イオンビームを用いた物性改質および分析
Ion Beam Material Modifications & Analysis

松波紀明 (N. Matsunami)

International Conference, Symposium(国際会議):

- Ion Beam Modifications of Materials (IBMM),
- Ion Beam Analysis (IBA),
- Radiation Effects in Insulators (REI) ,
- Atomic Collisions in Solids (ACS),
- Swift Heavy Ions in Matter (SHIM),
- Plasma Surface Interactions (PSI), • PFMC,
- Plasma Based Ion Implantation & Deposition (PBIID),
- Surface Modifications of Materials by Ion Beam (SMMIB),

Acknowledgements

Many staffs Nagoya University,

AIST(産総研), JAEA(原研),

NIFS (核融合研)

Many students

Outline

1. Interaction of ions with solids
2. Fundamentals of Ion Beam Analysis
3. Channeling
4. Ultra high-resolution proton energy loss spectroscopy
5. Ion beam material modification
   (a)TiO_2, catalysis, (b) doped-ZnO
   (c) Reaction of N ions with nitride film
6. Plasma Surface Dynamics with IBA
   in-situ D detection under plasma exposure
7. Electronic sputtering
8. Ion impact effects on graphene, Mn-doped ZnO
9. Concluding remarks

Collision of Energetic Ions with Atoms in Solids

1.Resulting in energy deposition

Elastic Collision（弾性衝突）;

[atom knock-on（はじき出し）]

collisions without electronic excitation

dpa (displacement per atom) is a measure of elastic collisions

Inelastic Collision（非弾性衝突）

electronic excitation & ionization, usually no effects, however, in some cases leading to atomic displacement

*イオンビームによる物性改質

1. Energy Deposition（エネルギー付与）

2. Reaction of Ions with Atoms（イオンと物質との化学反応）

3. Reaction between Ions（イオン間化学反応）

·<u>電子·原子構造改質</u>: Electronic & Atomic Structure Modification

·電気特性、光学特性、化学特性、磁気特性の改質

<u>Characteristic Effects by Ion Impact?</u>

*熱力学的非平衡：Non-thermal processing

*[損傷(damage)というイメージからの脱却]

*Ion Beam Analysis (non-destructive) イオンビーム分析（非破壊）

組成、不純物、薄膜の厚さ（composition, impurities, film thickness）

不純物（特に、H, C, N, O等軽元素, light impurities）

2009 brings with it the 100th anniversary of the first Rutherford Backscattering Spectroscopy experiment performed by H. Geiger and E. Marsden (a student) under the supervision of Ernest Rutherford at the University of Manchester.

Ion Beam Analysis (イオンビーム分析)

k (kinematic factor) ---> m_2 (質量)

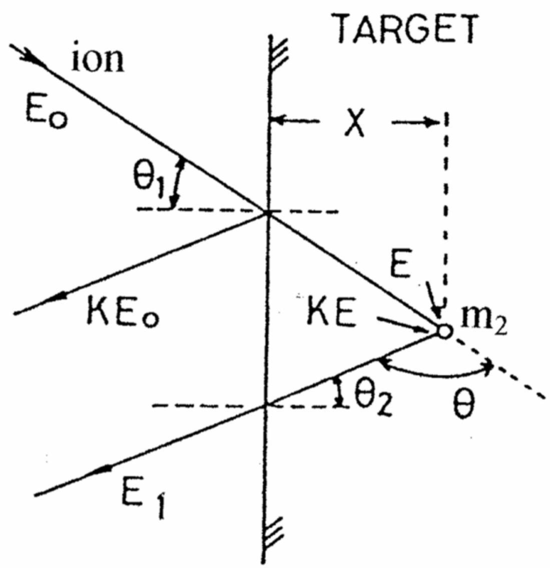
$\Delta E=(kE_o - E_1) =[dE/dx]*x$ ---> depth x (深さ)

[dE/dx]: stopping power factor (阻止能因子)

$$\Delta E = k\int dx(dE/dx)in/\cos\theta_1 + \int dx(dE/dx)in/\cos\theta_2$$

For small x (surface approximation, 表面近似),

$$[dE/dx] = \{k(dE/dx)_{Eo}/\cos\theta_1 + (dE/dx)_{kEo}/\cos\theta_2\}$$



Single scattering approximation in IBA

イオン散乱分析法における 1 回弾性散乱過程

RBS: Rutherford Backscattering Spectroscopy （ラザフォード後方散乱法）

NRA: Nuclear Reaction Analysis （核反応分析法）

ERD: Elastic Recoil Detection （弾性反跳法）

Samples (mainly Polycrystalline Thin Films）

Oxides；ZnO, ZnO(Al, In, Mn), Cu_2O, CuO, TiO_2, SiO_2, WO_3, Fe_2O_3, $SrCeO_3$, High Tc superconductors etc.

Nitrides；Si_3N_4, AlN, (TiN), Cu_3N, WN etc

Others；C(graphite, graphene), Si, Sapphire, MgO, W, SiC

Equipments

In campus; Accelerators ２ MV AN VG,
KNVG (shut down March 2013)
２００kV ion accelerator
XRD、RF-sputter film deposition

Off campus; optical、AFM（AIST）
Plasma・Material Interaction（NIFS、JAEA）
High-energy ion、RF-sputter depo.（JAEA）

