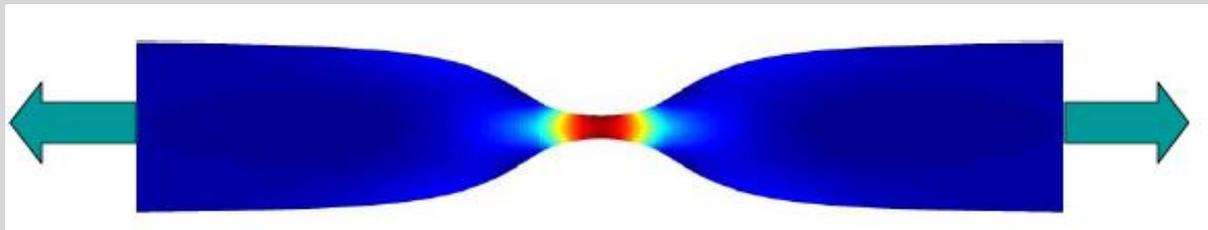




# From Supercooled Liquid to Glasses: Current Challenges for Amorphous Materials

## Discontinuous behavior in metallic glasses



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Beijing, China

# Acknowledgements

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**Dr. Xilei Bian (Shanghai University)**

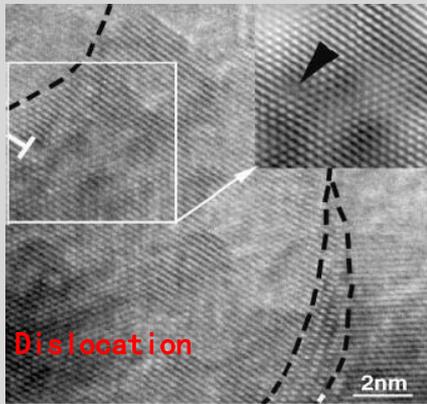
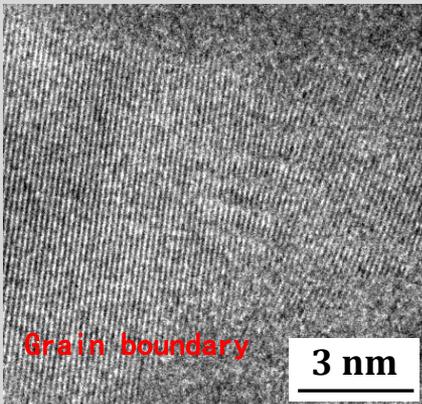
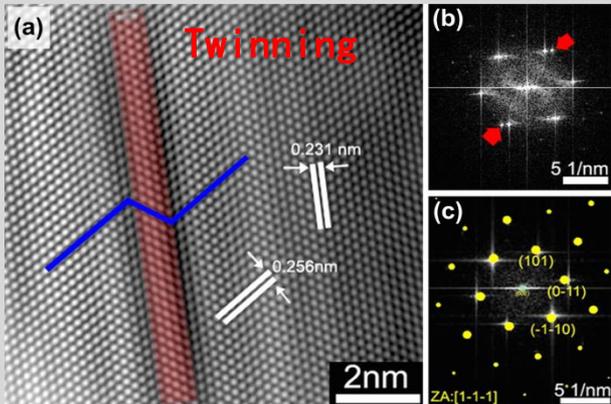
**Ms. Dongxue Han (Shanghai University)**

**Mr. Xing Tong (Shanghai University)**



# Background

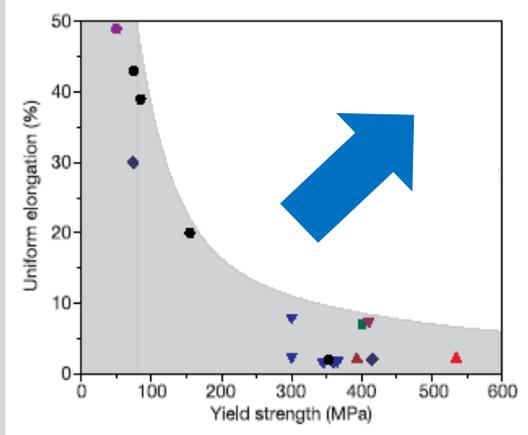
Crystallographic defects dominating the plastic deformation of crystalline materials.



Strength and plasticity - the most important properties, which can be modified by the modification of the defects.

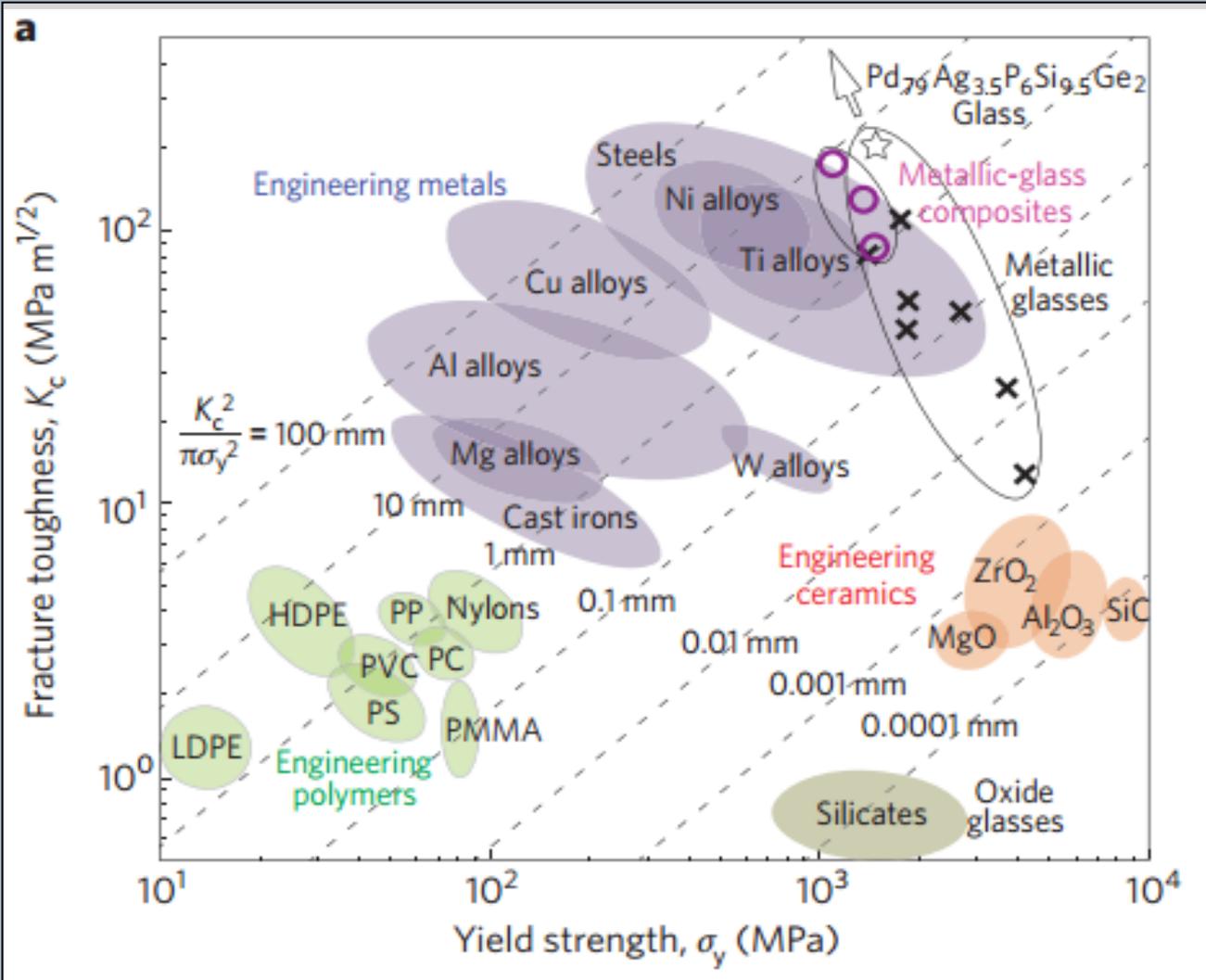
$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

Hall-petch relationship





# Background



High fracture toughness

High yield strength

High hardness

High corrosion resistant



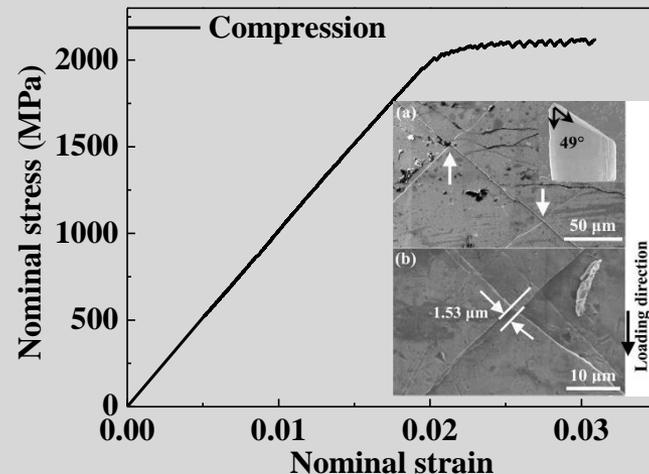
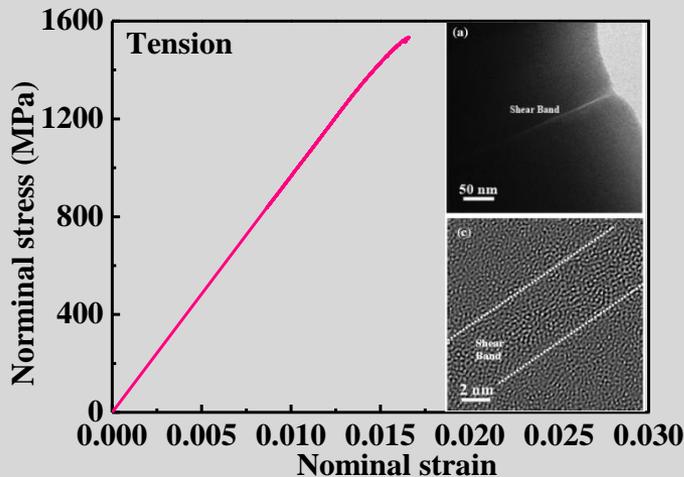
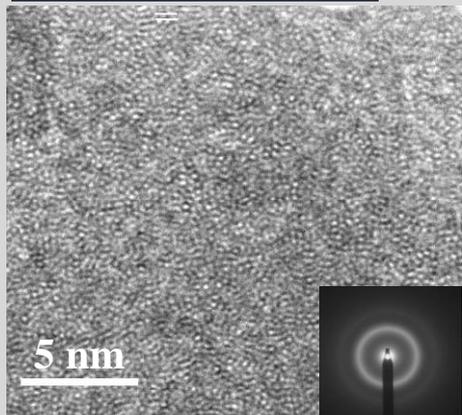
Application?



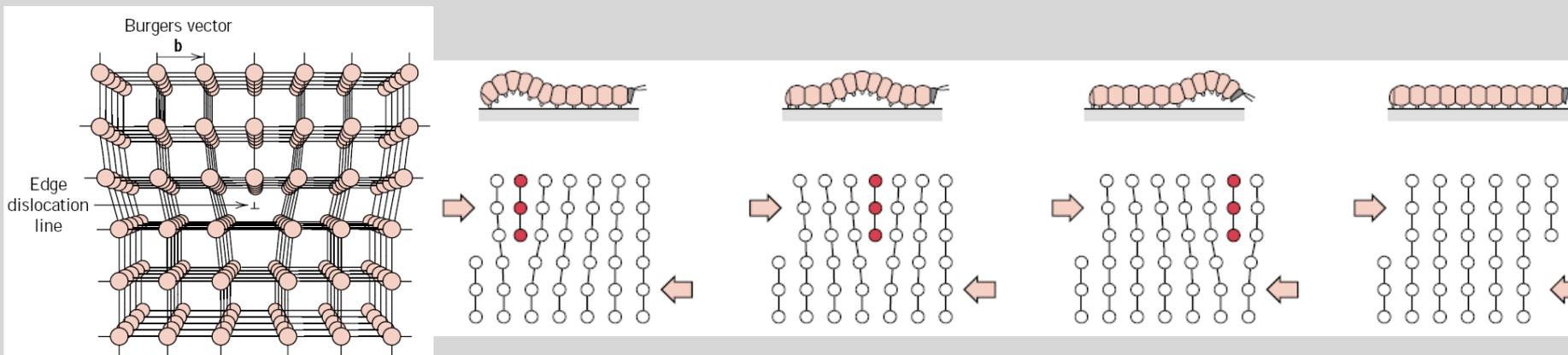
# Some problems

High toughness  
High strength

≠ Good plasticity    Work-hardening mechanism?



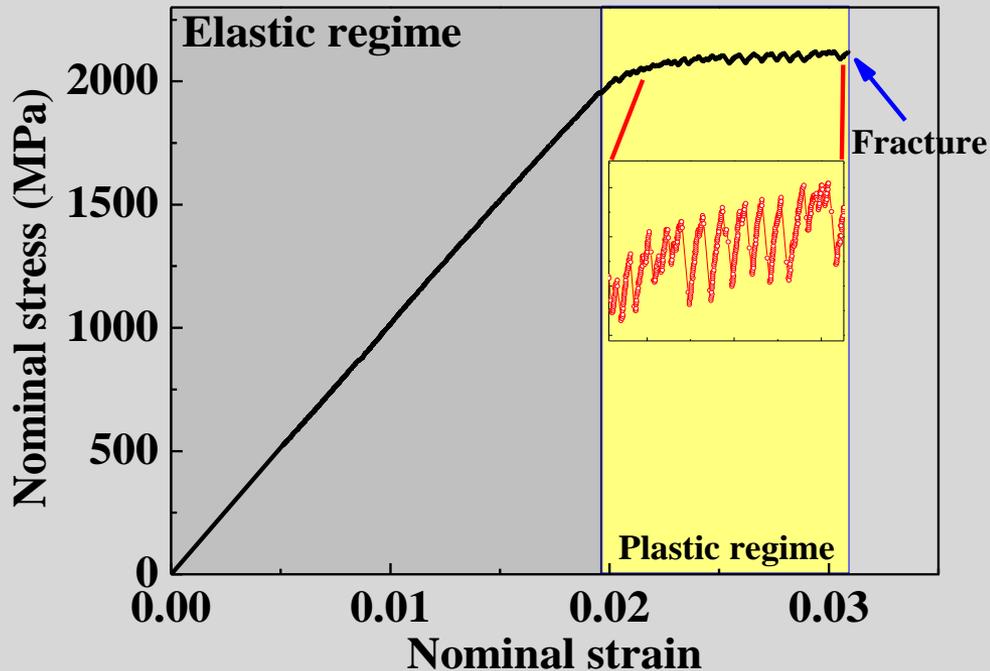
## ✉ Plastic deformation micromechanism in crystalline materials



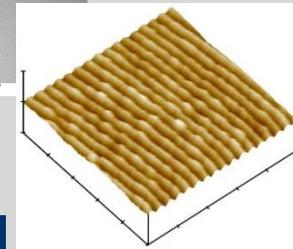
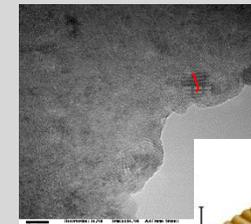
PRL 96, 245502 (2006); APL 89, 251909 (2006); JMR 22, 869 (2007)



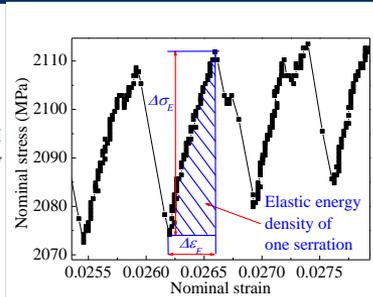
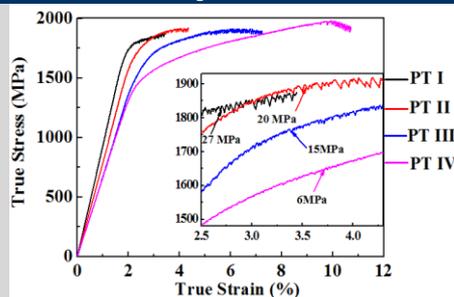
# Research scope (Outline)



(b)  
Fracture : Crack propagation ;  
Release of fracture energy; Fracture toughness



(a)  
Plastic deformation : Intermittent shear bands formation and propagation ; The plastic deformation ability.





**Part I Intermittent plastic deformation**

**Part II Influences of structures on on  
intermittent plastic deformation**

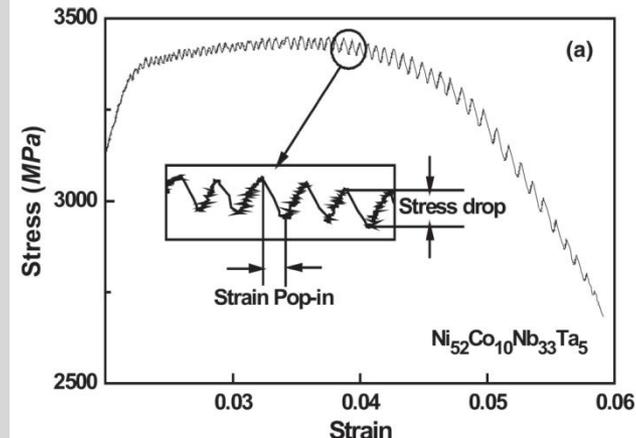
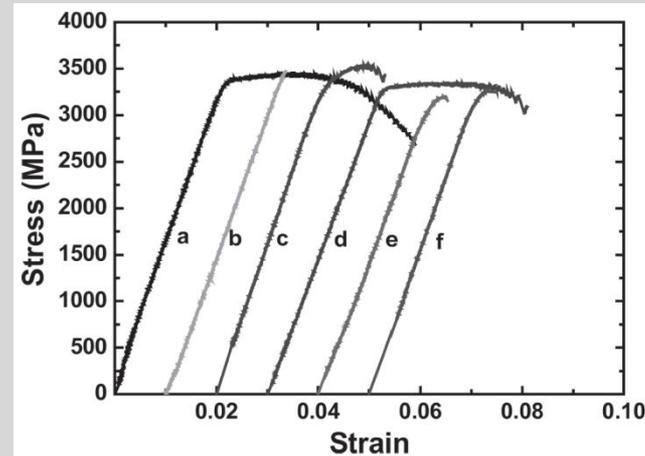
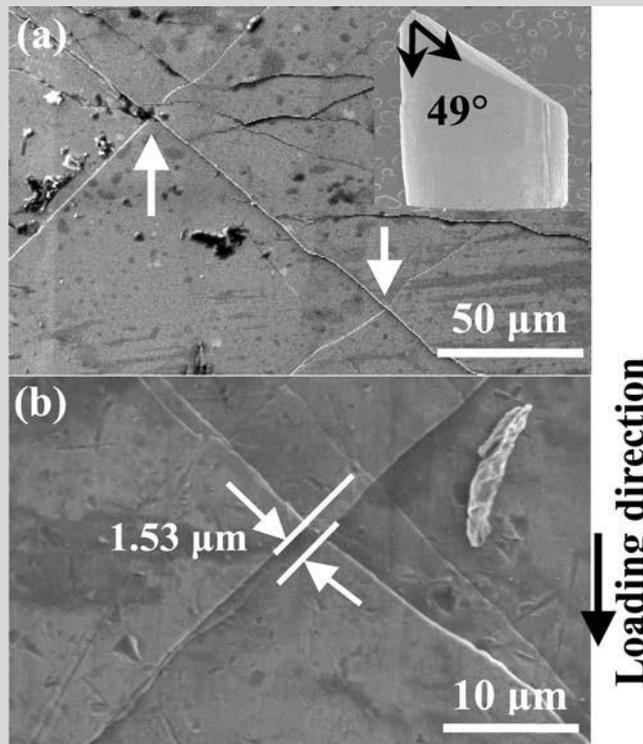
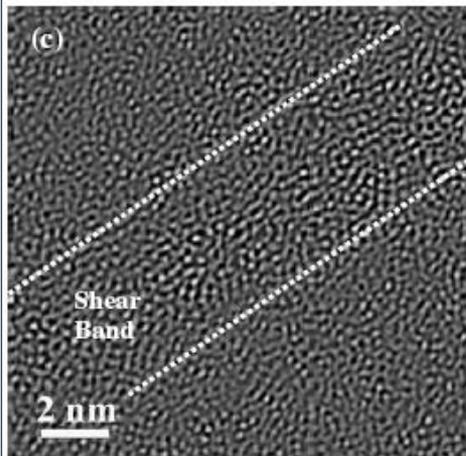
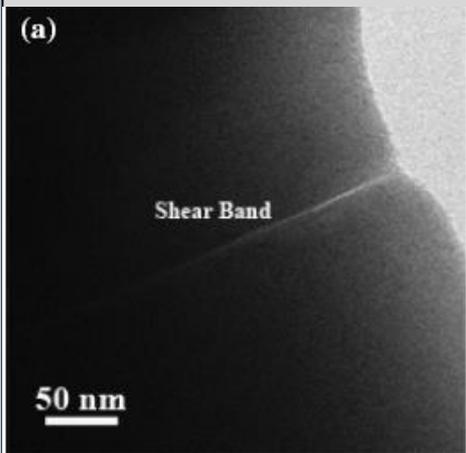
**Part III Stick-slip behavior in nanoscratch**

