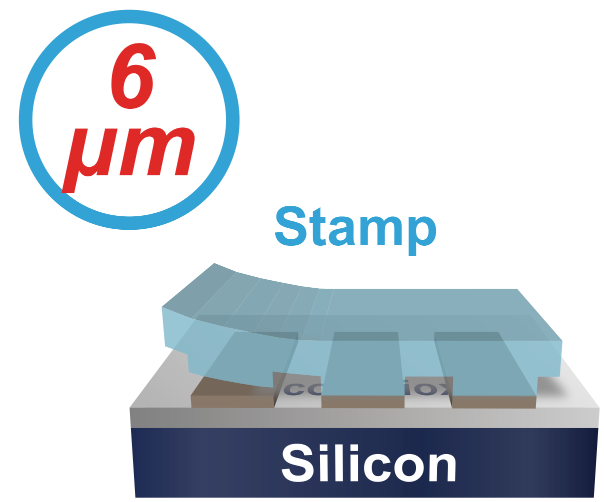
Laser direct writing



Low resolution,
Low throughput

Yong, Z. et al. Adv. Mater. 2010, 22, (1), 67-71.

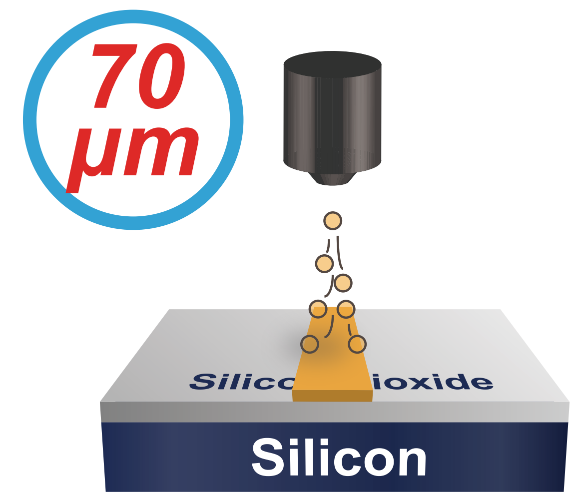
μ-contact printing



Low transfer precision,
Undesired Residues

George, A. et al. Small 2013, 9, (5), 711-5.

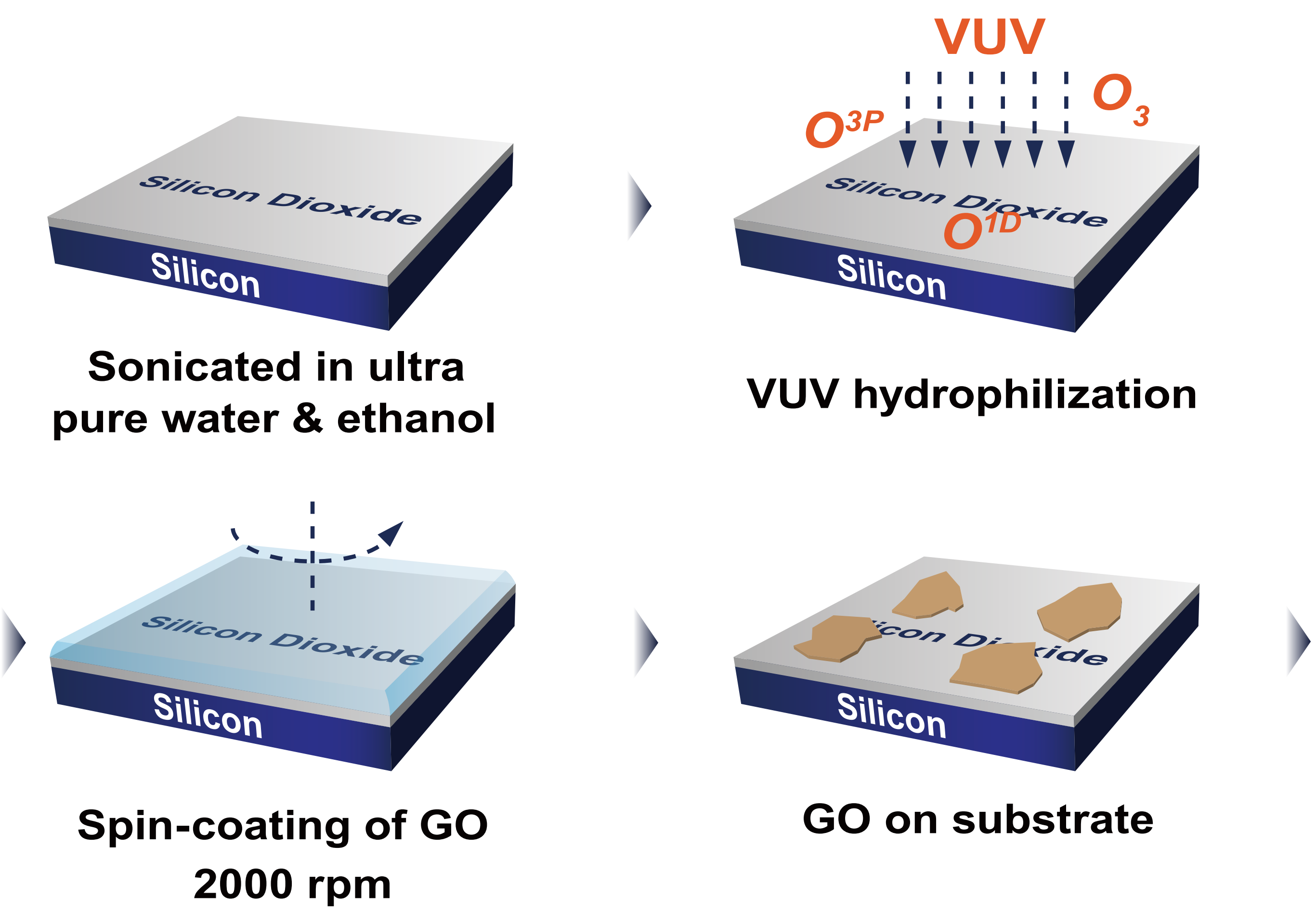
Inkjet printing

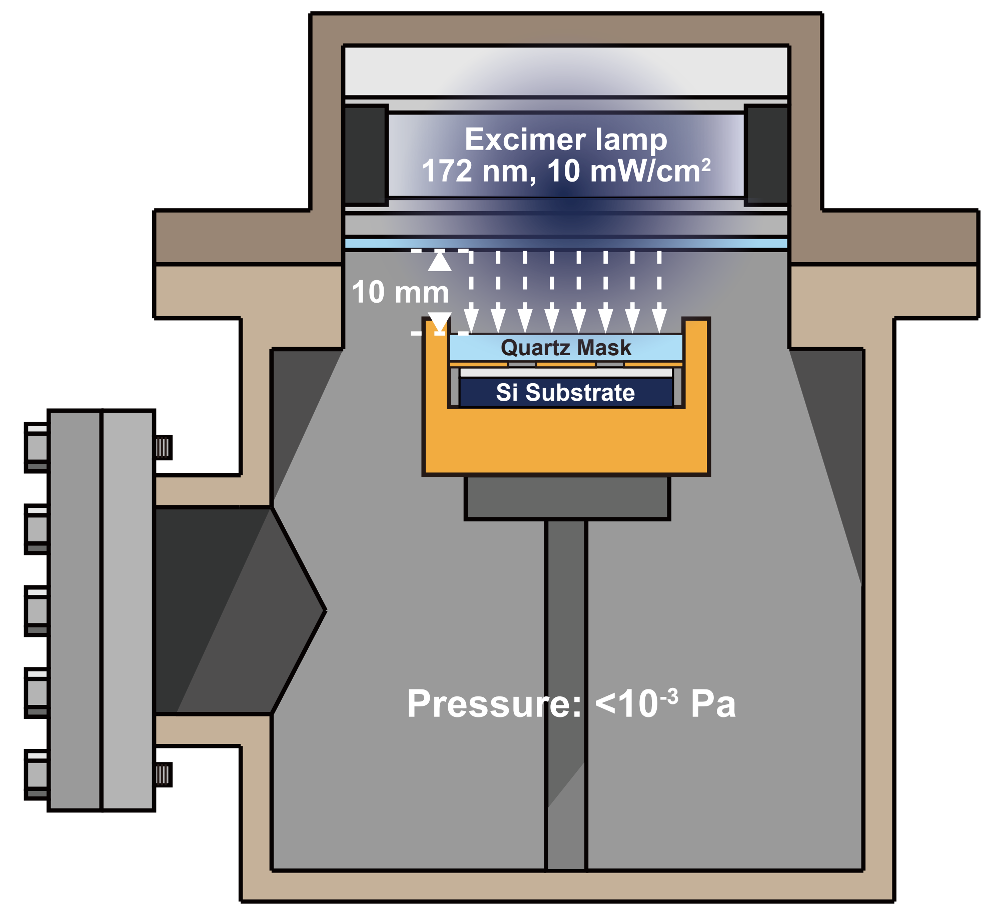


Low resolution,
Spray head blockage

Secor, E. B. et al. J. Phy. Chem. Lett. 2013, 4, (8), 1347-1351.