Energy; ~ 200 MeV

Ion; H – Au

10 eV/u - 2 MeV/u

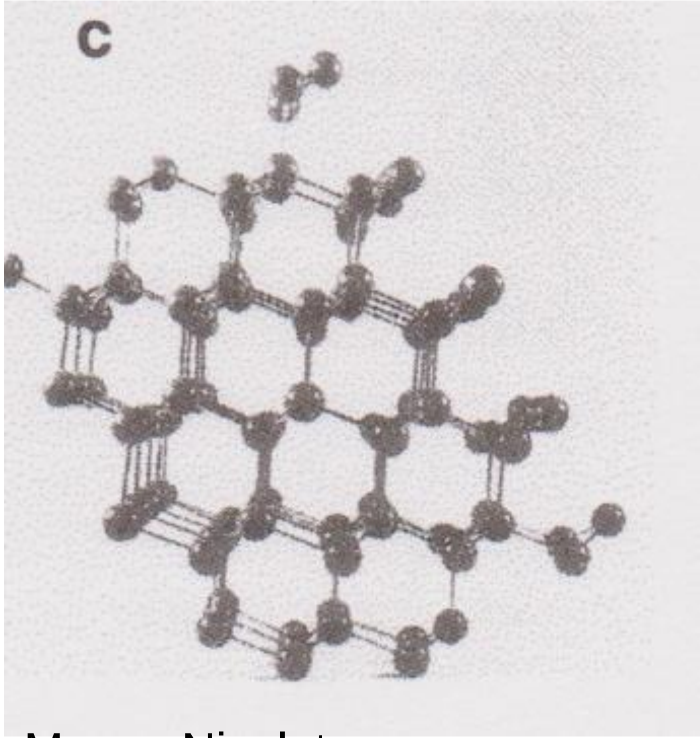
Low energy < 10 keV,

mainly elastic energy deposition

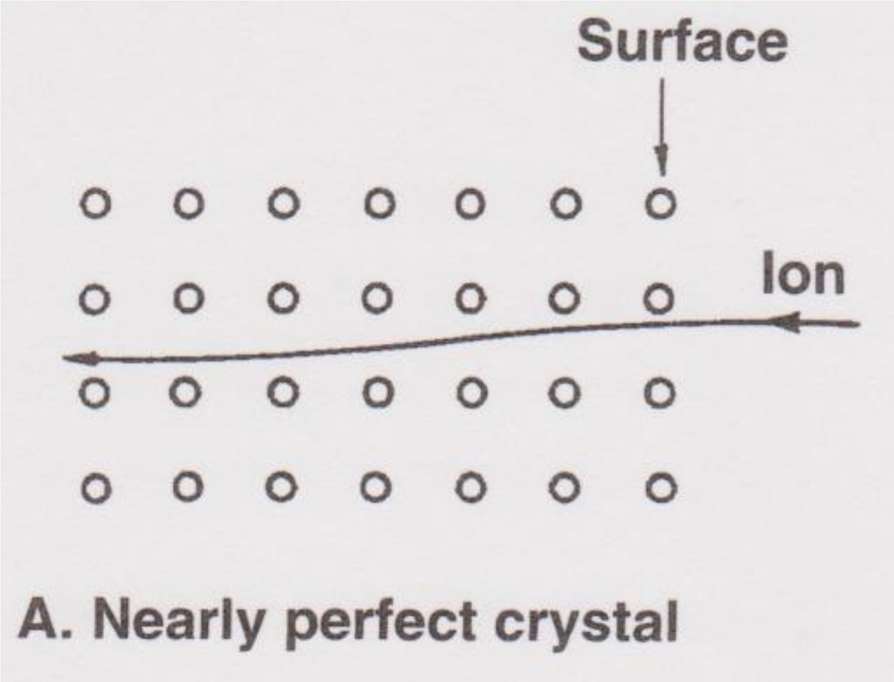
High energy >1 MeV

mainly inelastic energy deposition

Ph. D. Thesis: Uses of Channeling Technique for Determination of Defect Concentration and Structures in Crystals (1976)

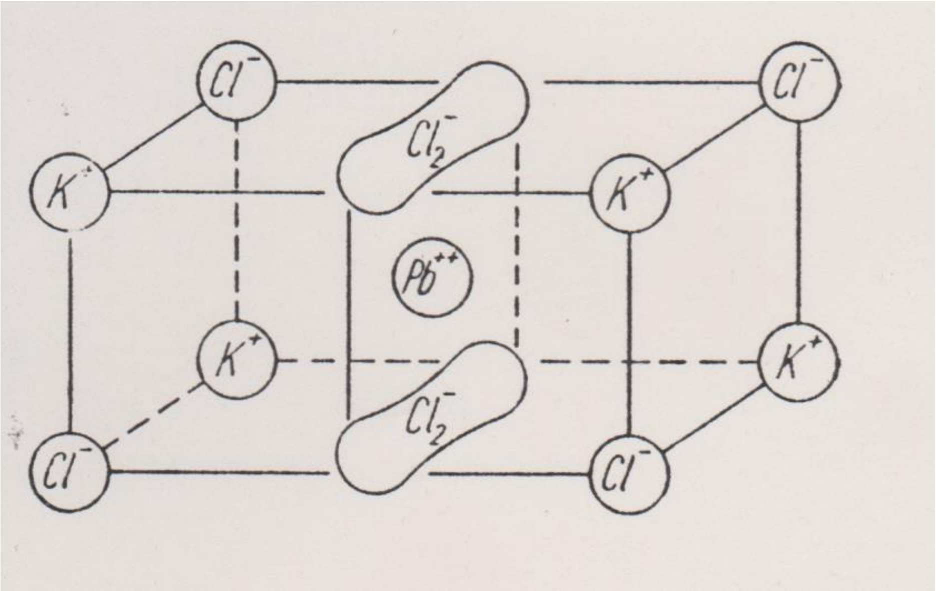


Chu, Mayer, Nicolet, Backscattering Spectrometry, Academic Press, 1978



Tesmer et al. ed. Handbook of modern ion beam material analysis , MRS, 1995

Location of Pb impurities in Pb-Cl interstitials in KCl



Pb is located near face center within 0.04 nm.

Matsuanmi, Yokoyama, Itoh, Phys. Stat. Sol. b75(1976)483.