**Part IV Discontinuous crack propagation**



# Part I Intermittent plastic deformation

Stress  $\Rightarrow$  STZs  $\Rightarrow$  Shear localization  $\Rightarrow$  Shear banding  $\Rightarrow$  Catastrophic fracture



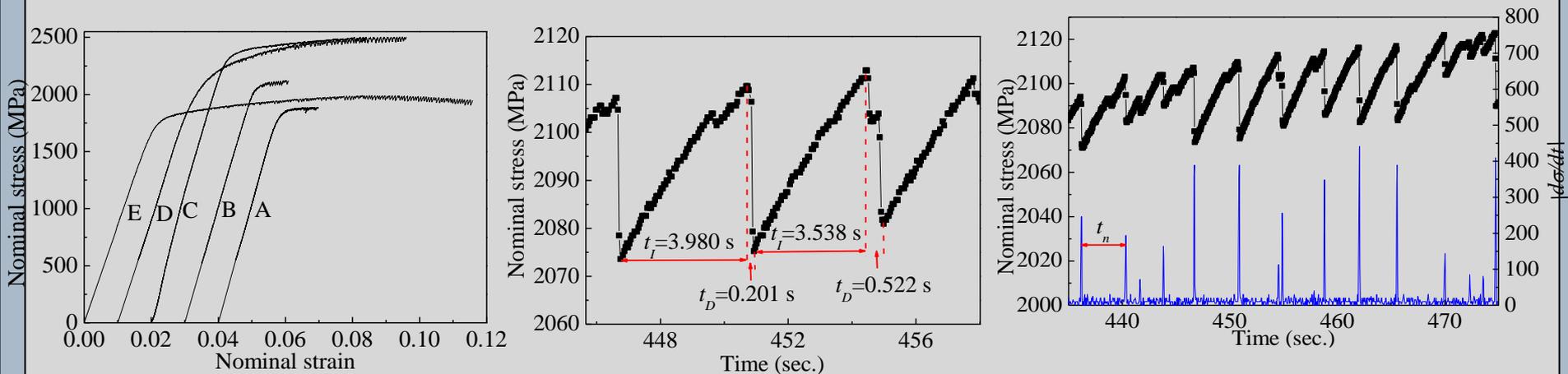


# Part I Intermittent plastic deformation

## ✉ Serration events (*Typical characteristics*)

Plastic deformation of BMGs generally exhibits serrated flow, i.e. repeated cycles of a sudden stress drop followed by reloading elastically

Serrations correspond to the shear bands formation and propagation



**A:**  $Zr_{55}Ni_5Cu_{30}Al_{10}$

**B:**  $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$

**C:**  $Cu_{42.5}Ti_{42.5}Zr_{2.5}Hf_5Ni_{7.5}$

**D:**  $Zr_{51}Cu_{23.25}Ni_{13.5}Al_{12.25}$

**E:**  $Cu_{47.5}Zr_{47.5}Al_5$

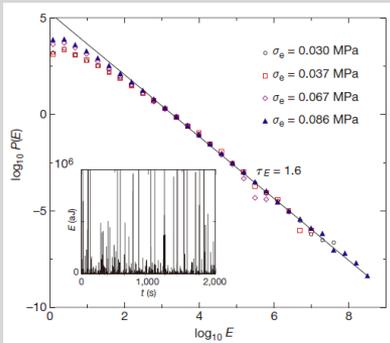
### Characteristics:

- ✉ Serration events lack any typical time scale ( $t_0 \neq t_1 \neq \dots \neq t_{n+1}$ )
- ✉ Process under external stress (stress increase) is much slower than the internal relaxation process (stress drop). ( $t_I > t_D$ )
- ✉ A large number of interacting entities. (The number of serration events is about 30)



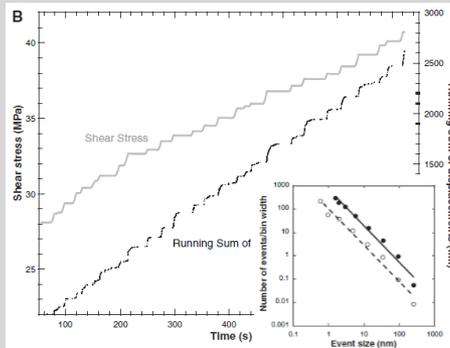
# Part I Intermittent plastic deformation

The continuum approach fails to account for microscopic plastic deformation because of discontinuous defect motions in crystalline materials.



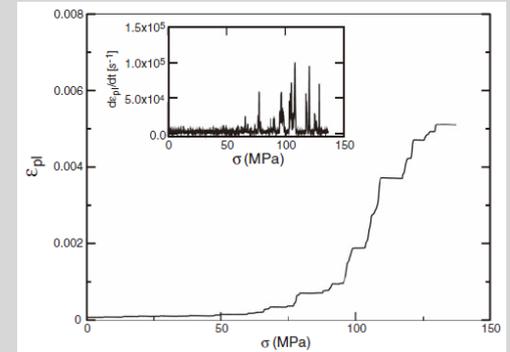
Single crystal (ice)

Science 2006, 312: 1188;  
 Science 2007, 318: 251;  
 Nature 2001, 410: 667.



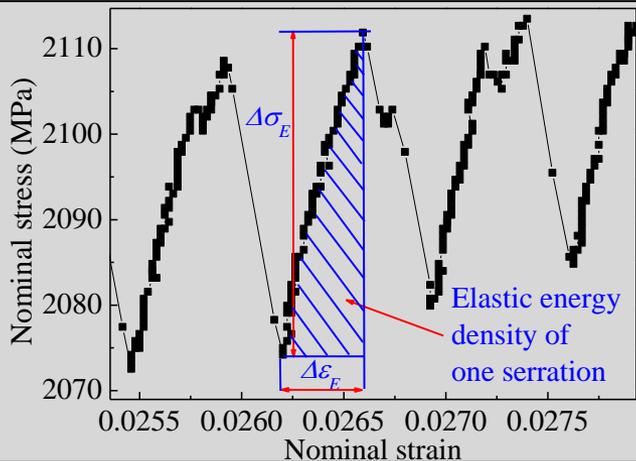
Polycrystal

Power law:  $P(E) \sim E^{-\tau}$



Microcrystal

$P(E)$ : propability



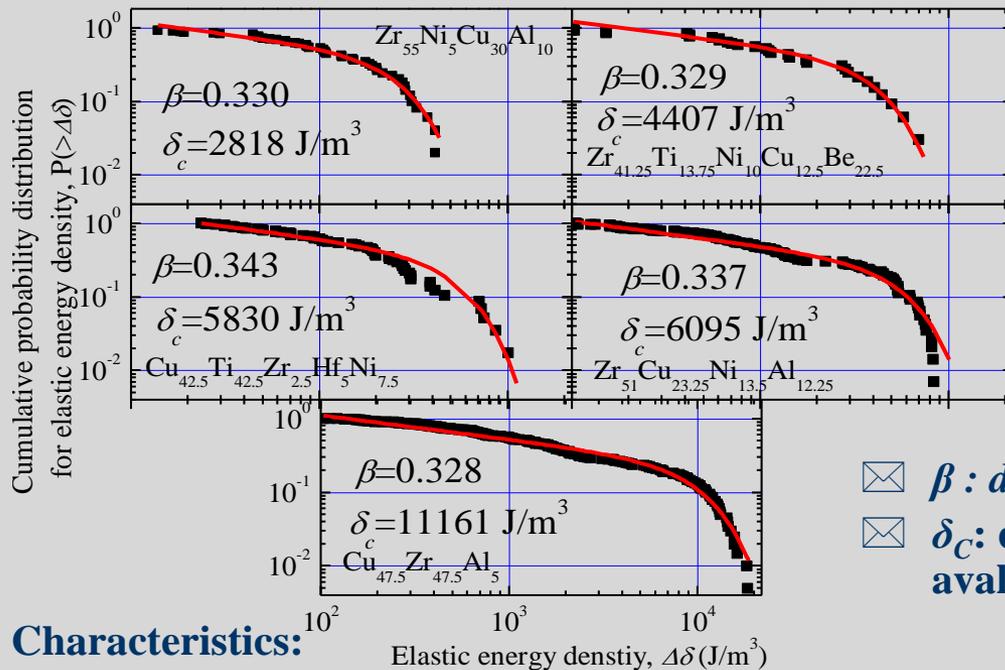
$$\Delta\delta = \frac{1}{2} \Delta\sigma_E \Delta\varepsilon_E$$

The elastic energy density of one serration event ( $\Delta\delta$ )



# Part I Intermittent plastic deformation

## Ergodic process of the elastic energy density in five BMGs



$$P(\geq \Delta\delta) = A\Delta\delta^{-\beta} \exp\left[-(\Delta\delta/\delta_c)^2\right]$$

Scattering points:  $\Delta\delta$  (measured from stress-strain curves)

Red solid lines: fitted by Power-law function

$$\beta = 0.335 \pm 0.008$$

- ⊠  $\beta$  : depending on the deformation mechanism
- ⊠  $\delta_c$ : depending on the characteristic length of avalanche

### Characteristics:

- ⊠ Serration events lack any typical time scale ( $t_0 \neq t_1 \neq \dots \neq t_{n+1}$ )
- ⊠ Process under external stress (stress increase) is much slower than the internal relaxation process (stress drop). ( $t_I > t_D$ )
- ⊠ A large number of interacting entities. (The number of serration events is about 30)
- ⊠ **Power-law distribution**

⇒ **Self-organized criticality (SOC)**

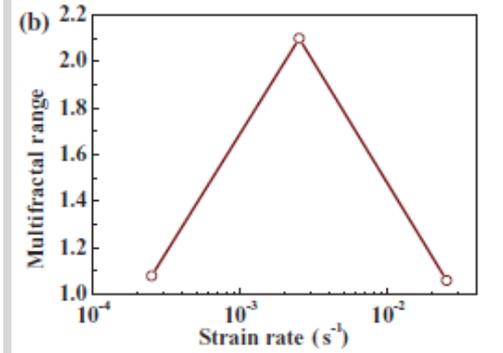
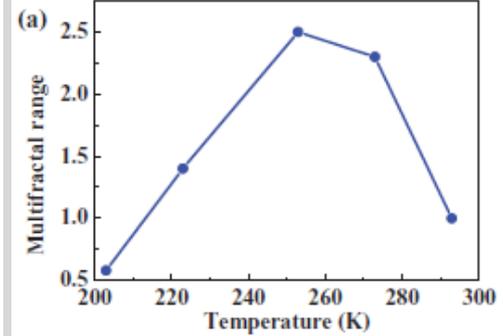
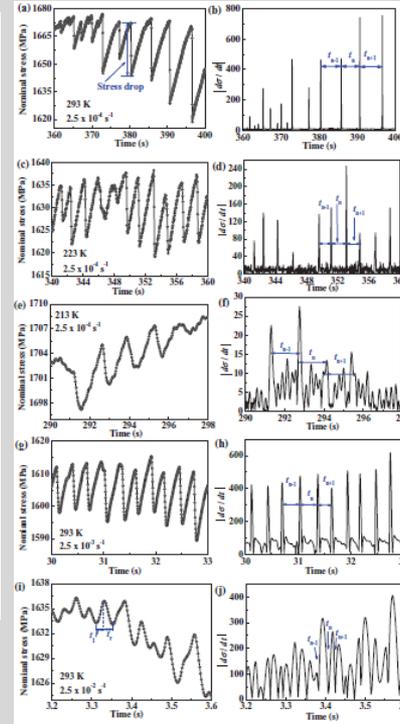
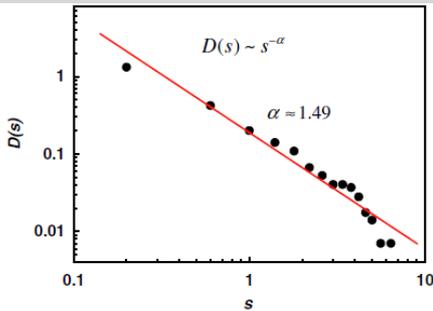
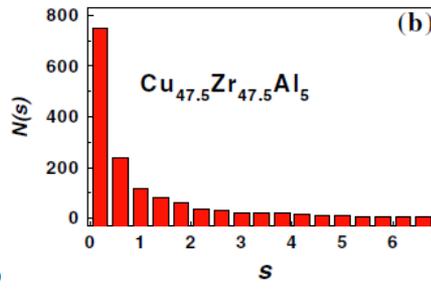
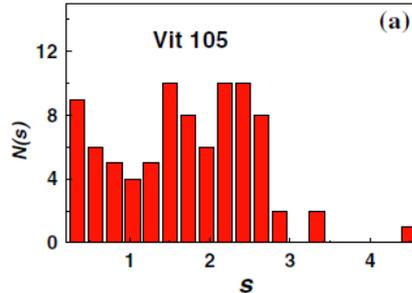
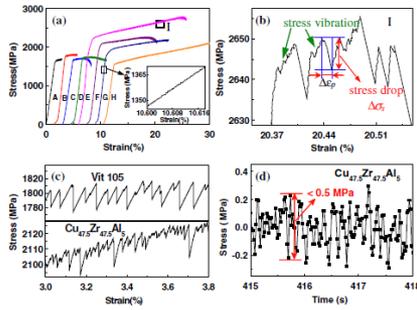
[Acta Materialia 57, 6146 (2009)]



# Part I Intermittent plastic deformation

- ☒ Ductile: Self-organized critical behavior
- ☒ Brittle: Chaotic behavior

- ☒ Low rate: Self-organized critical behavior
- ☒ High rate: Chaotic behavior



**Chaos ----- Self organized critical (SOC) behavior**

**Loading rate, temperature, chemical components**

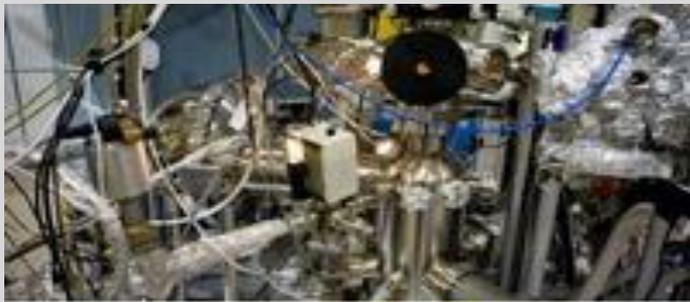
**Chaos ----- Multifractal ----- SOC  
多重分形**

B.A. Sun et al. PRL **105**, 035501 (2010);  
R. Sarmah et al. Acta Mater. **59**, 4482 (2011)

J.L. Ren, et al. Phys. Rev. B **86**, 134303 (2012);  
J.L. Ren, et al. J. Appl. Phys. **116**, 033520 (2014);  
J.L. Ren, et al. Phys. Rev. E **92**, 012113 (2015)



# Part II Influences of structures on on intermittent plastic deformation



A terminal of 320 kV High-Voltage Experimental platform equipped with an electron cyclotron resonance ion source in Institute of Modern Physics, Lanzhou, China, providing a **7 MeV Xe<sup>26+</sup> beam** for irradiation.

The incident flux was about  $3.43 \times 10^{14}$  ions/cm<sup>2</sup>s<sup>-1</sup>.

Base pressure lower than  $5 \times 10^{-5}$  Pa.



