Basic 14
Micro-Nano Tribology

- Ultra low friction of Carbon Nitride (CNx)
and
Low adhesion and friction of rubber -

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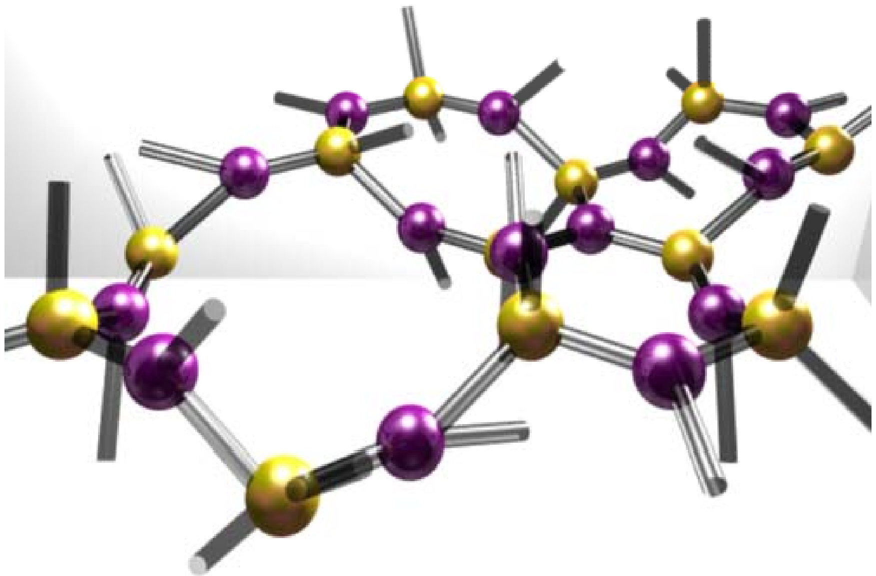
Outline

1.Ultra low friction of Carbon Nitride (CNx)
・Mechanism

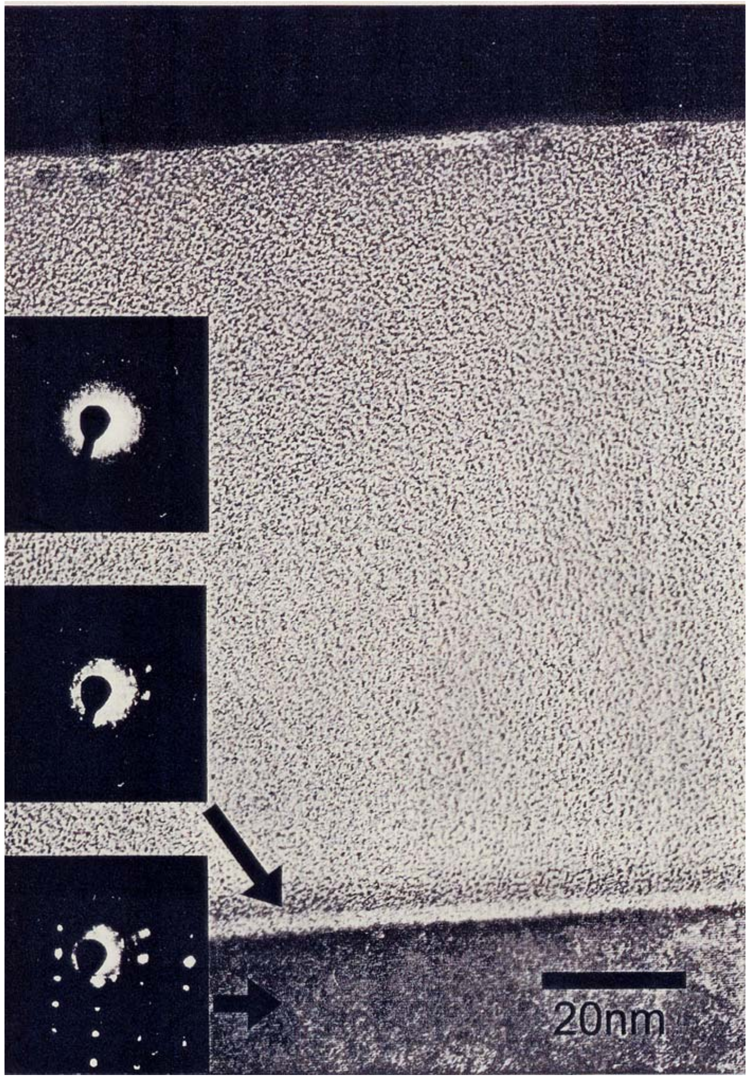
・Effect of carbon overcoat on friction

2.Low adhesion and friction of rubber
・High dense plasma irradiation to CIIR
・UV ray irradiation to TPE with PFPE

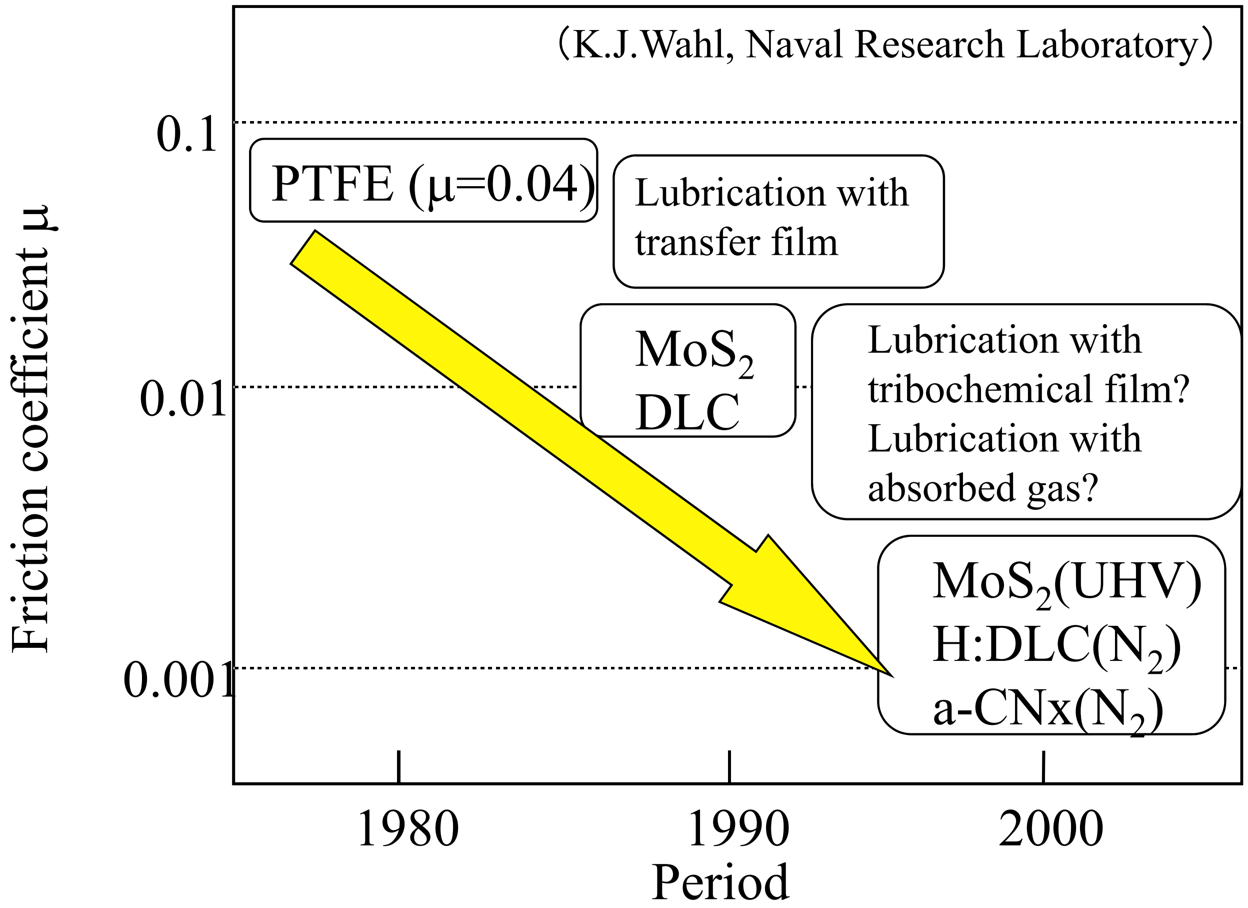
1. Ultra low friction of Carbon Nitride(CNx)



A.Y.Liu, M.L.Cohen, Prediction of new low compressibility solids, Science, 245 (1989) 841-842.



Introduction



After the annual meeting of STLE, 2001

MoS_2; W.E.Jamison (1986)
DLC; A.Erdemir (1991), J.Franks, K.Enke and A.Richardt (1990)
H:DLC; A.Erdemir (1999), C.Donnet(1998)
a-CNx; N.Umehara, K.Kato(1998)

Introduction

Carbon nitride(a-CNx) coating

High hardness
High wear resistance
Low friction

↓

Excellent tribological properties

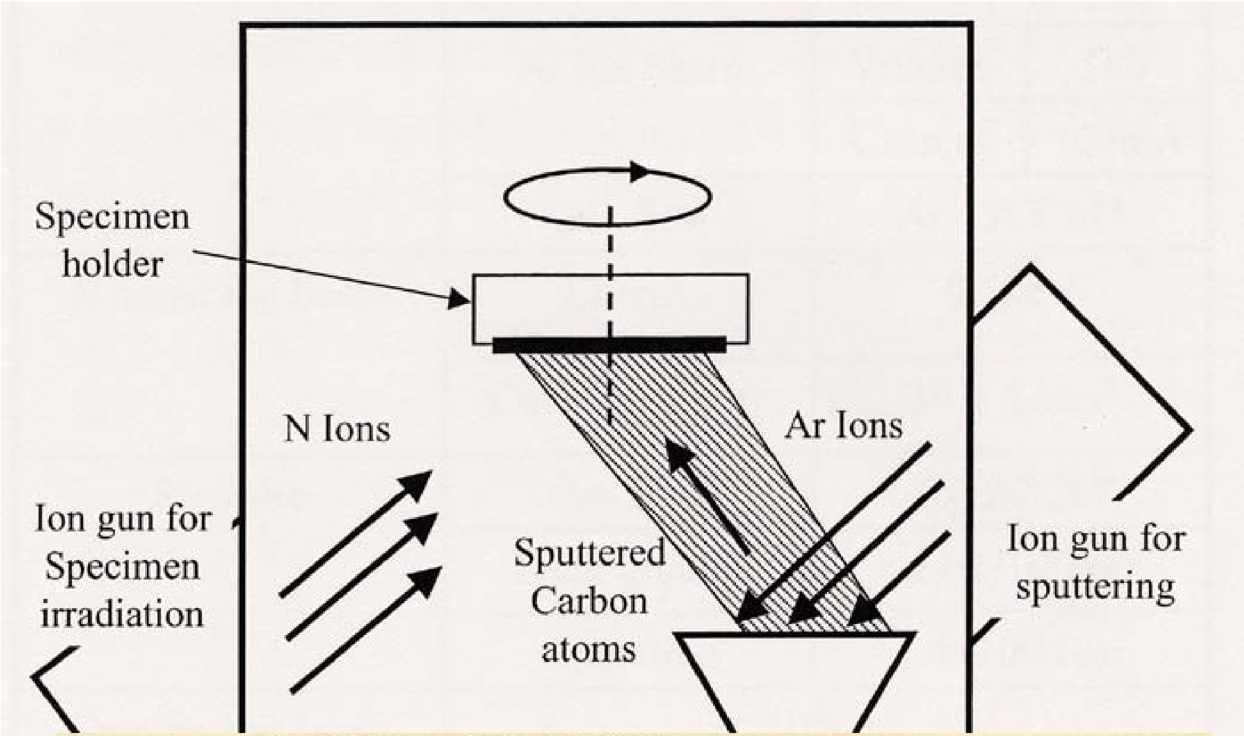
Hardness: $H_{a\text{-}CNx}/H_{a\text{-}C}=1.31$
Low friction coefficient(against Al_2O_3/TiC slider)

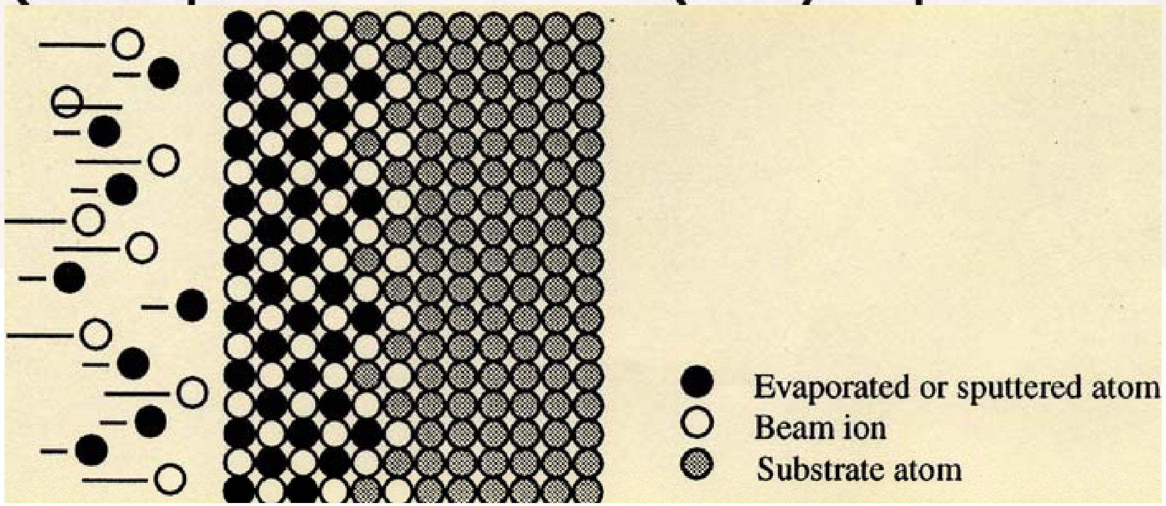
B.Wei et al. (1998)

Durability: $D_{a\text{-}CNx}/D_{a\text{-}C}=3\sim4$ (against Al_2O_3/TiC pin)

E.C.Cutiongco et al. (1996)