VUV micropatterning





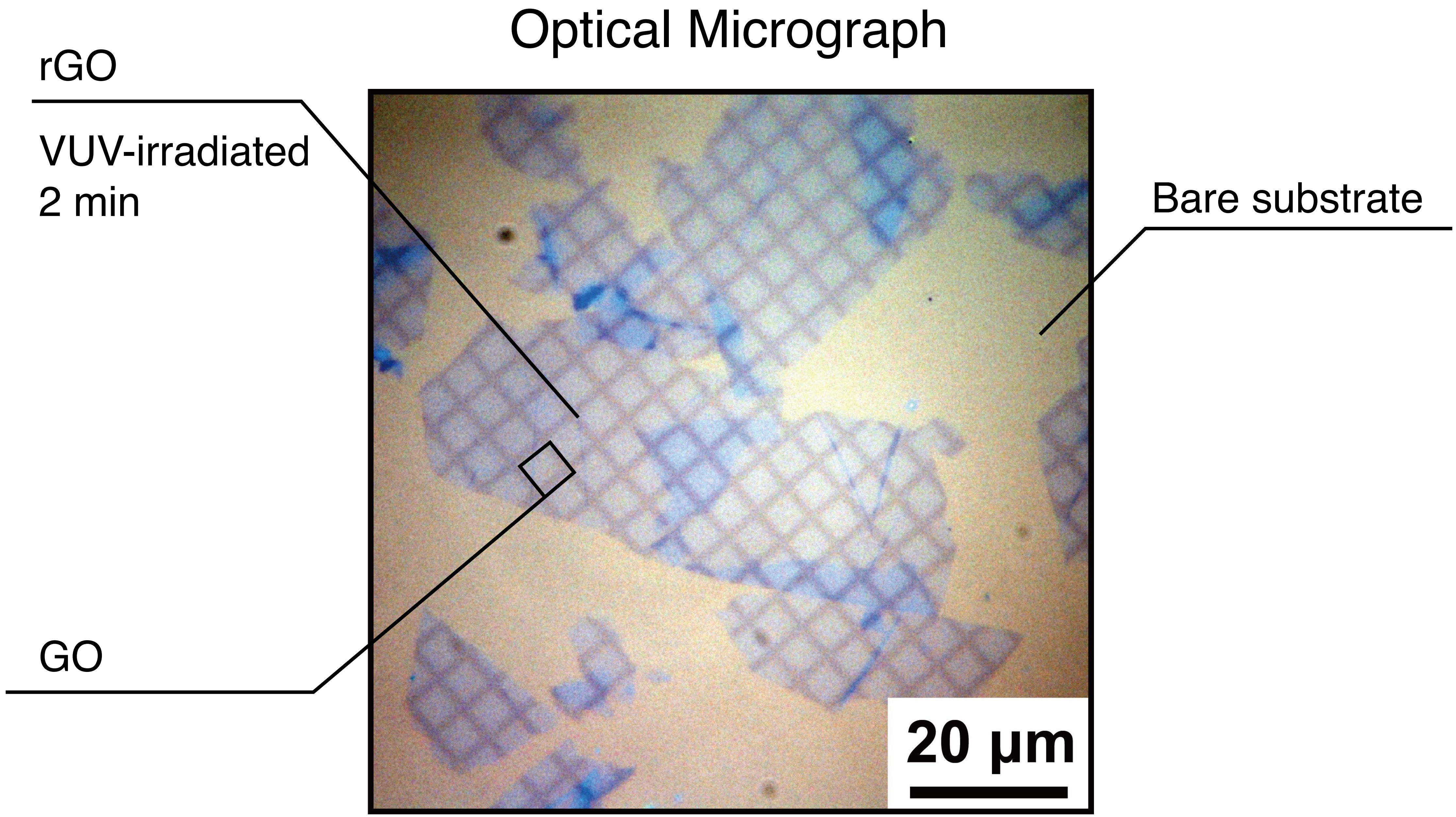
High vacuum (HV) VUV equipment

- X-ray photoelectron spectroscopy (XPS)
- Optical microscopy
- Atomic force microscopy (AFM)
- Kelvin-probe force microscopy (KFM)

Quartz photomask

Region	A	B	C	D
Line / µm	1	2	4	2
Space / µm	0.5	0.5	0.5	1

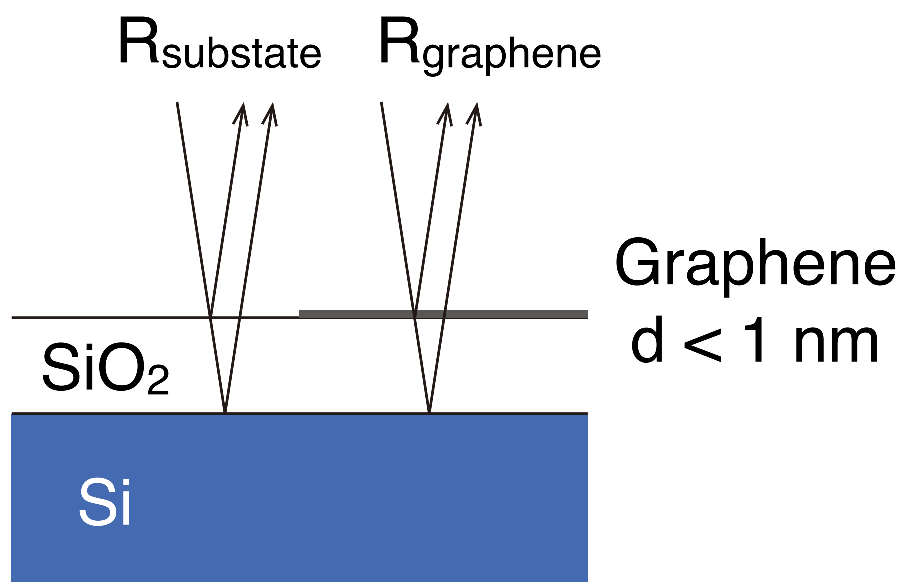
Micropatterned GO



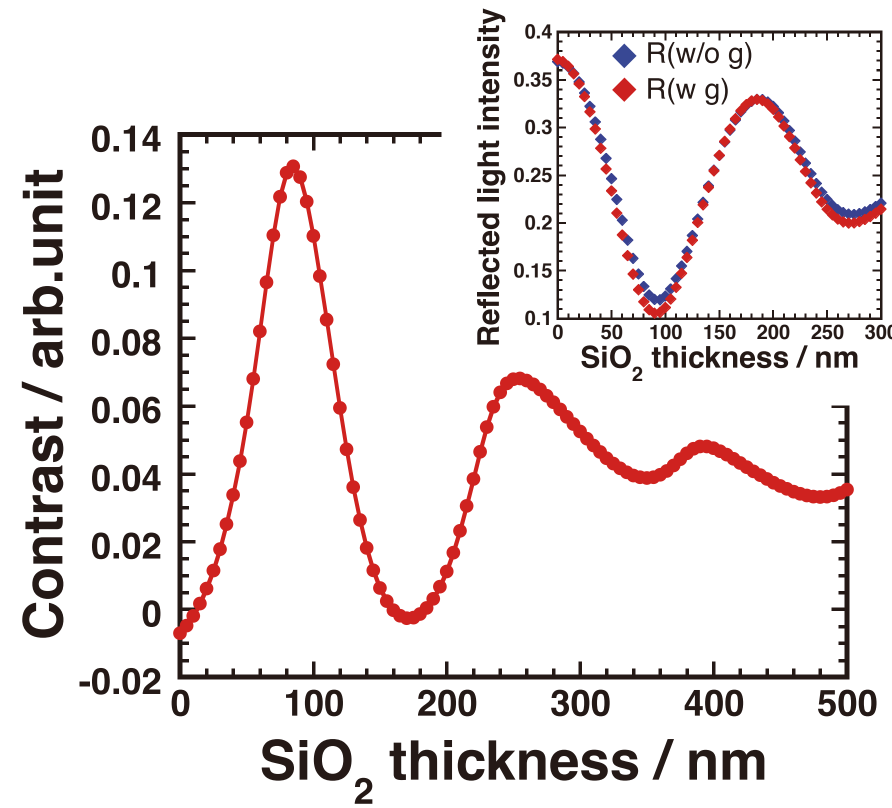
Substrate; SiO_2 (d = 90 nm) /Si

1 nm-thick graphene sheets *as well as the* ***contrast between GO/rGO*** *can be seen in optical microscopy.*