脉冲高精度二极磁铁和四极透镜



兰州重离子加速器冷却储存环



实验环二极磁铁



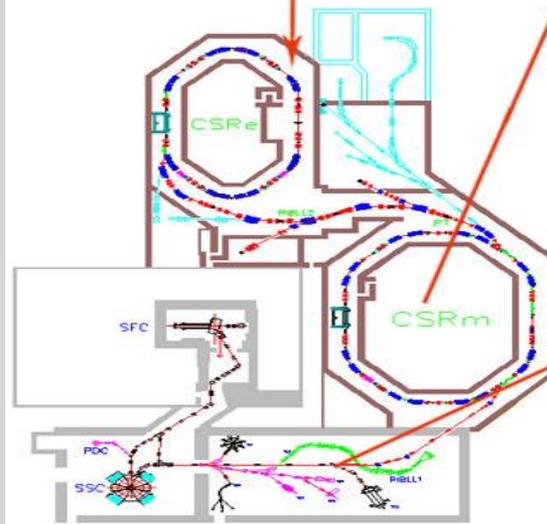
探测器



真空装置



重离子加速器 (SSC) 注入到主环 (CSRm) 接口的脉冲四极透镜

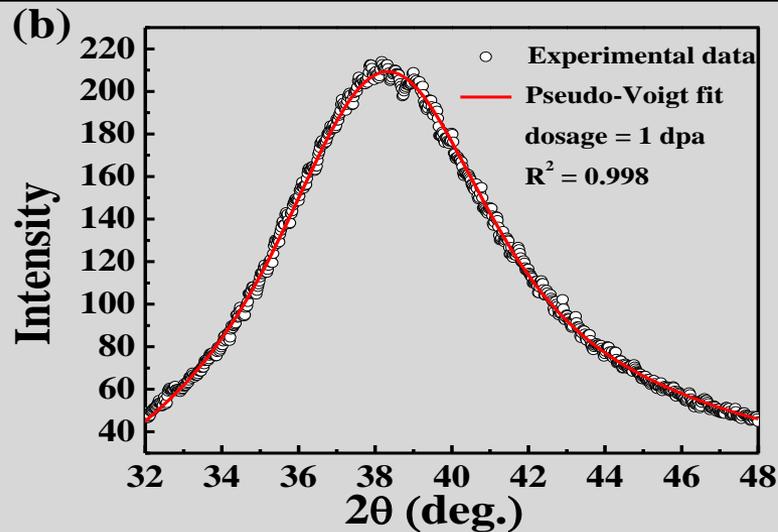
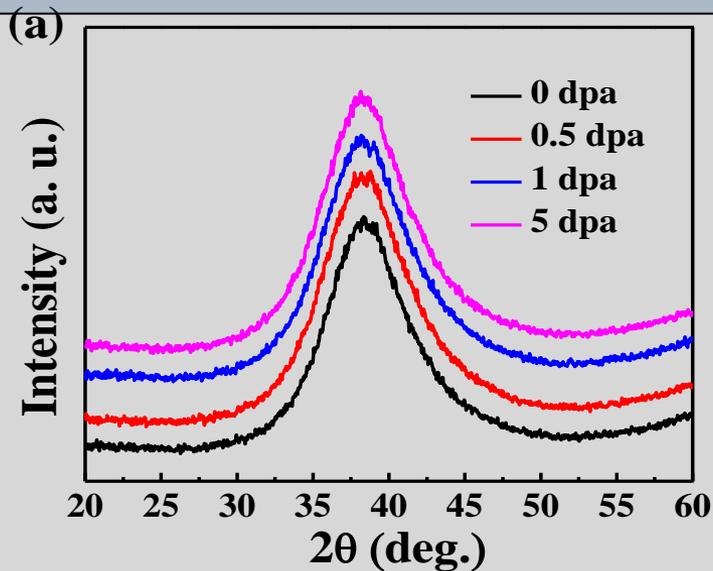


HIRFL-CSR平面图

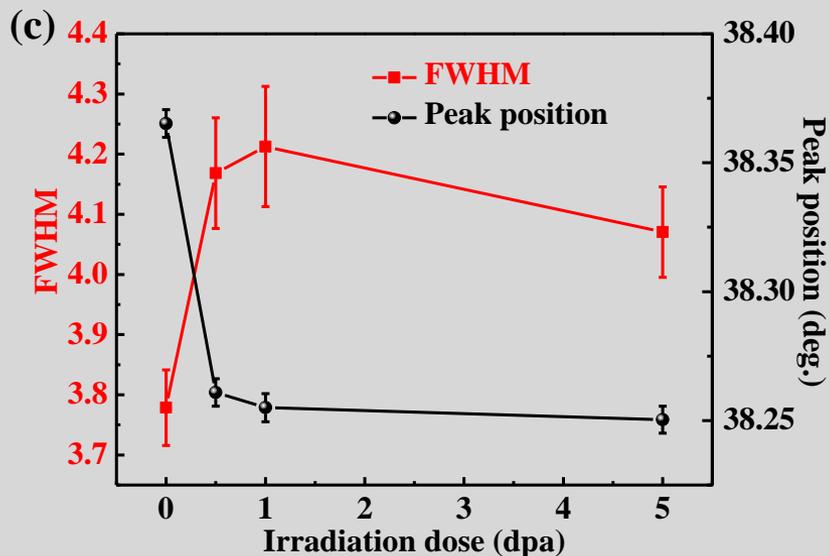
Heavy Ion Research Facility In Lanzhou (HIRFL)



# Part II Influences of structures on on intermittent plastic deformation



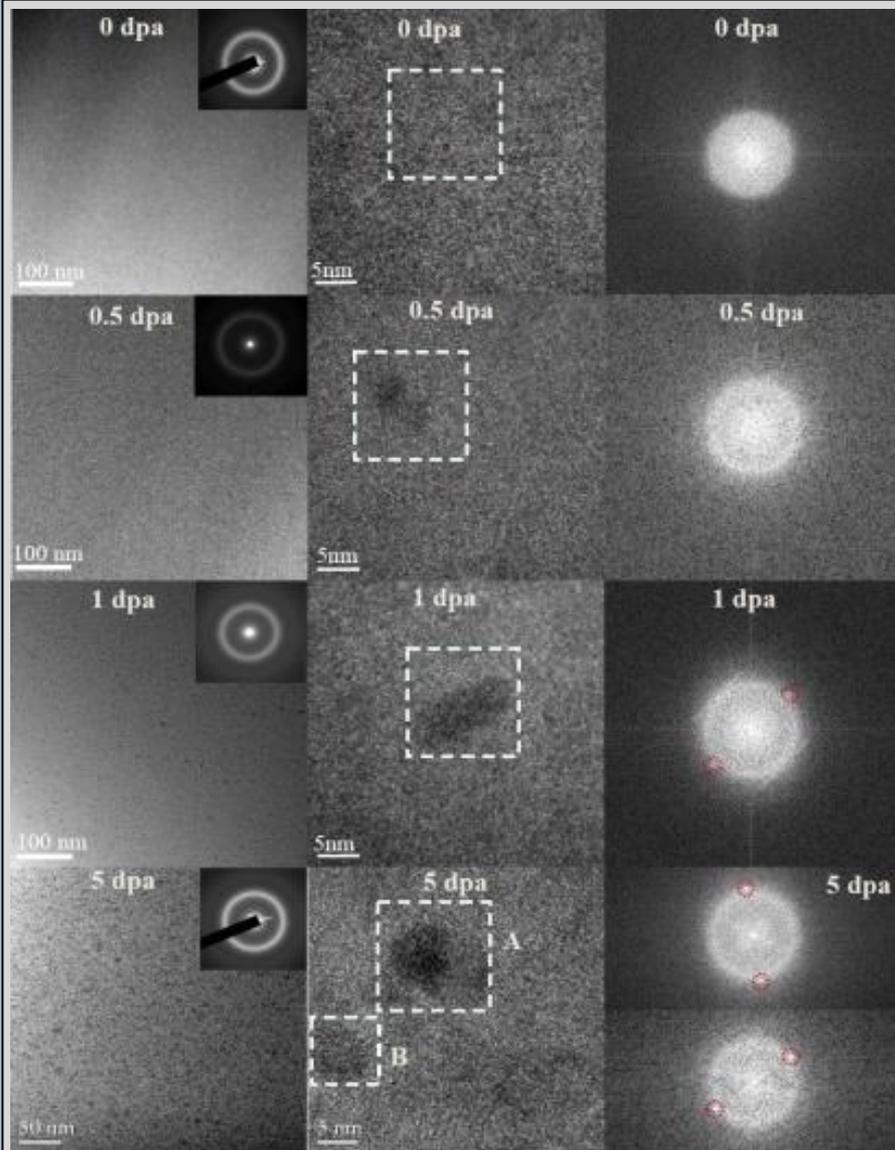
- ☒ Degree of ordering decreases
- ☒ Expansion in the interatomic distance



dpa (displacement per atom) is defined as the average number of displacements per atom per unit volume per unit time for a given irradiation dosage



# Part II Influences of structures on on intermittent plastic deformation



**Fully amorphous (0 dpa)**

**Some changes (0.5 dpa)**

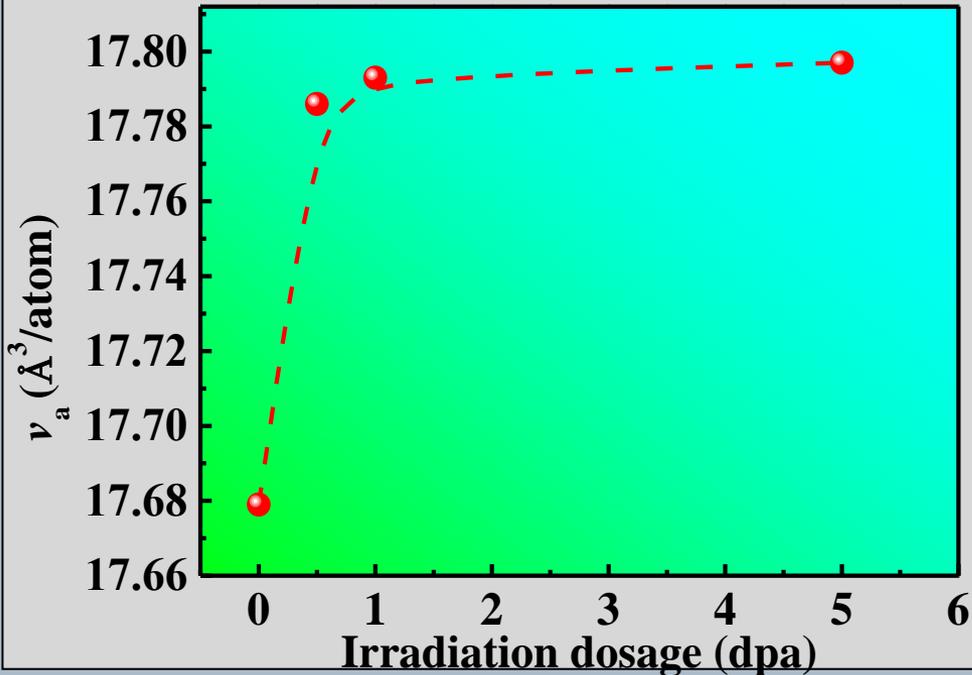
**Nanocrystals (1 dpa)**

**Crystalline phase (5 dpa)**



# Part II Influences of structures on on intermittent plastic deformation

Dosage (dpa)	Peak position (° )	FWHM	H (GPa)
0	$38.365 \pm 0.005$	$3.779 \pm 0.063$	<b>6.353</b>
0.5	$36.261 \pm 0.005$	$4.168 \pm 0.092$	<b>6.211</b>
1	$38.255 \pm 0.005$	$4.213 \pm 0.100$	<b>6.105</b>
5	$38.250 \pm 0.005$	$4.070 \pm 0.075$	<b>6.202</b>

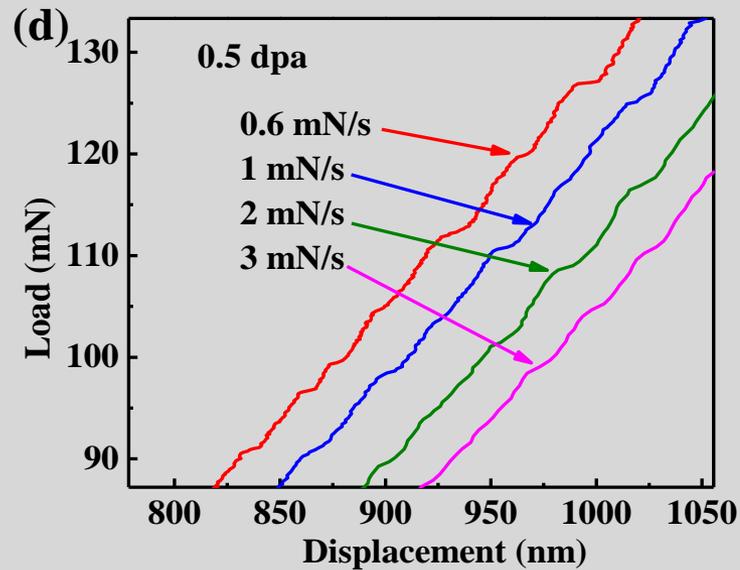
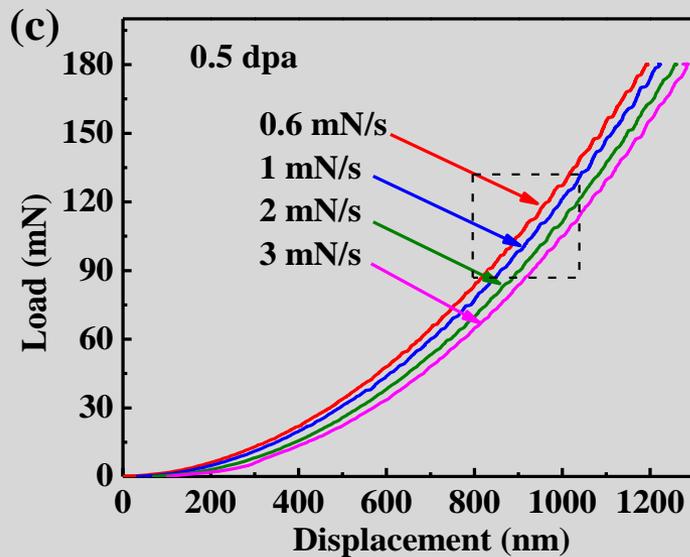
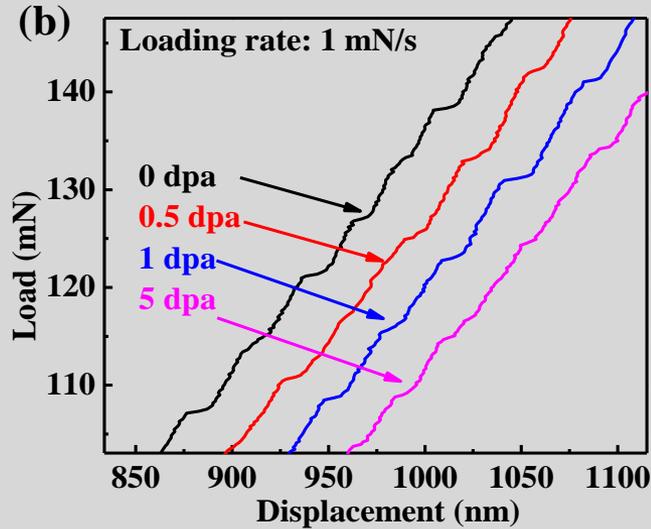
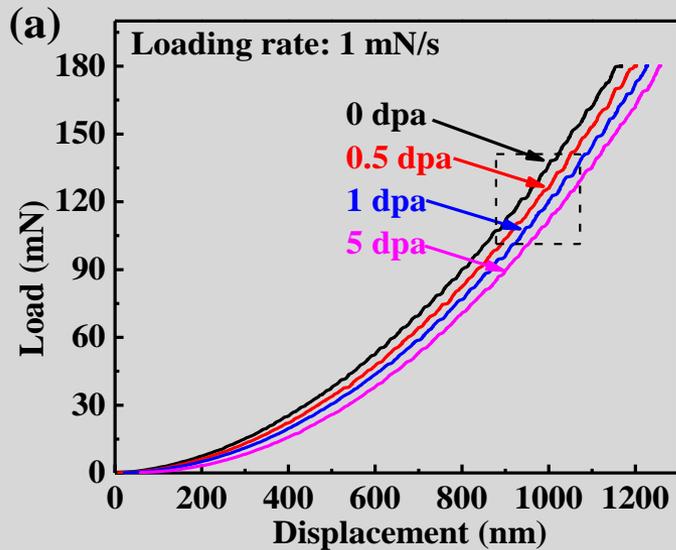


$$q \cdot v_a^{0.433} = 9.3$$

**Irradiation causes Dilatation**

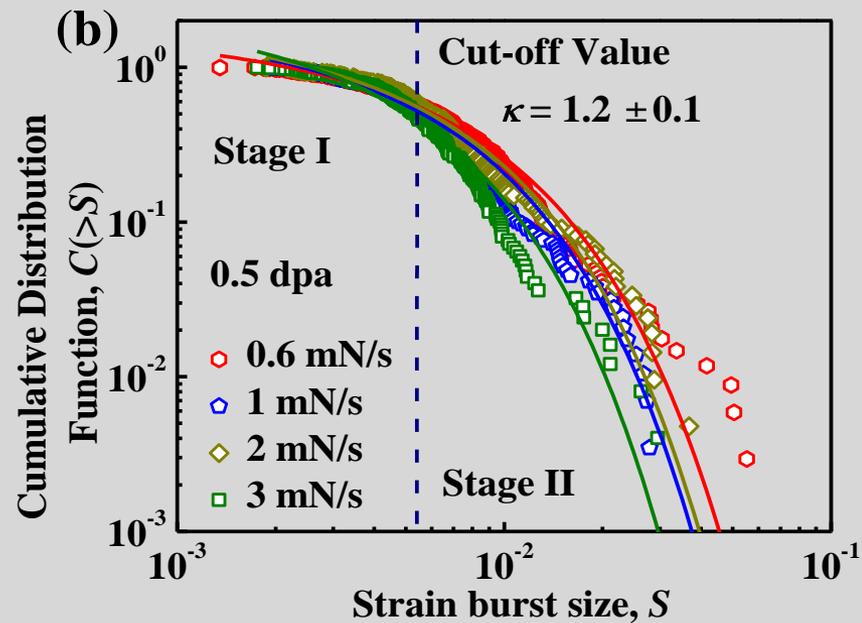
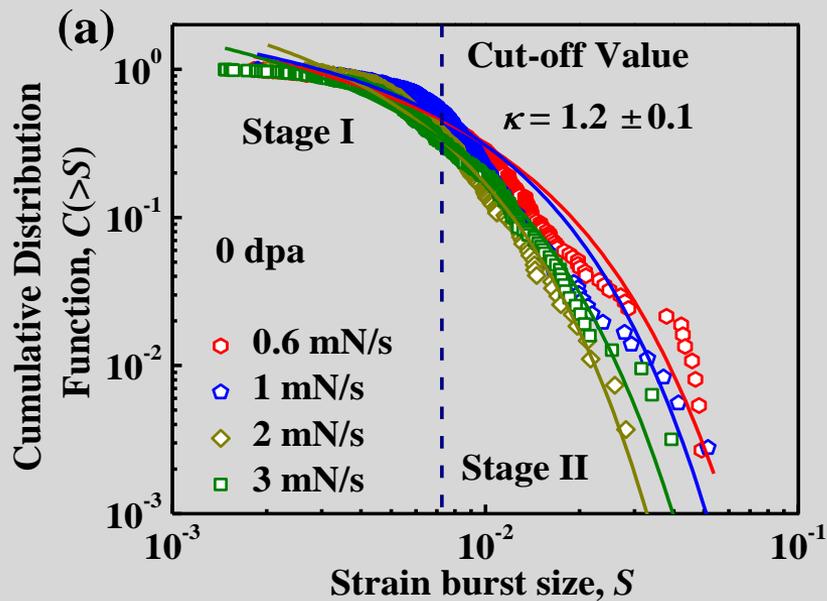
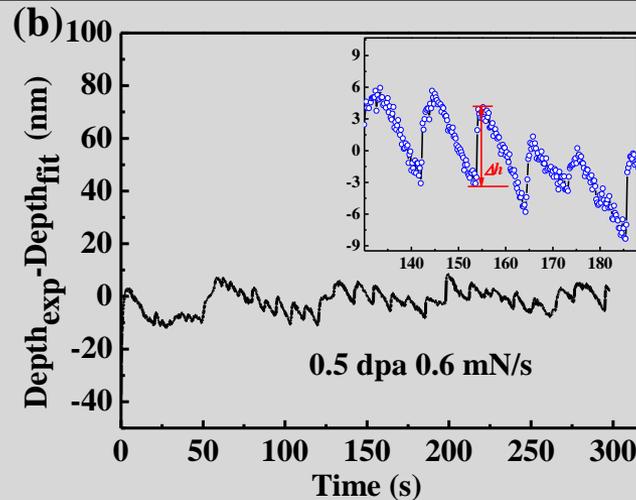
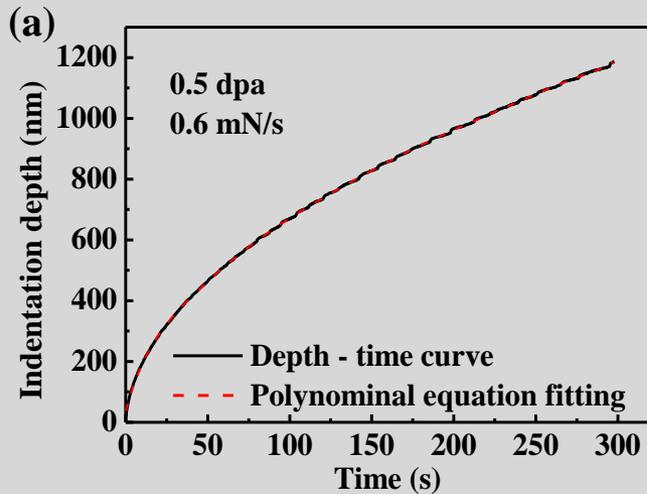