Ion Beam Assisted Deposition





Sputtering：

Ar ion beam 1kV, 100mA

Mixing：

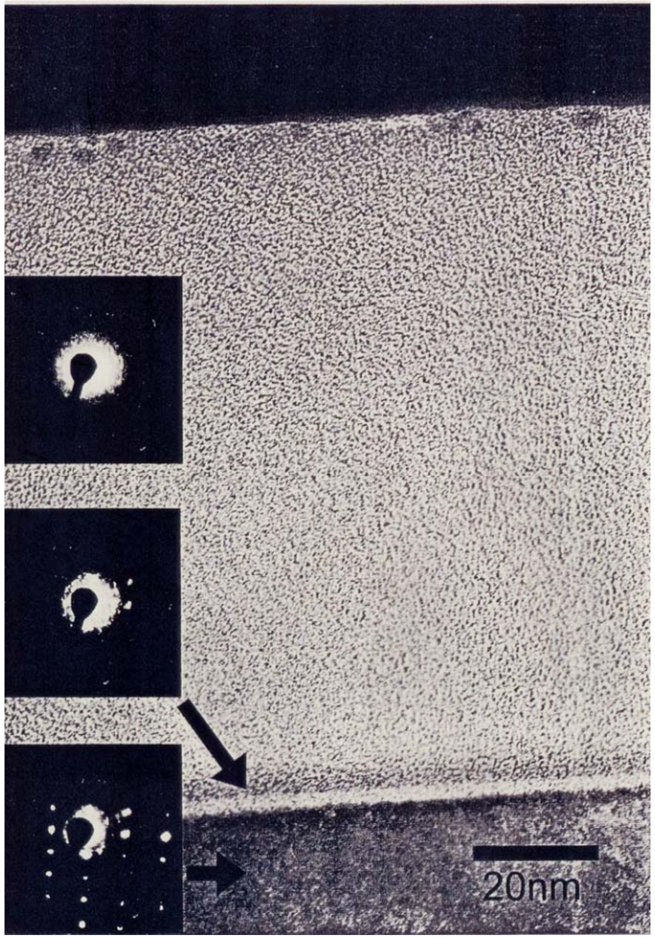
N ion beam 0.5keV,

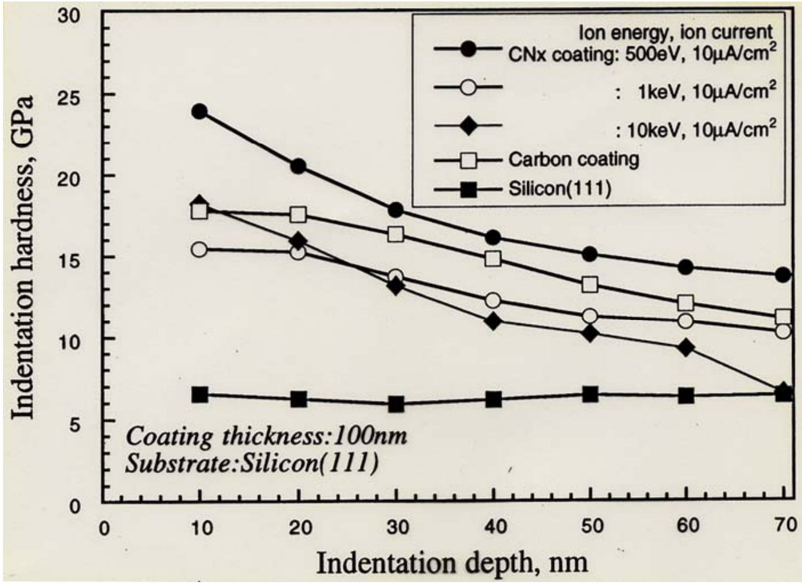
30μA/cm^2

Coating time：90min

Thickness of coating：100nm

TEM photo of CNx by IBAD and Hardness

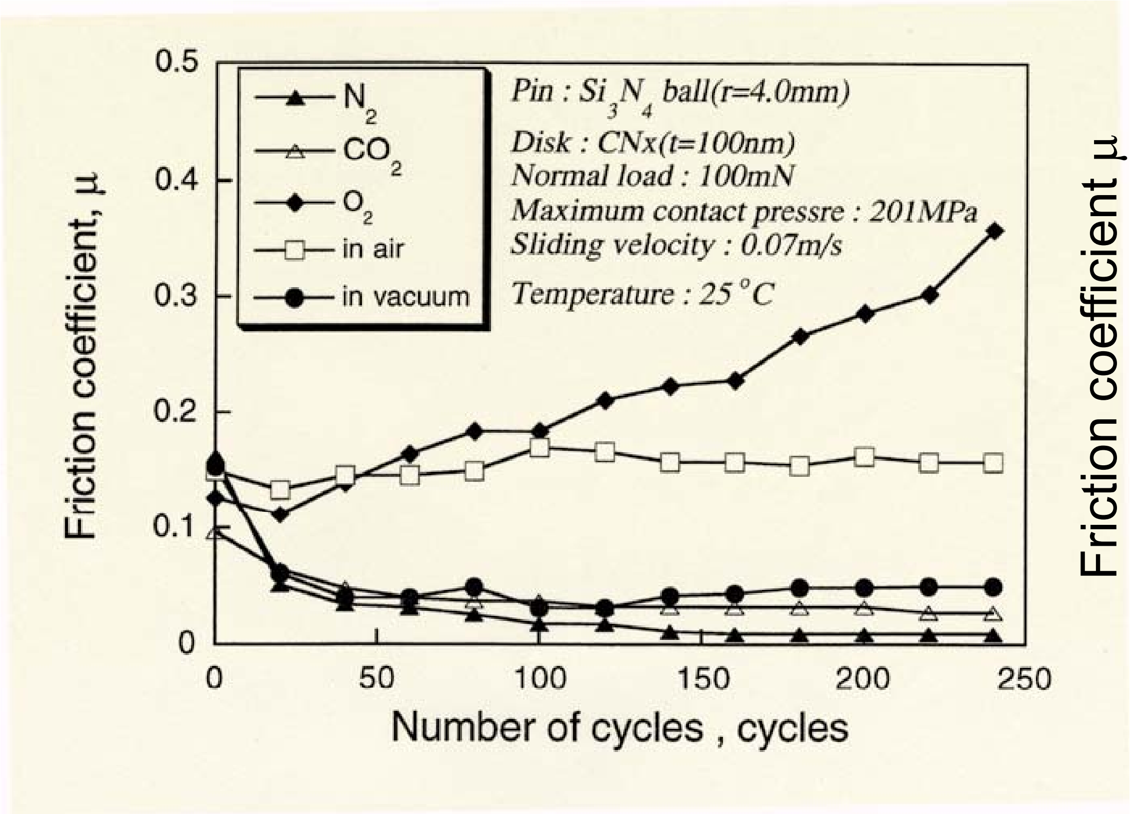


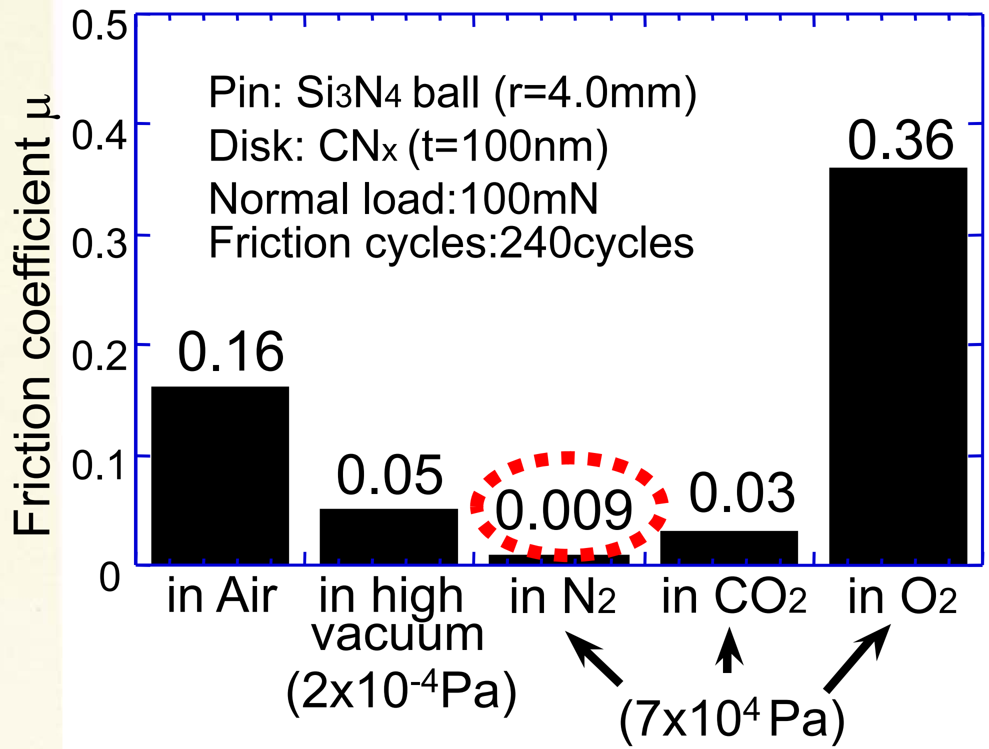


- Hardness 21GPa
- Amorphous structure
- N=C bonds

38) Micro-wear Mechnaisms of Thin Hard Coatings Sliding against Diamond Tip of AFM, ASME, Advances in Information Storage Systems, 9 (1998)289-302.
K. Kato, H. Koide, and N. Umehara

Effect of ambient gas on friction coefficient

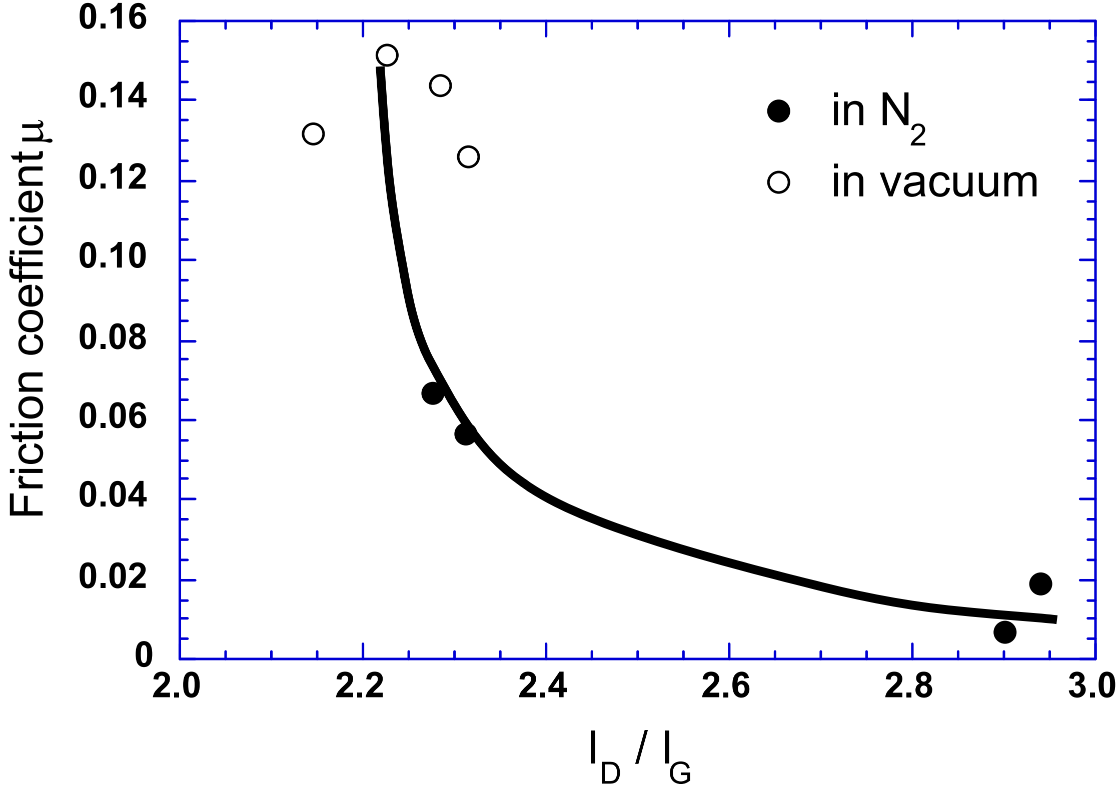




(N. Umehara and K. Kato , 1998)

Running-in is important for ultra low friction of CNx.
Something changed during running-in.

Raman spectroscopy after running-in

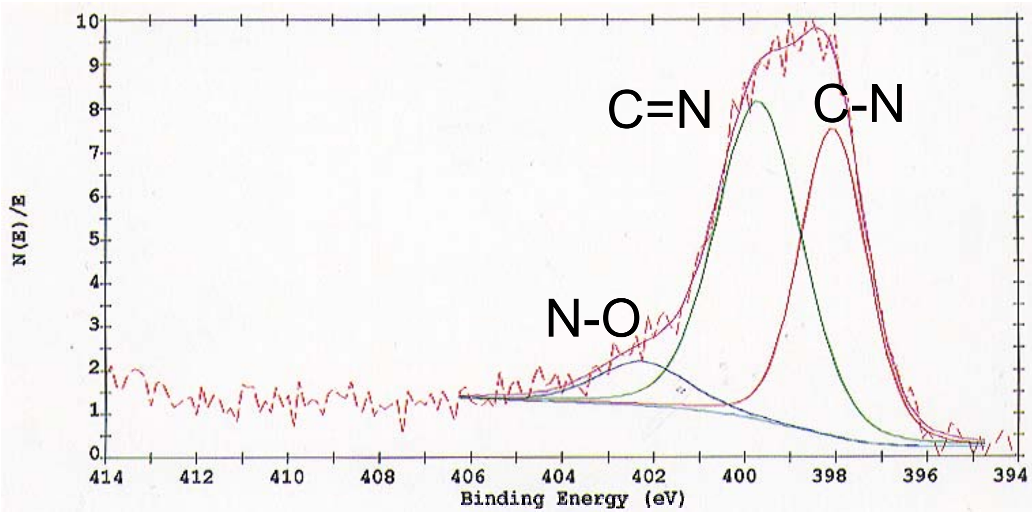


Large I_D/I_G provides small friction coefficient

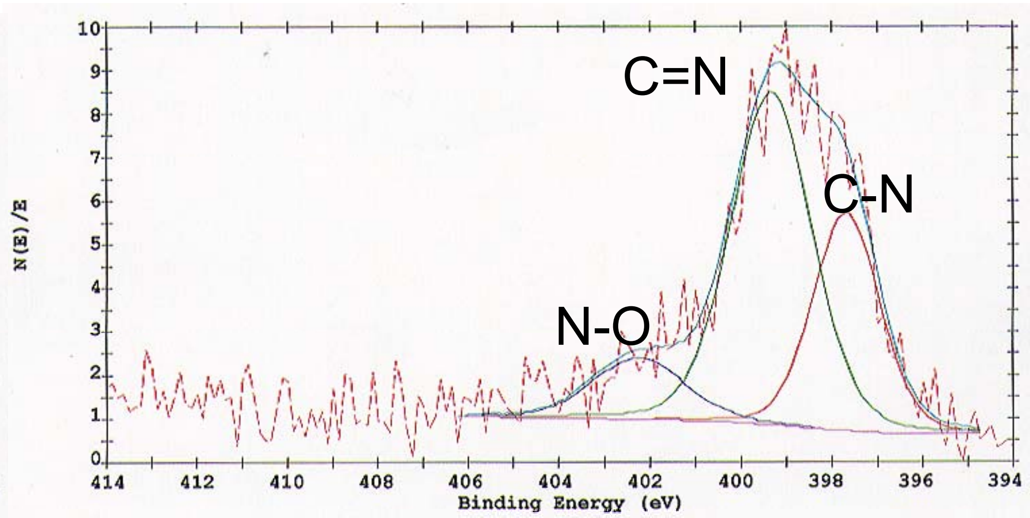
Increase in the number or size of small graphitic domain

N. Umehara, M. Tatsuno, K. Kato, Proc. Int. Trib. Conf. Nagasaki(2000)1007.

XPS before and after running-in



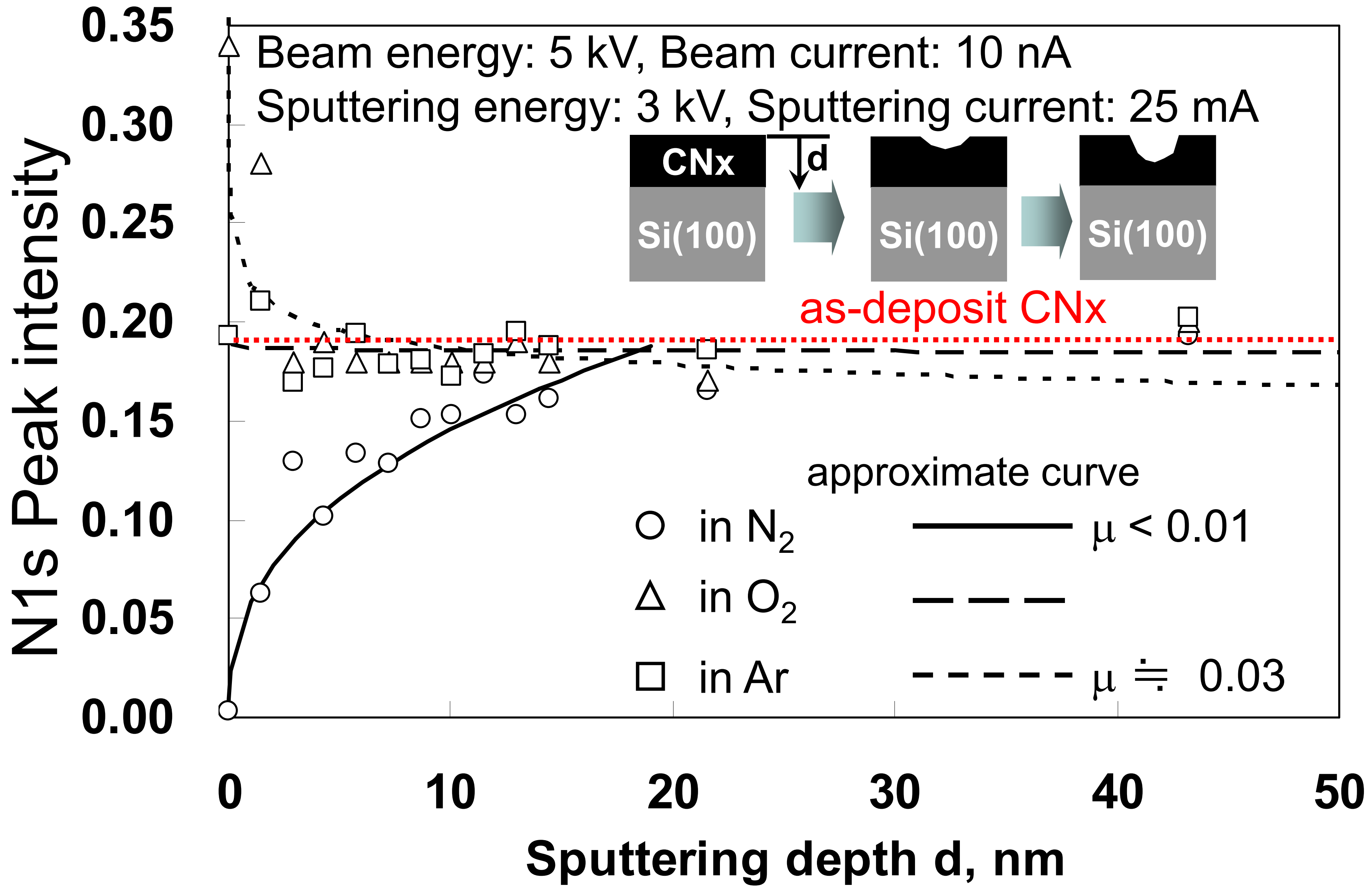
(a) a-CNx coating



(b) wear track after 240 cycles in N_2 gas

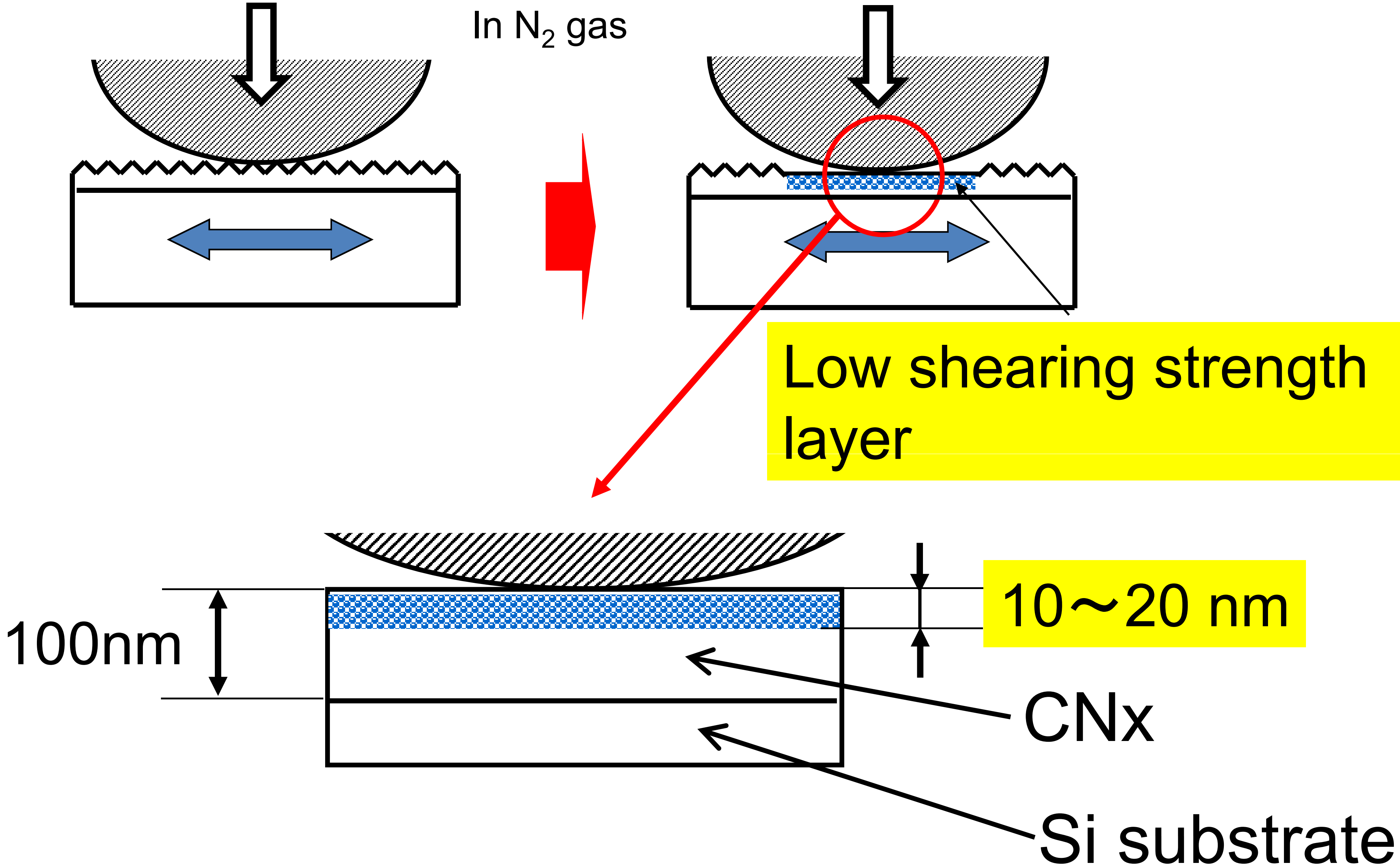
After running-in in N_2 gas, C=N increases larger than C-N.