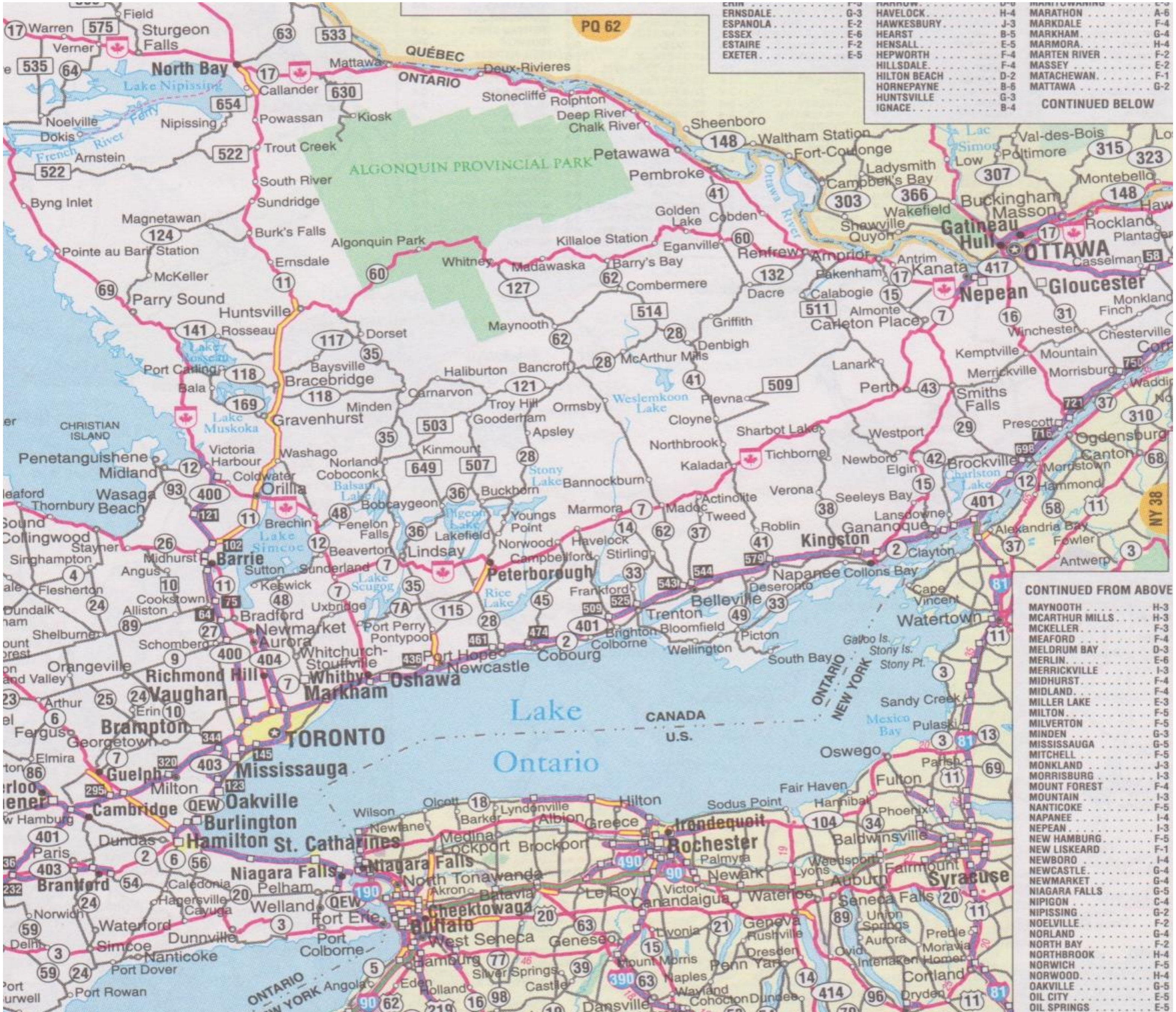
For Al-0.1%Mn, location of Mn solute in Mn Al-interstitial (mixed dumbbell, <100> split configuration).

Matsuanmi, Swanson, Howe, Can. J. Phys. 56(1978)1057.

1976~1978,
Solid State Science Branch, Chalk River Nuclear Laboratories, Atomic Energy of Canada Limited (AECL), Chalk River, Ontario, Canada


CANADA
ARCTIC OCEAN
Ellesmere Island
GREENLAND
0 600 km
0 360 miles
ALASKA (USA)
Melville Island
Banks Island
Devon Island
Baffin Bay
Arctic Circle
Baffin Island
Victoria Island
Dawson City
Nunavut
Auyuittua
Yukon
Northwest Territories
ATLANTIC OCEAN
Whitehorse
Watson Lake
Yellowknife
Great Slave Lake
Newfoundland
Hudson Bay
Wood Buffalo
British Columbia
Alberta
L'Anse-aux-Meadows
Churchill
Prince George
Manitoba
St John's
Rocky Mountains
Edmonton
Quebec
Prince Edward Is
Vancouver
Saskatchewan
Lake Winnipeg
Gaspésie Park
Charlottetown
The Prairies
Victoria
Calgary
Ontario
Bay of Fundy
Regina
Winnipeg
Quebec City
Halifax
Lunenburg
Montreal
Algonquin Park
Ottawa
UNITED STATES OF AMERICA
Toronto
Niagara Falls
ATLANTIC OCEAN