# Part II Influences of structures on on intermittent plastic deformation



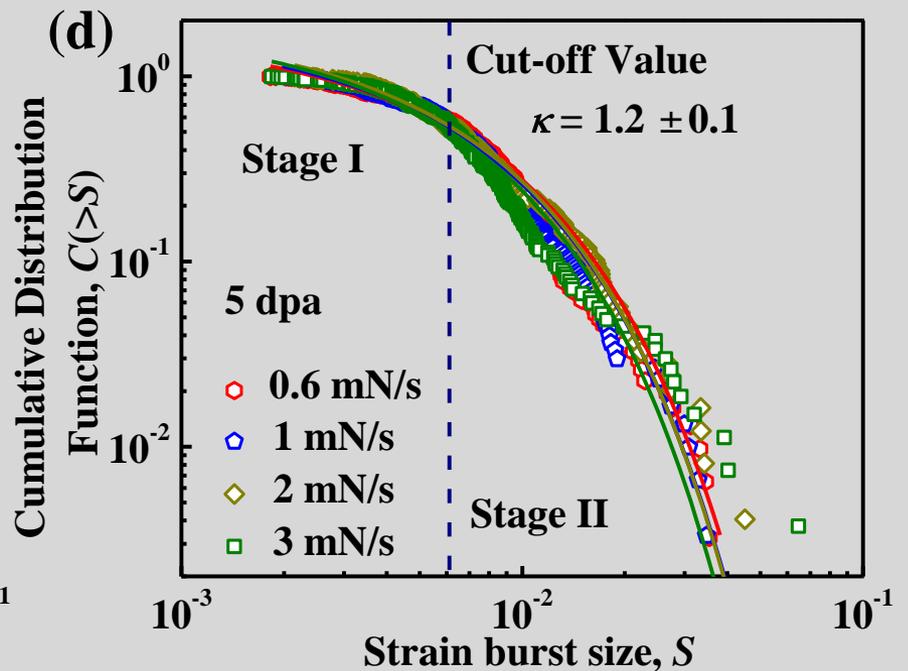
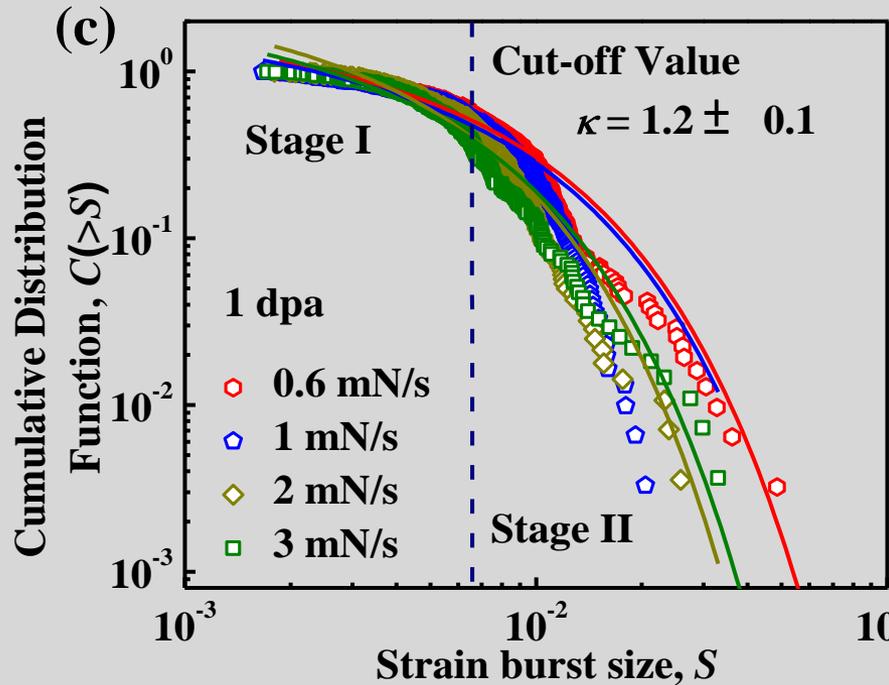


# Part II Influences of structures on on intermittent plastic deformation





# Part II Influences of structures on on intermittent plastic deformation



$$C(S) \sim S^{-(\kappa-1)} F(S/S_C)$$

$F(S/S_C)$  [=  $\exp(-(S/S_C))$ ]: a quickly decaying scaling function

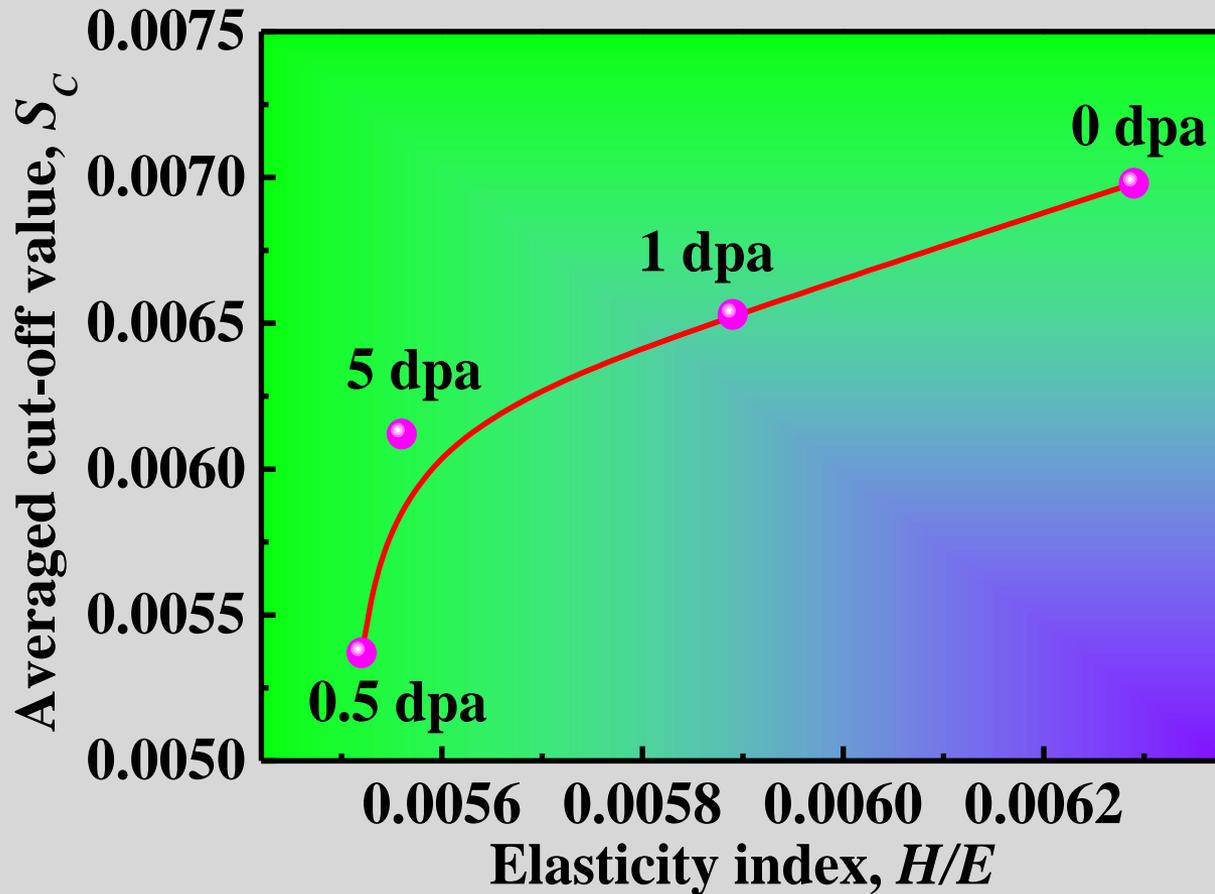
$\kappa$ : a scaling exponent ( $\kappa = 1.5$  in the mean field theory)

$S_C$ : the size of the largest typical “critical” avalanche that acts as a cut-off in  $F(S/S_C)$ , and decays exponentially to leading order for large  $S/S_C \gg 1$ .

Mean-field theory: 把一些单个的涨落现象, 平均于周围环境中。<sup>19</sup>



# Part II Influences of structures on on intermittent plastic deformation



Elastic index: The energy for supporting the shear slip of flow units



# Part II Influences of structures on on intermittent plastic deformation



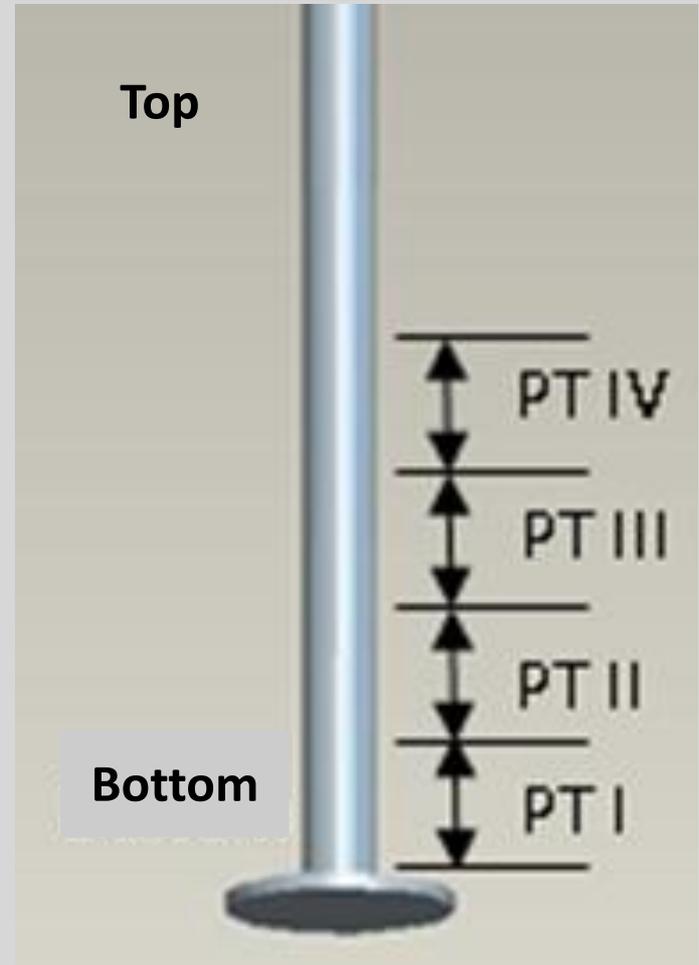
**Low glass forming ability**

**Arc-melting**



Titanium-gettered argon

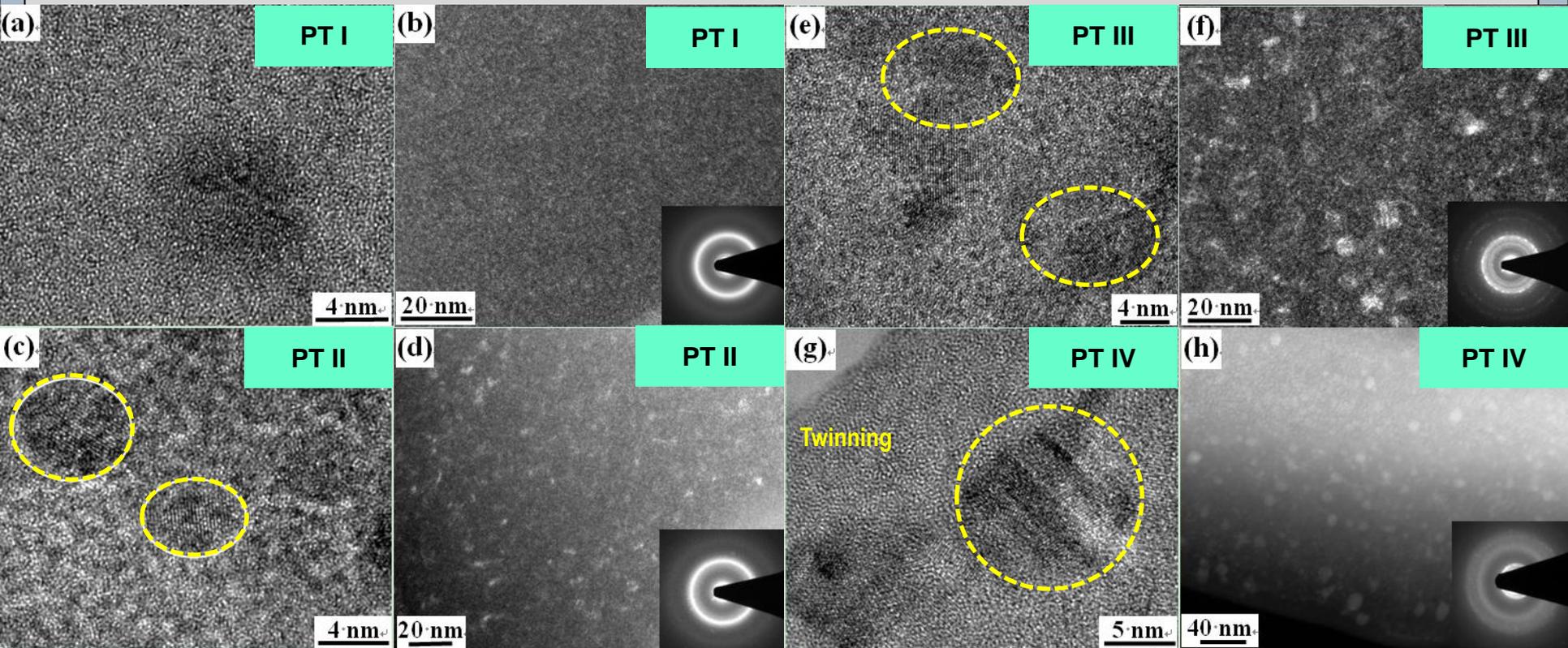
**Suction casting**



A rod-like sample



# Part II Influences of structures on on intermittent plastic deformation



**PT I:** Homogeneous contrast; Monolithic amorphous; Two diffraction halos

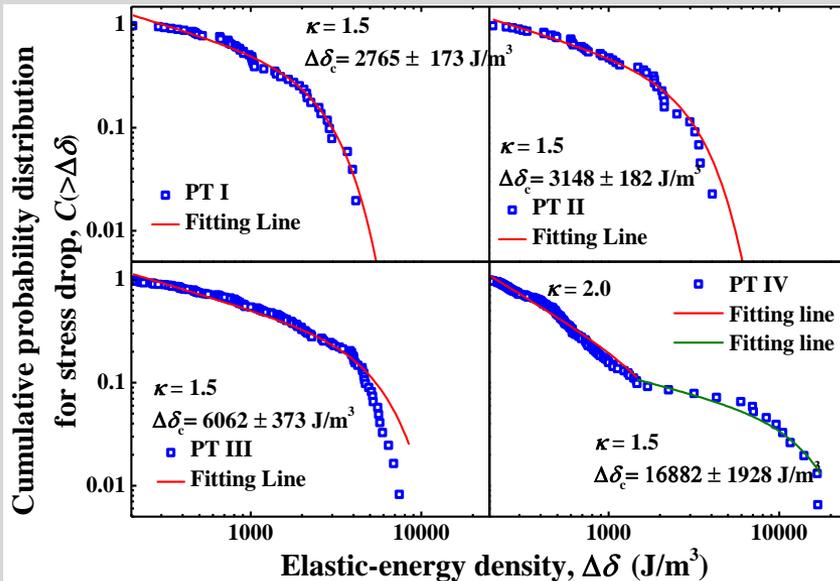
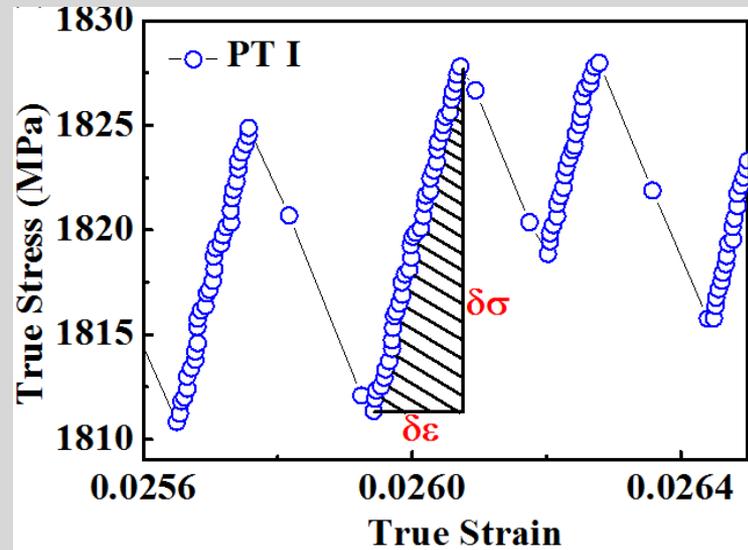
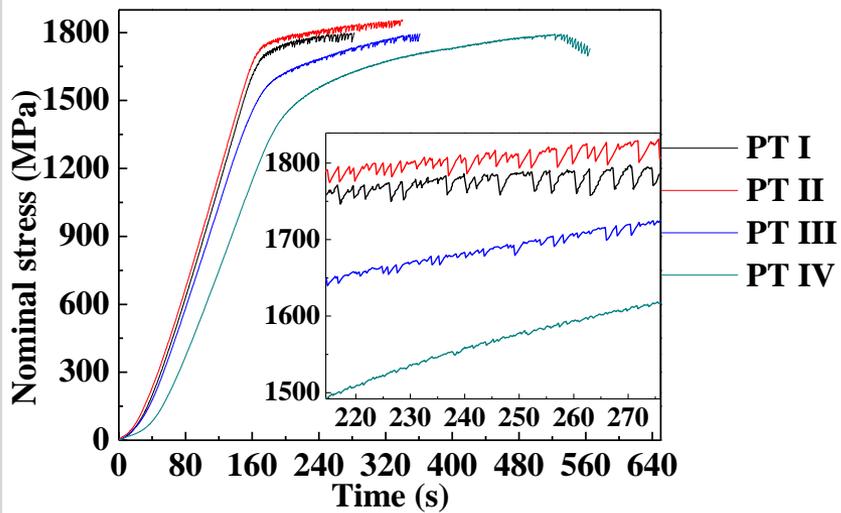
**PT II:** Small nanocrystals; White spots