Depth profile of N after running-in in various environment



Tokoroyama, Umehara, IIP Session, Annual meeting of JSME, Sept. 11,2007

Self surface modification in the running-in process



Outline & Summary

1.Ultra low friction of Carbon Nitride (CNx)

- Mechanism Self modification in nm thickness
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- Effect of Ultraviolet (UV) ray irradiation on friction

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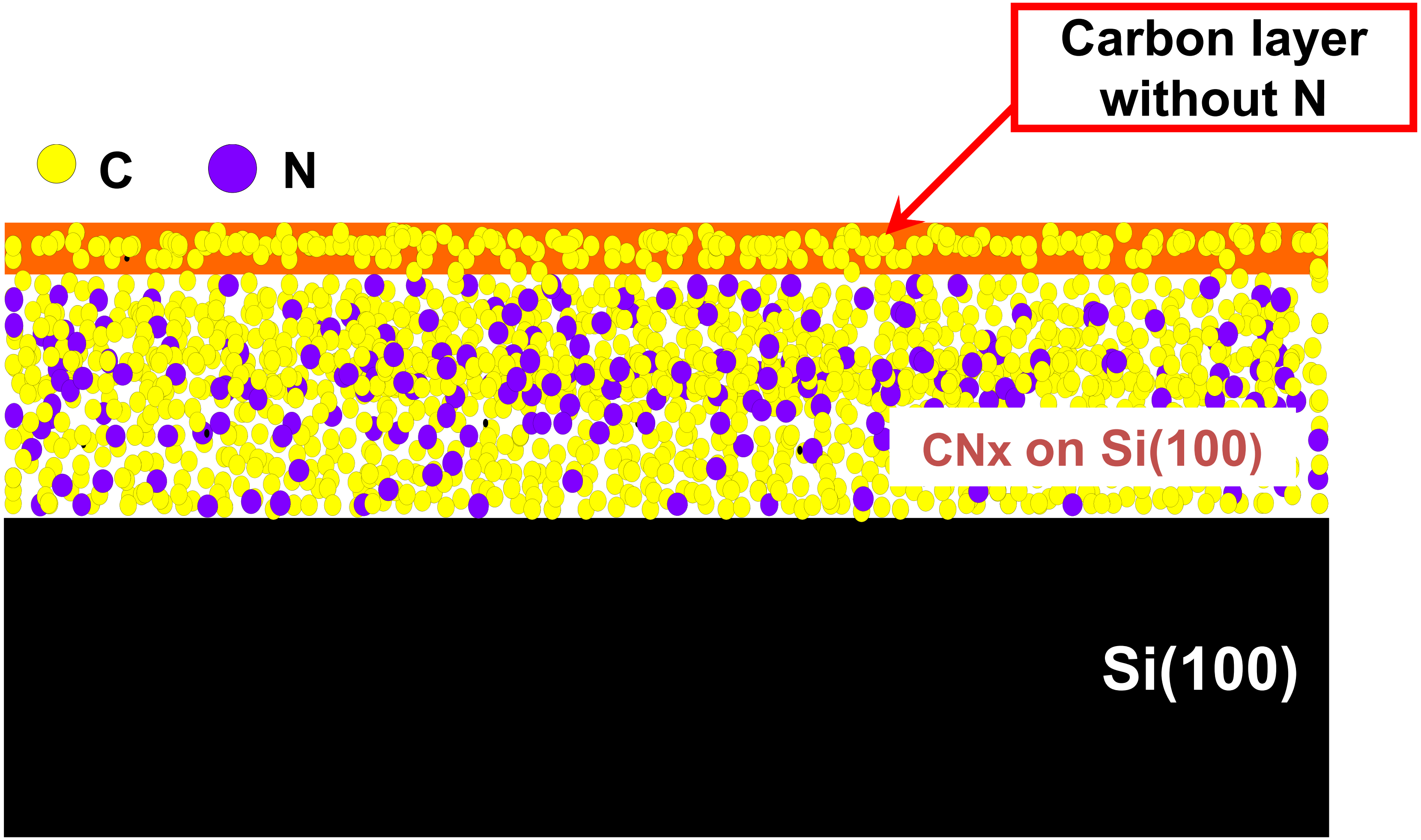
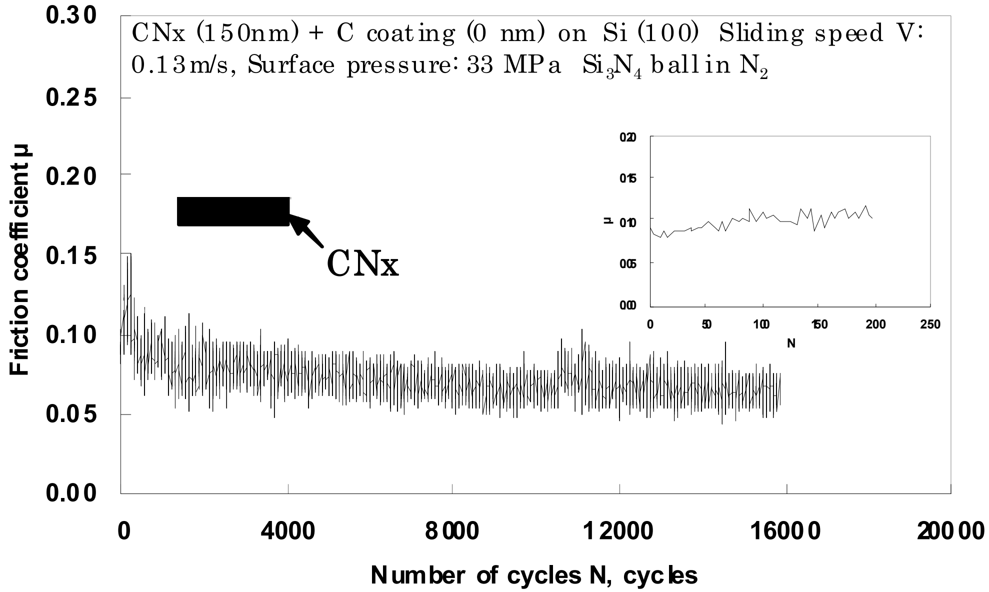
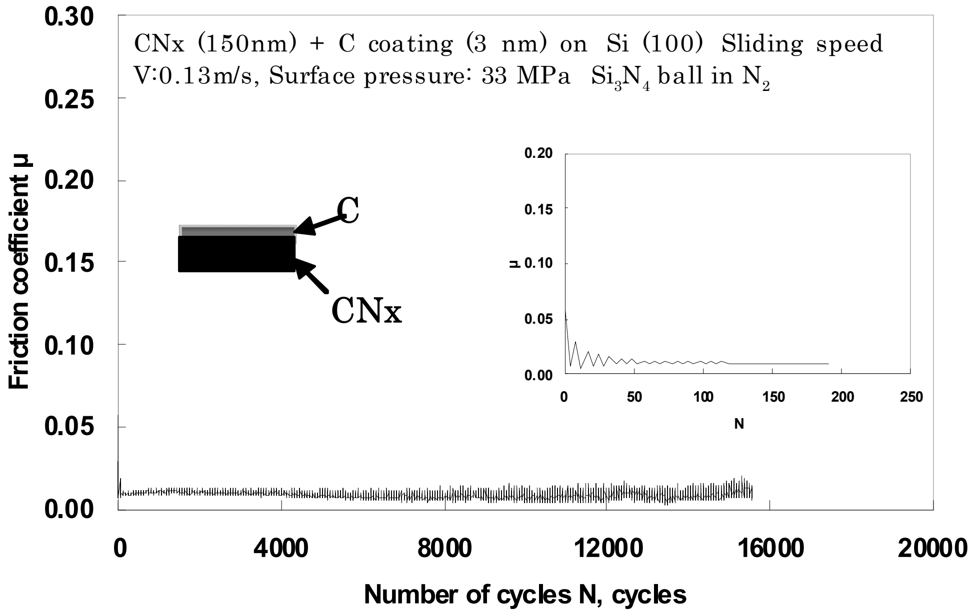
Enhancement of running-in of CNx with nm thickness carbon overcoat



Effect of 3nm thickness carbon overcoat on friction of CNx



Only CNx



3nm C + CNx

Proc. ICMDT Sapporo,2007, Tokoroyama, Wang, Umehara, Fuwa

Outline & Summary

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  not need running-in
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The expectation of ultraviolet ray irradiation to CNx

C-N bond: 305 kJ/mol

The light energy

Energy of photon

$$E = h\nu = h\frac{c}{\lambda}$$

h: Planck's constant, ν: frequency,
c: light velocity, λ: wavelength

Energy of photon per mol

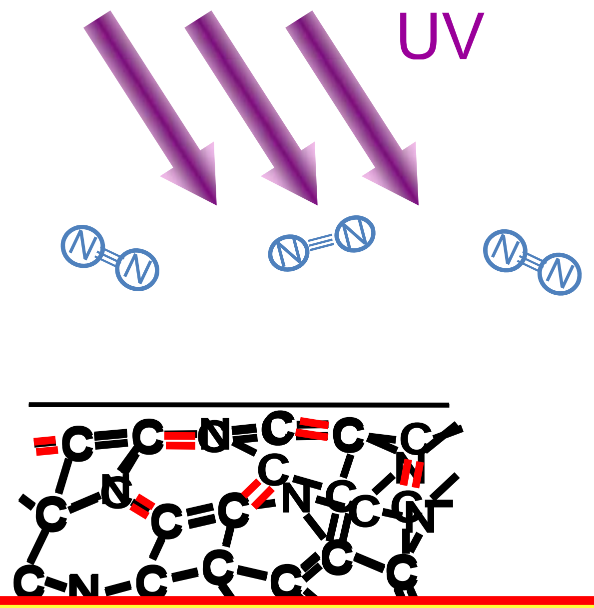
$$E = h\frac{c}{\lambda} \times N_A$$

N_A: Avogadro's constant

Wavelength
＜390 nm

Braking of
C-N bond

Expected result



Nitrogen desorption ⇒ Structural change

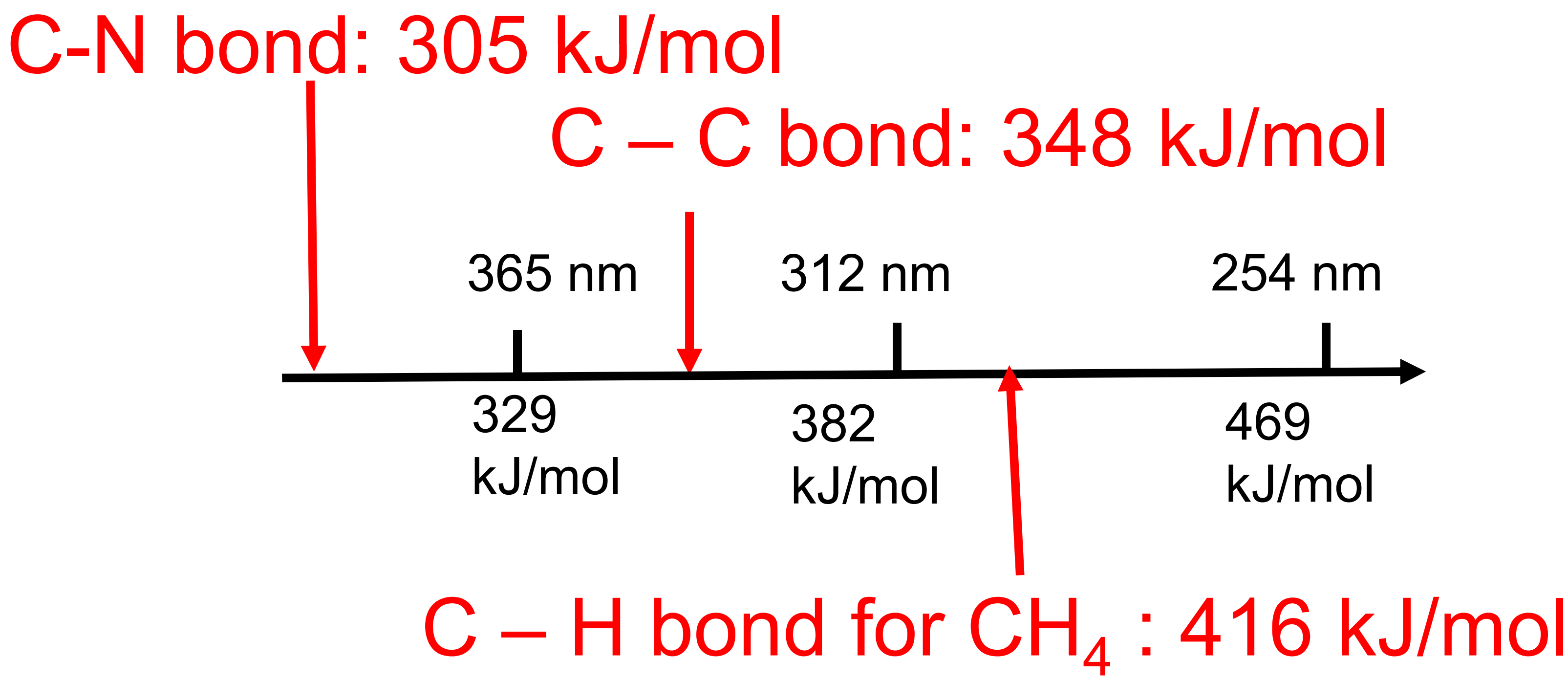
We focused on Nitrogen content in CNx. J. Wei et al. Surf Interface Anal. 28(1999) 208-211

We assumed that the variable UV wavelength to obtain superlow friction changed with the Nitrogen content in CNx coating because of its structure.

Nitrogen content ratio 0,9,12,19% was prepared

e.g.
$CN_{0.09}$(x=content)

Background –Effect of UV irradiation



Energy of photon

$$E = h\nu = h\frac{c}{\lambda}$$

h: Planck's constant, ν: frequency,
c: light velocity, λ: wavelength

Experimental – Ultraviolet ray irradiation to CNx coating

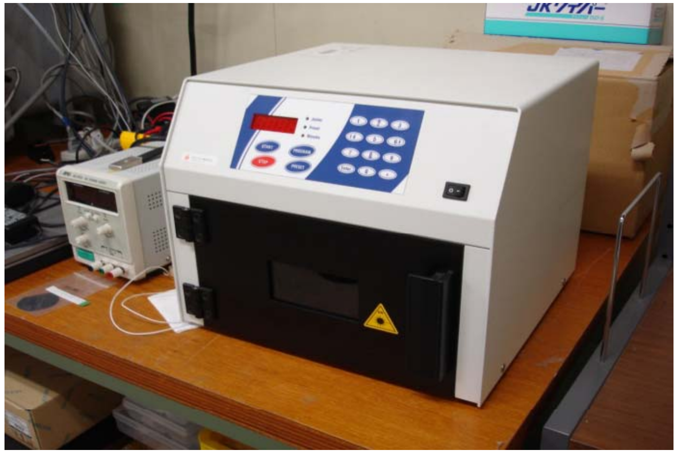
Did Nitrogen atoms desorb from CNx coating with UV irradiation?

Table 1 The energy of each wavelength

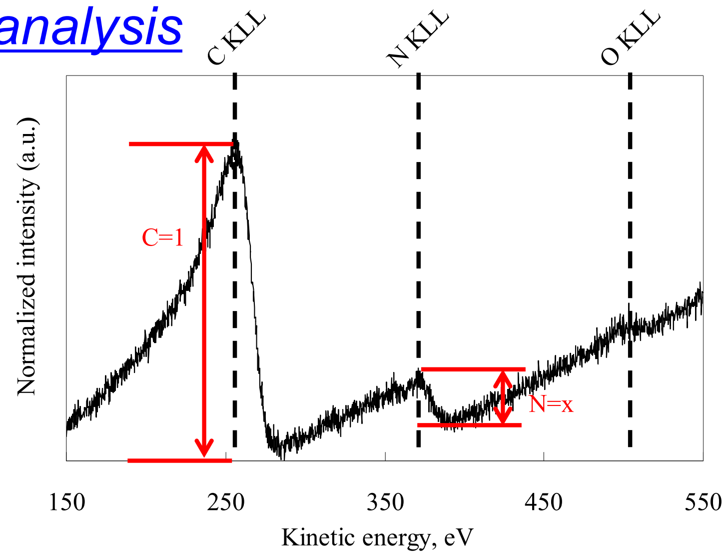
Wavelength λ, nm	Energy, kJ/mol
365	326
312	382
254	469

Table 2 UV irradiation condition

Test pieces	Irradiation time
•CN_0	•60 min
•$CN_{0.09}$	•120 min
•$CN_{0.12}$	•180 min
•$CN_{0.19}$	•240 min