Magic substrate for optical imaging of graphene

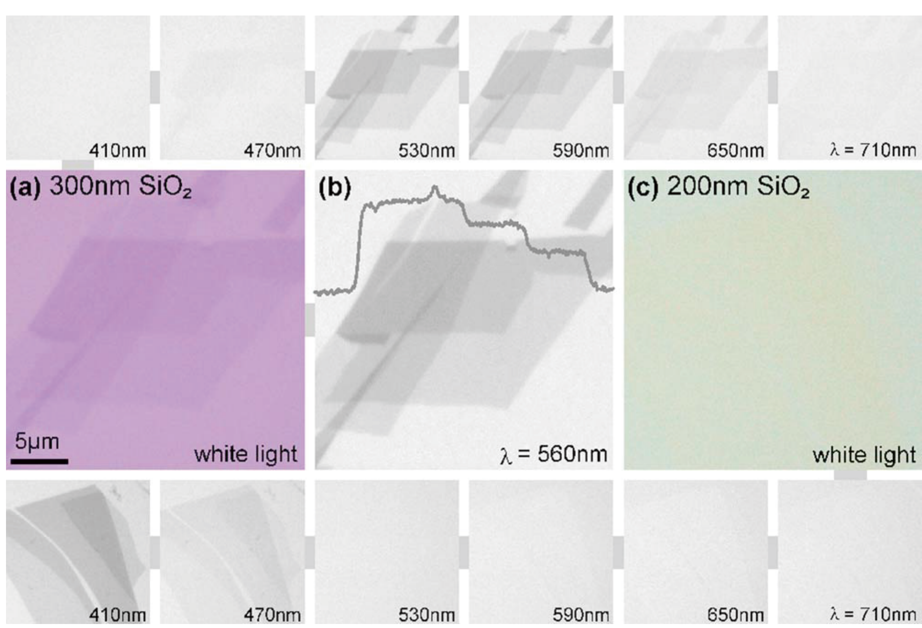


Contrasts apper
due to the optical interference.



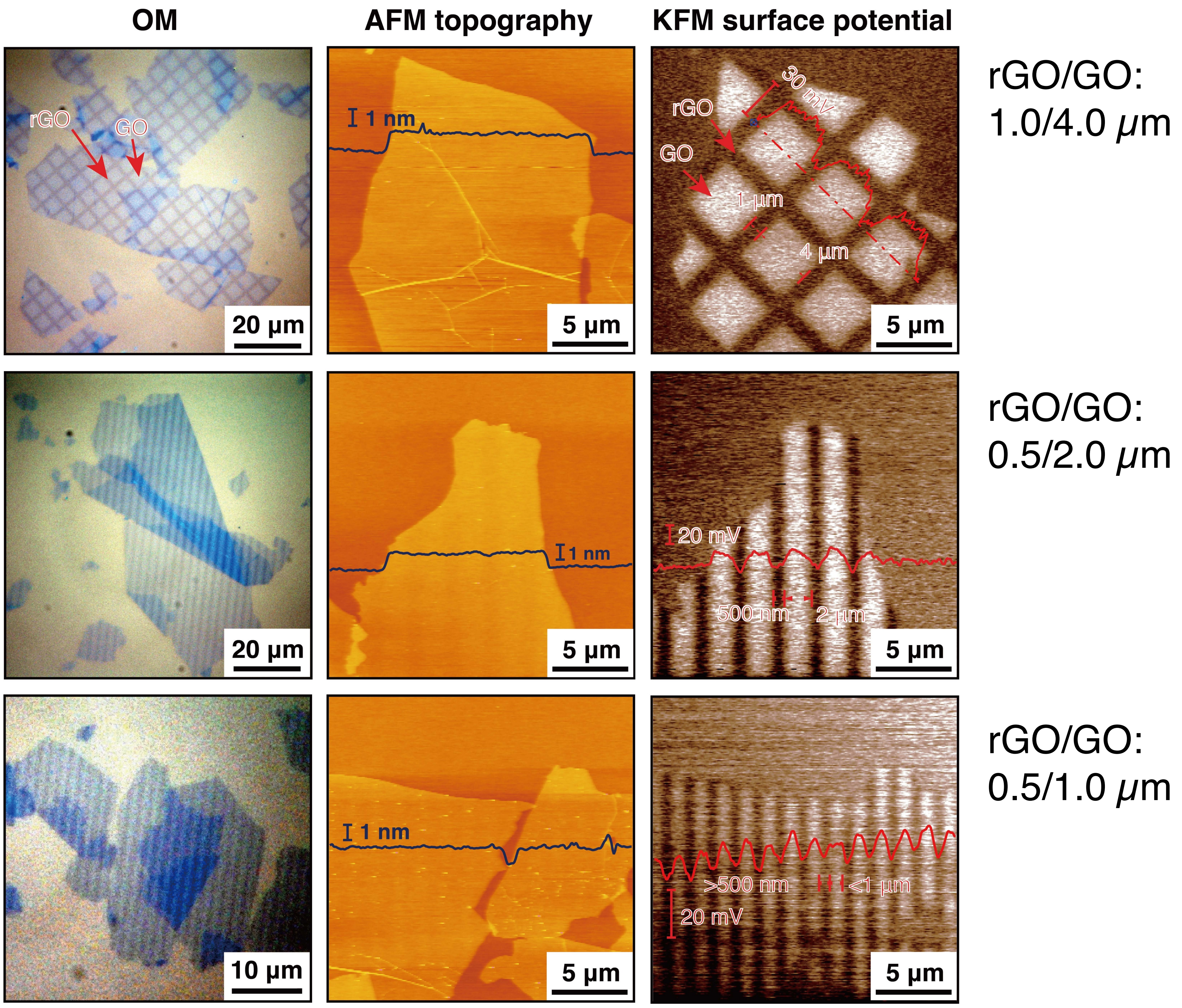
White light λ = 450 〜 750 nm

Relative contrast vs. SiO_2 thickness (Ref. 2)



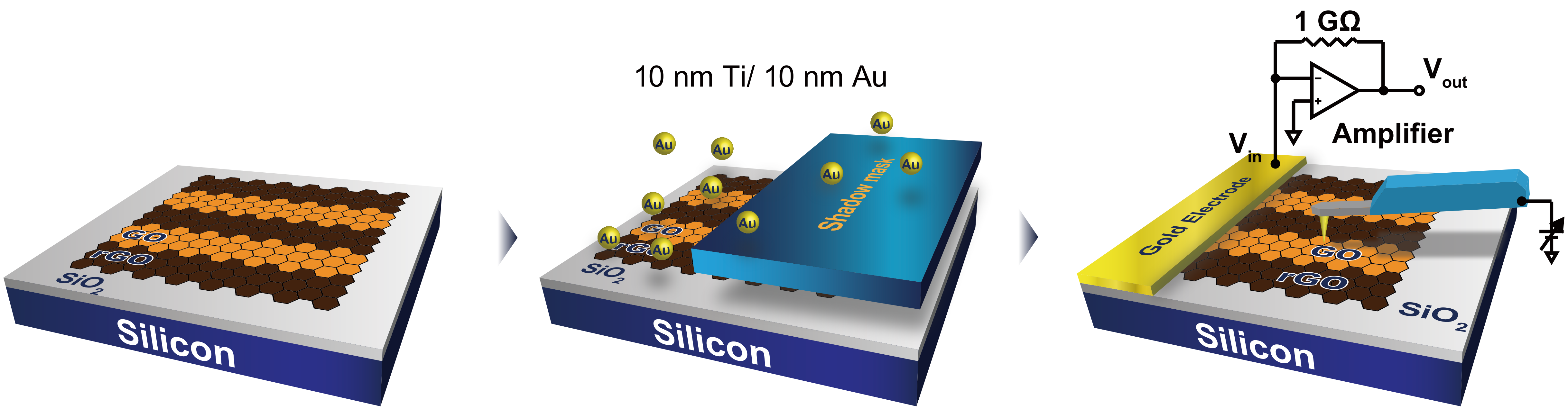
Optical micrographs of GO on SiO_2/Si (Ref. 1)
The contrasts changed with
thickness and wavelength.

1) P. Blake et al. *Appl. Phys. Lett.* **91** (2007) 063124.
2) K. Nagashio et al. *Appl. Phys. Exp.* **2** (2009) 025003.



The resolution of **500 nm** was achieved.