**PT III:** Large nanocrystals; A larger size and volume fraction than PT II

**PT IV:** Twinning nanocrystals



# Part II Influences of structures on on intermittent plastic deformation

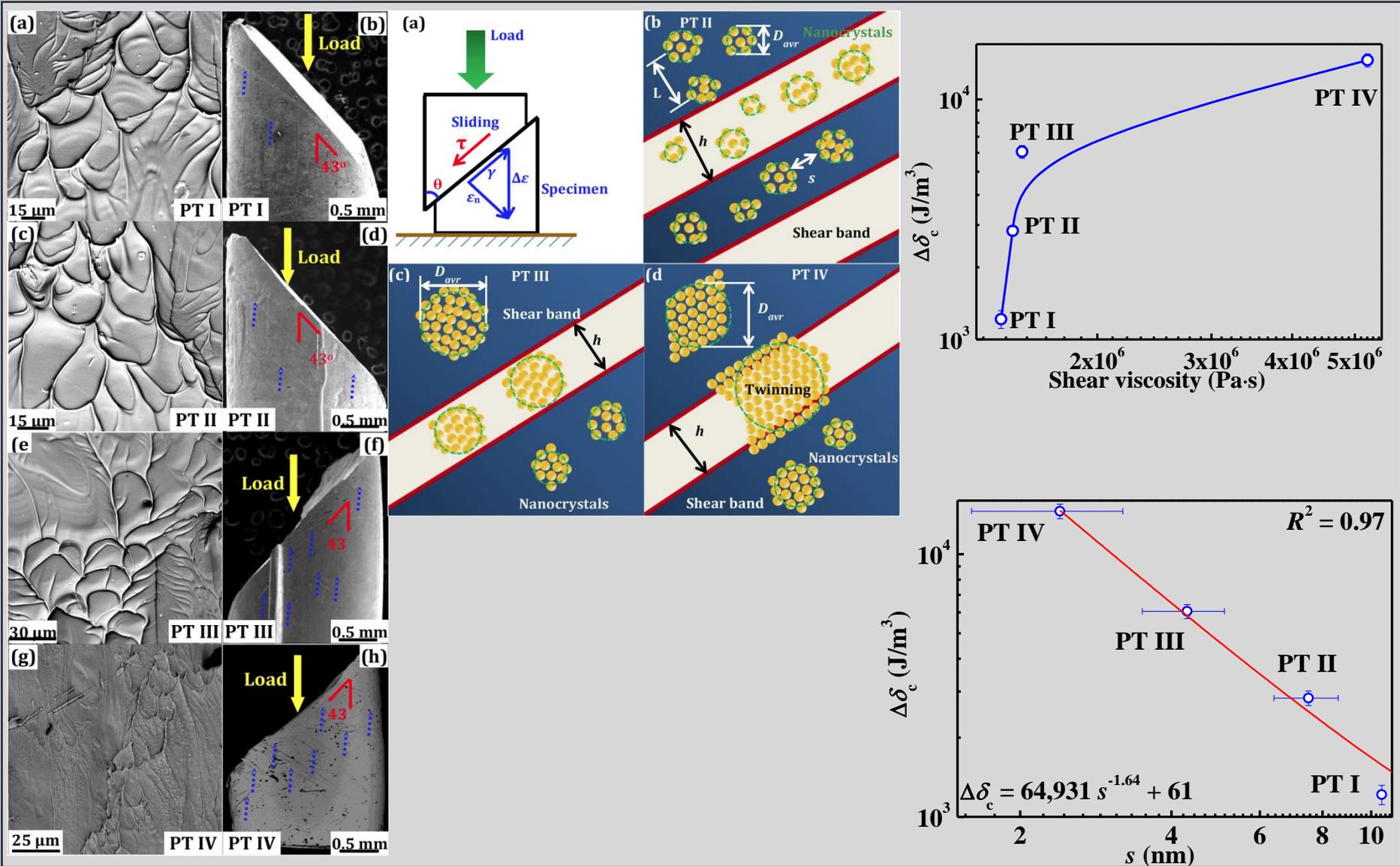


$$P(\geq \Delta\delta) = A\Delta\delta^{-\beta} \exp[-(\Delta\delta/\delta_c)^2]$$

$\Delta\delta_c$  : critical size for large shear avalanche

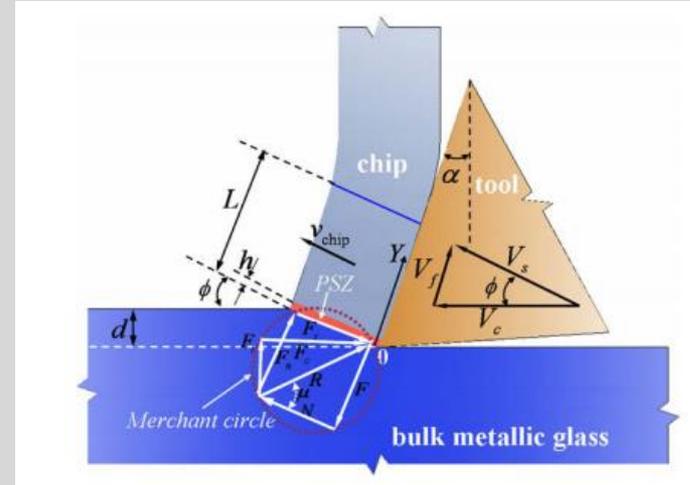


# Part II Influences of structures on on intermittent plastic deformation

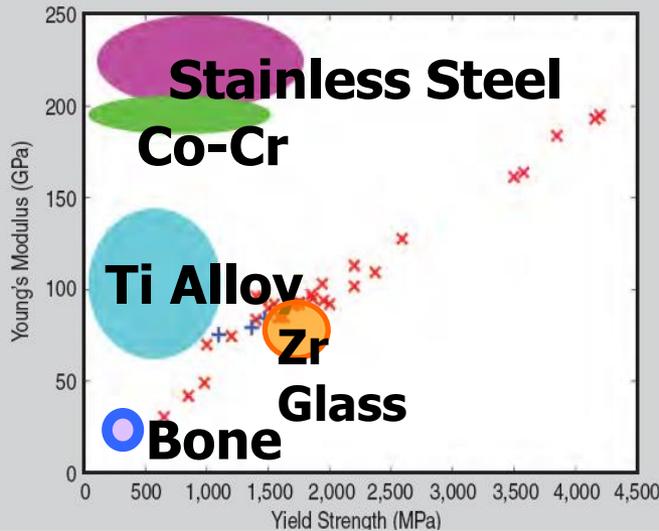




# Part III Stick-slip behavior in nanoscratch



- Good glass forming ability
- High yielding strength [(1660 ± 20) MPa]
- Low elastic modulus (80-90 GPa)
- High toughness (53 MPa.m<sup>1/2</sup>)
- Small density (5.9 g/cm<sup>3</sup>)
- ◆ Most important
- Without Fe element

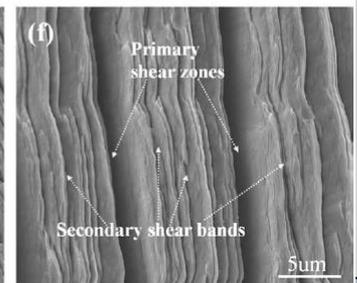
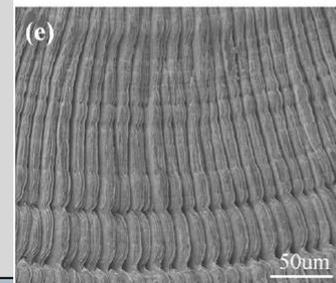
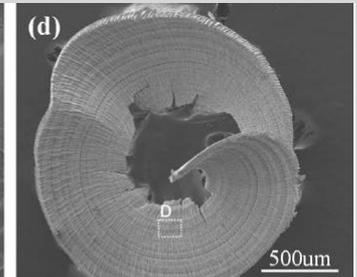
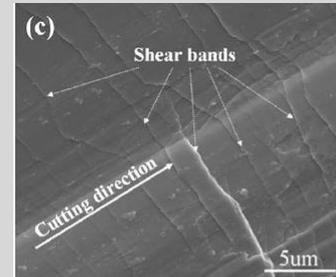
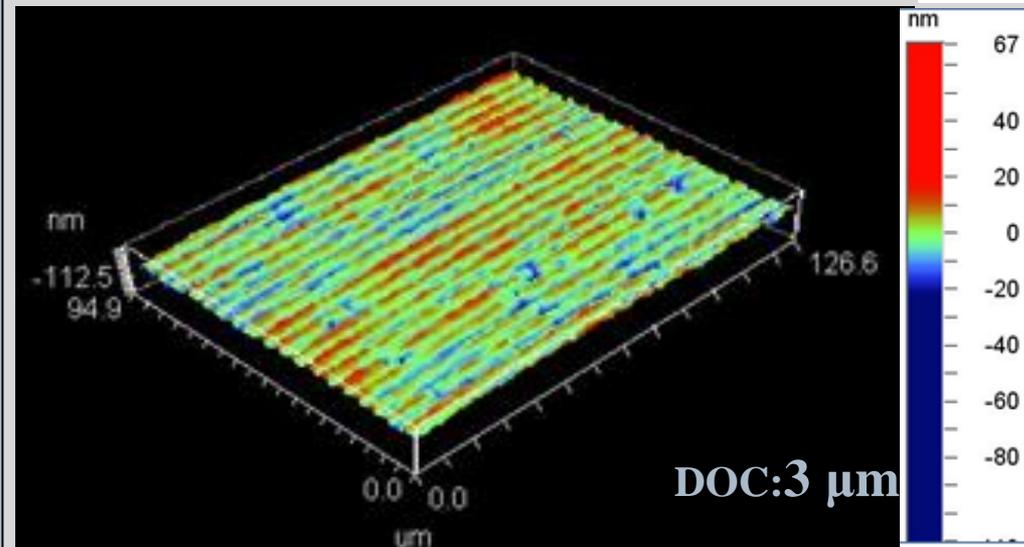
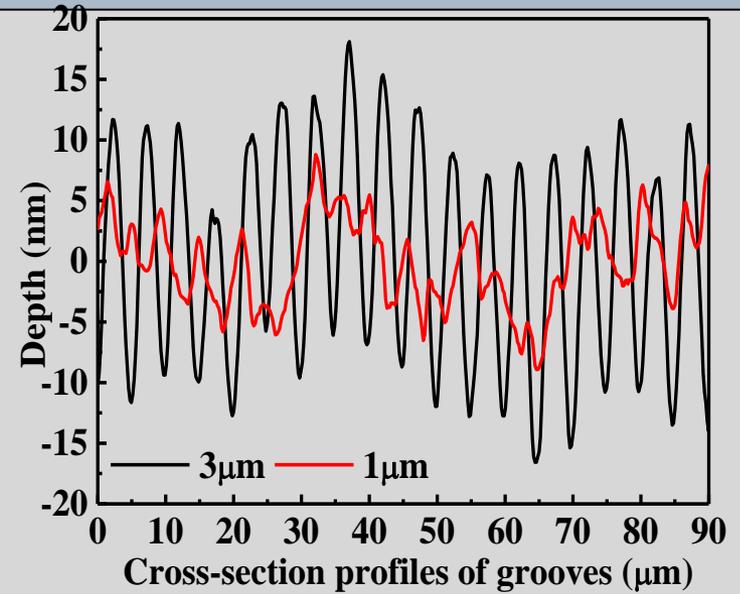
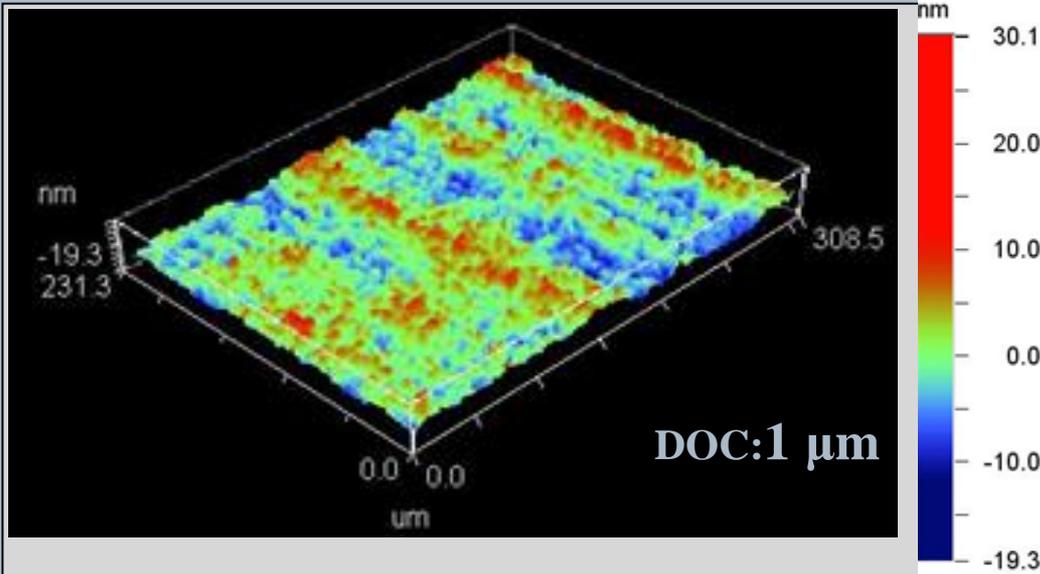


M.D. Demetriou. JOM 62(2) 83 (2012)

L.H. Dai, et al. Acta Mater. 2009

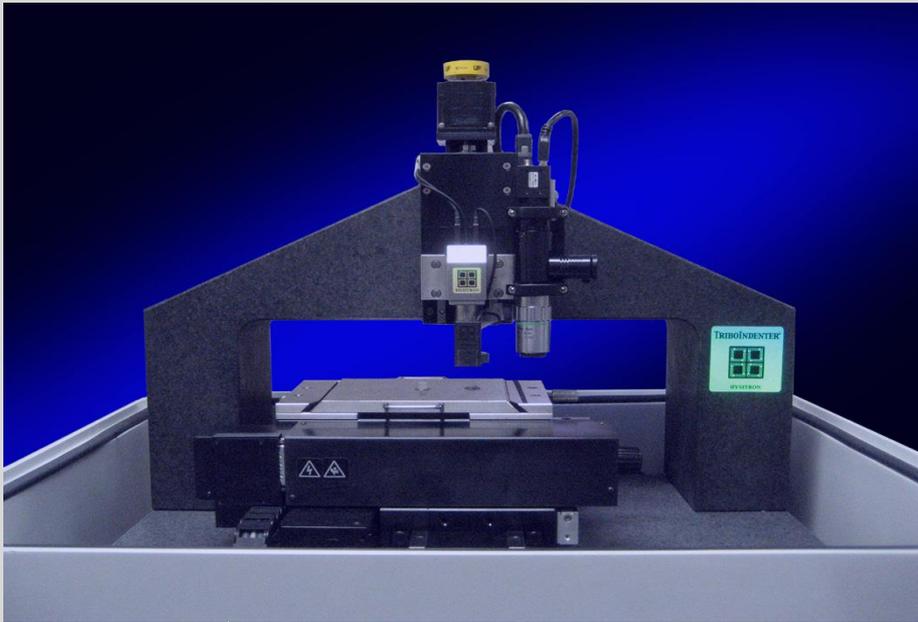


# Part III Stick-slip behavior in nanoscratch





# Part III Stick-slip behavior in nanoscratch



**TI-900**

Nanoindention:

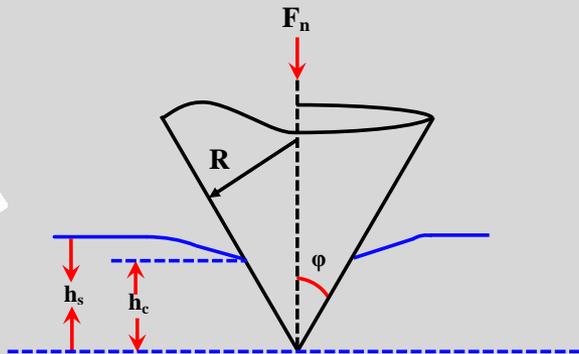
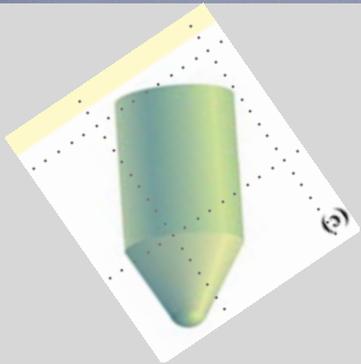
load resolution: 1nN

displacement resolution: 0.006 nm

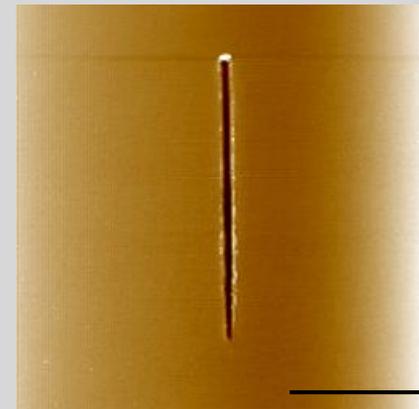
Nanoscratch:

load t resolution: 50 nN

displacement resolution: 0.02nm



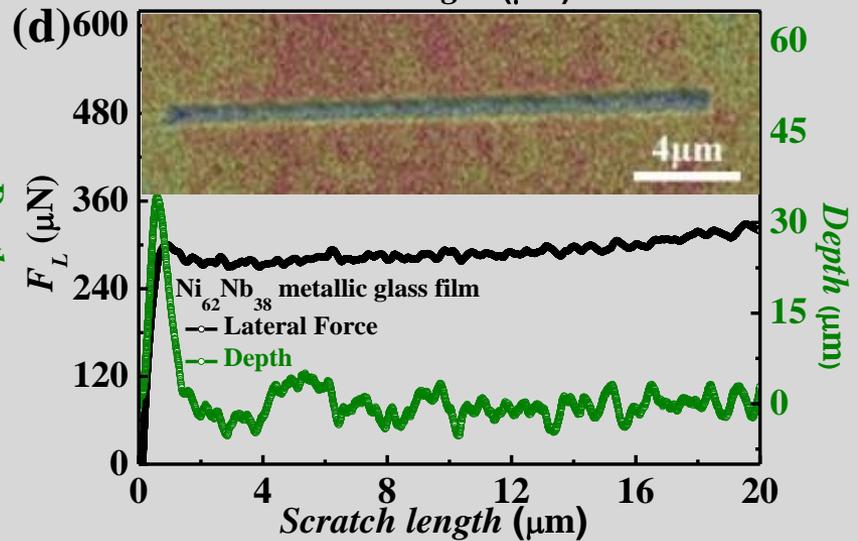
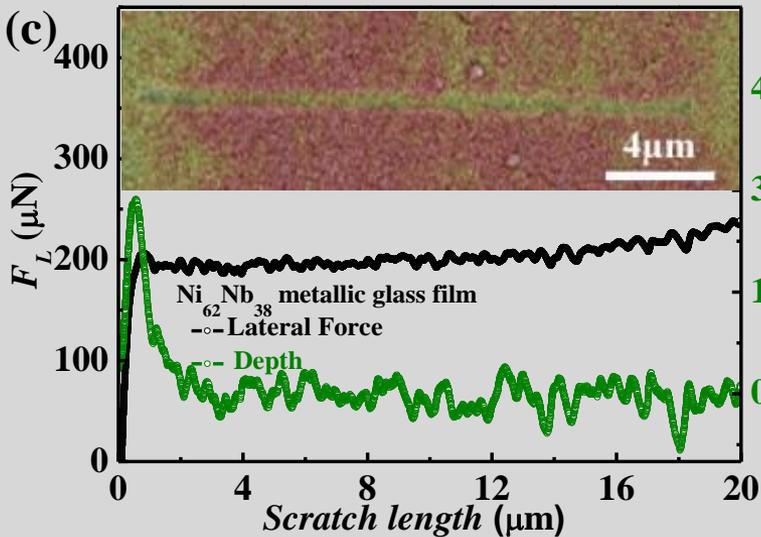
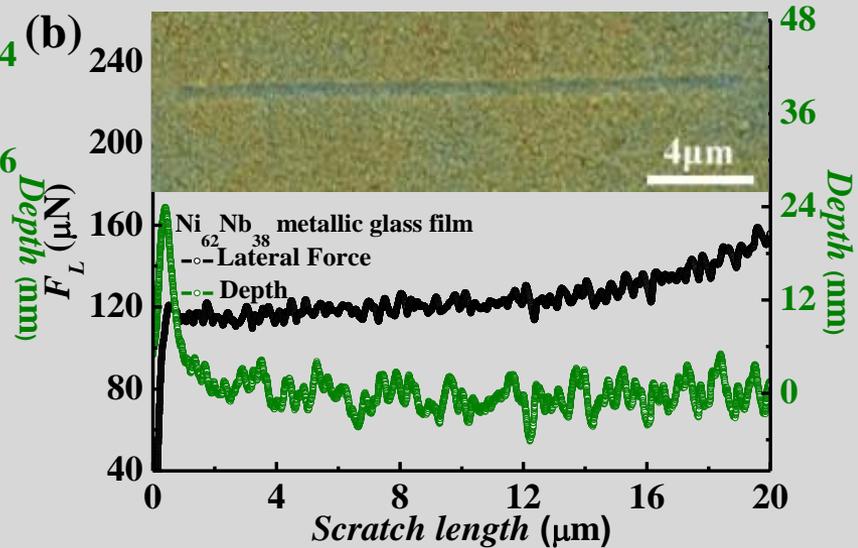
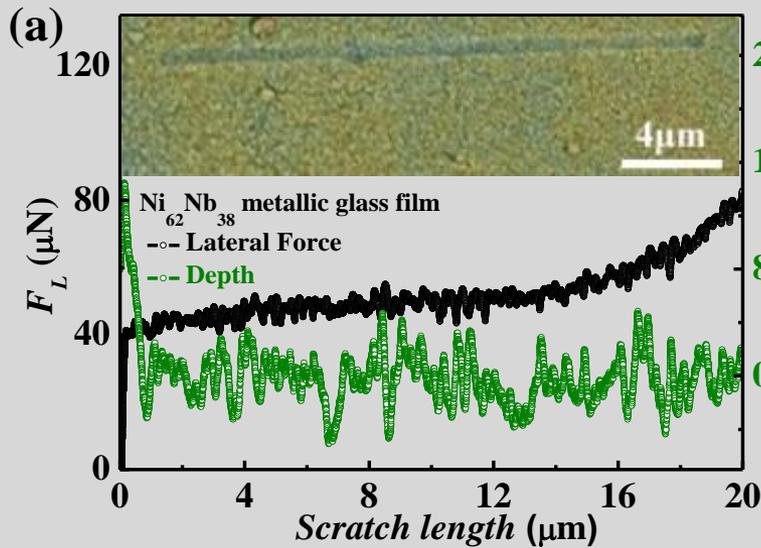
conical indenter



*the scratch length was 20  $\mu\text{m}$ ,  
the moving speed of the nanoindenter  
was 2  $\mu\text{m/s}$ .*

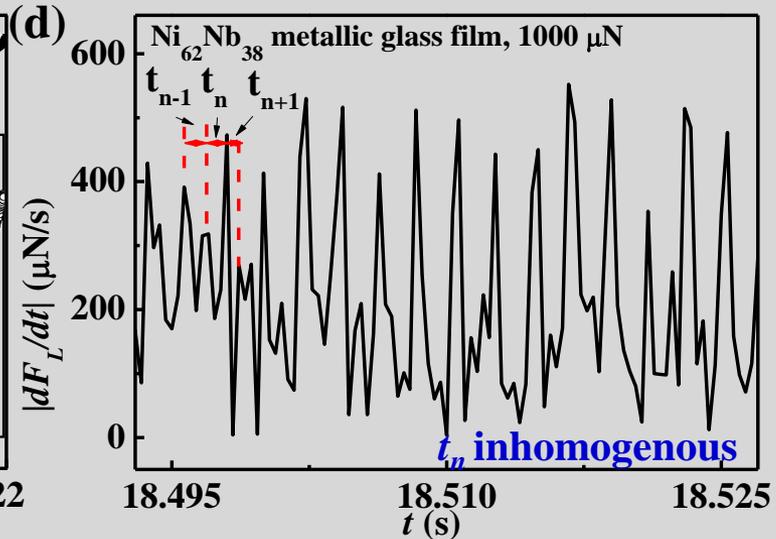
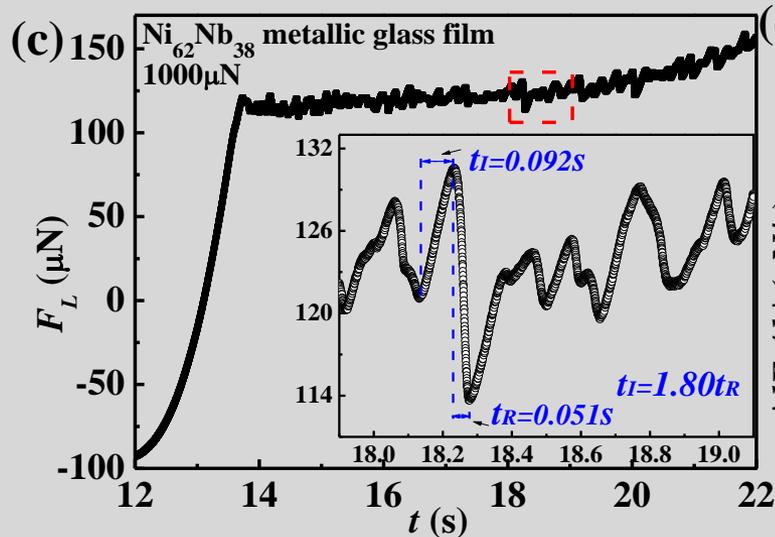
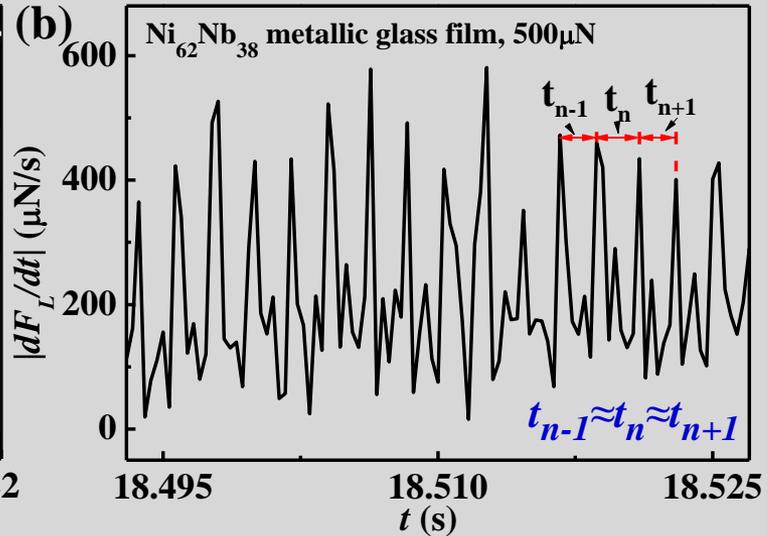
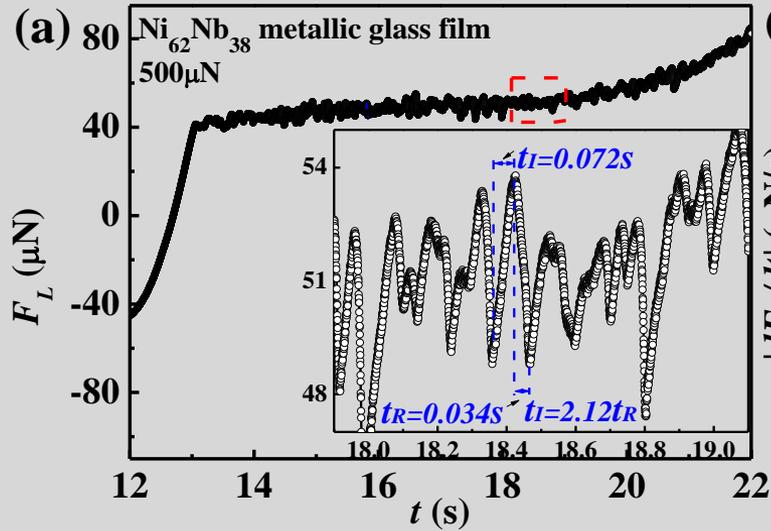


# Part III Stick-slip behavior in nanoscratch



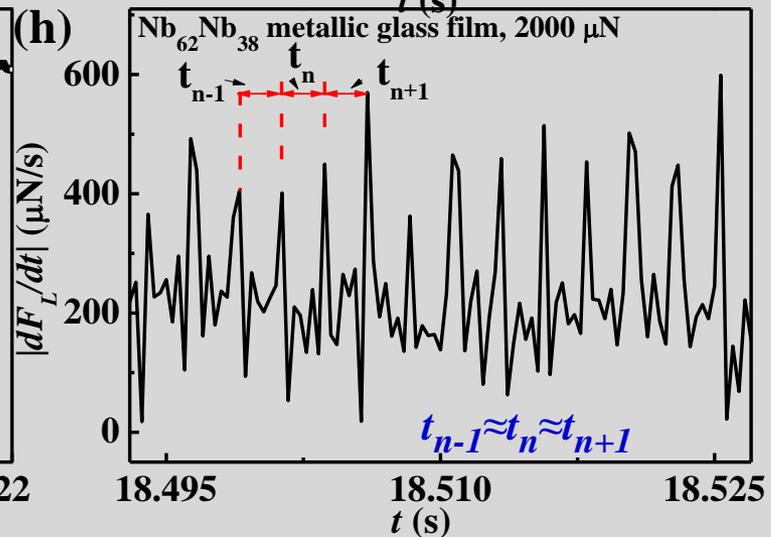
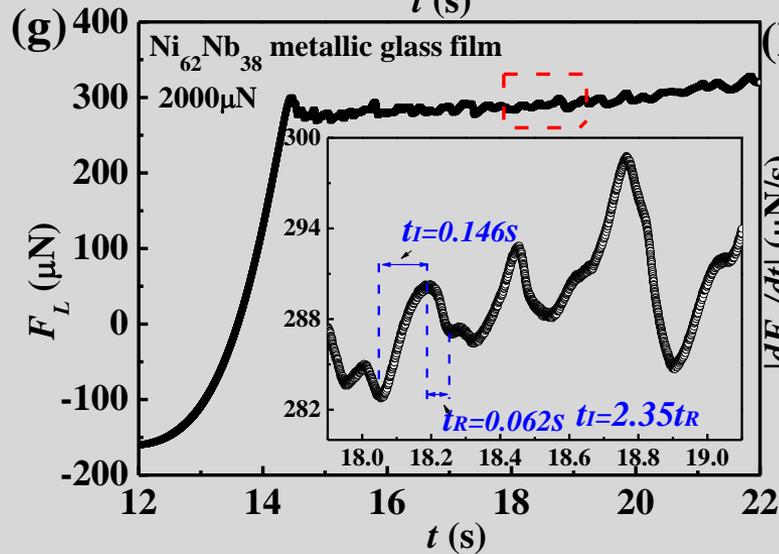
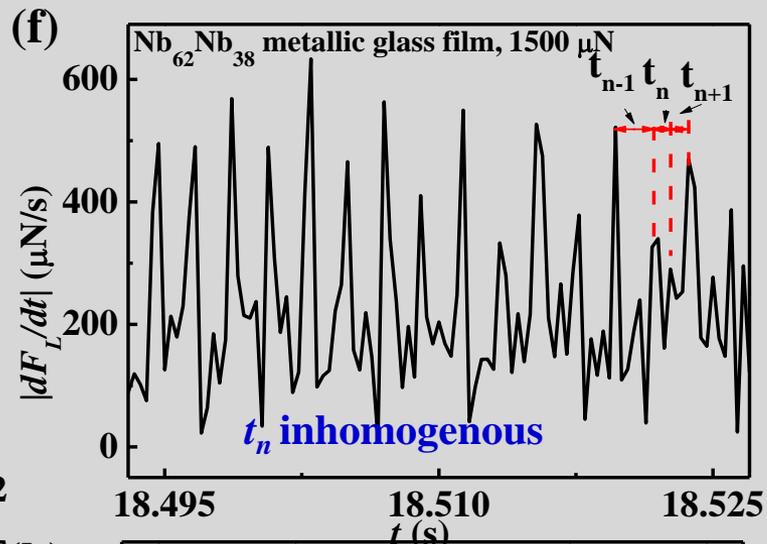
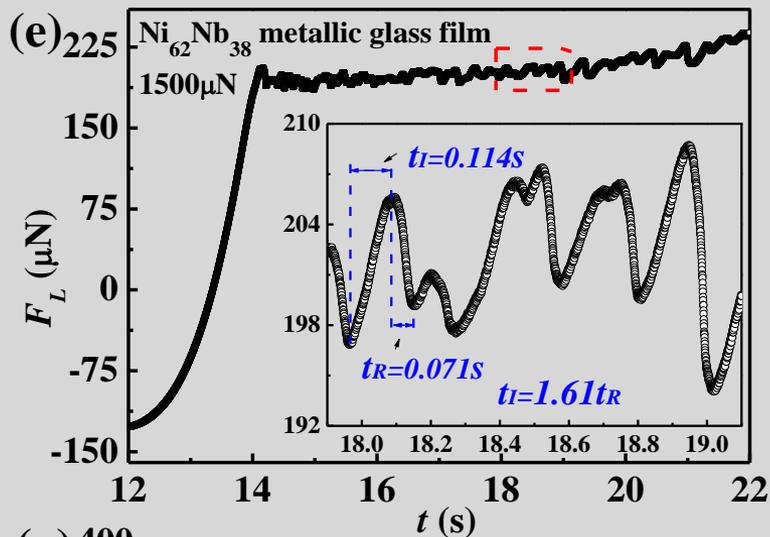


# Part III Stick-slip behavior in nanoscratch



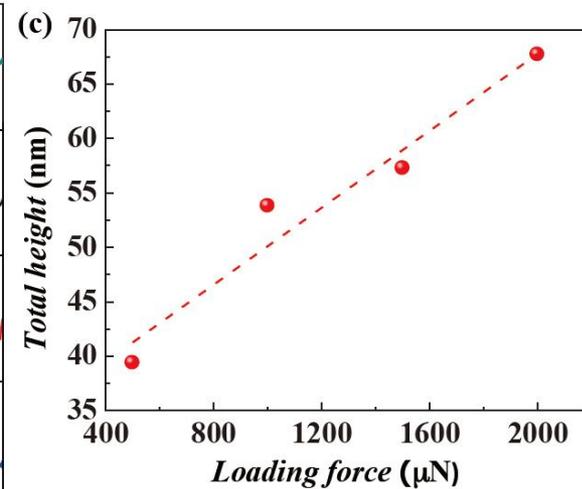
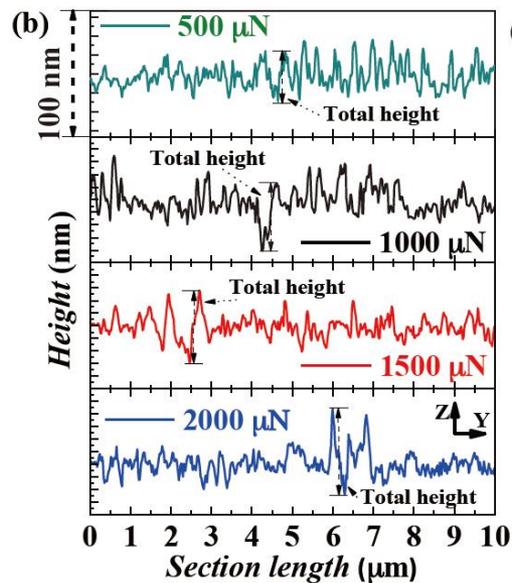
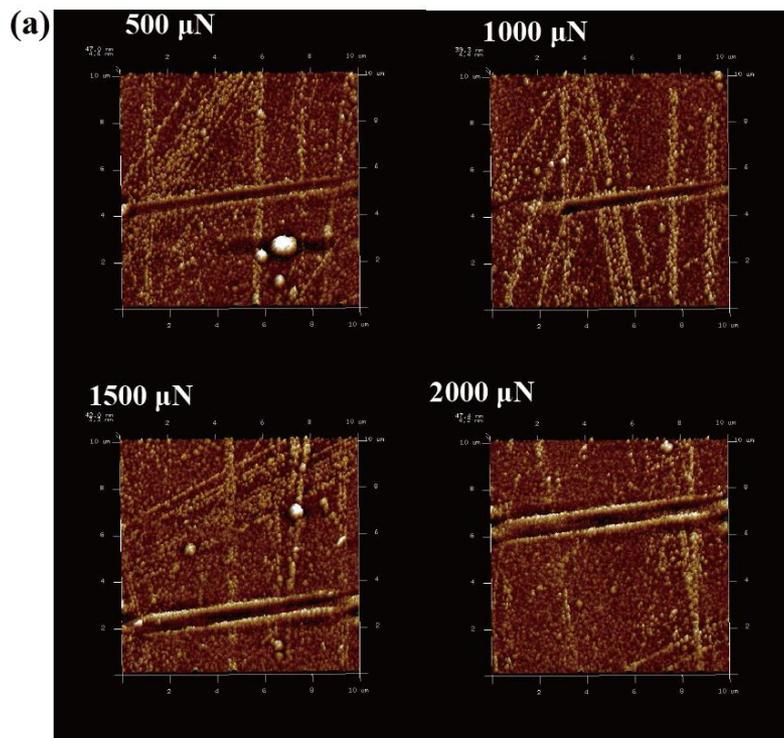


# Part III Stick-slip behavior in nanoscratch



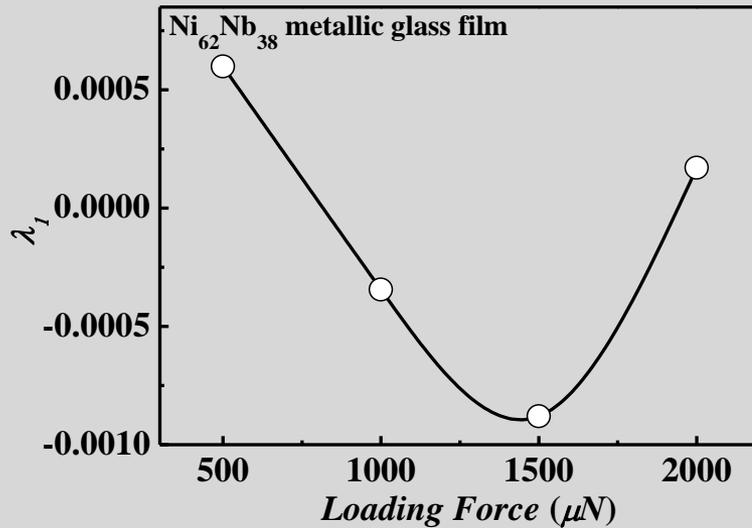


500  $\mu\text{N}$ : without pile-up





# Part III Stick-slip behavior in nanoscratch



$\lambda < 0$ , the phase-space adjacent track is convergent

$\lambda > 0$ , the phase-space adjacent track is diverging

Lyapunov exponent

Loading Force (μN)	500	1000	1500	2000
$t_I(s)$	0.068	0.050	0.078	0.211
$t_R(s)$	0.028	0.028	0.420	0.099
$R$	2.403	1.799	1.850	2.135

$t_I(s)$ : lateral force accumulation time

$t_R(s)$ : lateral force relaxation time



# Part III Stick-slip behavior in nanoscratch

## ✉ Plastic dynamics analysis (**Load-time sequence analysis**)

The Lyapunov exponent in a dynamical system is a quantity that characterizes the rate of separation of infinitesimally close trajectories.