AES analysis



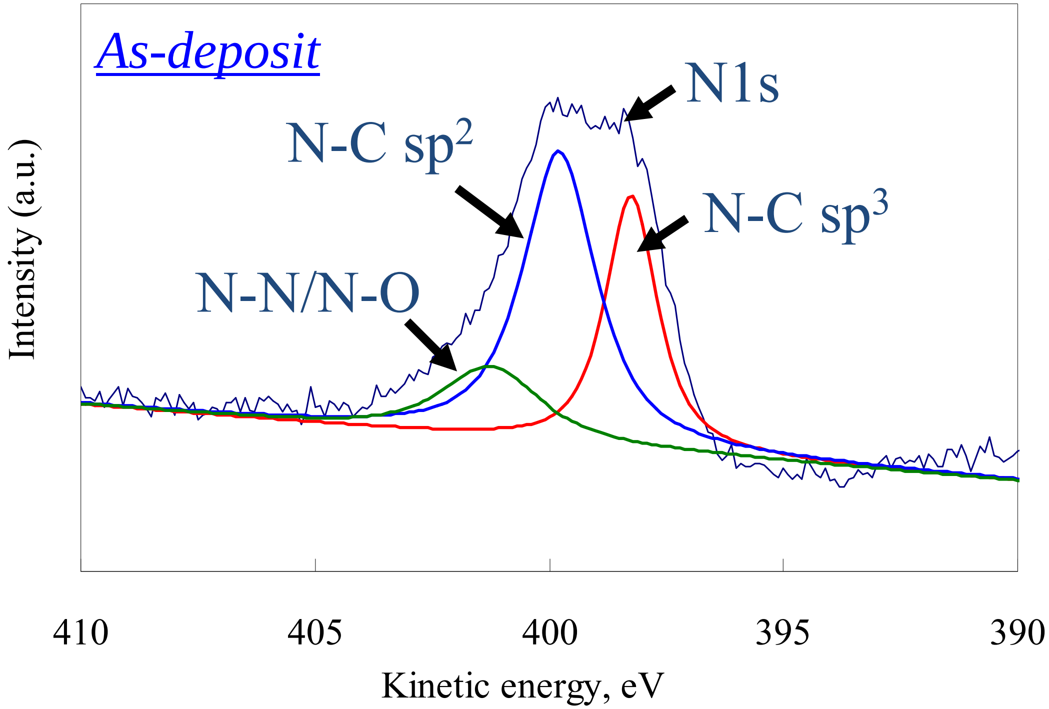
N/C ratio: N/C=x/1

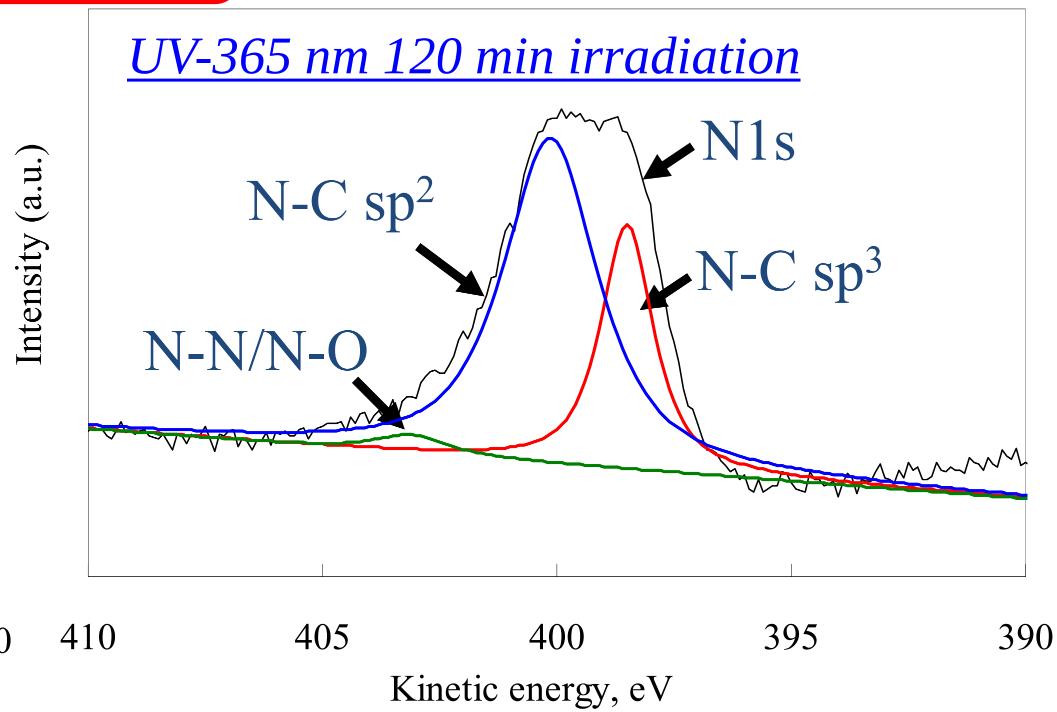
XPS analysis results

J. M. Ripalda et al. Diam. Relat. Mater. 7(1998) 402-406.

What kind of deformation did it take place?

$CN_{0.12}$ N1s peak

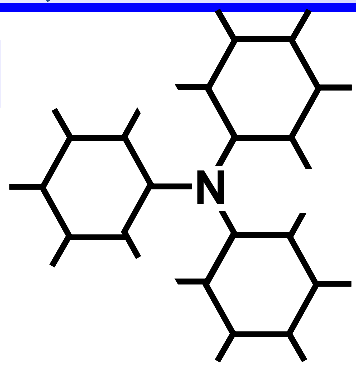




In the case of no nitrogen desorption, structural deformation took place.

$CN_{0.09}$, $CN_{0.19}$ showed deformation.

In the case of UV irradiation to CNx, the bond originated from N-C sp^2 increased.

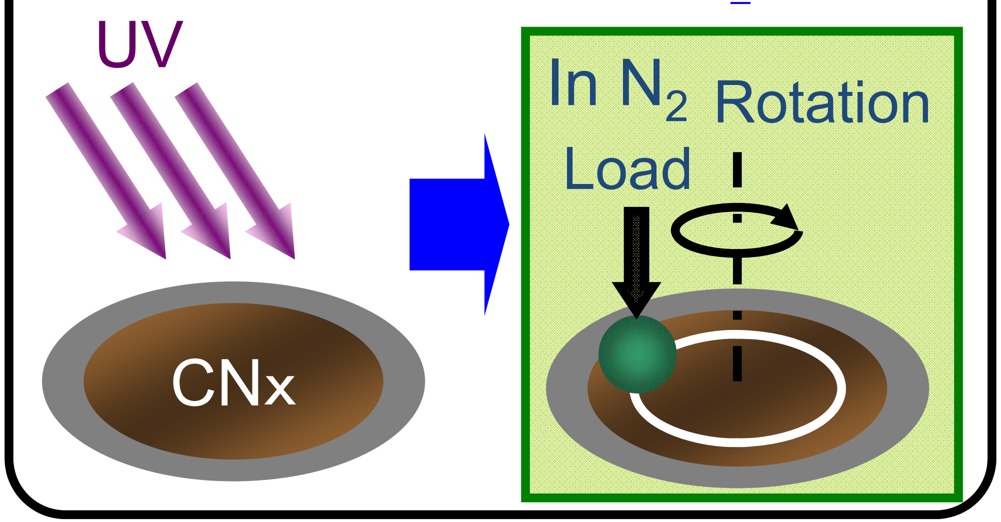


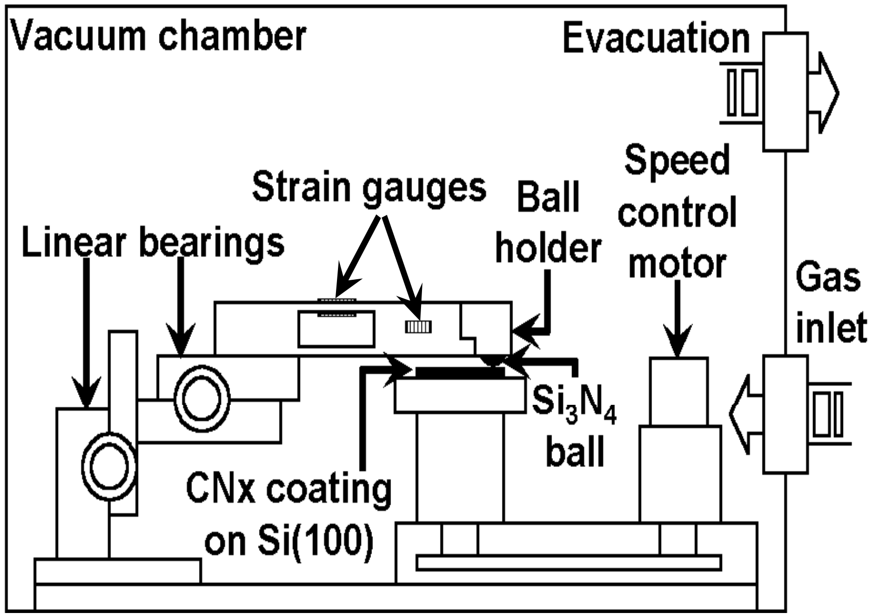
Triphenilamine

The bond shows like graphite was assumed to increase.

Experimental of tribological property under N_2

UV irradiation ⇒ Friction in N_2





UV irradiation conditions

Wavelength λ	Irradiation time
•365 nm	•60 min
•312 nm	•120 min
•254 nm	•180 min
	•240 min

Friction test conditions

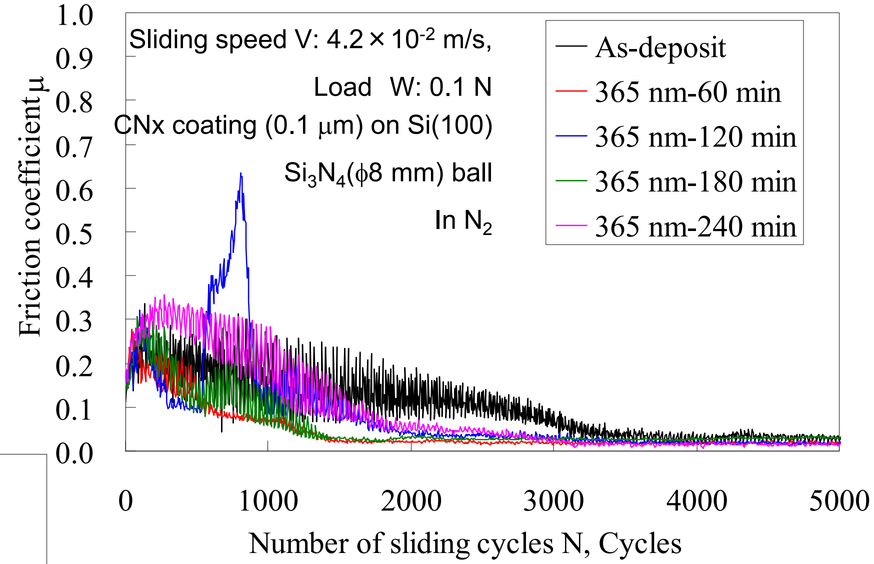
Load	0.1 N
Sliding speed	4.19×10^{-2} m/s
Rotation speed	200 rpm
Rotation radius	2.0 mm
Ambient	Nitrogen

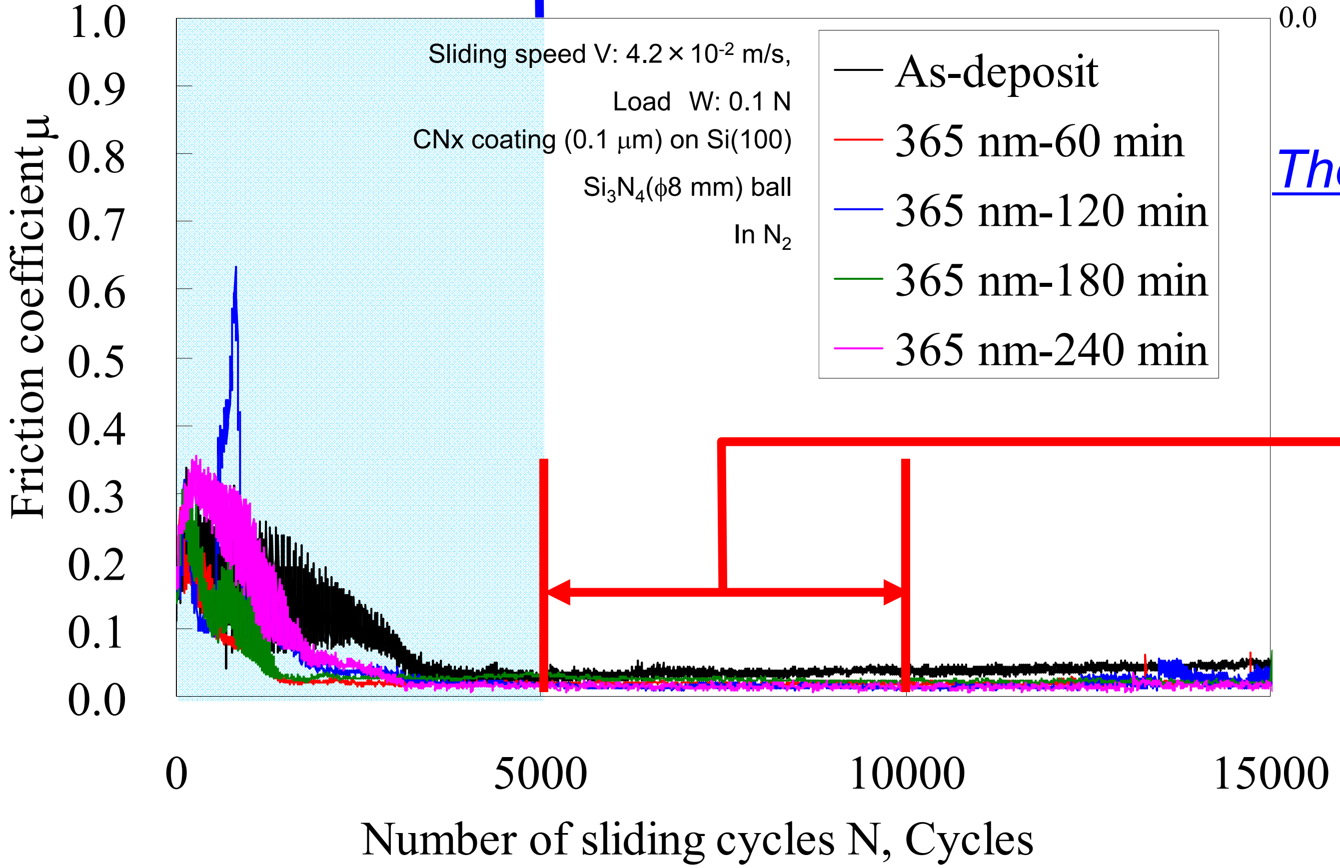
Friction test results under N_2 environment

$CN_{0.12}$ 365 nm-UV irradiation

The running-in period of $CN_{0.12}$ was decreased by UV irradiation

The variation of μ with number of cycles





The average of 5000~10000 cycles

As-deposit: μ=0.040

60 min: μ=0.019↓

120 min: μ=0.018↓

180 min: μ=0.022↓

240 min: μ=0.015↓

μ decreased by UV irradiation.

The effect of UV irradiation on running-in period

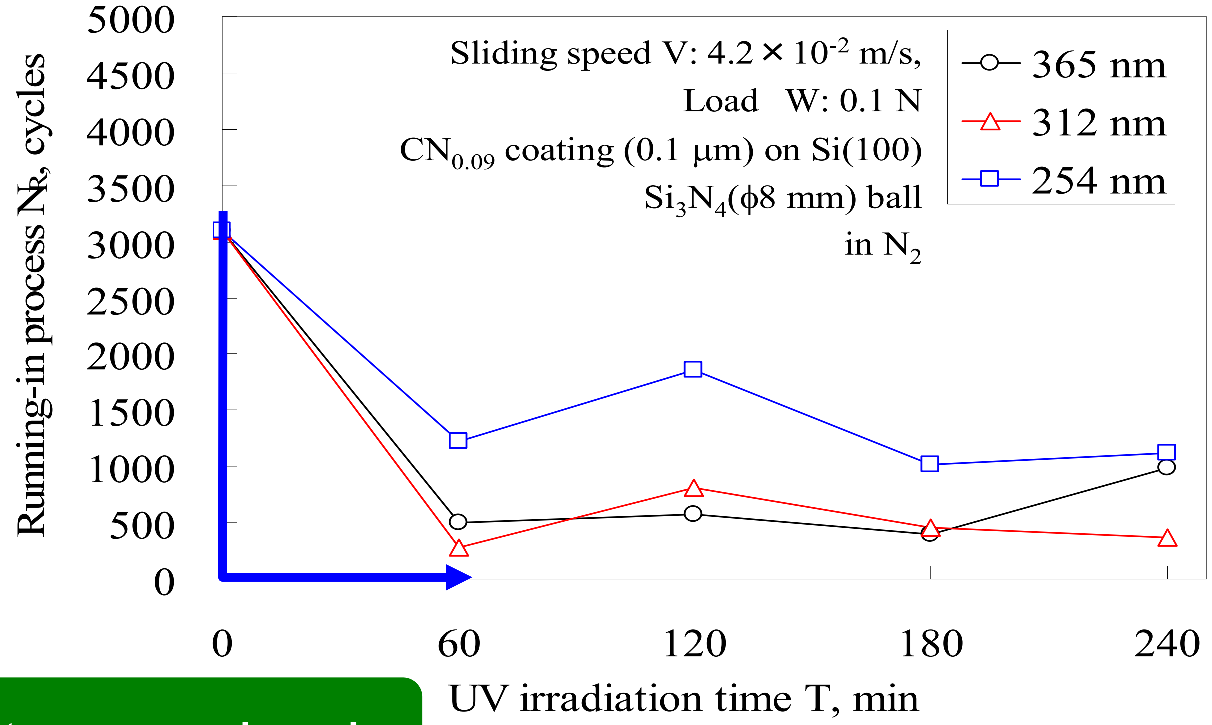
Running-in

$\mu<0.05$, $\Delta\mu<0.02$

As-deposit:3100 cycles

⇒ 312 nm-60 min:280 cycles

$CN_{0.09}$



The effect of shorten running-in

$CN_{0.12}$ As-deposit: 3100 cycles ⇒ 365 nm-60 min: 563 cycles

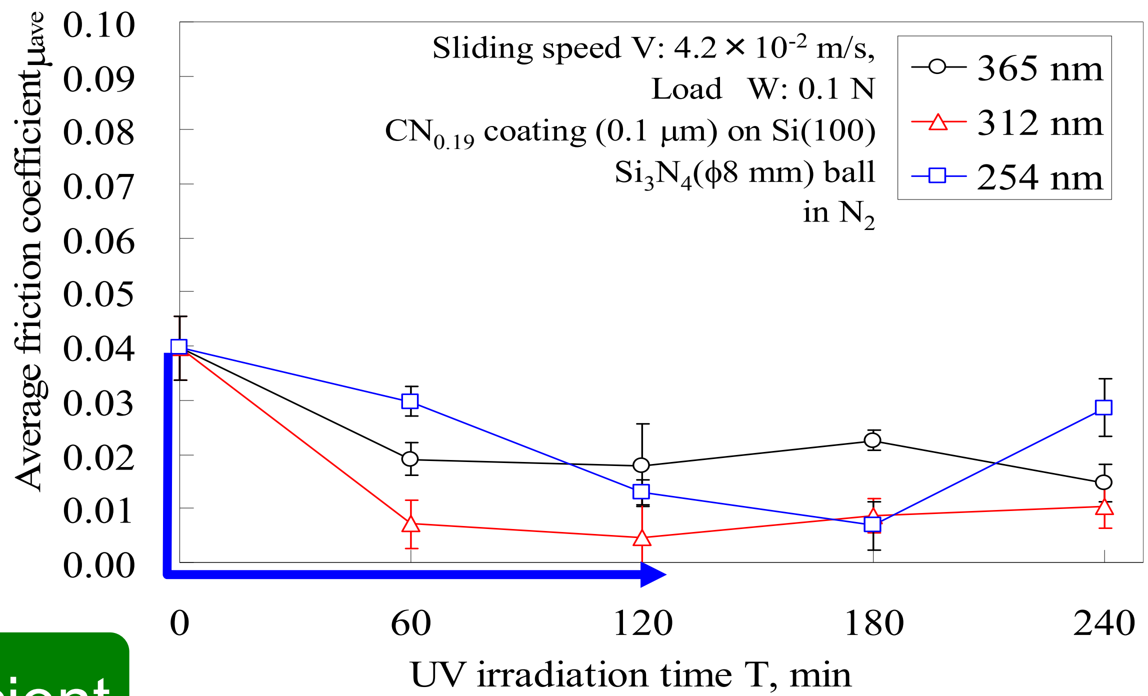
$CN_{0.19}$ As-deposit: 2440 cycles ⇒ 312 nm-240 min: 750 cycles

3.4 The effect of UV irradiation on minimum m

CN$_{0.19}$

The minimum friction coefficient: μ_{min}

As-deposit: μ=0.040 ⇒ 312 nm-120 min: μ=0.004



Minimum friction coefficient

CN$_{0.09}$ As-deposit: μ=0.028 ⇒ 254 nm-120 min: μ=0.002

CN$_{0.12}$ As-deposit: μ=0.033 ⇒ 365 nm-60 min: μ=0.008

The friction coefficient decreased by UV irradiation.