LOW
HILLS
MTS
CLICK HERE FOR LARGER MAP
Fort Severn
Manitoba
Winisk
250 mi
250 km
Winisk River
James Bay
Severn River
Attawapiskat River
Ontario
Akimiski Is.
Canadian Shield
Albany River
Moosonee
Ear Falls
Quebec
Kenora
Lake Seul
Missinaibi River
Lake of the Woods
Lake Nipigon
Lake Abitibi
Thunder Bay
Kirkland Lake
Lk. Superior
©GraphicMaps.com
Sault Ste. Marie
Ottawa River
MN
GREAT LAKES
Sudbury
North Bay
Ottawa
Lk. Huron
St. Paul
WI
Kingston
Owen Sound
Toronto
Madison
Lk. Mich.
MI
Mississauga
Lk. Ontario
NY
London
Niagara Falls
IA
Detroit
St. Catharines
Chicago
Chatham
Lk. Erie
Hamilton
PA

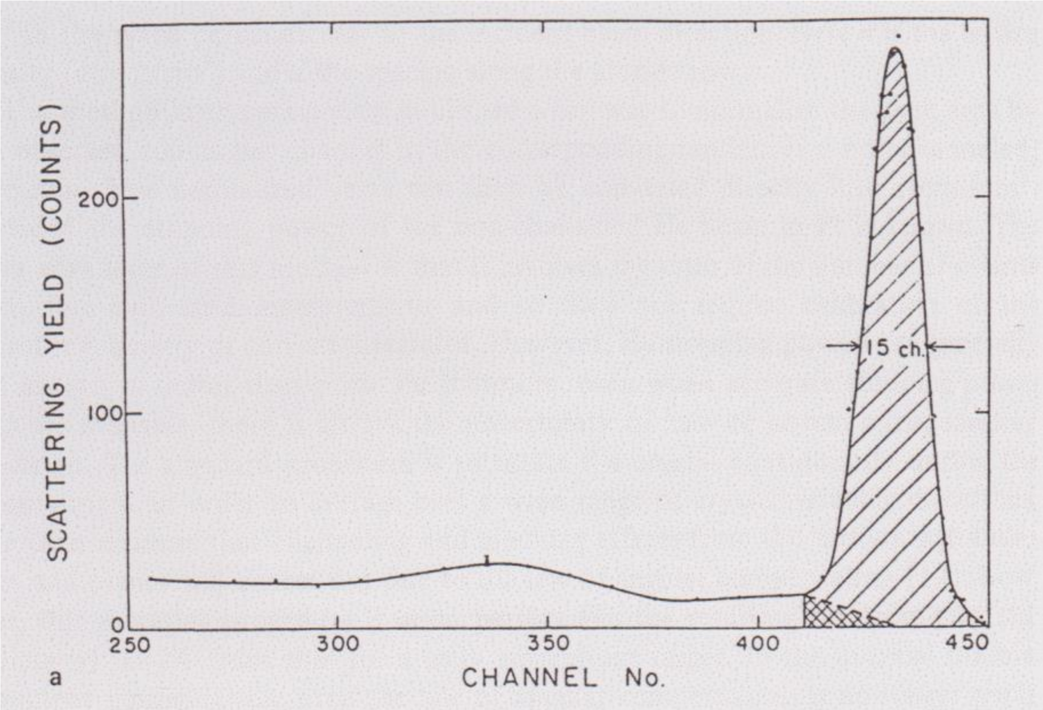


CONTINUED BELOW

CONTINUED FROM ABOVE

Mont-Tremblant Prov. Park

Surface relaxation of Pt(111)



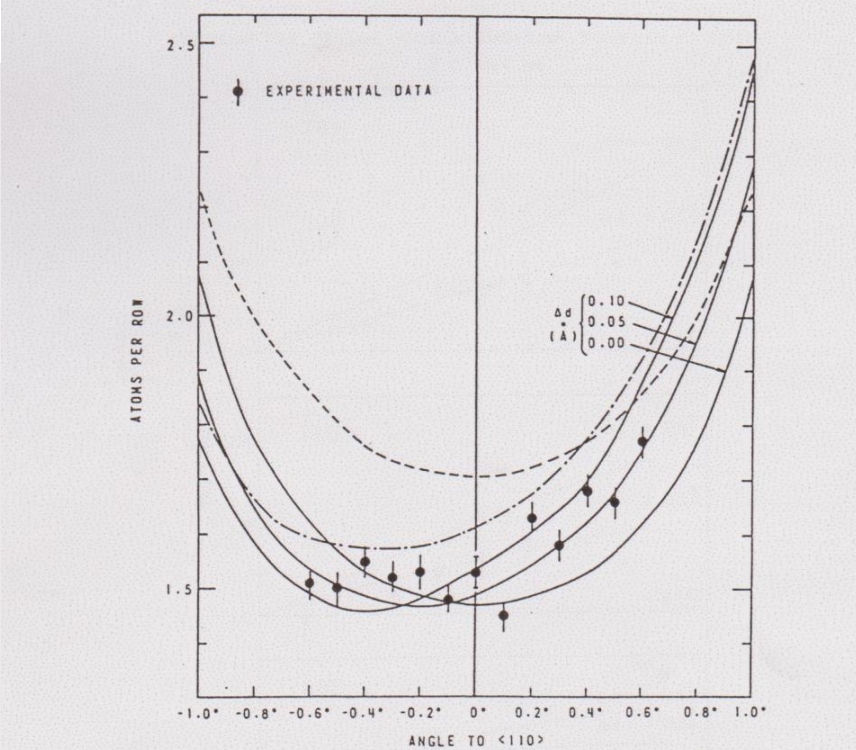


Fig. 6. Angular scan of the ⟨110⟩ surface peak on Pt(111) at 120 K using a 2.0 MeV He beam. The upper (– – –) curve is a Monte Carlo simulation, based on Somorjai's [21] anisotropic surface vibration value (i.e. $\theta_\perp$ = 111 K) and assuming Δd = 0. The other curves are based on the same set of assumptions, as in fig. 5.

Outward relaxation by 0.003 nm

Davies, Jackson, Matsunami, Norton, Andersen, Surf. Sci. 78(1978)274.