**Method:** Phase space reconstruction

[D.A. Egolf, Nature Phys. 9, 288 (2013). ]

### **Features of SOC behavior**

✉ Negative largest Lyapunov exponent means that the stress –time sequence evolution is convergent.

✉ Stable state

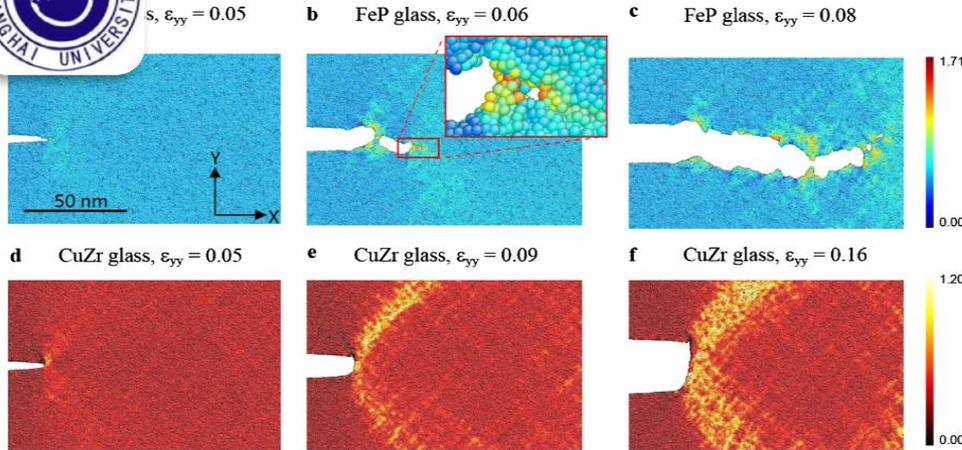
### **Features of chaotic behavior**

✉ Positive largest Lyapunov exponent means that the stress- time sequence evolves separately.

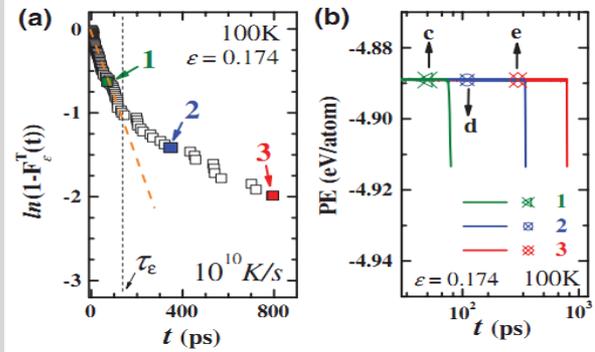
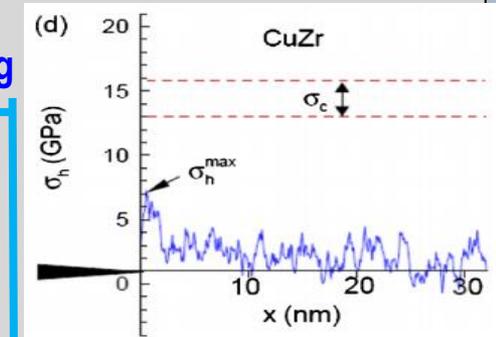
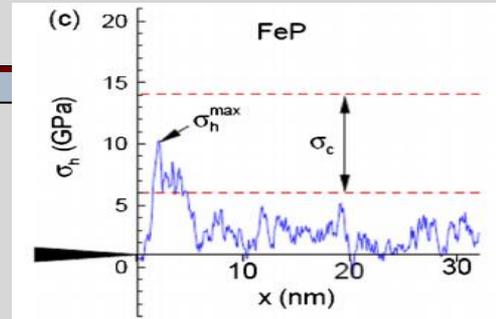
[J.L. Ren and G. Wang, et al .Phys. Rev. B. 86, 134303 (2012)]

[Z.Y. Liu and G. Wang et al. J. Applied Physics. 114, 033521 (2013)]

# Part IV Discontinuous crack propagation



**Brittle:**  
 Cavitation, Nanoscale void nucleation and coalescence  
 Nanoscale density fluctuations, high free volume.  
**Ductile:**  
 Extensive shear banding

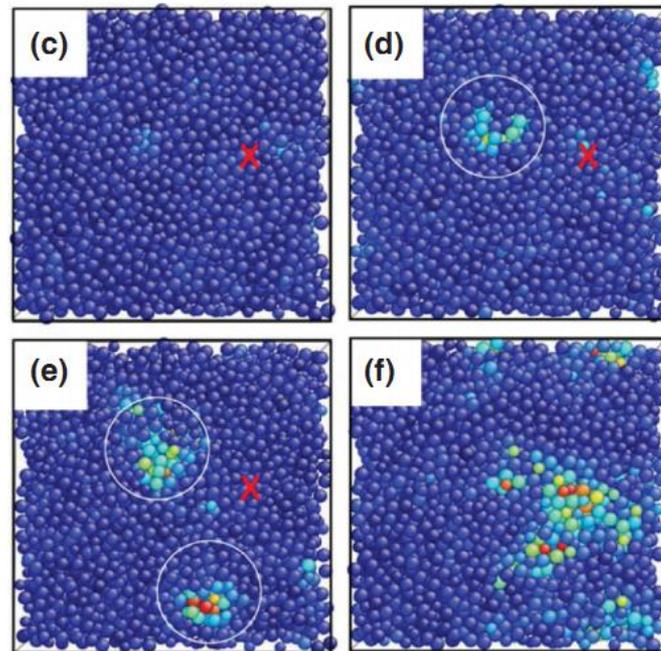


Sudden decrease of PE:  
 cavity nucleation event

Free energy barrier to cavitation

$$\Delta F_c = \frac{4}{3} \pi r_c^3 K (\epsilon - \epsilon_c) - 4 \pi \gamma r_c^2$$

nucleation event. We conclude that cavitation in MG is controlled by the spatial heterogeneity in the glass with preferential nucleation sites able to cavitate by surmounting a free energy barrier that is significantly lower than would be expected in the absence of the effect of cavity radius on surface energy. The relatively smaller activation



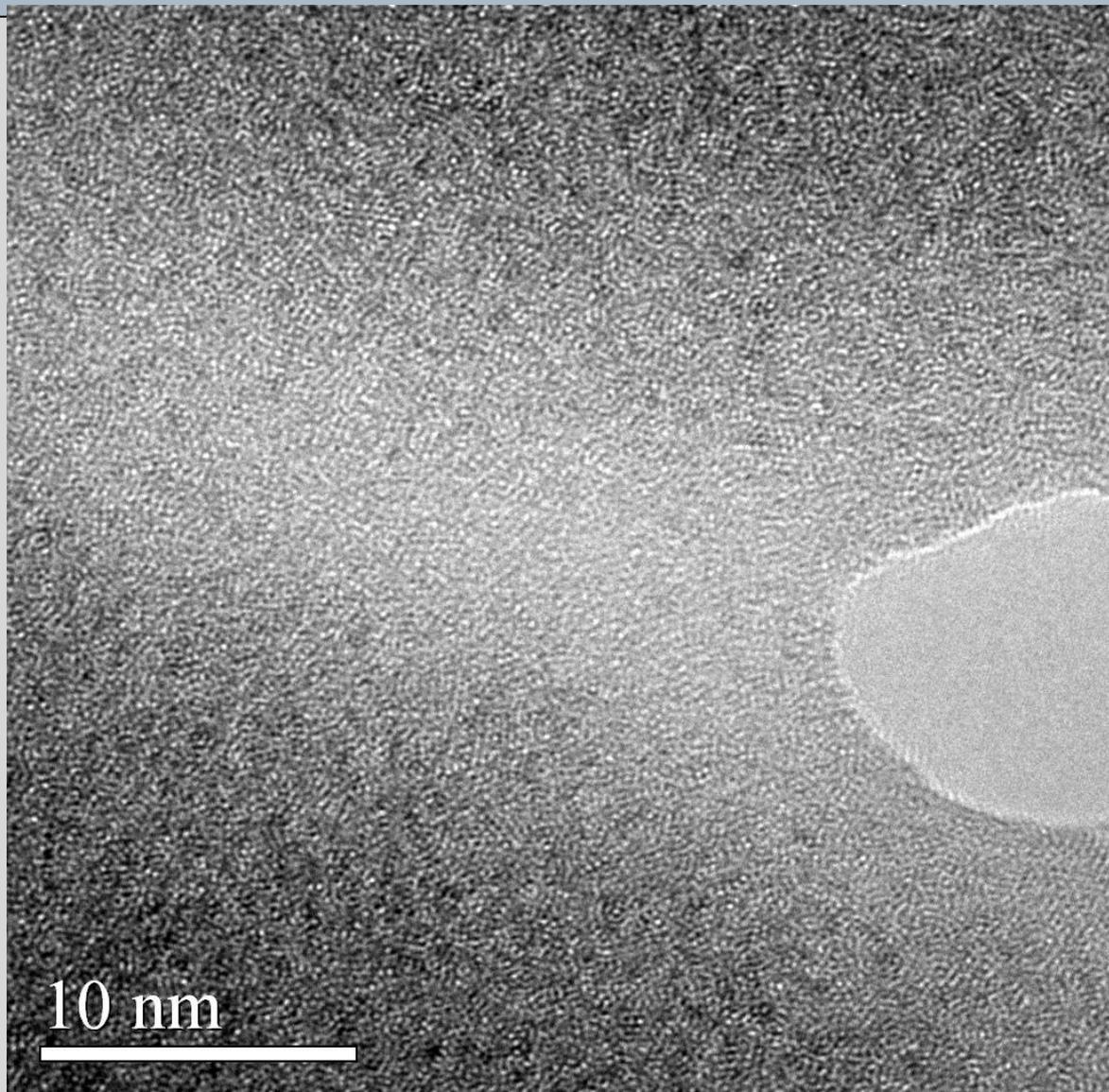
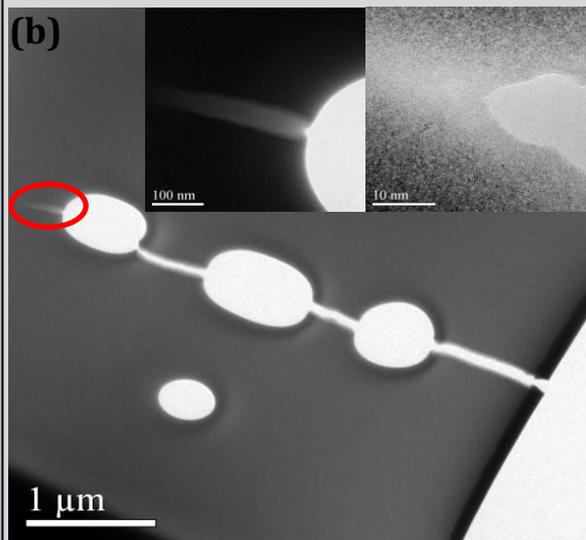
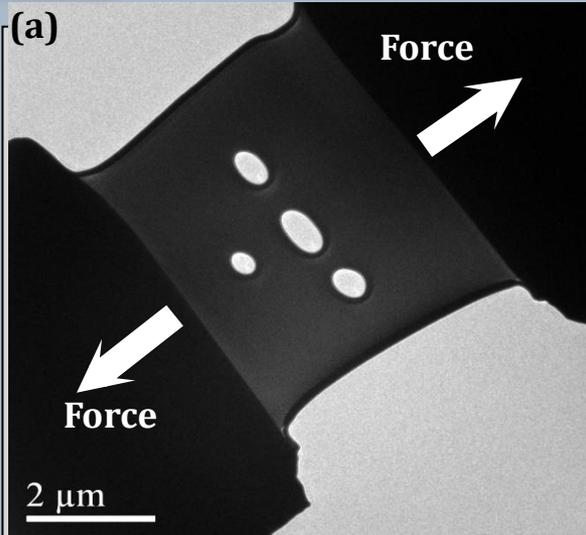
High strain regions

*Phys. Rev. Lett.* 107, 215501 (2011)

*Phys. Rev. Lett.* 110, 185502 (2013)

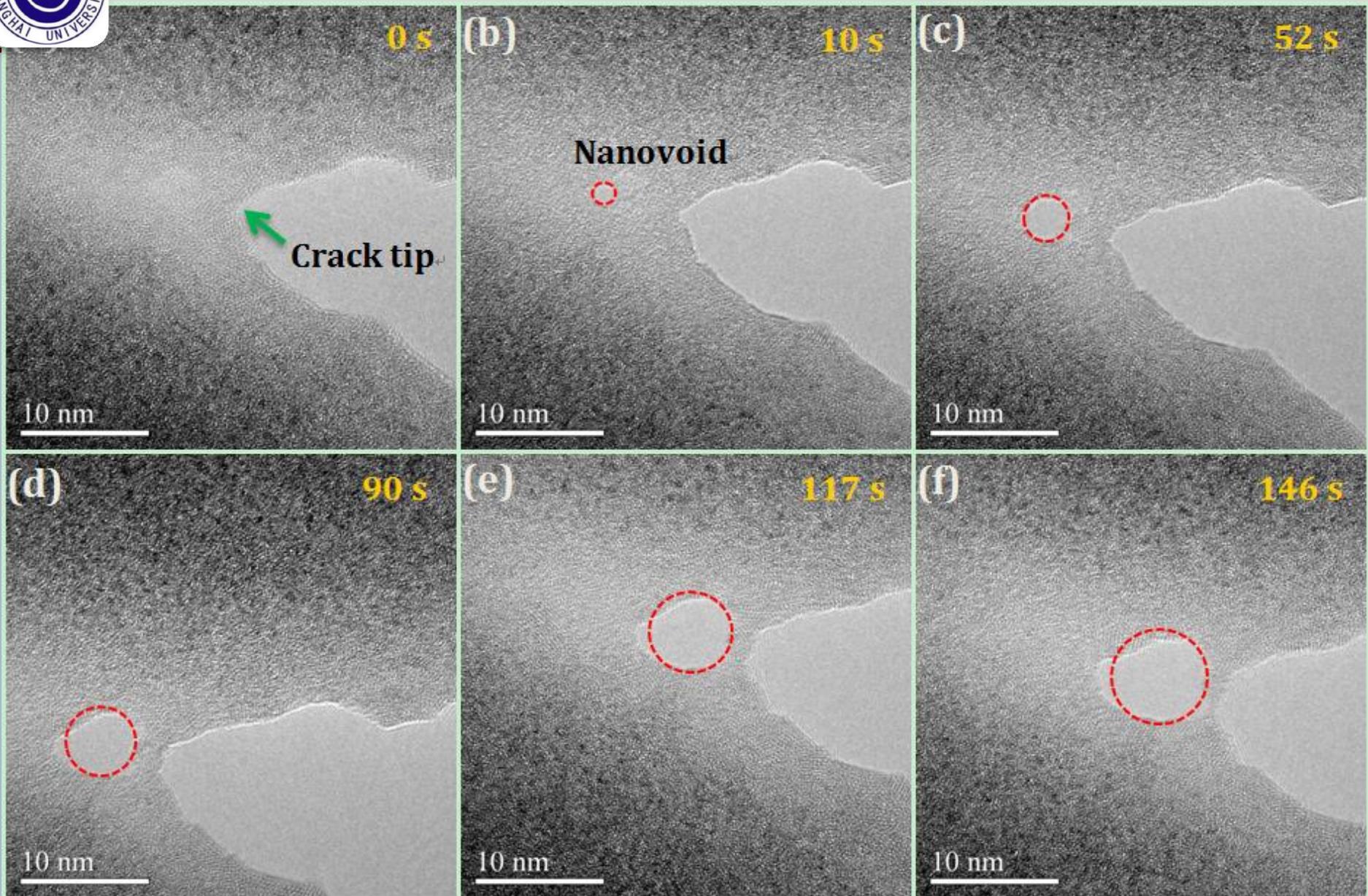


# Part IV Discontinuous crack propagation

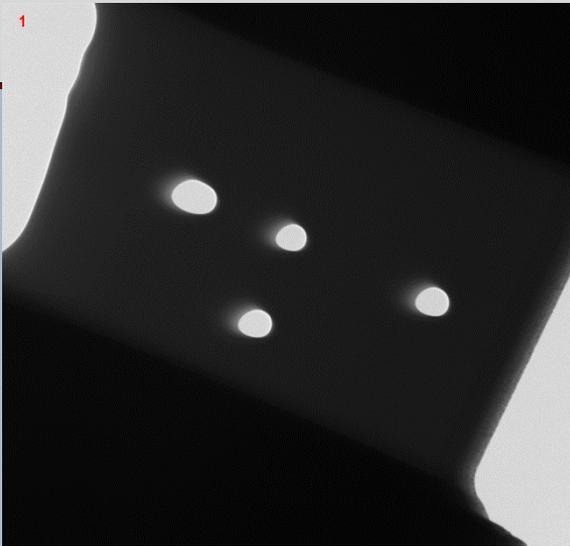




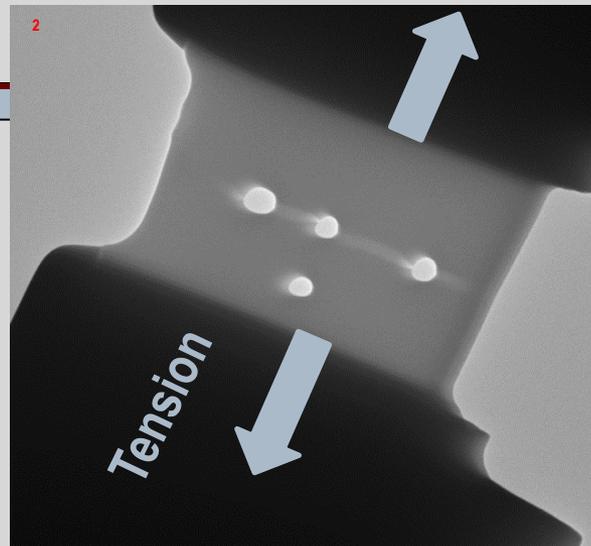
# Part IV Discontinuous crack propagation