Outline & Summary

1.Ultra low friction of Carbon Nitride (CNx)

・ Mechanism　Self modification in nm thickness

・ Effect of carbon overcoat on friction

not need running-in

・ Effect of Ultraviolet (UV) ray irradiation on friction　More rapid running-in by 1/10 , Lower minimum friction by 1/10

2. Low adhesion and friction of rubber

・ High dense plasma irradiation to CIIR

・ UV ray irradiation to TPE with PFPE

Industrial products and issue

Rubber Products

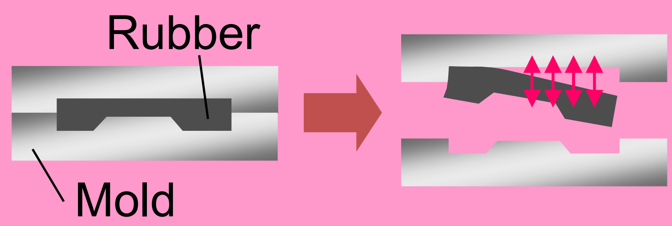
Widely used as components of various industrial products
as Oil seal, Packing, Tire etc.

Production methods

Injection forming

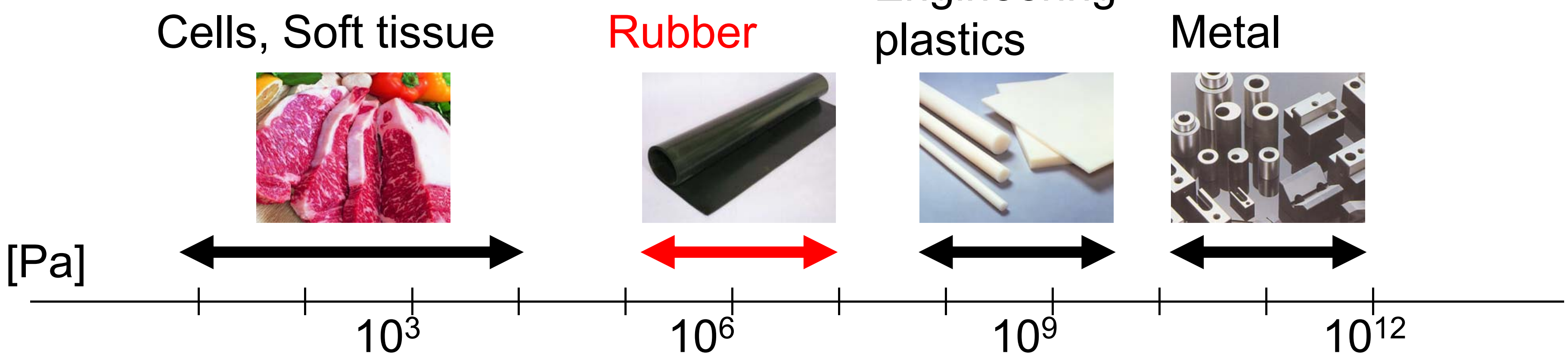
Press forming

Issue: Adhesion to mold or conveying equipment



Why rubber can stick to surface?

Elastic modulus of various materials



■The Contact between Rubber and Steel

Elastic energy

$$U_{el} \approx E\lambda h^2$$

Adhesion energy

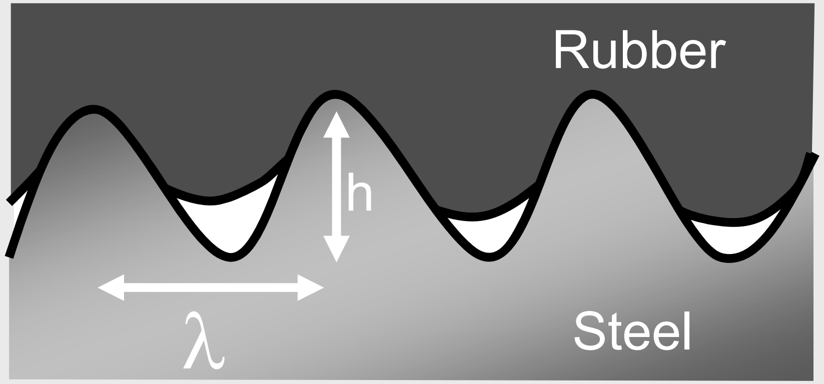
$$U_{ad} \approx -\Delta\gamma\lambda^2$$

Adhesion parameter

$$\theta = -\frac{U_{el}}{U_{ad}} \approx 10^{-1}$$

→ $\theta < 1$

Adhesive!



$\Delta\gamma$ ~ 10mJ/m^2 = 10^{-2} J/m^2

λ ~ 1 μm = 10^{-6} m

E ~ 10 MPa = 10^7 Pa

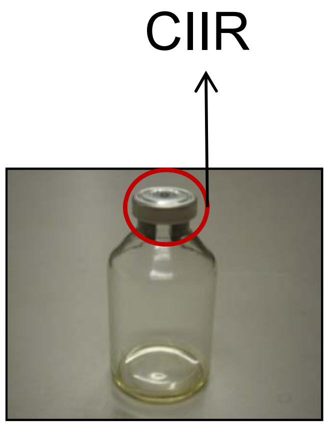
h ~ 0.01 μm = 10^{-8}m

B.N.J. Persson at el.

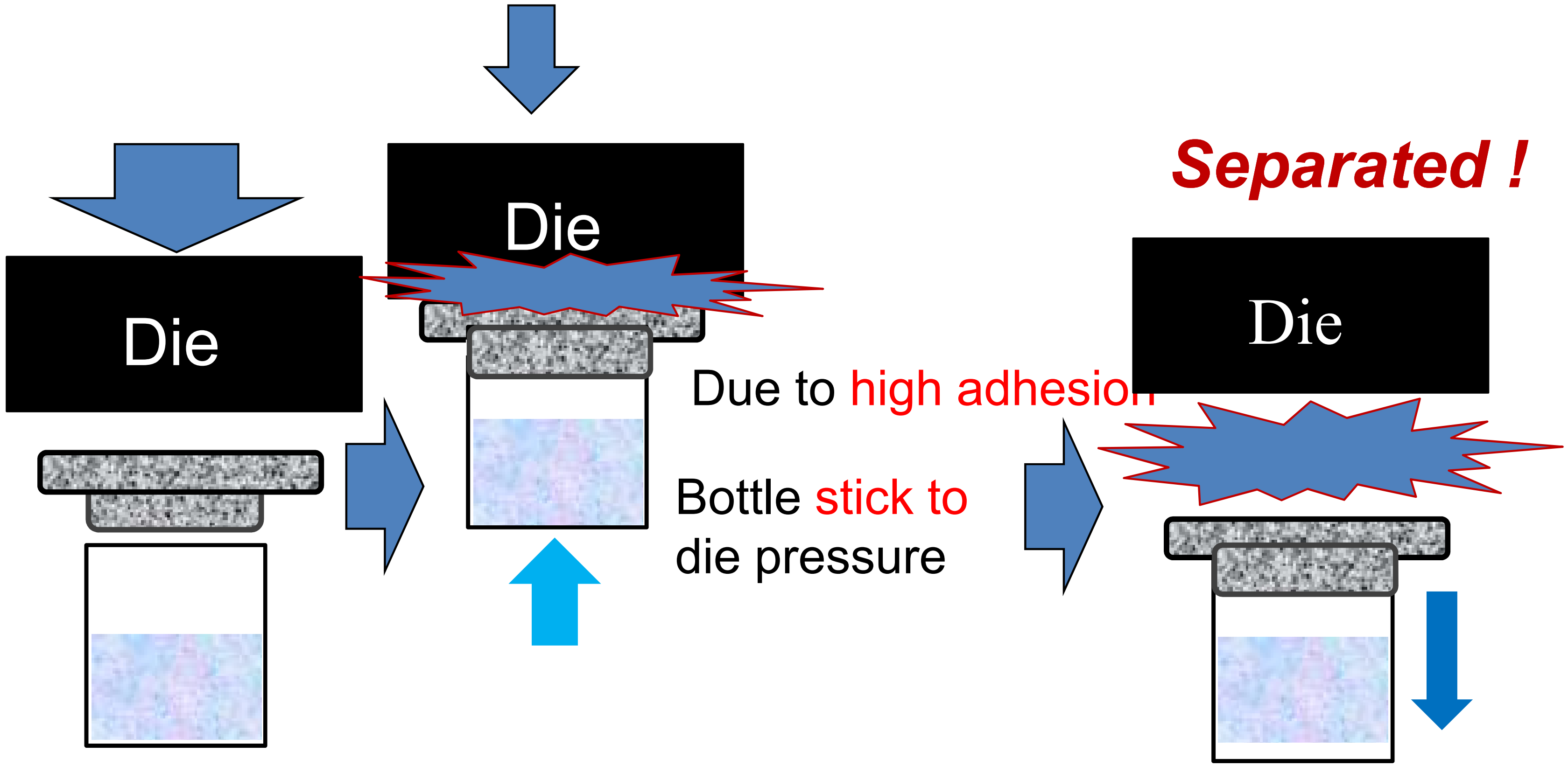
Another issue for medicine bottle

Issue:

Strong adhesion of rubber for medicine bottle against mold

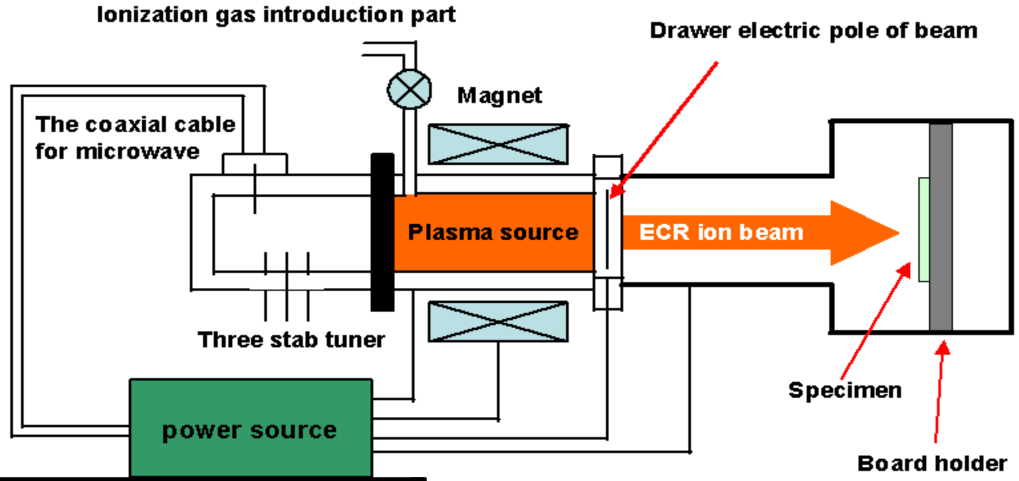


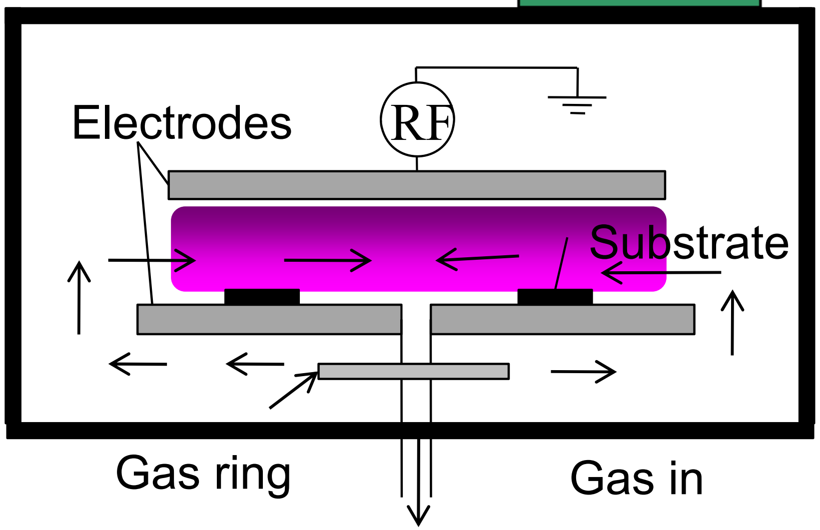
Medicine bottle

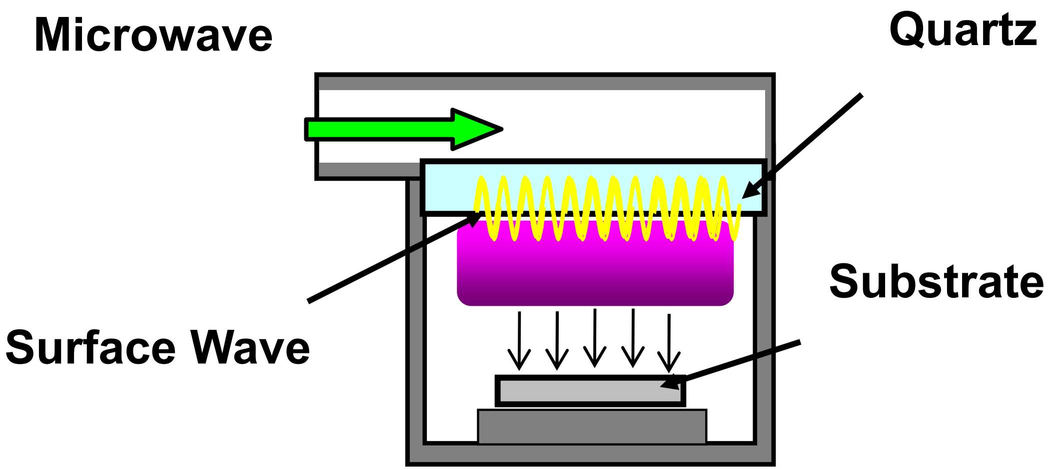


Various plasma treatment

The generator of ion beam irradiation treatment







$n_e \approx 10^8$-10^{10} cm^{-3}

RF plasma treatment

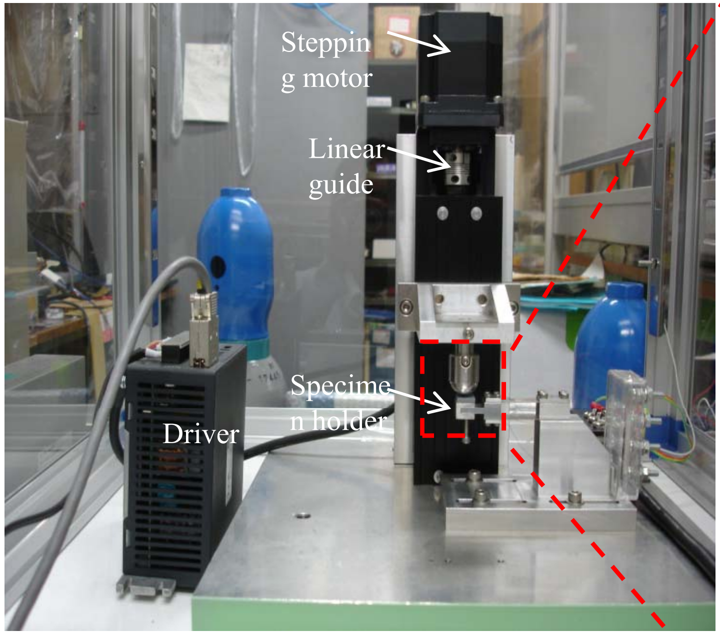
$n_e \approx 10^{11}$-10^{13} cm^{-3} at a frequency of 2.45 GHz