Electrical characterization by conductive-AFM



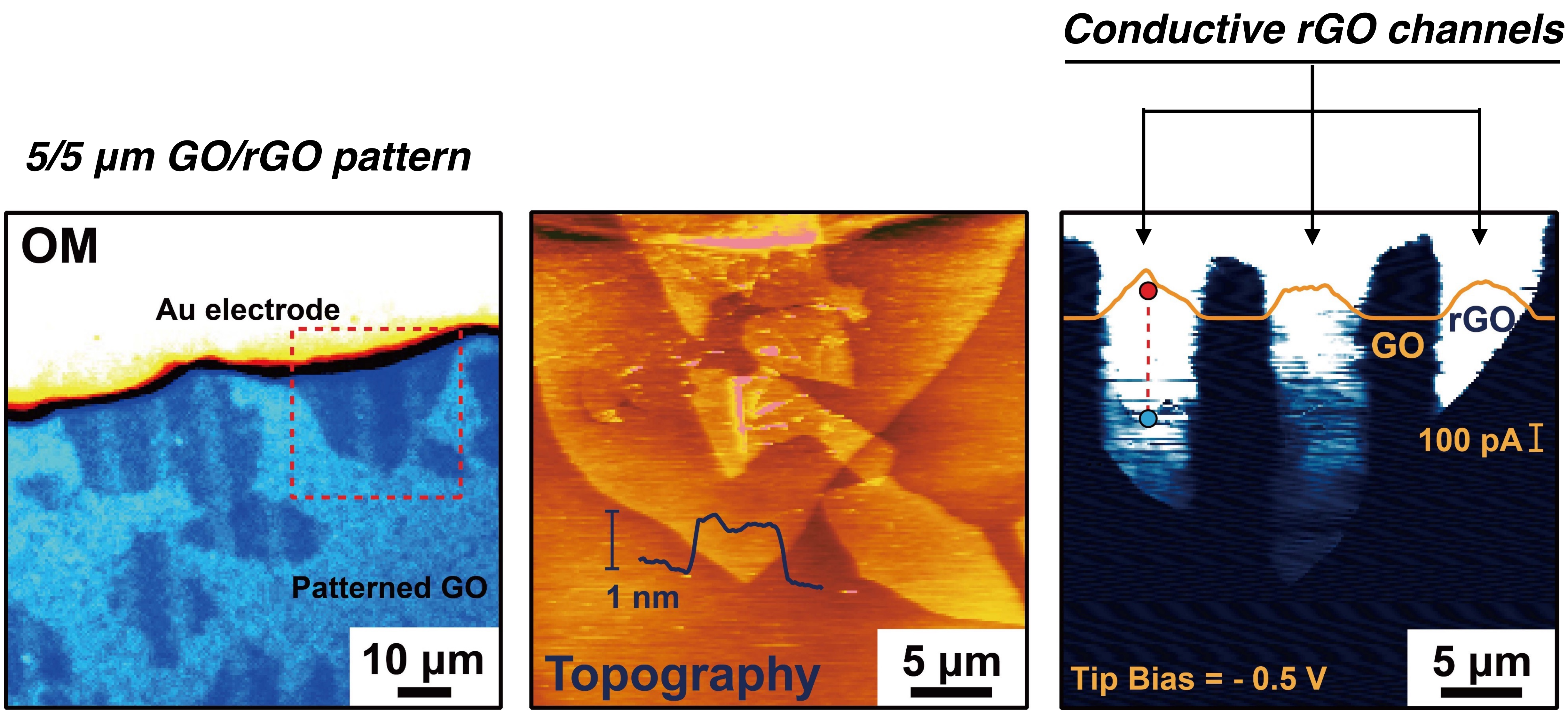
GO/rGO pattern

Electrodes PVD

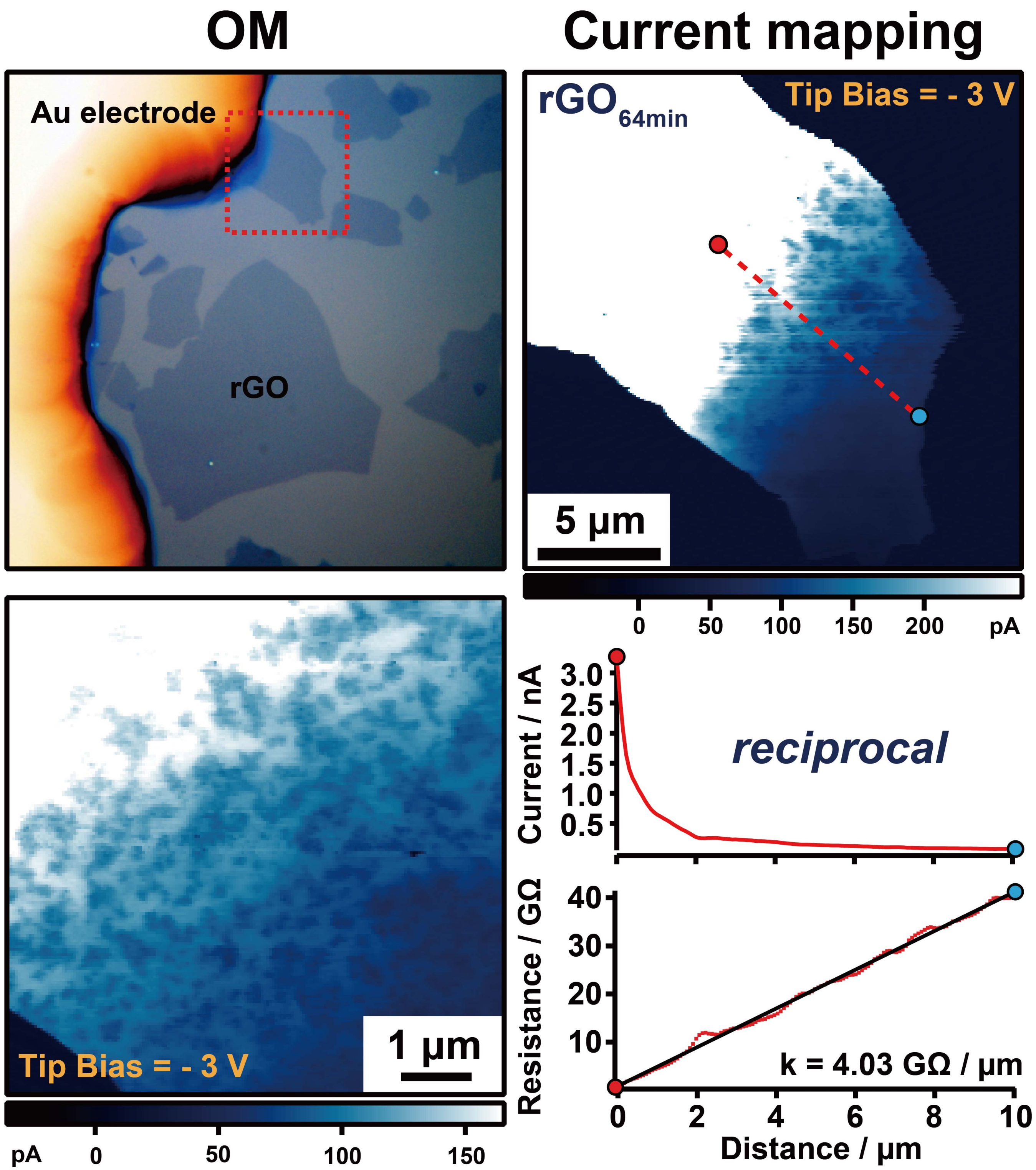
C-AFM measurement

100 nm Rh coated Si cantilever
(SI-DF-3R(100), 1.6 N / m,
resonance frequency = 23 kHz)