Unpublished data,

Explanation is difficult to the observations.

Proton Energy Loss Spectroscopy

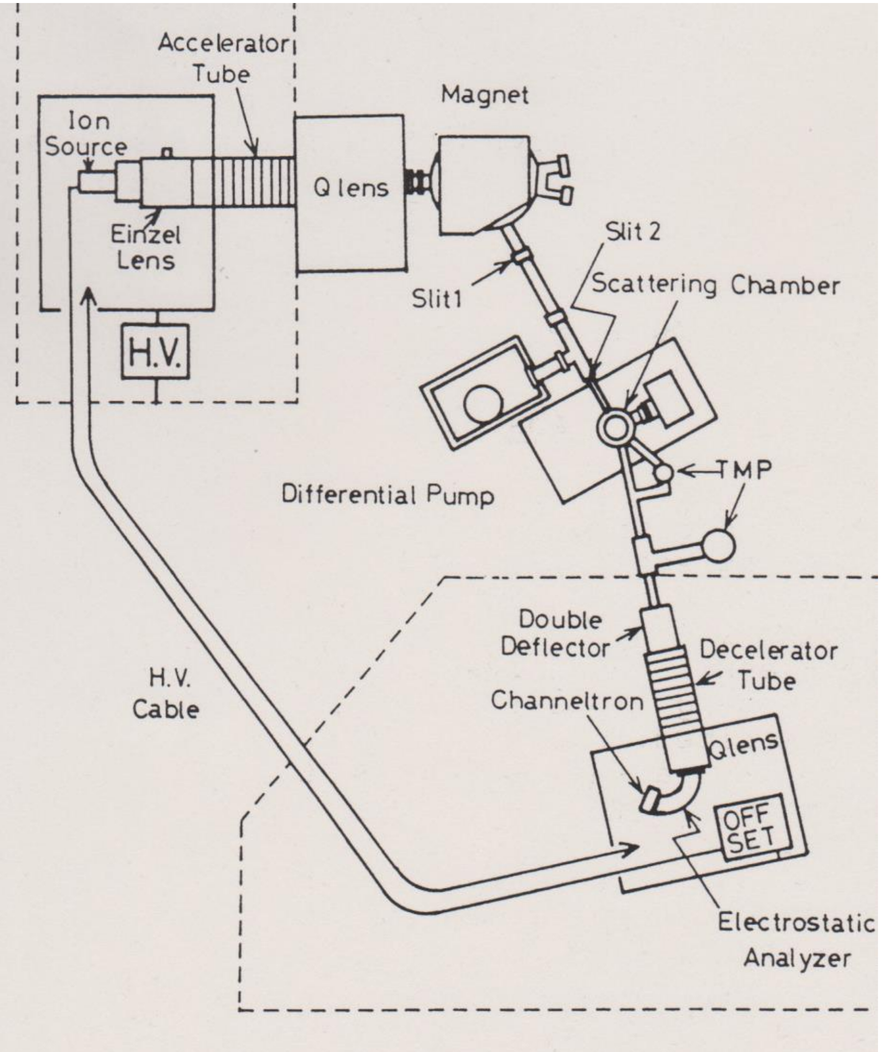


Fig. 1. A sketch of the high-resolution proton energy-loss spectrometer (after Oku et al., 1986).

100 keV Proton
Energy resolution ~20 eV, adequate to resolve surface monolayer.

Matsunami, Scanning Microscopy 1(1987)1593.

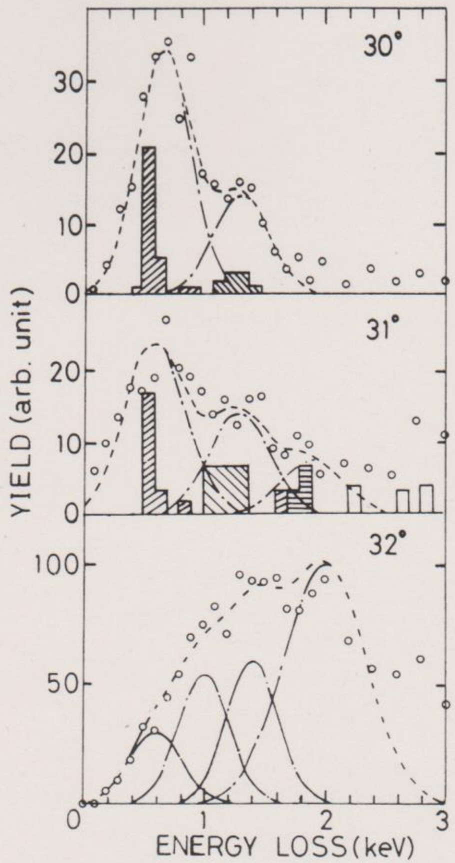


Fig. 2. Energy loss spectra of 100 keV H^+ on a W(111) surface obtained by PELS-I (open circles). Incoming and outgoing angles are 6° from the surface (scattering angle = 12°), and the azimuthal angle $\phi = 30°$ means the direction along ⟨211⟩. The dashed curves are the multi-Gaussian fit to the data, and each contribution is indicated by a dot–dashed line. Histograms are the results of computer simulations for a surface contraction of ~ 5 pm and a reduced Debye temperature 200 K of the normal component of surface atom vibration. The scattering intensity from each layer is indicated by (////) for the first, (\\\\) for the second, and (≡) for the third layer, respectively.

100 keV P on W(111) surface

Monolayer resolution

*Layer spacing

Lattice vibration of surface layer

Matsunami, Kitoh, Knasaki, Itoh, NIM B45(1990)412.

Au on Si(111),

Pd on Si(111), Pd-silicide formation

Kanasaki, Itoh, Matsunami, Appl. Phys. Lett. 51(1987)1072.