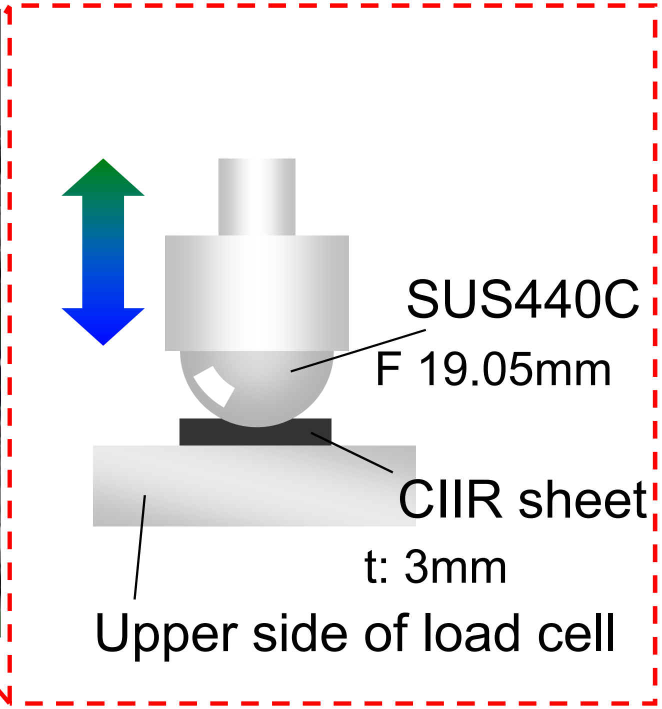
Surface -wave excited plasma treatment

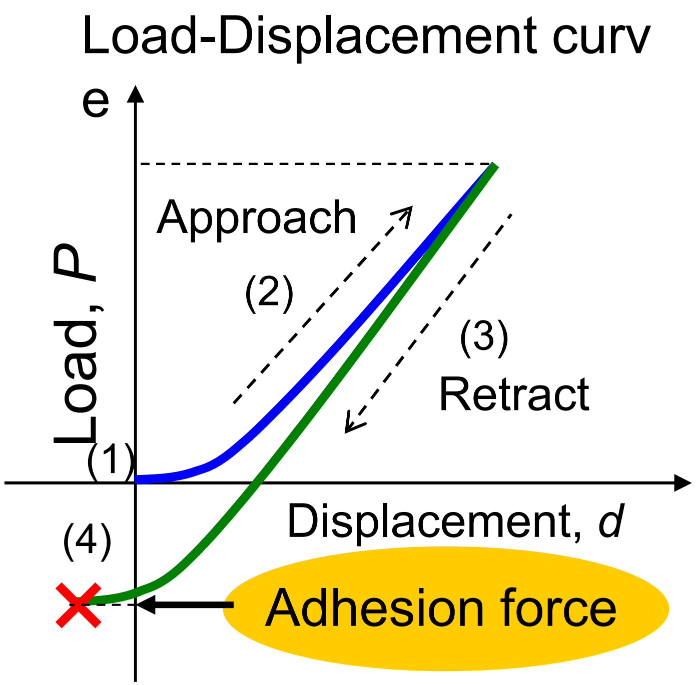
Plasma density : RF plasma < SWP plasma

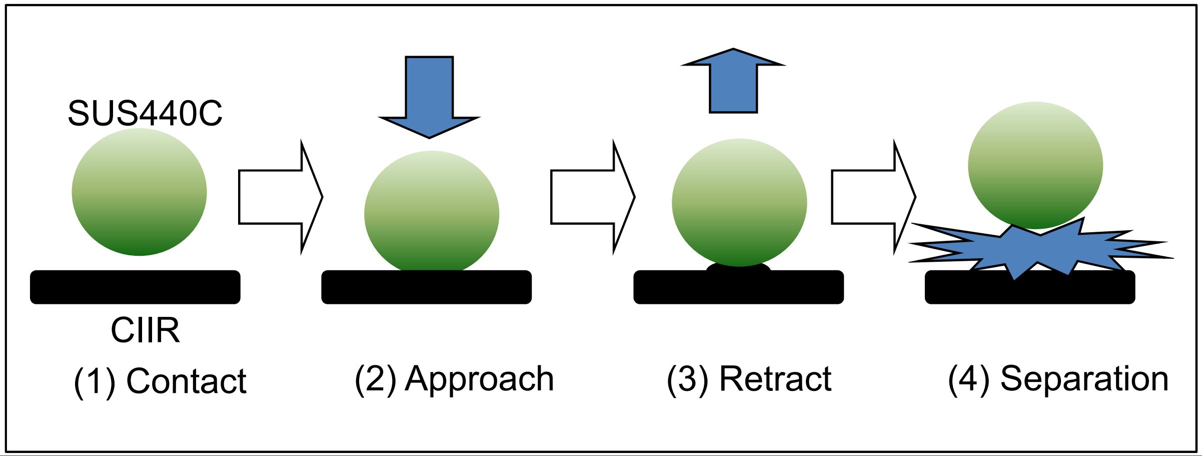
Adhesion force measurement

Adhesion force appartus



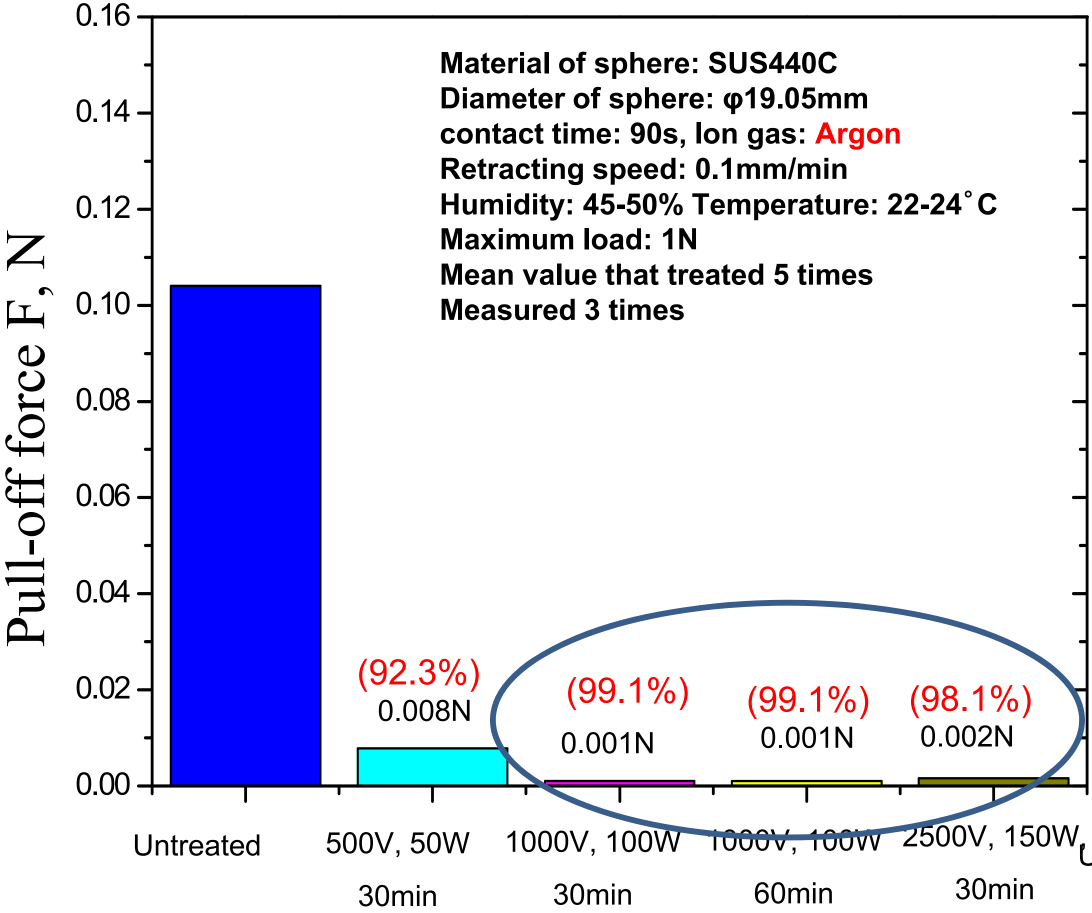




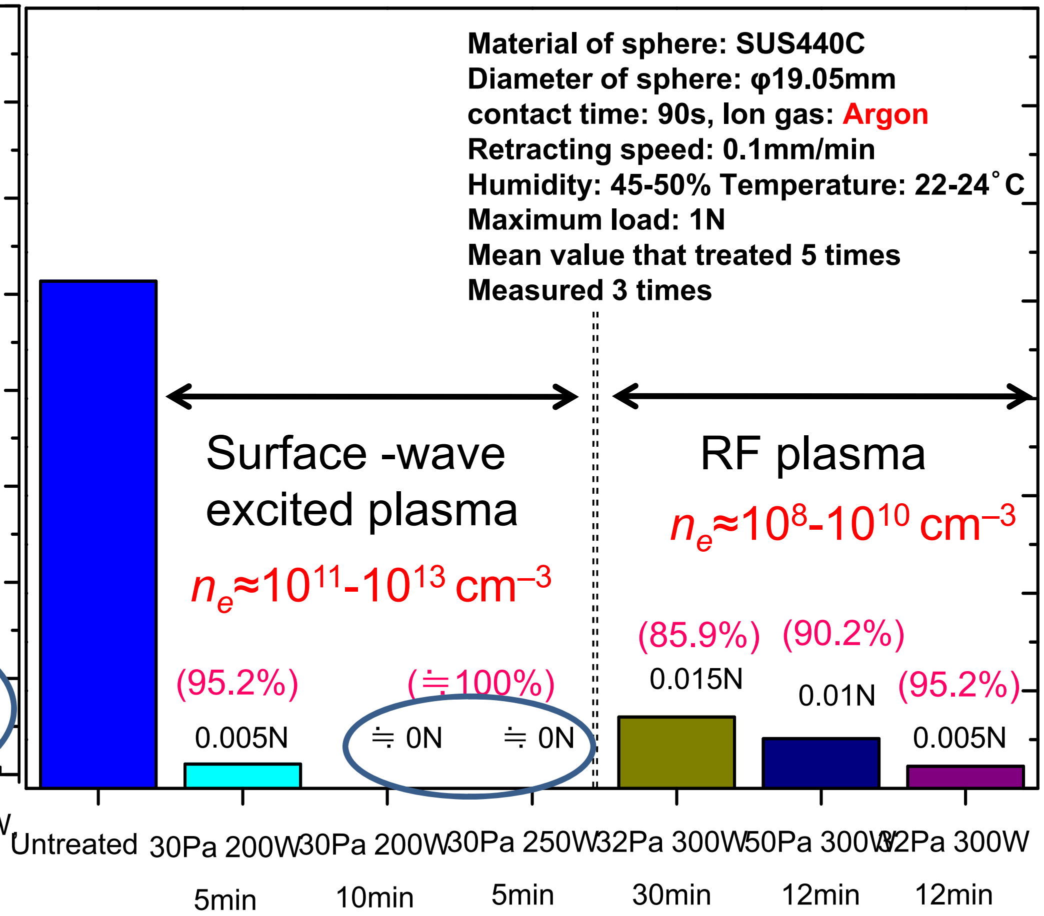


Effect of plasma irradiation on adhesion

Ion beam irradiation treatment



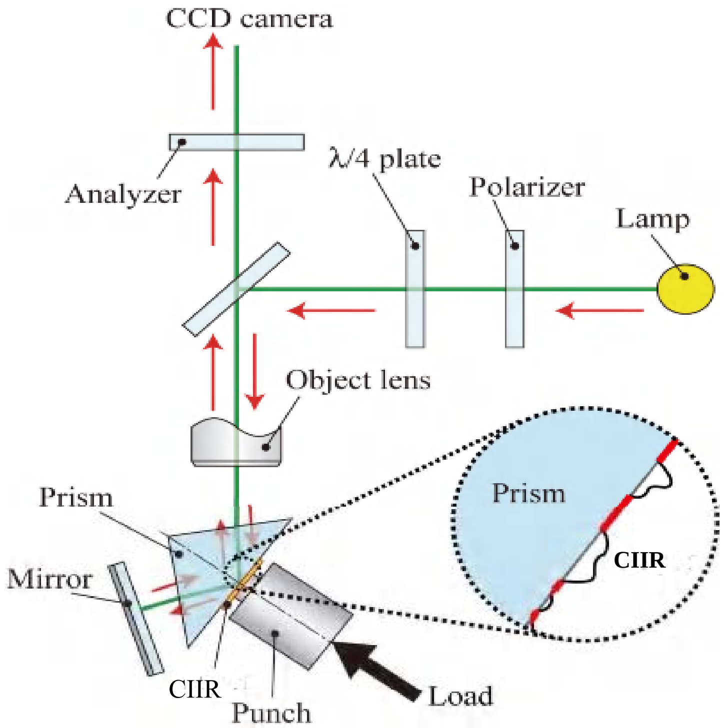
Plasma treatment



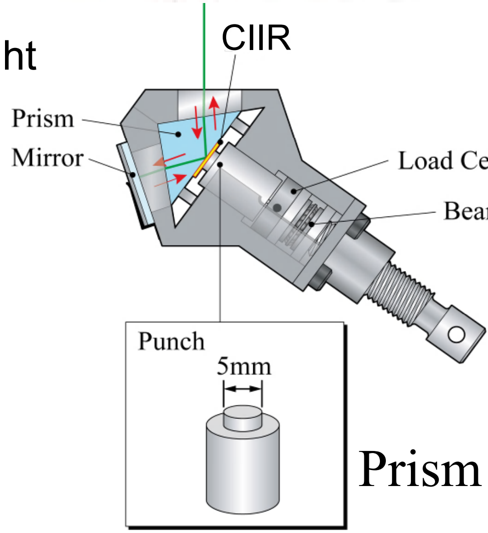
Treatment time Ion beam >> surface-wave plasma treatment Surface-wave plasma treatment reduced adhesion almost 0 N between stainless steel ball and CIIR sheet

Contact microscope device

Prof. Isami NITTA, Niigata University, Japan



Schematic diagram of a contact microscope with an elliptically polarized light



Prism fixed jig

The procedure of calculate the real contact area

Lights pass through the prism

↓

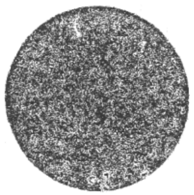
The analyzer blocks the light when the asperity exists between prism and CIIR

↓

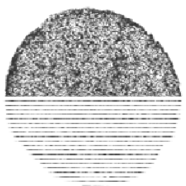
The asperity appear to be dark dot.

Real contact area

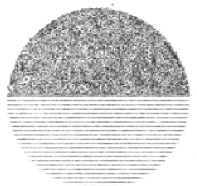
Unreated



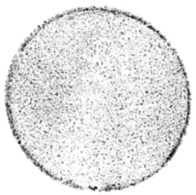
Argon−1 min



Oxygen−1 min



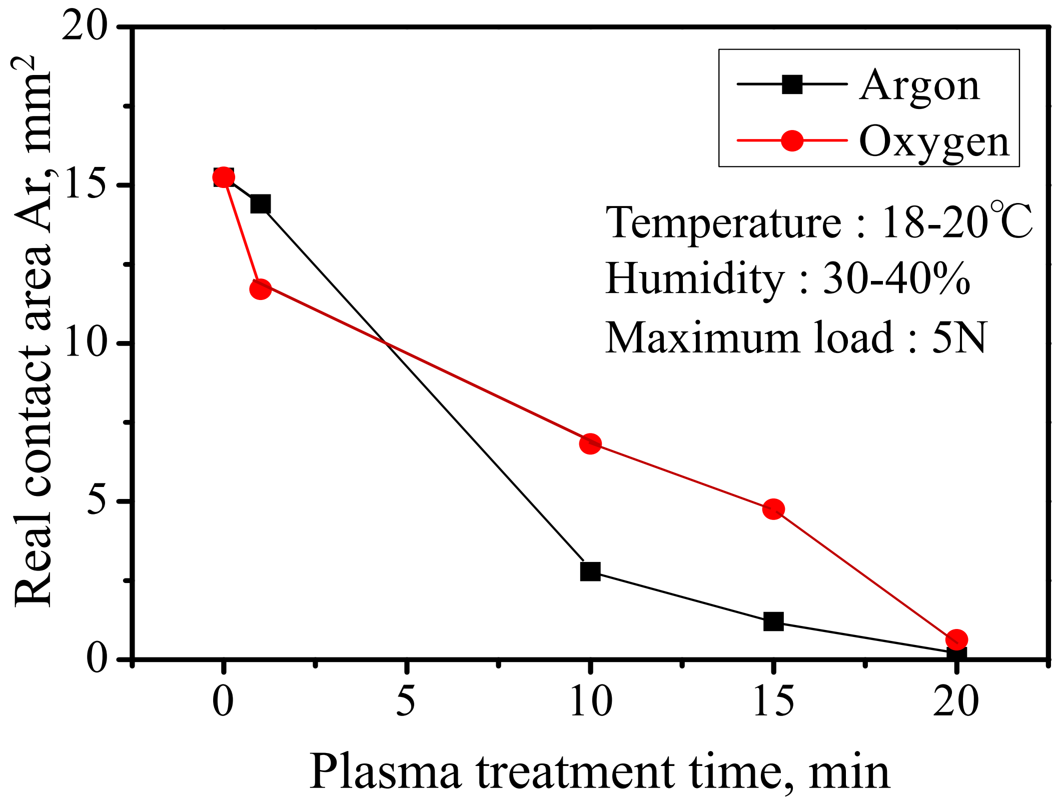
Argon−5 min



Oxygen−5 min

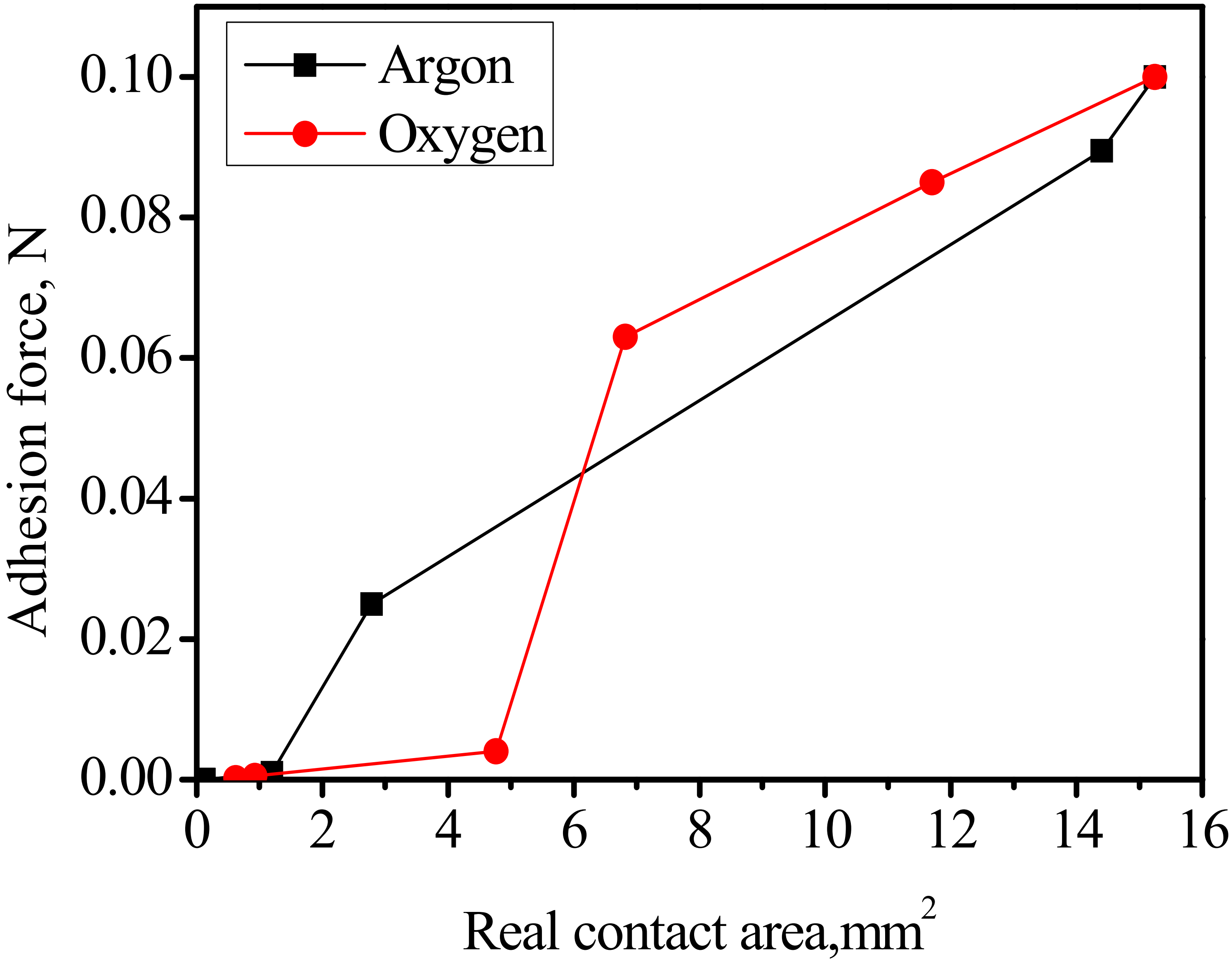
Argon−10 min

Oxygen−10 min



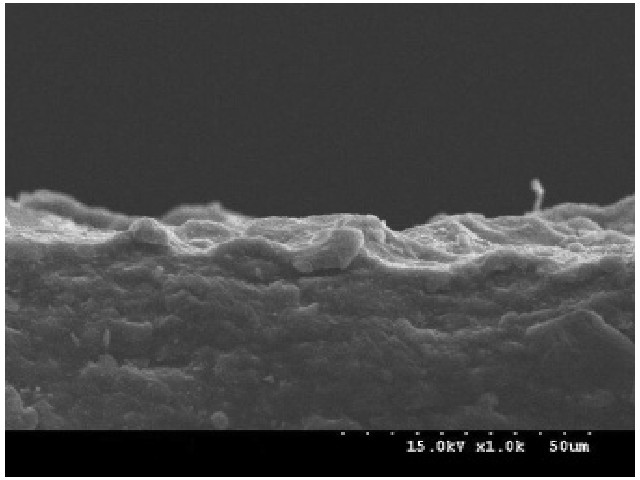
Real contact areas were decreased in all conditions !