Conductive lines fabricated in a GO sheet



Conductivity of rGO sheet



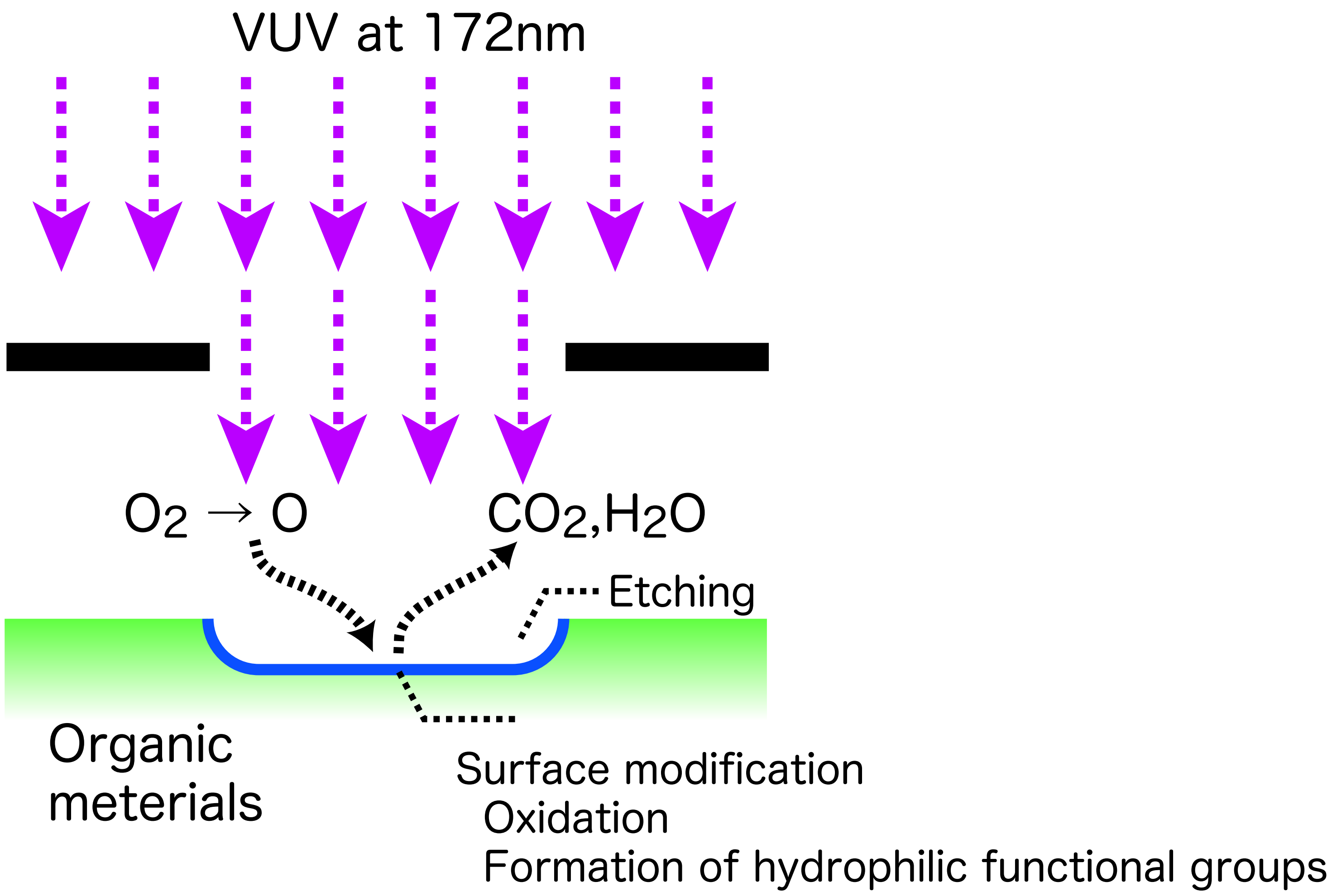
Sub-μm conductive rGO lines were successfully fabricated in a sheet.

Conductivity VUV-rGO (less than 1/1000 of graphene) is ***not sufficient*** for electronic applications. Its improvement is necessary.

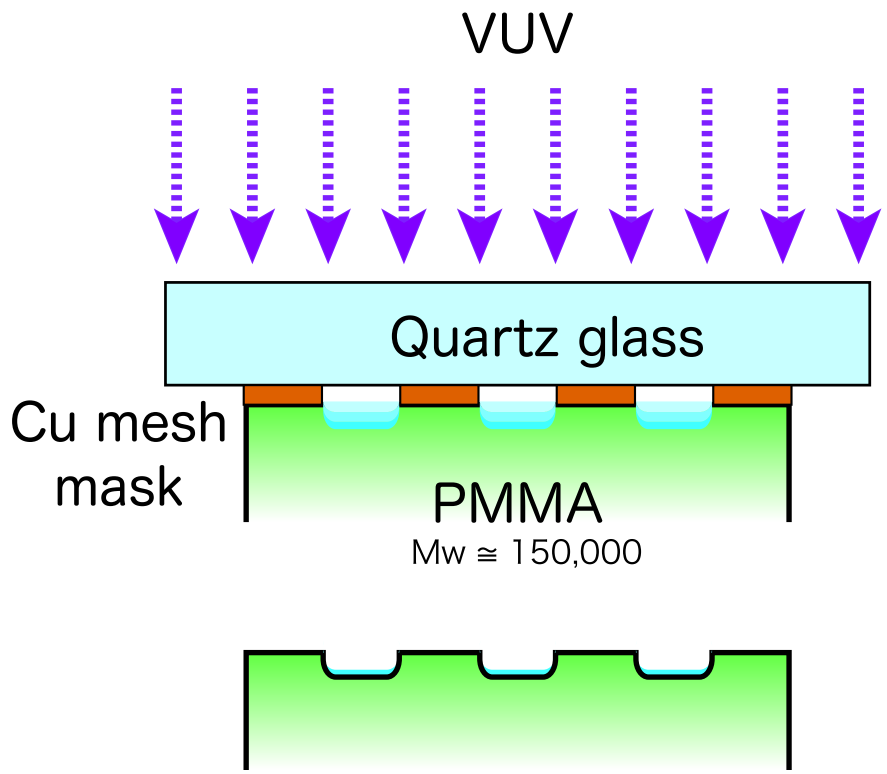
Defects in rGO served as **electro-active** sites in the chargetransfer at an electrode surface. *rGO is promising for* ***electrochemical devices***.

Electrochemistry at Chemically Modified Graphenes
A. Ambros et al. Chem. Eur. J. 17 (2011) 10763

VUV micro-ething



VUV etching of PMMA

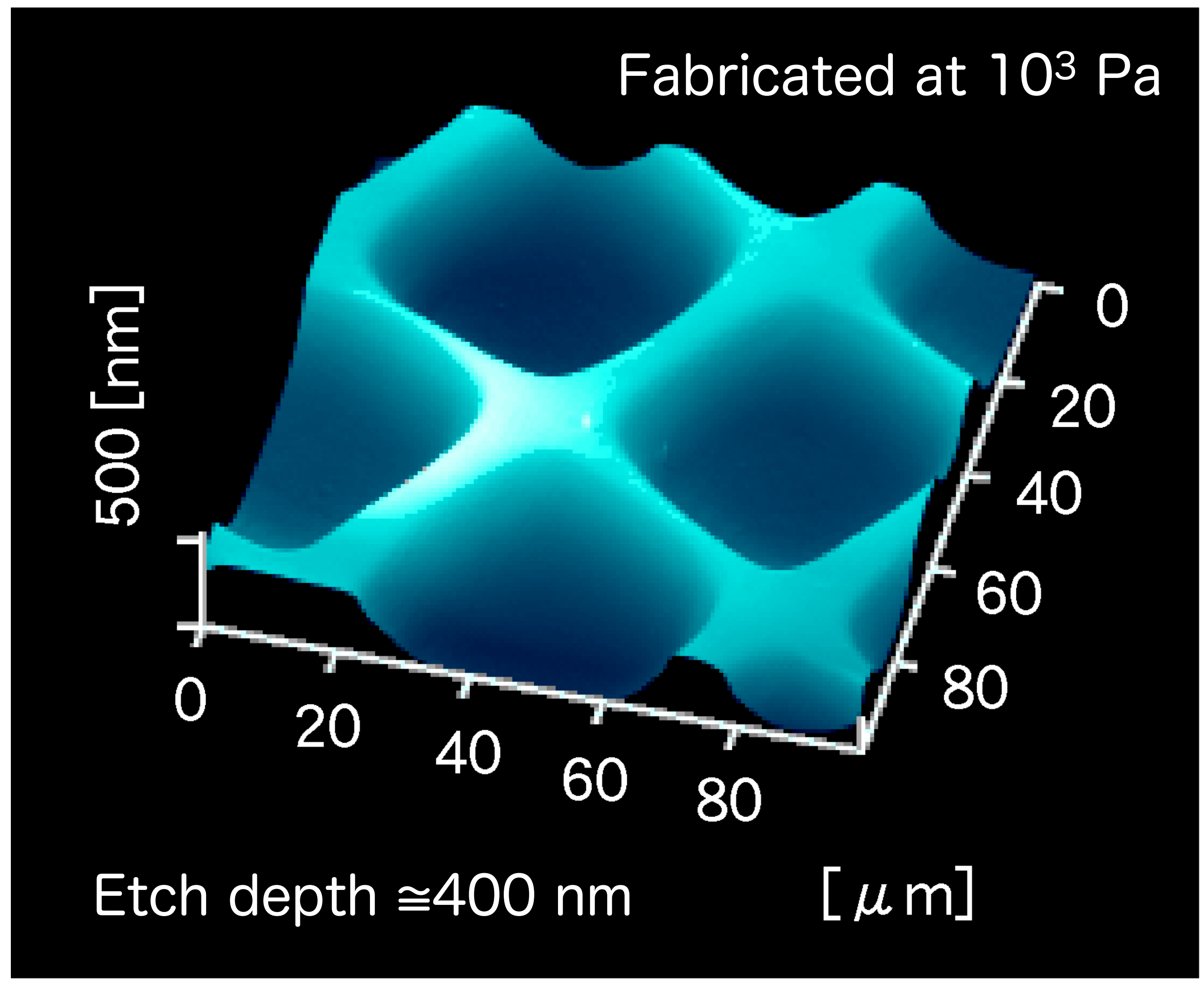


Etching rate

13.0 nm/min at 10 Pa

13.2 nm/min at 10^3 Pa

6.9 nm/min at 10^5 Pa



Collaboration with Dr. Hozumi, AIST

Langmuir **18** 9022 (2002)