Energy loss in Carbon films with PELS；100 keV Proton

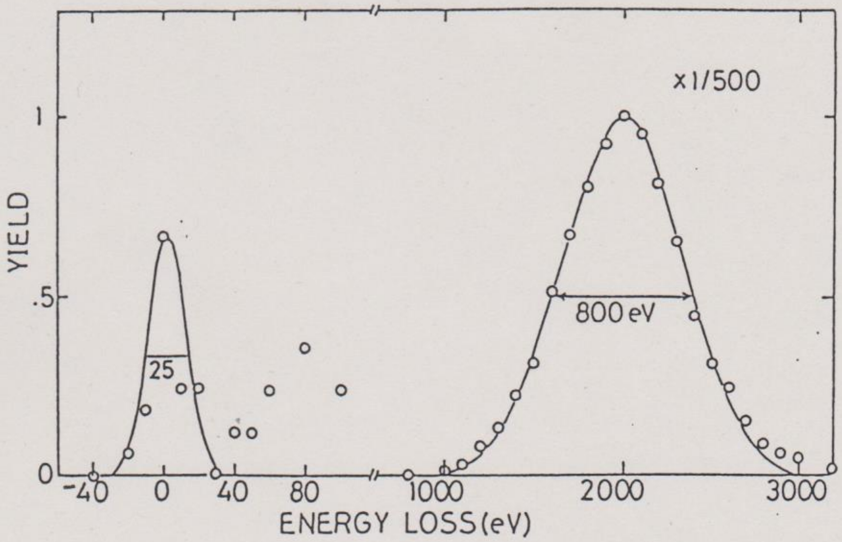


Fig.7 Energy loss spectra(ELS) for 100 keV H^+ transmitted through carbon film, showing the normal energy loss peak around 2 keV with the full width of 800 eV and the zero energy loss peak with the full width of 25 eV. Notice that the horizontal scale is different for the two peaks and x1/500 means that the yield of the normal energy loss peak is larger by 500 than that of the zero energy loss peak. The solid lines are the Gaussian fit.

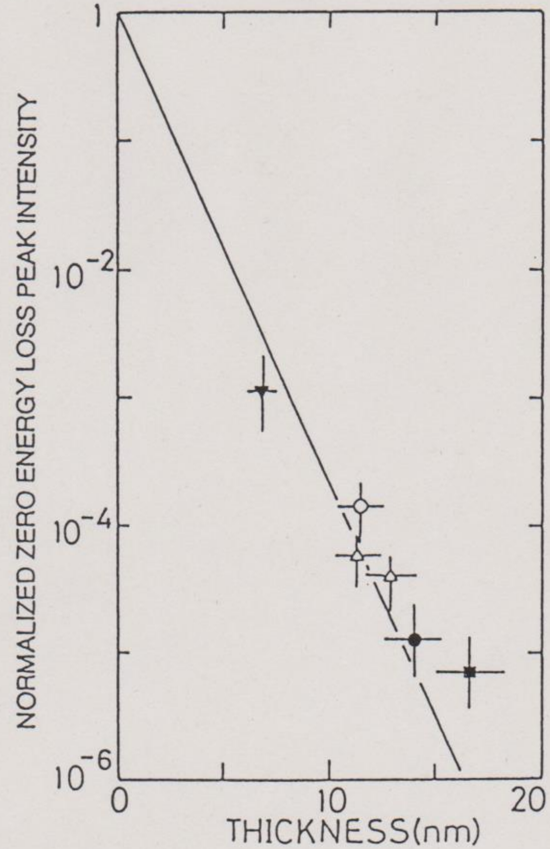


FIG.8 Normalized zero energy loss peak intensity vs thickness in nm 100 keV H^+ transmitted through carbon film. The solid line corresponds to the inelastic mean free path of 1.2 nm.

Zero energy loss;
No collisions with electrons
(no pin hole)

Matsunami, NIM B115(19996)14.
松波、科研費C(H4−5)

Inelastic mean free path (IMFP)

No collisions with electrons

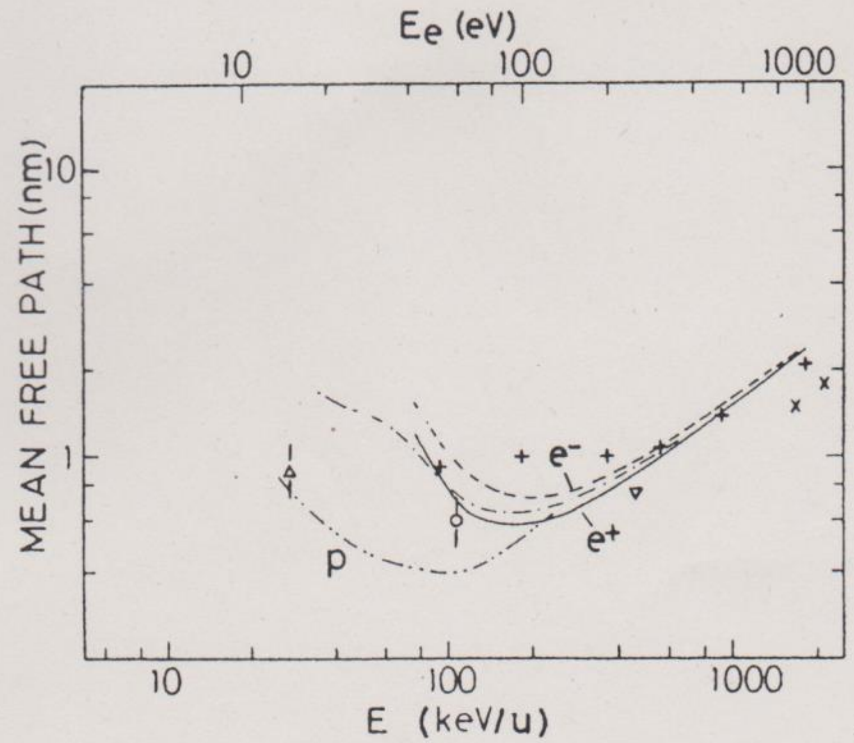


Fig. 3. Energy dependence of inelastic mean free path; present results for H^+ (○) and He^+ (△), calculated results for positrons (solid line) and electrons (dashed line) [17]. E and E_e are the energies of H^+, He^+ (per nucleon) and electron (or positron) having the same velocities. The dot-dashed and double dot-dashed lines show the calculated result for electrons including extension to low energies and protons, respectively, without the exchange effect after Ref. [19]. Experimental data source: ▽ = Ref. [21]; × = Ref. [22]; + = Ref. [23].