Effect of real contact area on adhesion

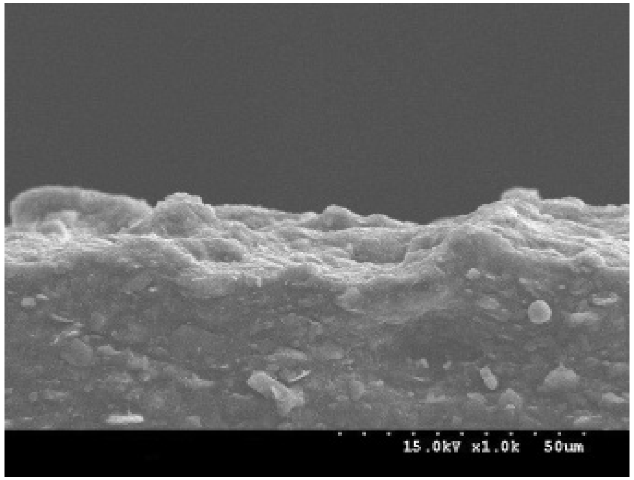


Surface topography of rubber surface

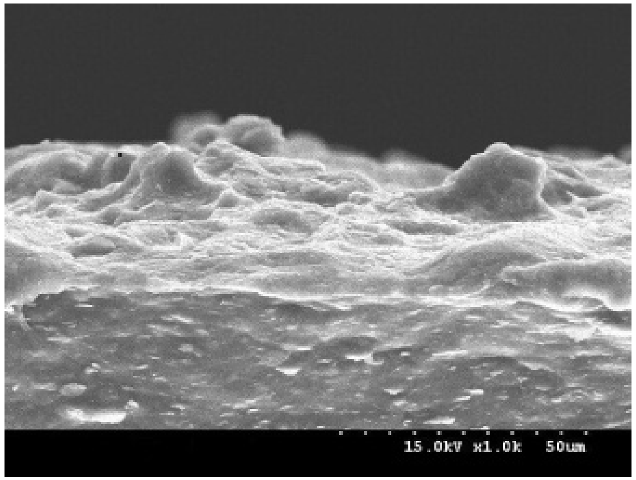
Sputter coated with platinum for 1mintues



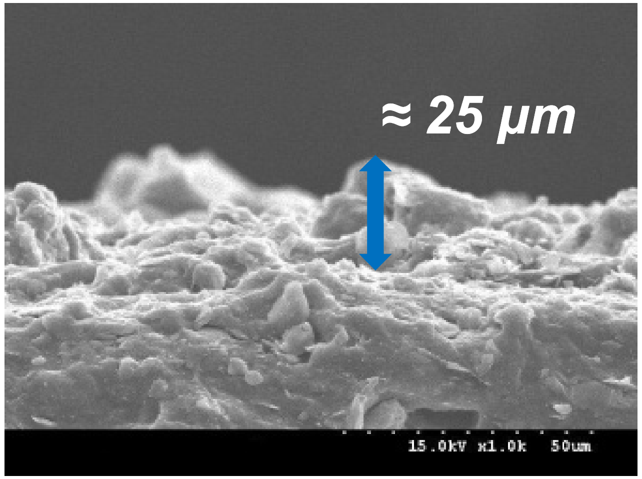
(a)



(b)



(c)



(d)

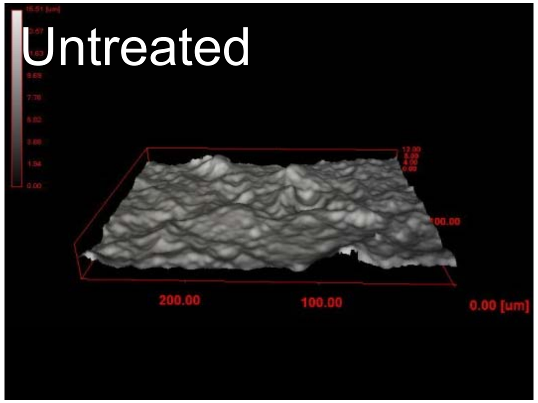
(a)
The subsurface on the CIIR looks less granular and generally has a smoother shape
(c)
Growing rougher as the treating time increasing

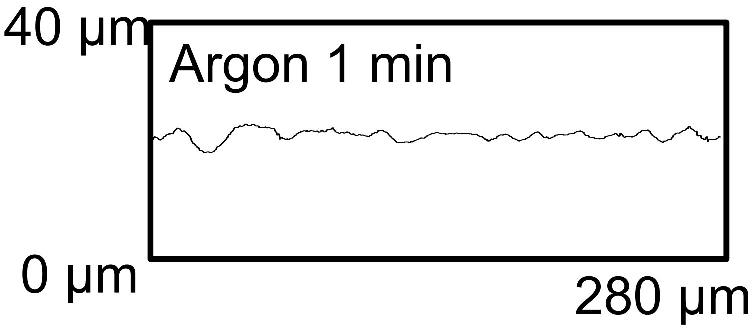
(d)
Microwave power pattern has changed
- Roughest surface observed

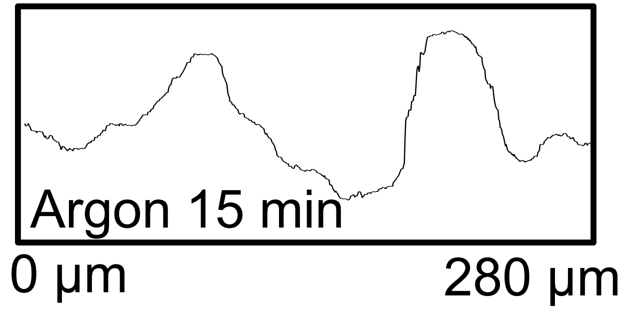
Etching effect !

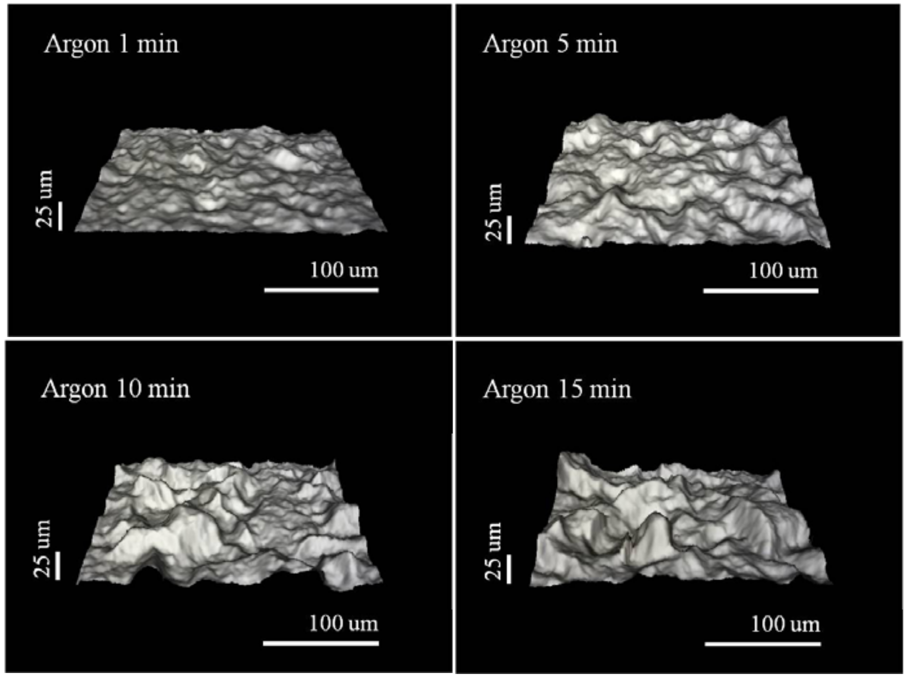
The cross-section FE-SEM micrographs of oxygen plasma treated to CIIR rubber for (a) Untreated (b) 200 W, 5 min (c) 200 W, 10 min and, (d) 200 W 20 min

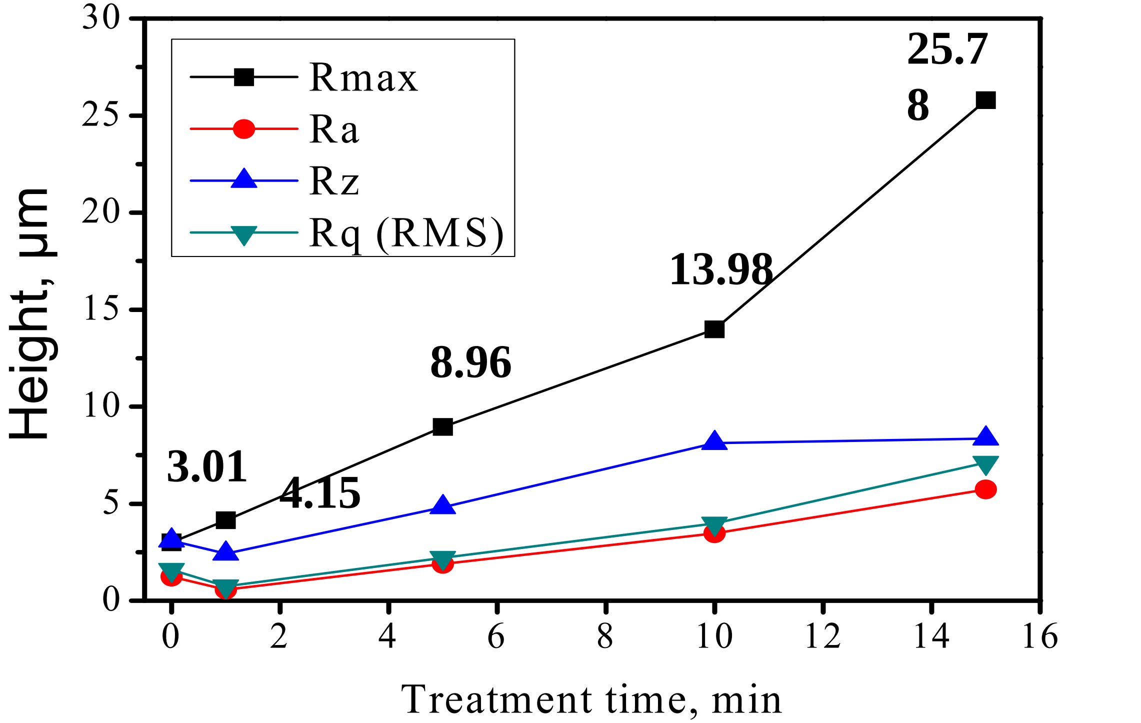
Surface roughness of argon plasma treated to CIIR rubber







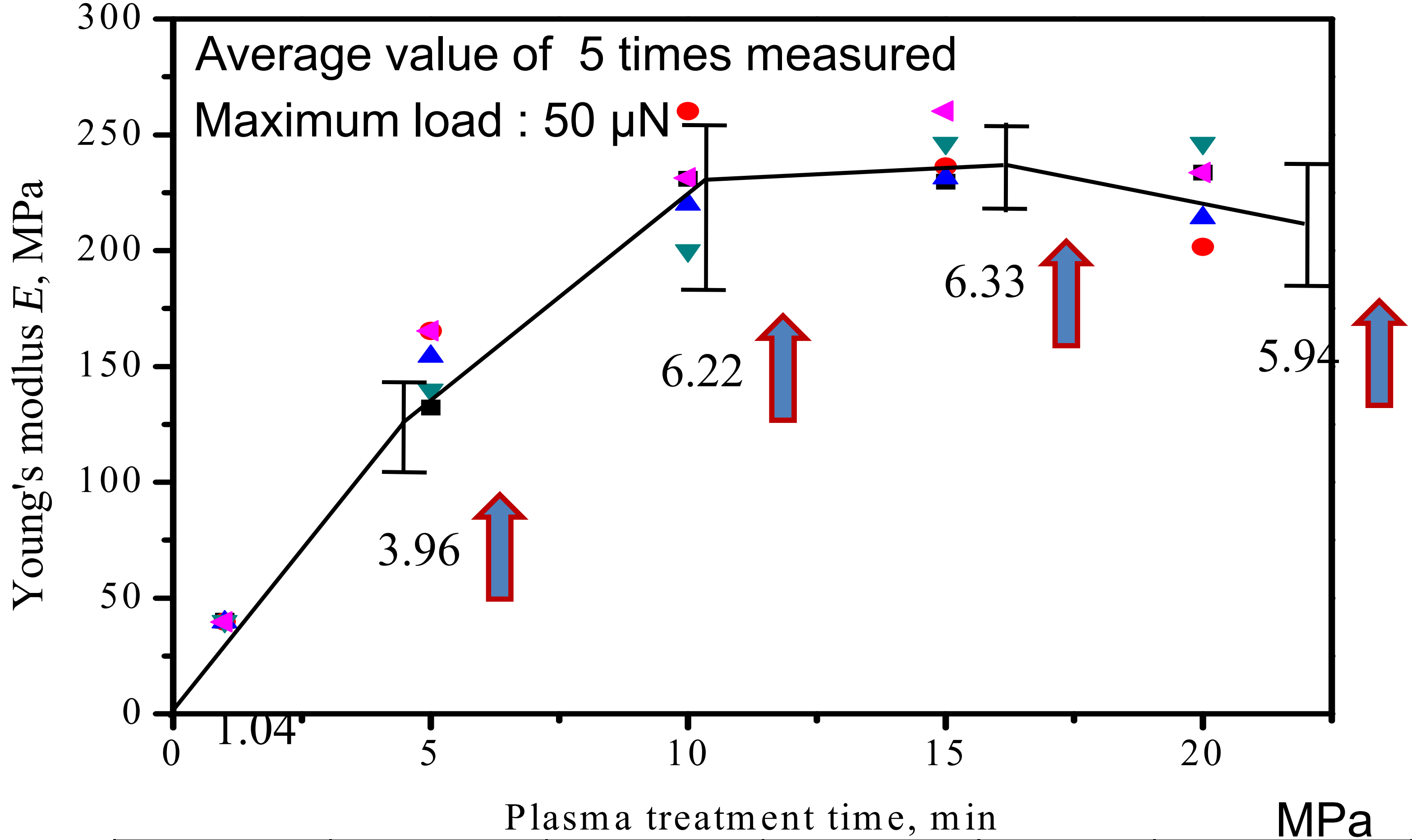




Surface profile with argon plasma treatment, as a function of treatment time

3D laser scanning microscope images of CIIR sheets after oxygen plasma treatment with 200 W at a gas pressure of 30 Pa for treatment times of (a)1, (b)5, (c)10, and (d)15 min.

Young's modulus of CIIR rubber

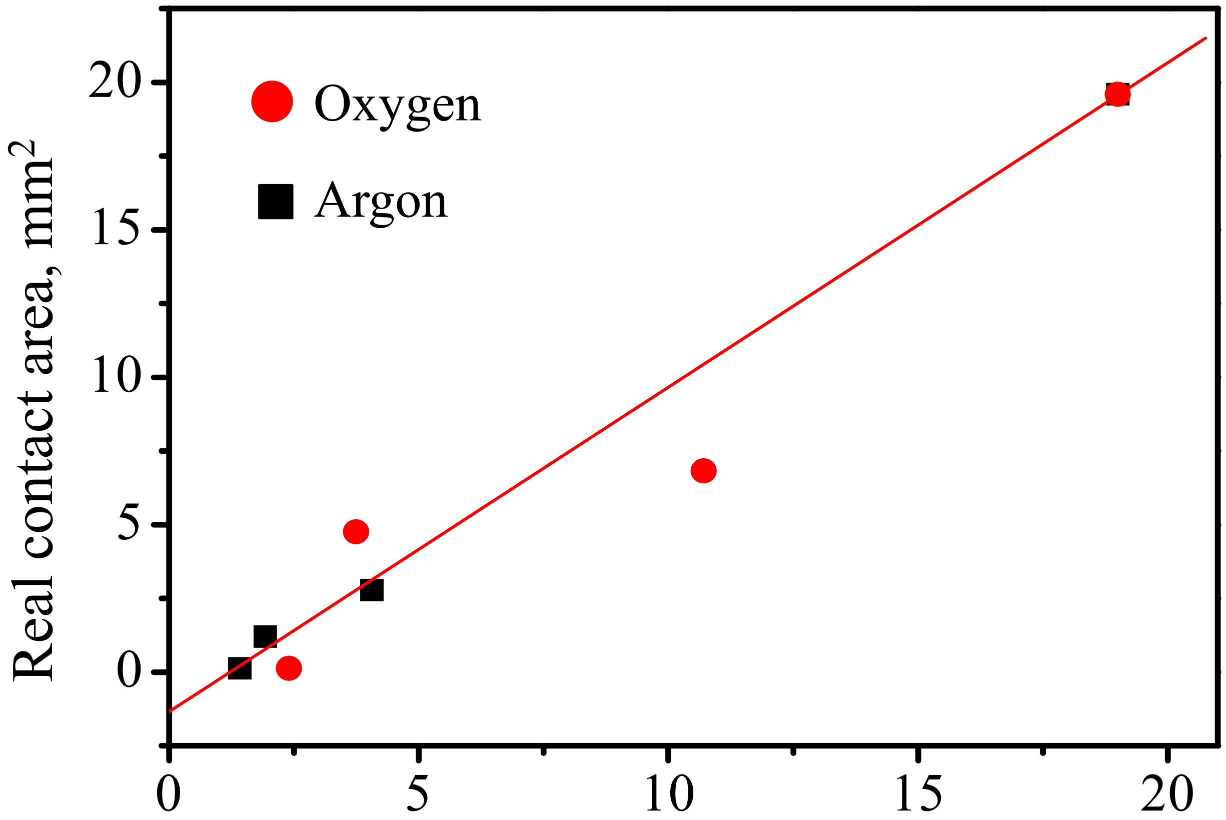


MPa

untreated	1	5	10	15	20
38	39.8	151.4	236.4	240.8	225.9

Explanation by the GW model

$$A_{re} \propto \frac{3.2 P_a A_a}{E^*(\sigma_p / R_p)^{1/2}}$$



$$\frac{1}{E^*(\sigma_p / R_p)^{1/2}}$$, μm^{-1}MPa^{-1}

$$\frac{1}{E^*} = \frac{(1-\nu_1{}^2)}{E_1} + \frac{(1-\nu_2{}^2)}{E_2}$$

σ_p : RMS
R_p : asperity of radius = 1μm
P_a : apparent pressure
A_a : apparent area

Poisson's ratio *v*
stainless steel ball : 0.3
CIIR rubber : 0.5

Young's modulus of
stainless steel ball : 210 Gpa
CIIR rubber : Measured

$$(W = P_r A_{re} = P_a A_a = 1N)$$

Comparison between GW model & real contact area (Stainless steel ball and CIIR contact)

Outline & Summary

1.Ultra low friction of Carbon Nitride (CNx)

- Mechanism　Self modification in nm thickness
- Effect of carbon overcoat on friction
  not need running-in
- Effect of Ultraviolet (UV) ray irradiation on friction　More rapid running-in by 1/10 ,
  Lower minimum friction by 1/10

2. Low adhesion and friction of rubber

- High dense plasma irradiation to CIIR **<1/100**
  by Larger E & Roughness ➡ Smaller Ar
- UV ray irradiation to TPE with PFPE

Tendency in Medical syringe products

Medical syringe

Glass syringe

- Easy to crack
- High cost
- inferior to the size accuracy

➡ **Undesirable**

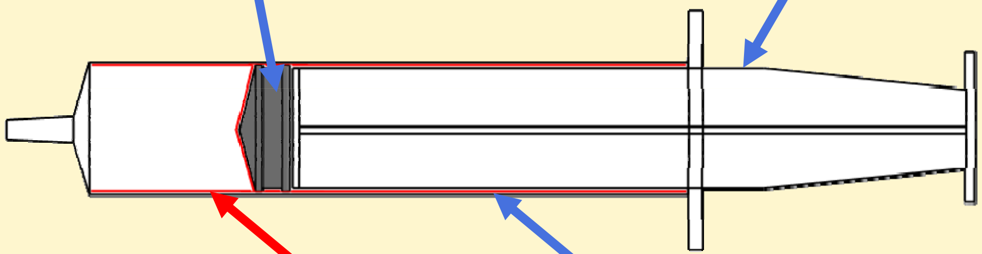
Plastic syringe

- Productive
- Lubricated with **silicone oil**

Replacing glass syringes with plastic ones is desired.