Photoreaction of Oxygen

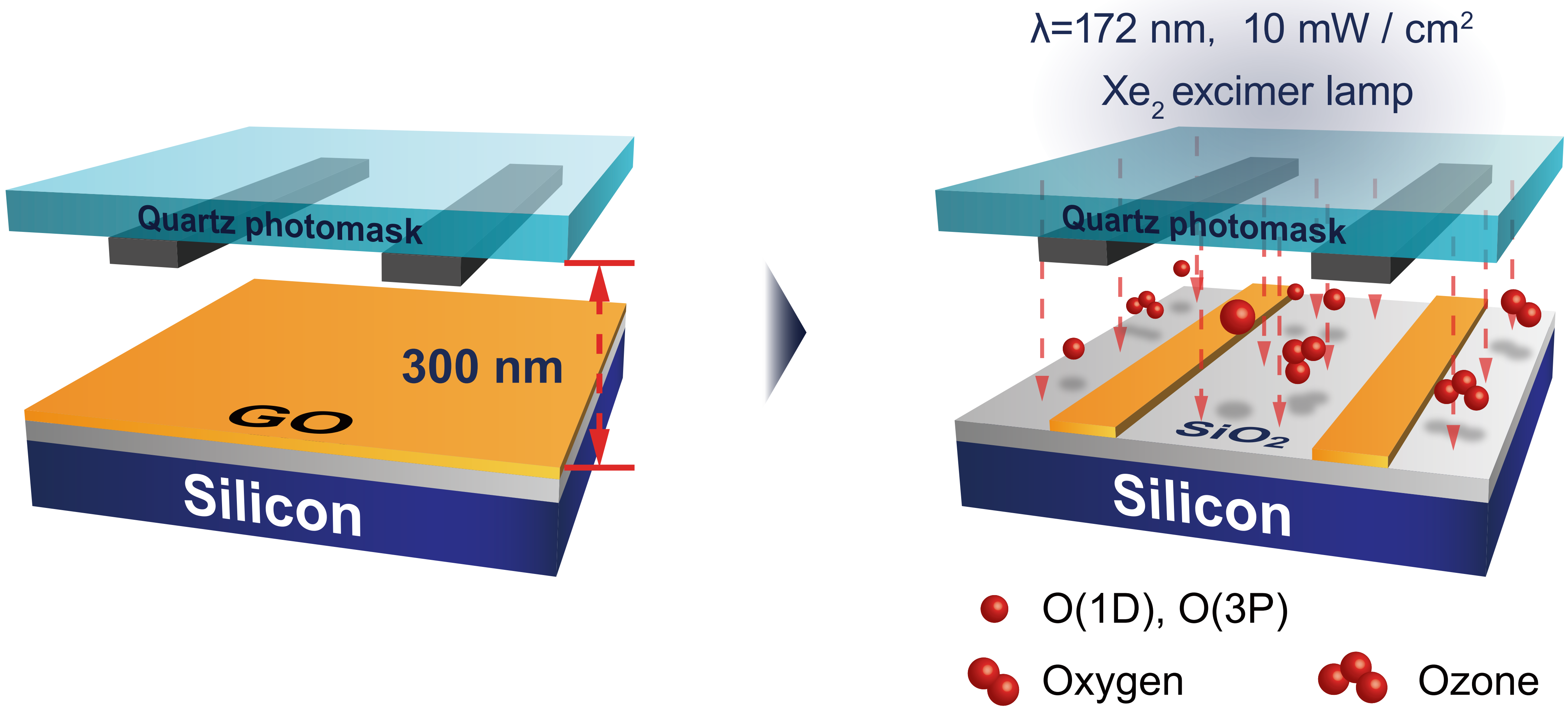
$O_2 + h\nu(\lambda \leq 175\ nm) \rightarrow O(1D) + O(3P)$

$O(1D) + M \rightarrow O(3P) + M$
$O(3P) + O_2 + M \rightarrow O_3 + M$

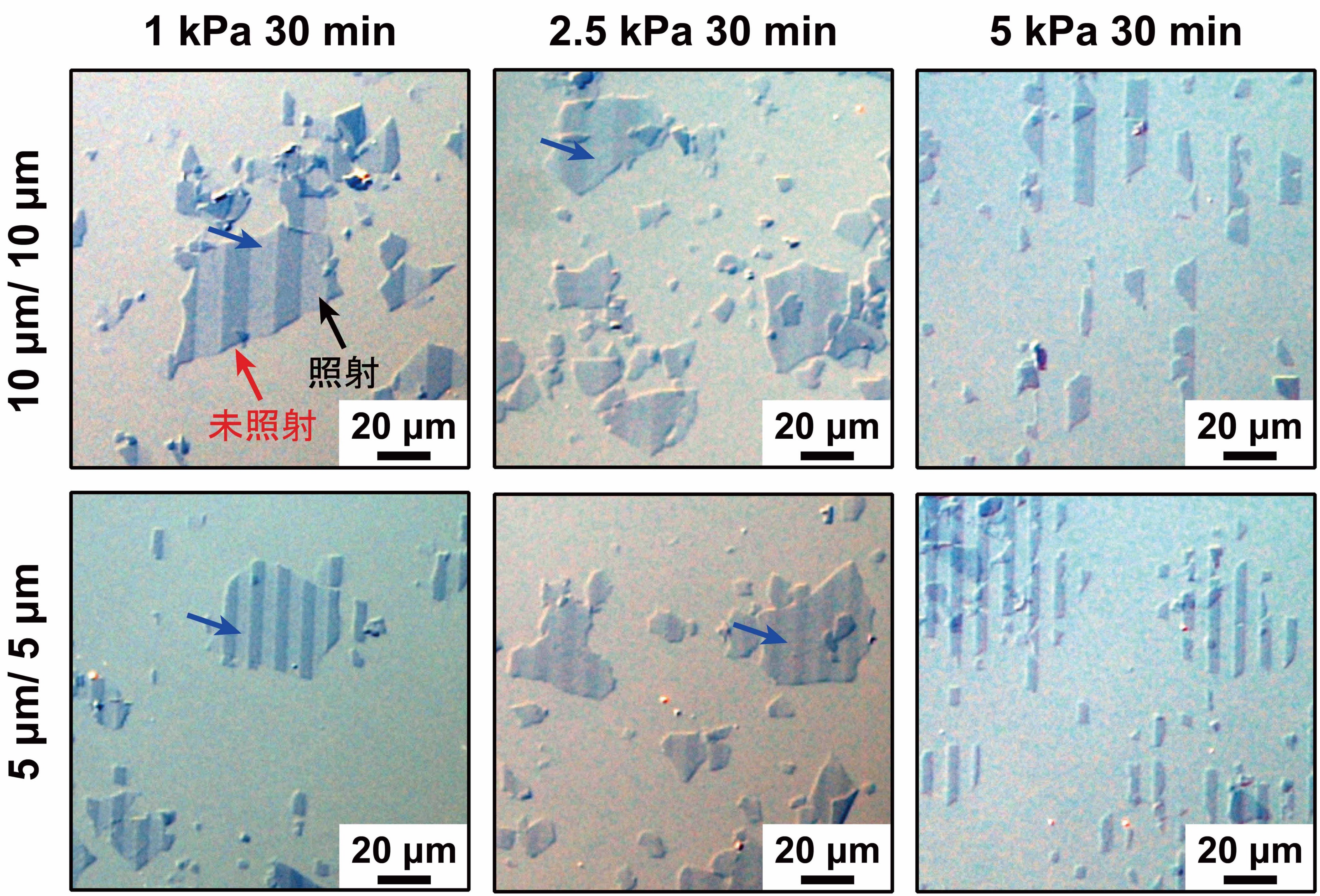
$O_3 + h\nu(\lambda \leq 300\ nm) \rightarrow O(1D) + O_2$

Active oxygen species, O(1D) , O(3P) , O_3 are generated by VUV irradiation of O_2 molecules.