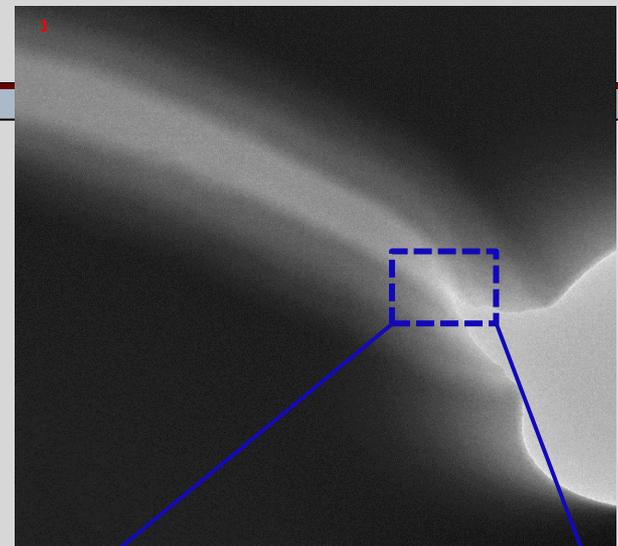
# In-situ TEM tension tests (E-beam irradiation)



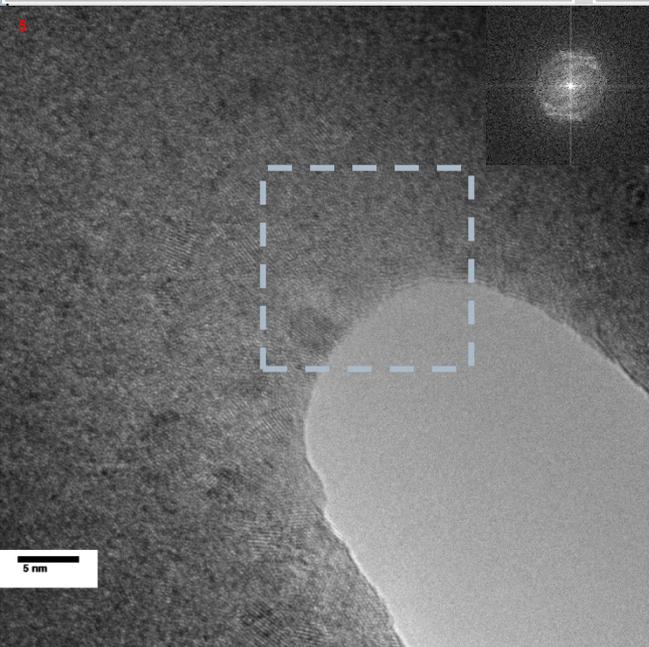
CuZrAl\_014  
Cal: 0.001264  $\mu\text{m}/\text{pix}$   
10:07:34 6/30/2015  
TEM Mode: Imaging  
Camera: , Exposure(ms): 1792 X 1 Gain: 1, Bin: 1  
Gamma: 1.00, No Sharpening, Normal Contrast



CuZrAl\_020  
Cal: 0.002532  $\mu\text{m}/\text{pix}$   
10:37:37 6/30/2015  
TEM Mode: Imaging  
Camera: , Exposure(ms): 250 X 1 Gain: 1, Bin: 1  
Gamma: 1.00, No Sharpening, Normal Contrast

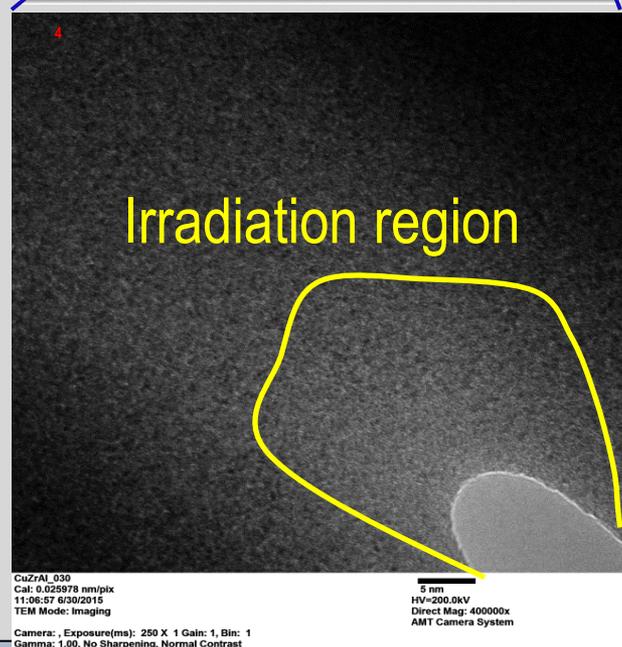


CuZrAl\_024  
Cal: 0.261091  $\text{nm}/\text{pix}$   
10:59:15 6/30/2015  
TEM Mode: Imaging  
Camera: , Exposure(ms): 250 X 1 Gain: 1, Bin: 1  
Gamma: 1.00, No Sharpening, Normal Contrast



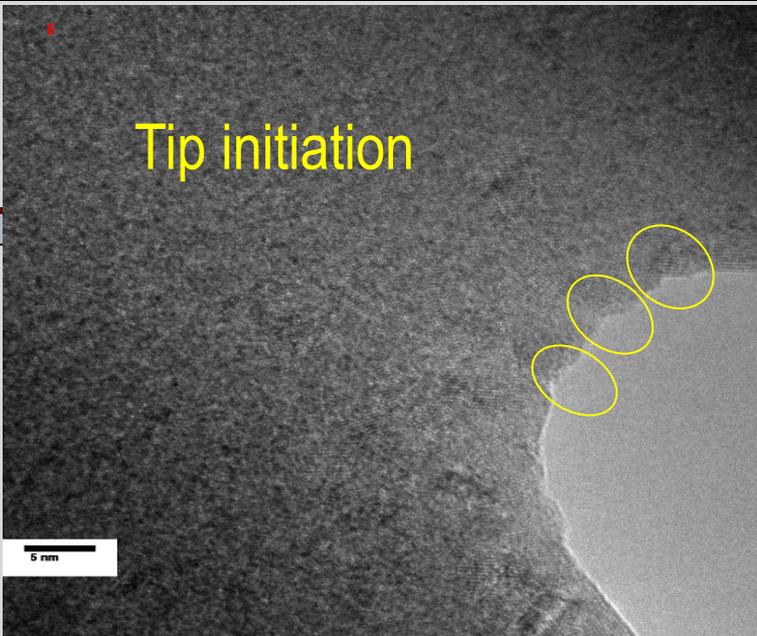
Beam current:  
20-30  $\text{pA}/\text{cm}^2$

Irradiation time:  
30 min

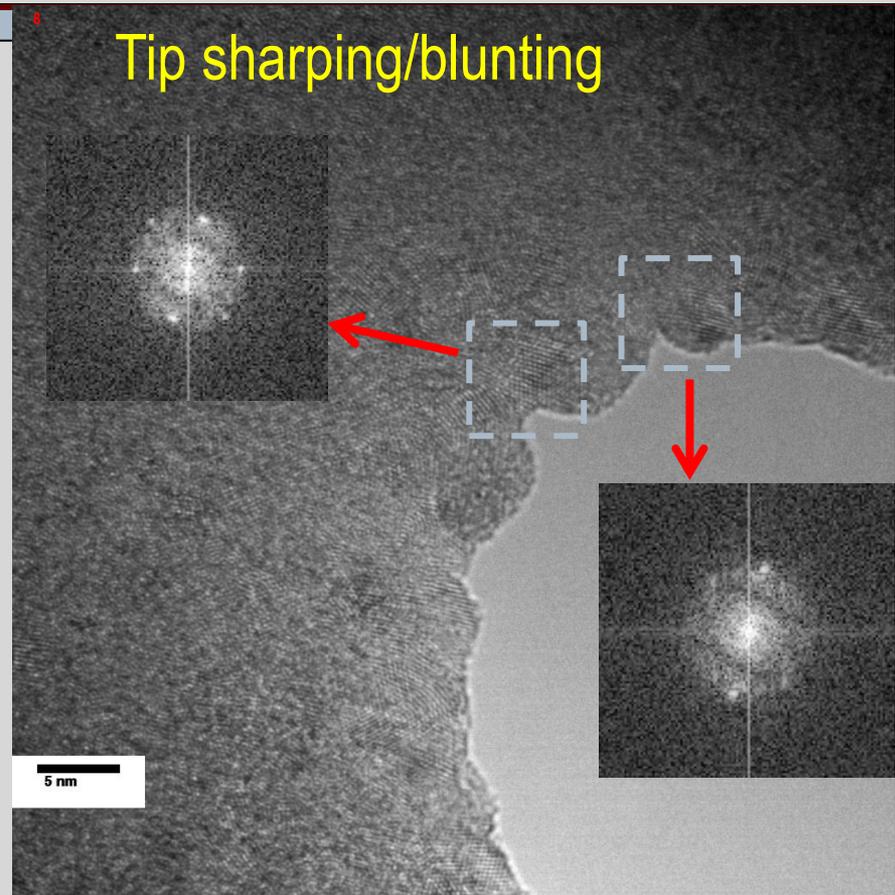


CuZrAl\_030  
Cal: 0.025978  $\text{nm}/\text{pix}$   
11:06:57 6/30/2015  
TEM Mode: Imaging  
Camera: , Exposure(ms): 250 X 1 Gain: 1, Bin: 1  
Gamma: 1.00, No Sharpening, Normal Contrast

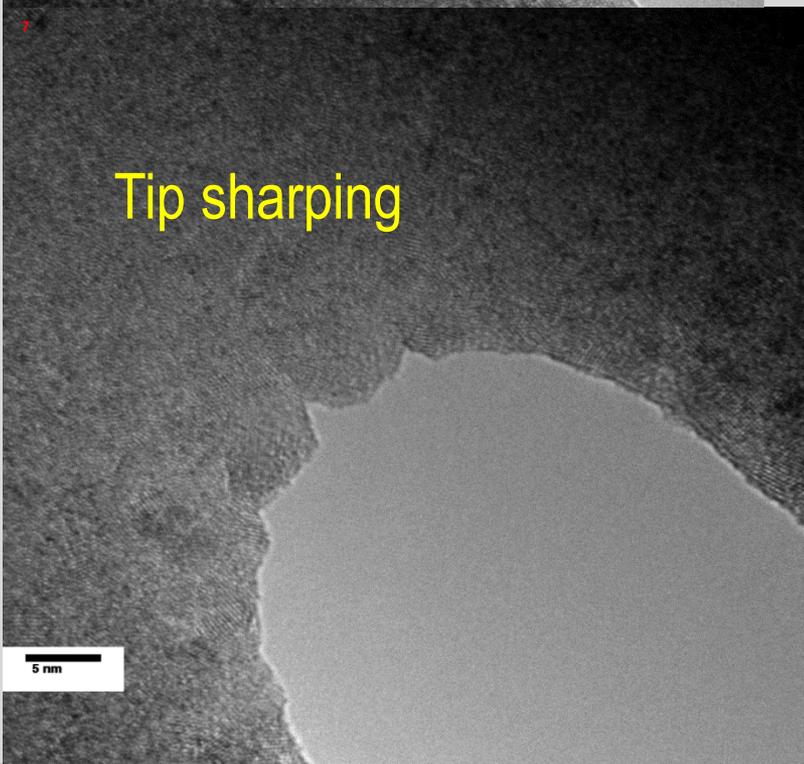
# Tip initiation



# Tip sharpening/blunting

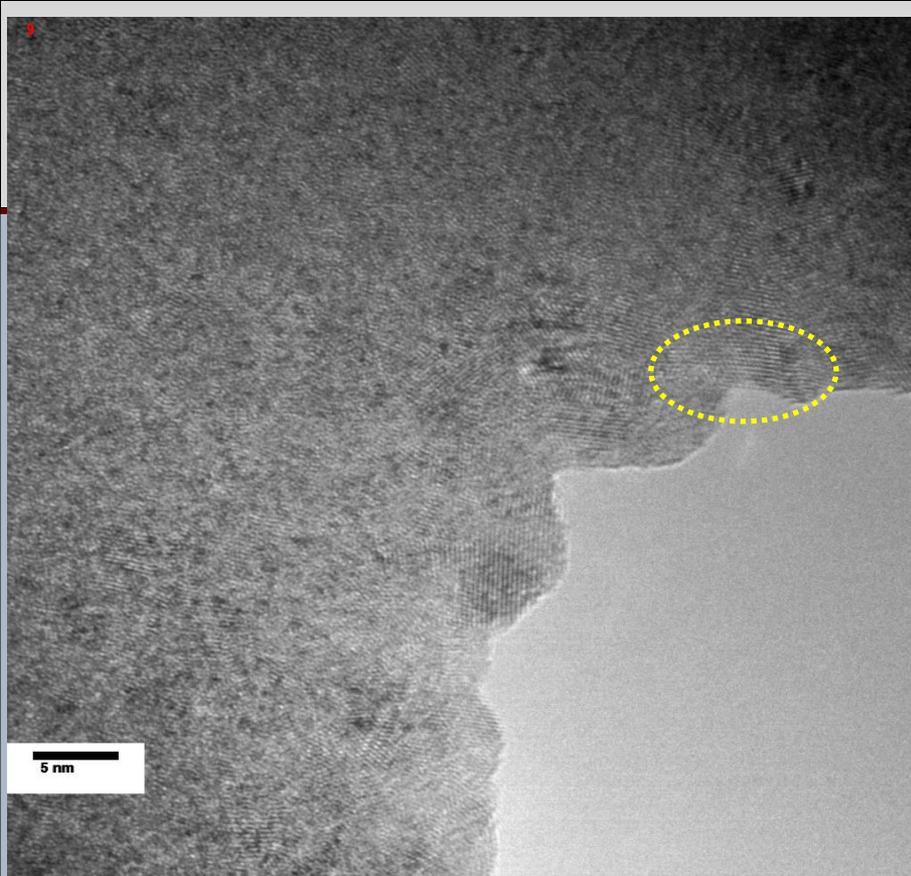


# Tip sharpening

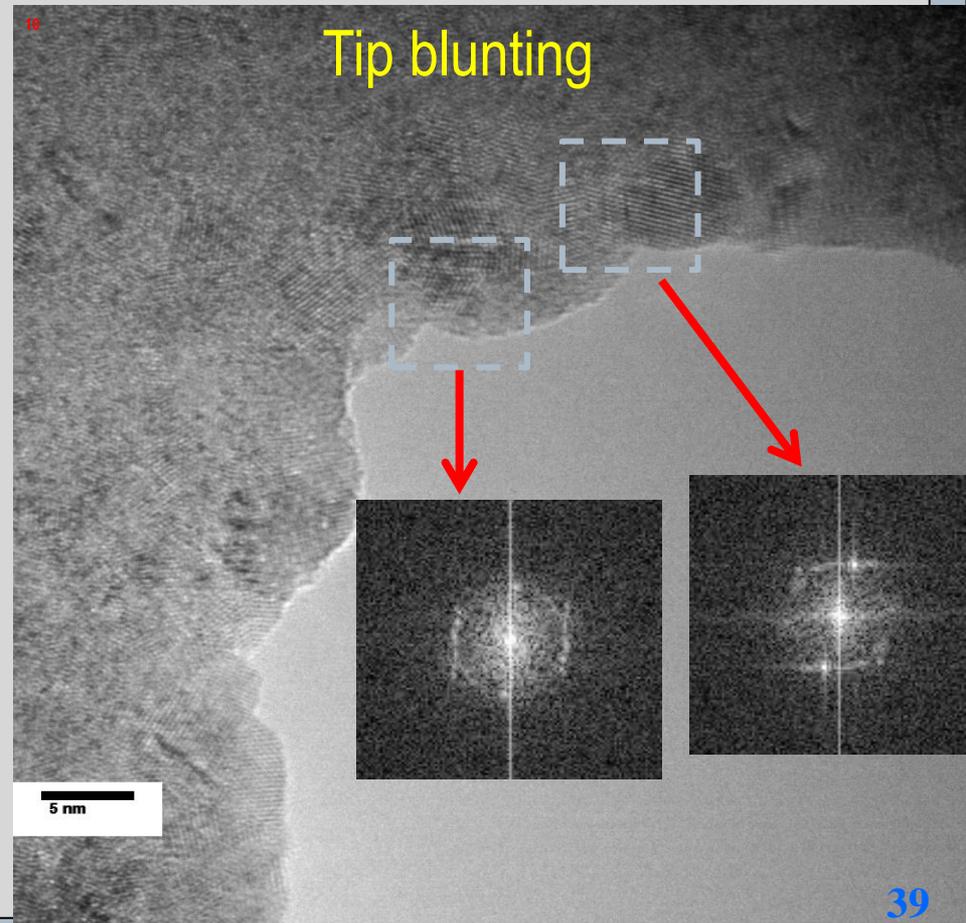


$$\sigma_{\text{effective}}(\text{tip}) = \sigma_{\text{applied}} (a/R_{\text{tip}})^{1/2}$$

The effective stress  $\sigma_{\text{effective}}$  at the tip drops and the crack is blunted, leading to increased toughness



Nanocrystals grow on the tip, and then hinder the crack propagation (delocalization of shear bands).





# Conclusions

## **I. Plastic dynamics of metallic glasses is correlated with chemical components, structures, loading rates and temperatures. SOC behavior can enhance the ductility of metallic glasses.**

- [1] Shear avalanche in plastic deformation of a metallic glass composite. *International Journal of Plasticity*. 2016, 77: 141-155.
- [2] Liaw. Manipulation of free volumes in a metallic glass through Xe-ion irradiation. *Acta Materialia*. 2016, 106: 66-77.
- [3] Scaling behavior and complexity of plastic deformation for a bulk metallic glass at cryogenic temperatures. *Physical Review E*. 2015, 92: 012113 (1-5).
- [4] Plastic Flow of a  $\text{Cu}_{50}\text{Zr}_{45}\text{Ti}_5$  Bulk Metallic Glass Composite. *Journal of Materials Science and Technology*. 2014, 30(6): 609-615.
- [5] Various Sizes of Sliding Event Bursts in the Plastic Flow of Metallic Glasses Based on a Spatiotemporal Dynamic Model. *Journal of Applied Physics*. 2014, 116: 033520 (1-7).
- [6] Low temperature dependent Dynamics Transition of Intermittent Plastic Flow in a Metallic Glass. I. Experimental Investigations. *Journal of Applied Physics*. 2013, 114: 033520 (1-8).
- [7] Low Temperature dependent Dynamics Transition of Intermittent Plastic Flow in a Metallic Glass. II. Dynamics Analysis. *Journal of Applied Physics*. 2013, 114: 033521 (1-8).
- [8] Plastic Dynamics Transition between Chaotic and Self-Organized Critical States in a Glassy Metal via a Multifractal Intermediate. *Physical Review B*. 2012, 86: 134303 (1-8).
- [9] Self-organized Intermittent Plastic Flow in Bulk Metallic Glasses. *Acta Materialia*. 2009, 57: 6146.

## **II. Nanoscratch tests suggest a discontinuous slip occurring on the surface.**

- [1] Cutting Characteristics of Zr-Based Bulk Metallic Glass. *Journal of Materials Science and Technology*. 2015, 31: 153-158.
- [2] Shear Avalanches in Metallic Glasses under Nanoindentation: Deformation Units and Rate Dependent Strain Burst Cut-off. *Applied Physics Letters*. 2013, 103: 101907.
- [3] Stick-slip dynamics in a  $\text{Ni}_{62}\text{Nb}_{38}$  metallic glass film during nanoscratching. *Acta Materialia*. 2017 .

## **III. Crack propagation is a discontinuous process.**

Thank you for your attention!