Matsunami, NIM B115(1996)14.

Energy loss of 100 keV Protons in C film

?Peak around 200 eV

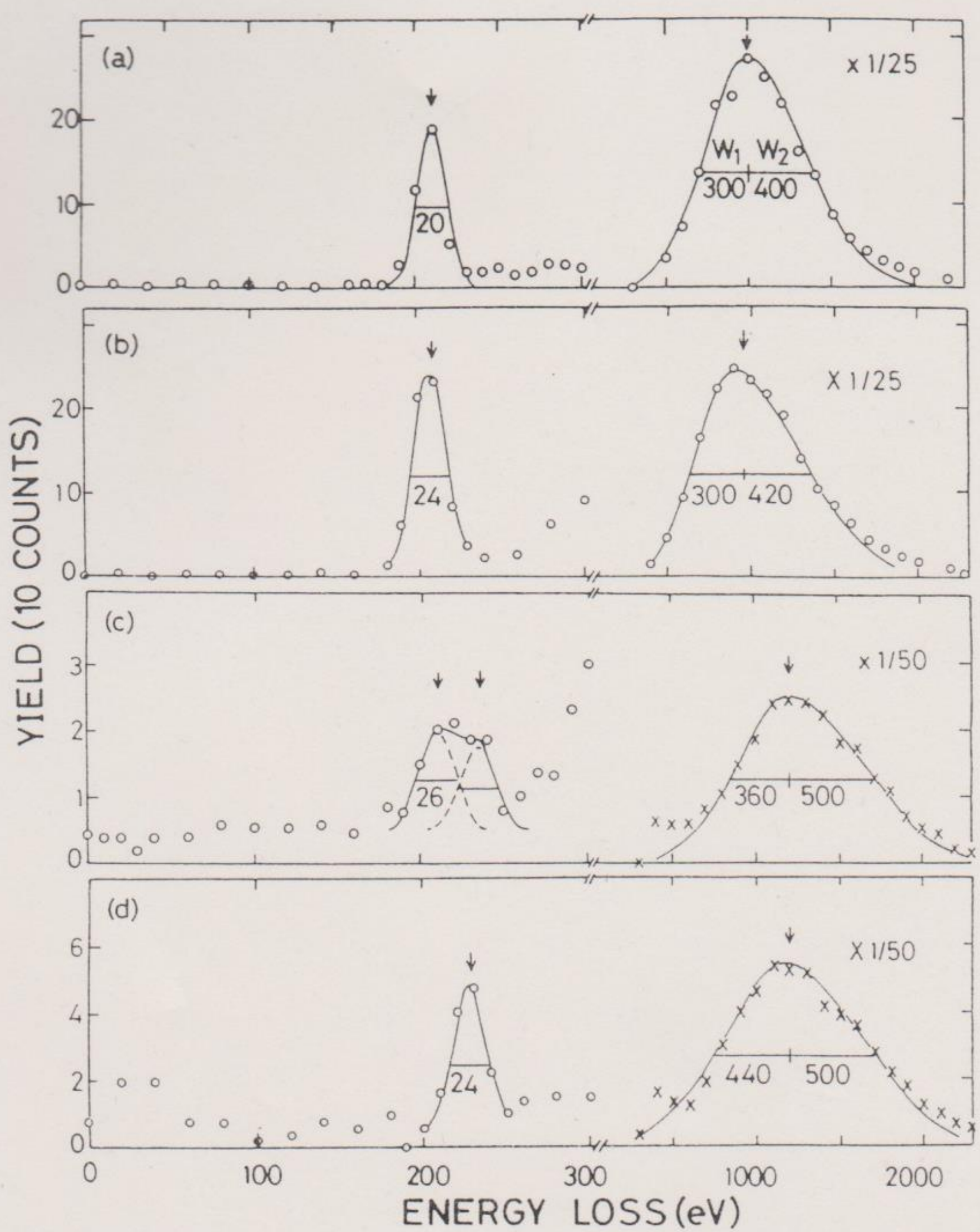


Fig. 2. Energy spectra of H^+ transmitted through thin carbon films; (a) and (c) for 100, and (b) and (d) for 120 keV. The solid lines around the energy loss of 1 keV are the asymmetric Gaussian fit to the data. The spectra around 1 keV indicated by crosses and open circles are obtained for the as prepared sample and after bombardment of H^+ to a dose of ~ 0.1 $\mu C/mm^2$, respectively. The numbers are the half-width at half maximum in eV. The solid lines around 210 eV are the single or double Gaussian fit to the data with the full width at half maximum indicated in the figure.