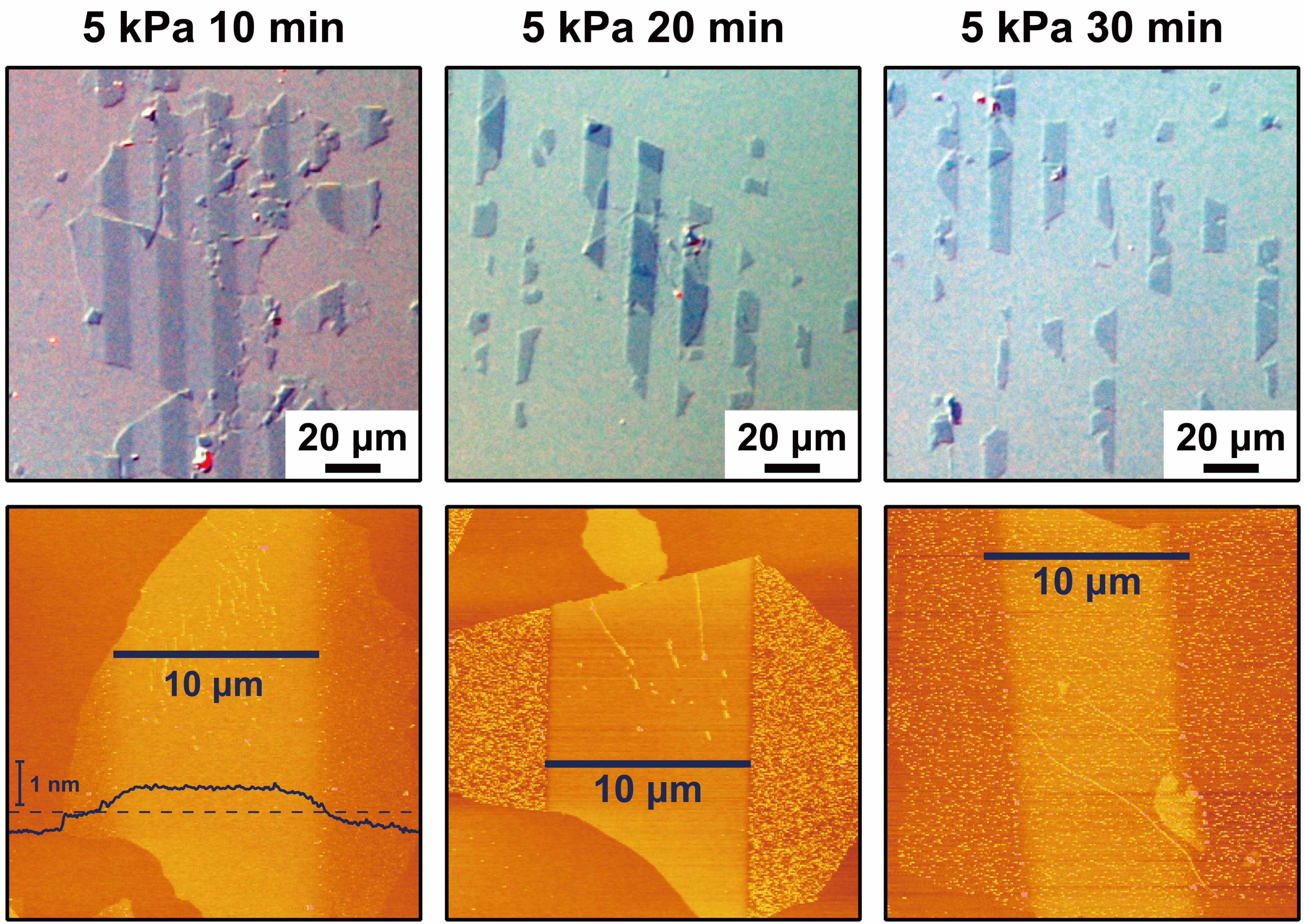
VUV/O micro-ething of GO



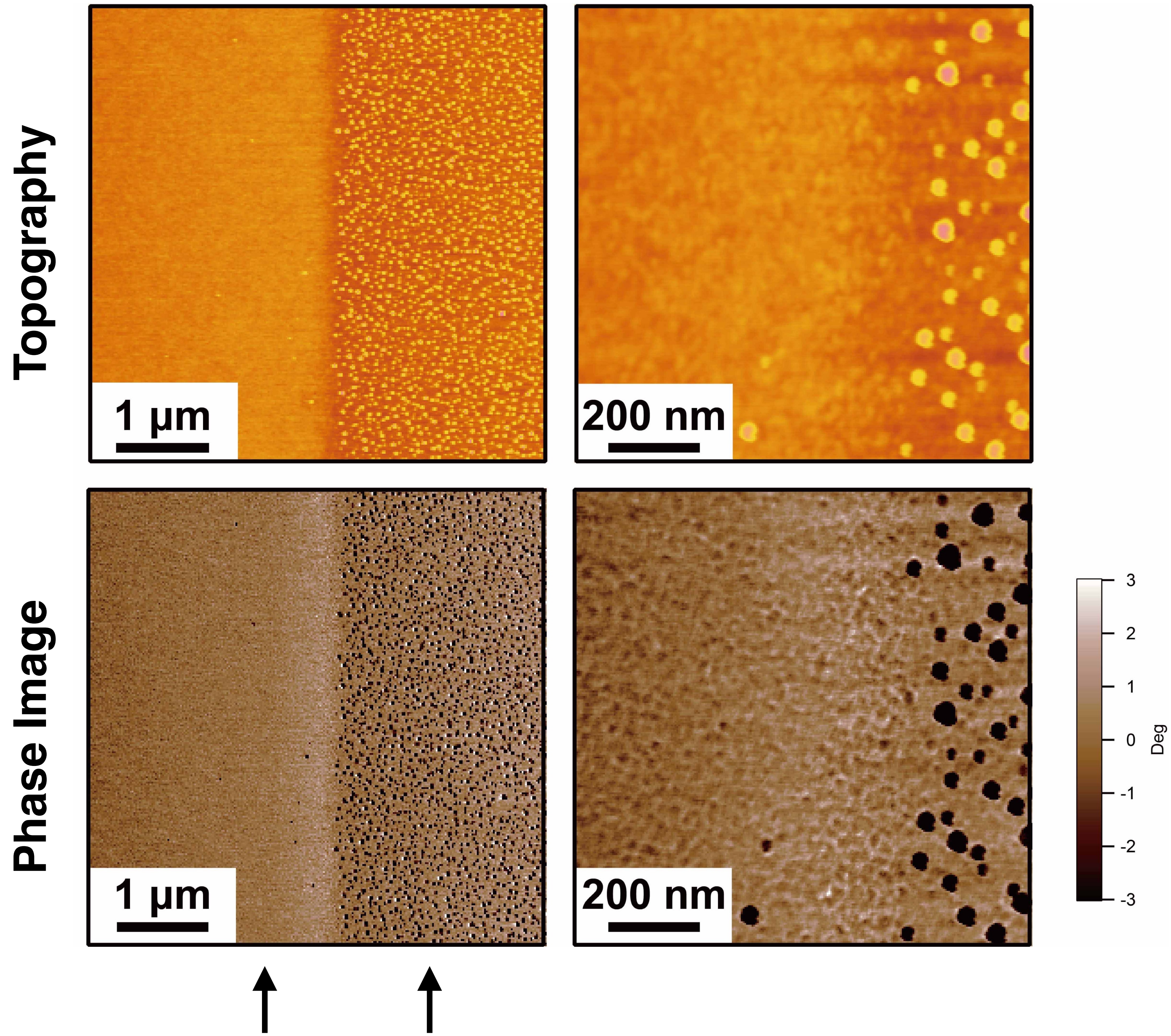
VUV/O ething : Pressure dependence



VUV/O ething : Pressure dependence

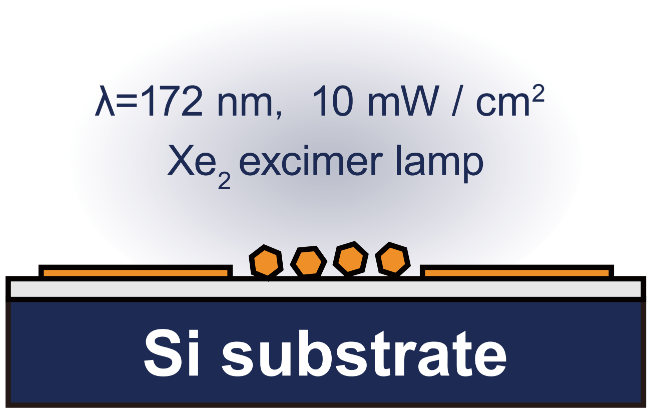


Remnant on the VUV/O etched area

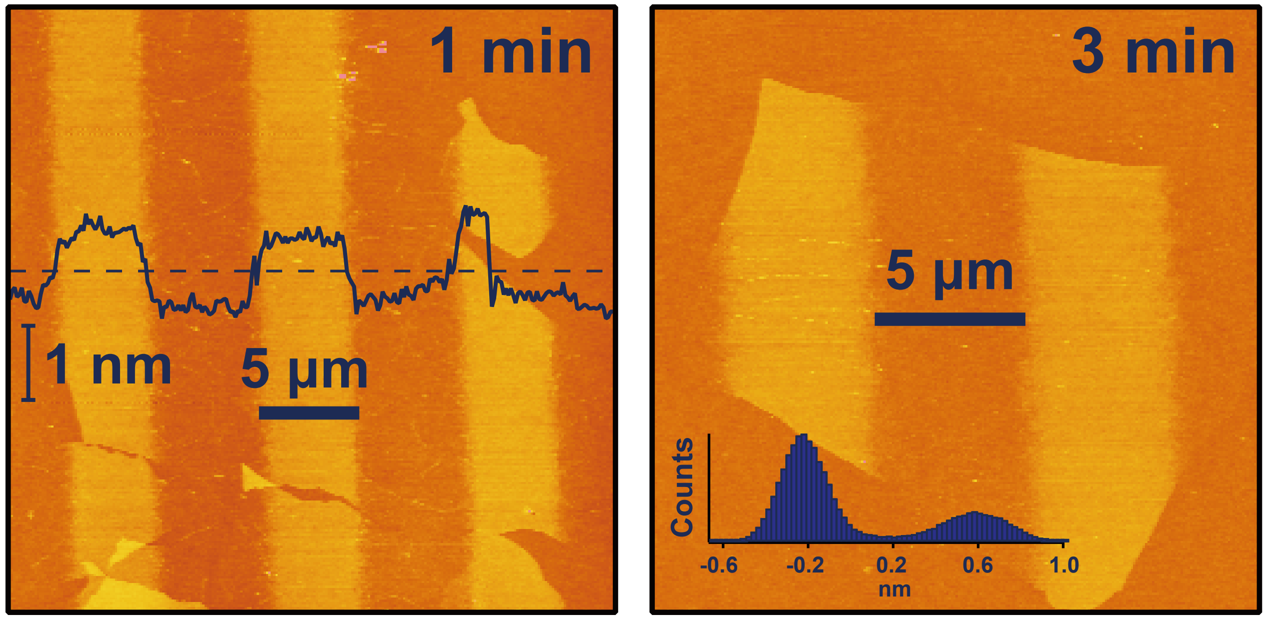


Distinct phase rag : Different nature - more adhesive

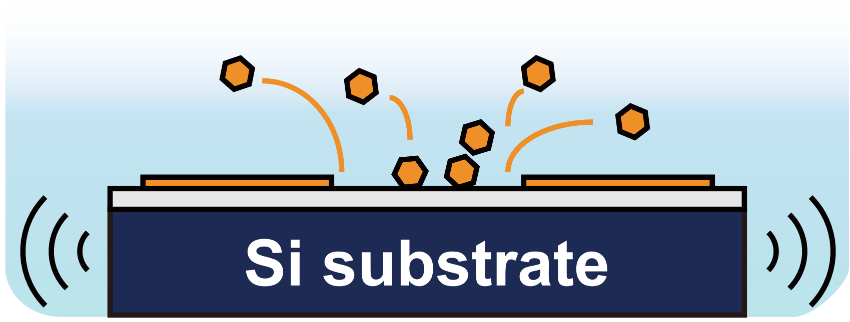
Sonication in water



Prior to sonication, the sample was reduced by VUV irradiation.

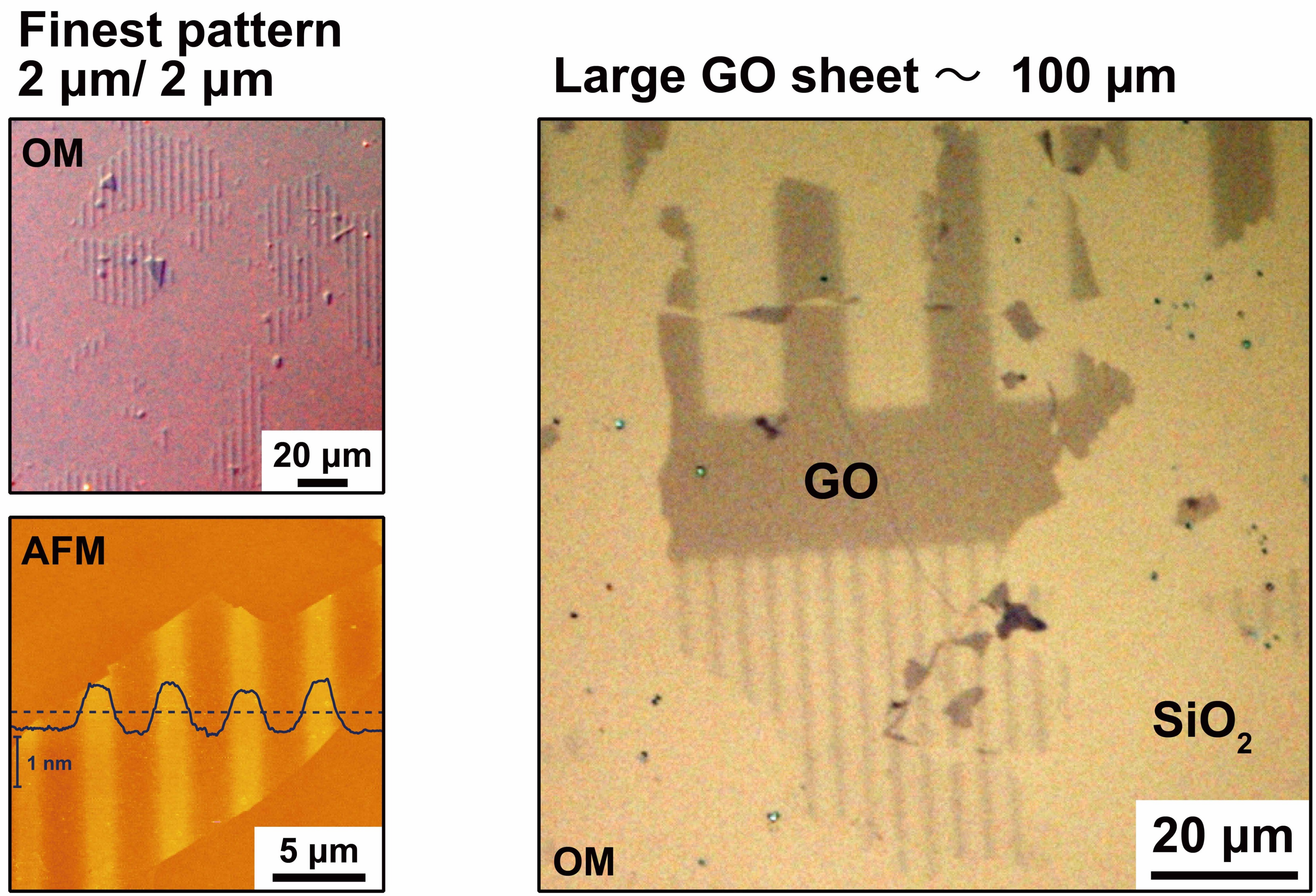


The sample sonicated in water.



Sonication in solvent
VS-F100, 100 W

UPW	○	**Ethanol**	×
Acetone	×	**Hexane**	×
Dibutyl ether	×	**THF**	×
DMF	×	**Toluene**	×
DMSO	×		


Finest pattern
2 µm/ 2 µm
OM
20 µm
AFM
1 nm
5 µm
Large GO sheet ～ 100 µm
GO
SiO2
20 µm
OM

Summary

VUV photochemistry has been applied for GO modification/sub-micro patterning both on the oxidation and reduction schemes.

Reduction approach:
Fabrication of conductive channels in GO.
Expected for printing graphene micro circuits.

Oxidation approach:
Micro-etching of GO layers.

Nanoscopic Surface Architecture Laboratory

http://www.nsa.mtl.kyoto-u.ac.jp

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