Issues in advanced plastic syringe

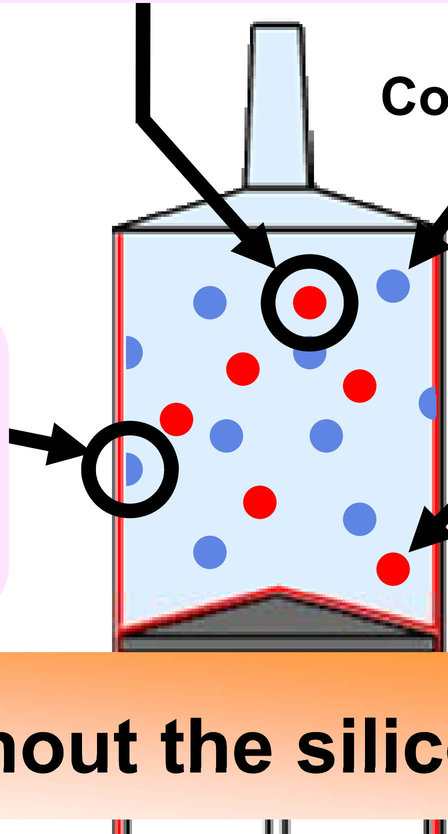
Plastic syringe



Float of silicone oil droplets

Issue ↓ ※In certain medicines

Risk of the accumulation in the body



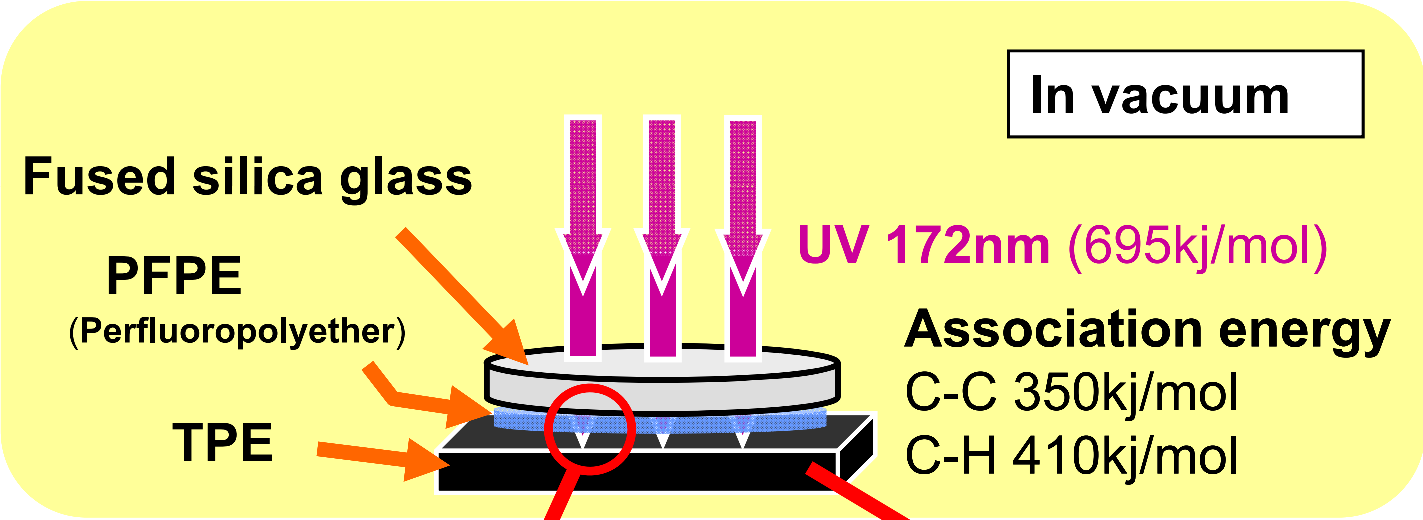
Adsorption of medicine

Issue ↓

Improper dosage

To design the plastic syringe without the silicone oil

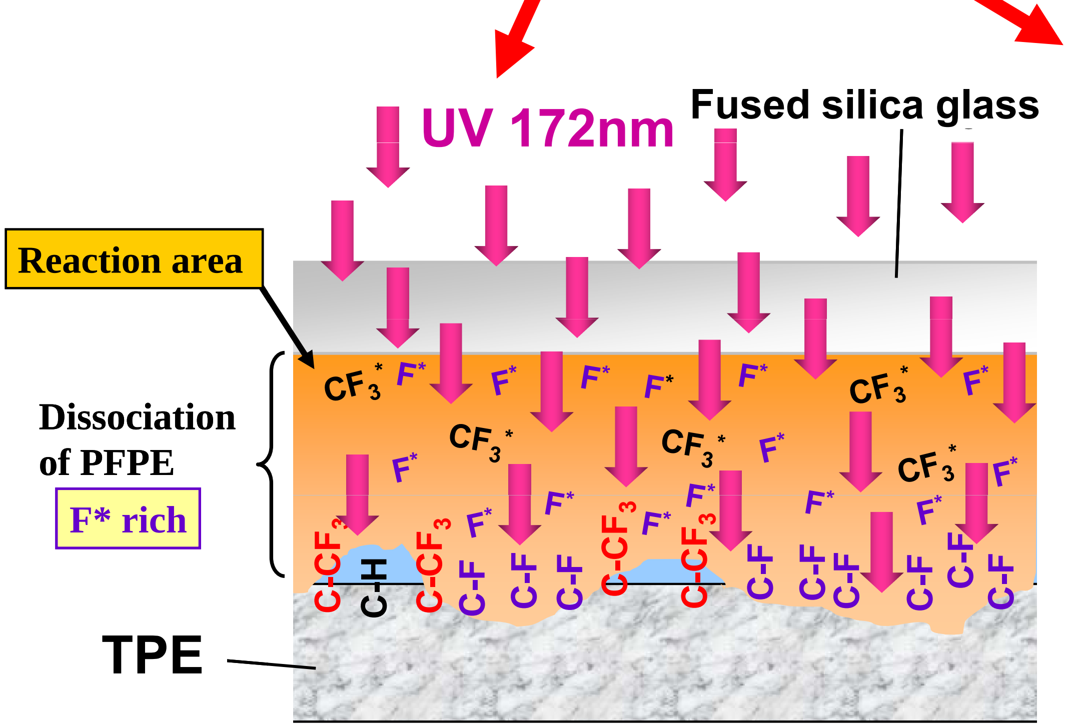
Photochemically fluorination

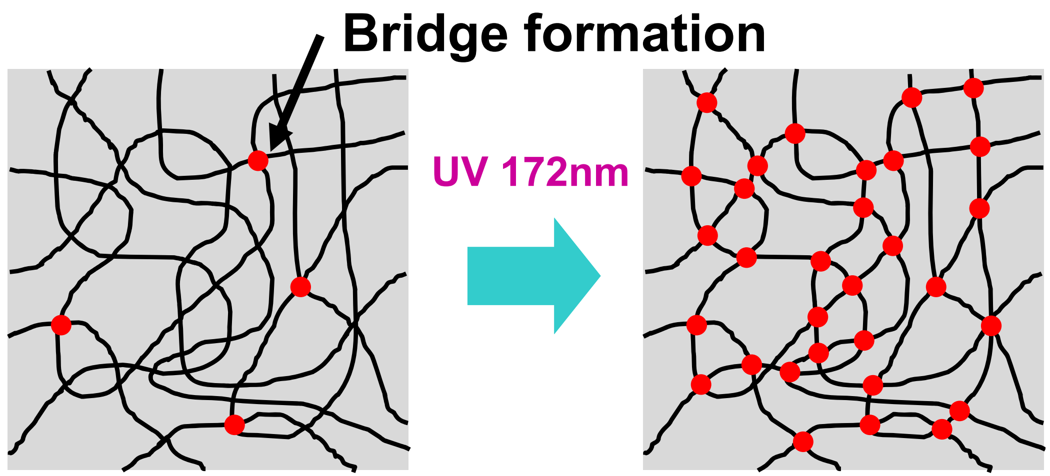


Surface free energy ↓
Real contact area ↓

↓

Low friction





Form bridge formation

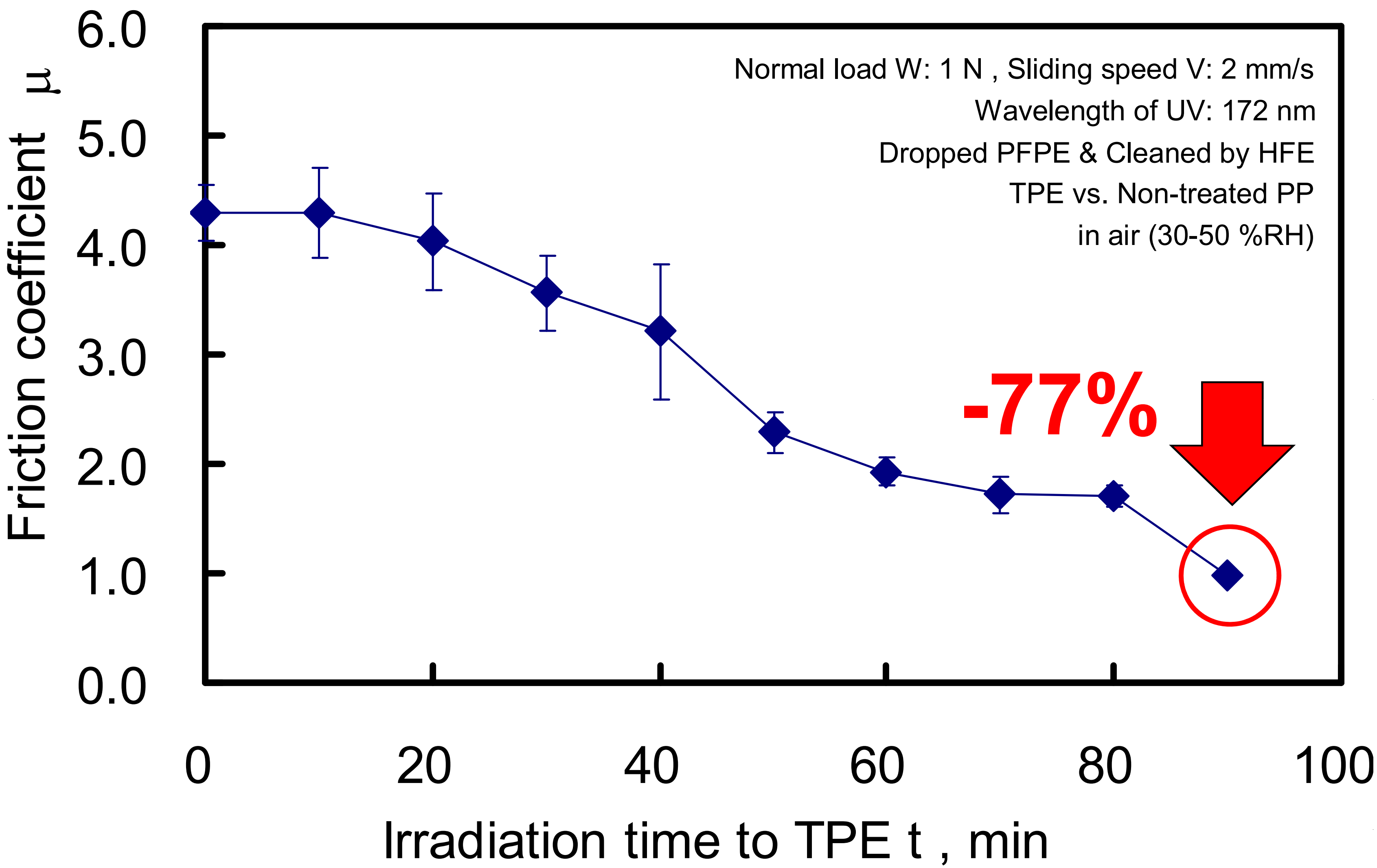
↓

Increase Young's modulus

Effect of Photochemically fluorination on friction

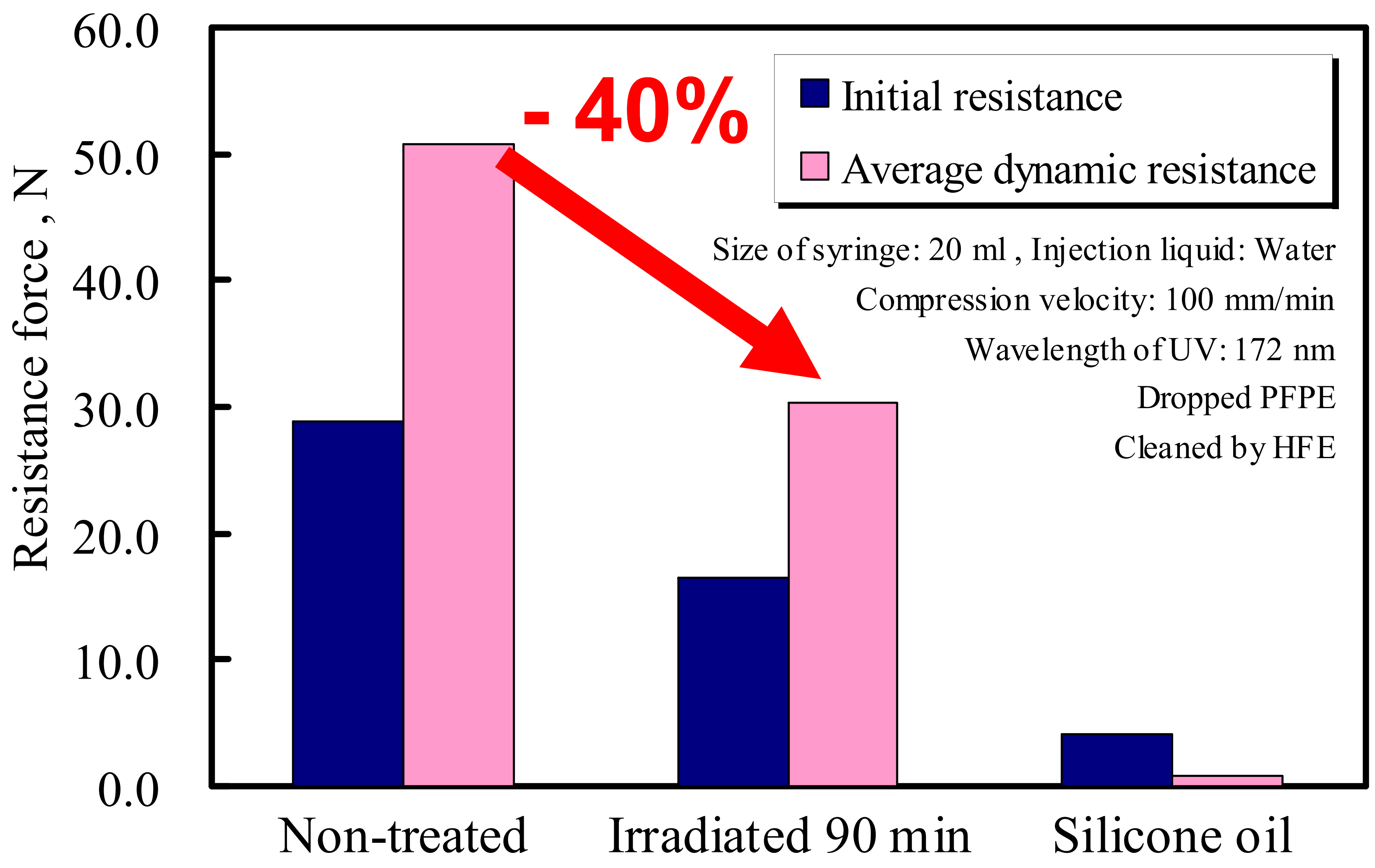
Friction test in flat specimen

W=1 N



Effect of Photochemically fluorination on friction

Friction test in TPE gasket



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  Lower minimum friction by 1/10

2. Low adhesion and friction of rubber

- High dense plasma irradiation to CIIR **<1/100**

  by Larger E & Roughness ➡ Smaller Ar
- UV ray irradiation to TPE with PFPE **1/4**

  by Larger E ➡ Smaller Ar, Smaller surface energy