Matsunami, Kitoh, NIM B85(1985)1994)556

Ag Nano cluster formation in SiO_2-glass

150 keV Ag ion into SiO_2-glass

Interactions between implanted Ag's

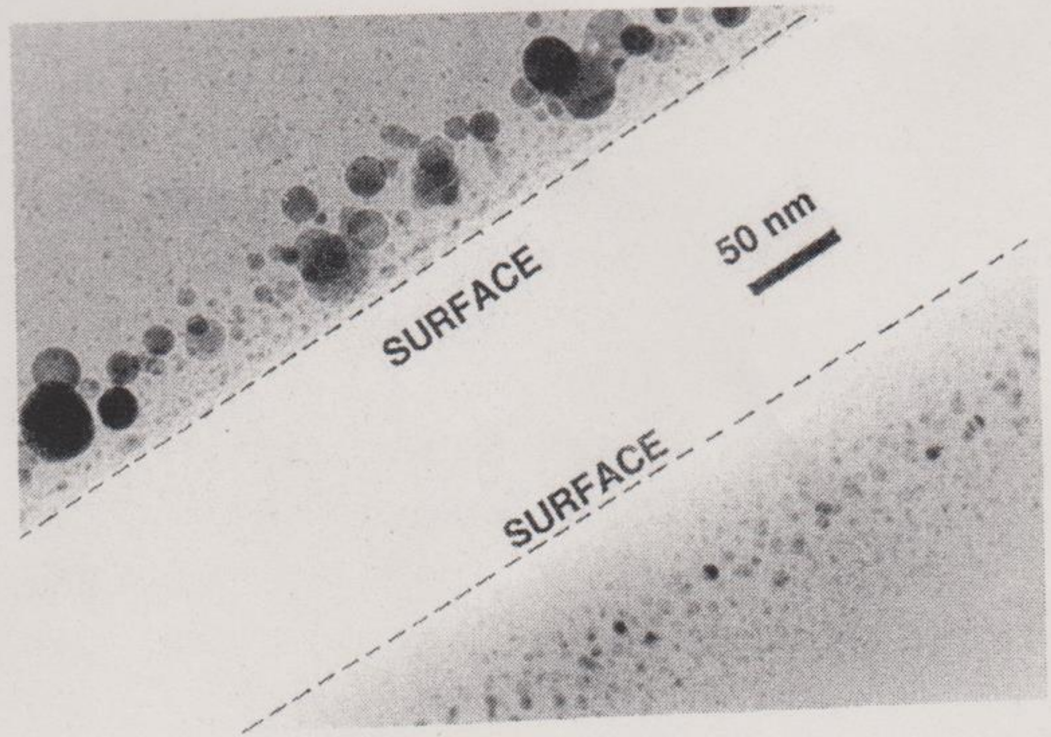
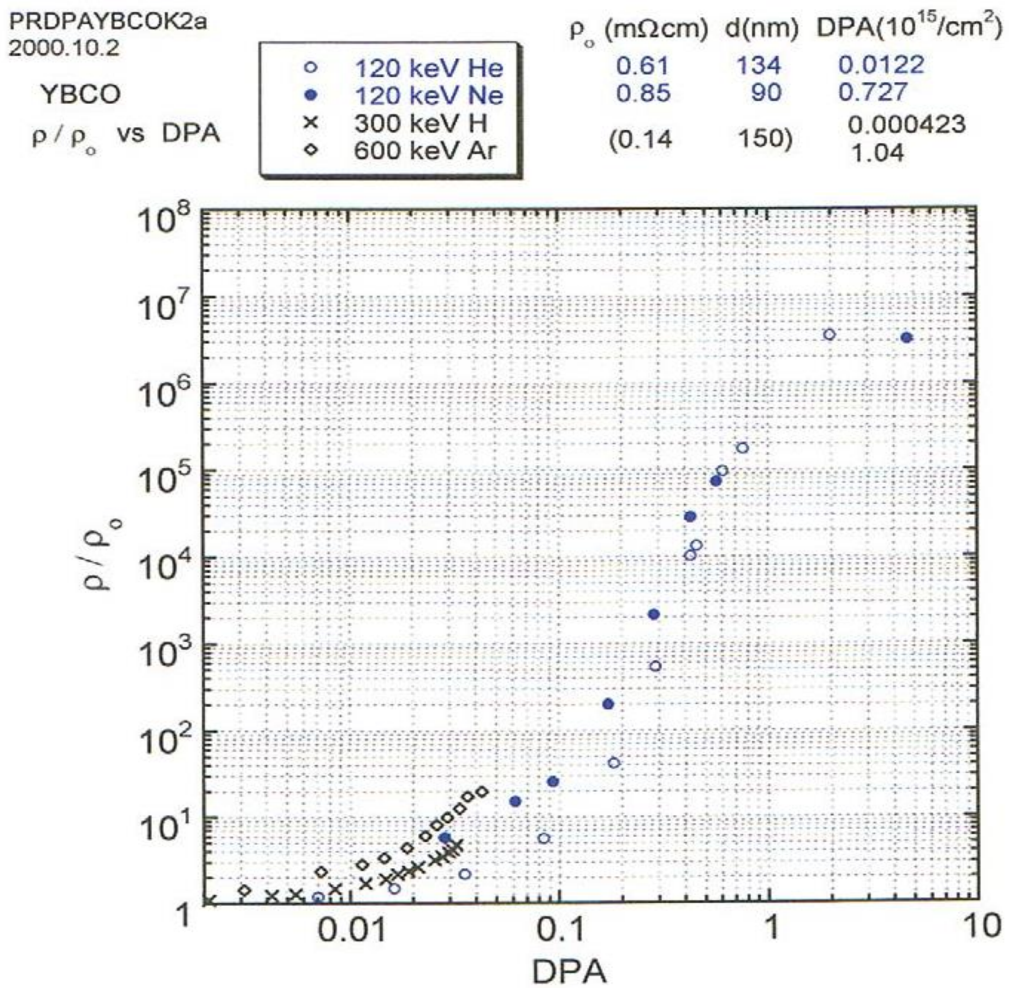


FIG. 3. X-TEM photographs of Ag implanted SiO_2 glasses for doses $2\times10^{16}/cm^2$ and $7.6\times10^{16}/cm^2$, showing small and large colloids for t small and large doses, respectively.

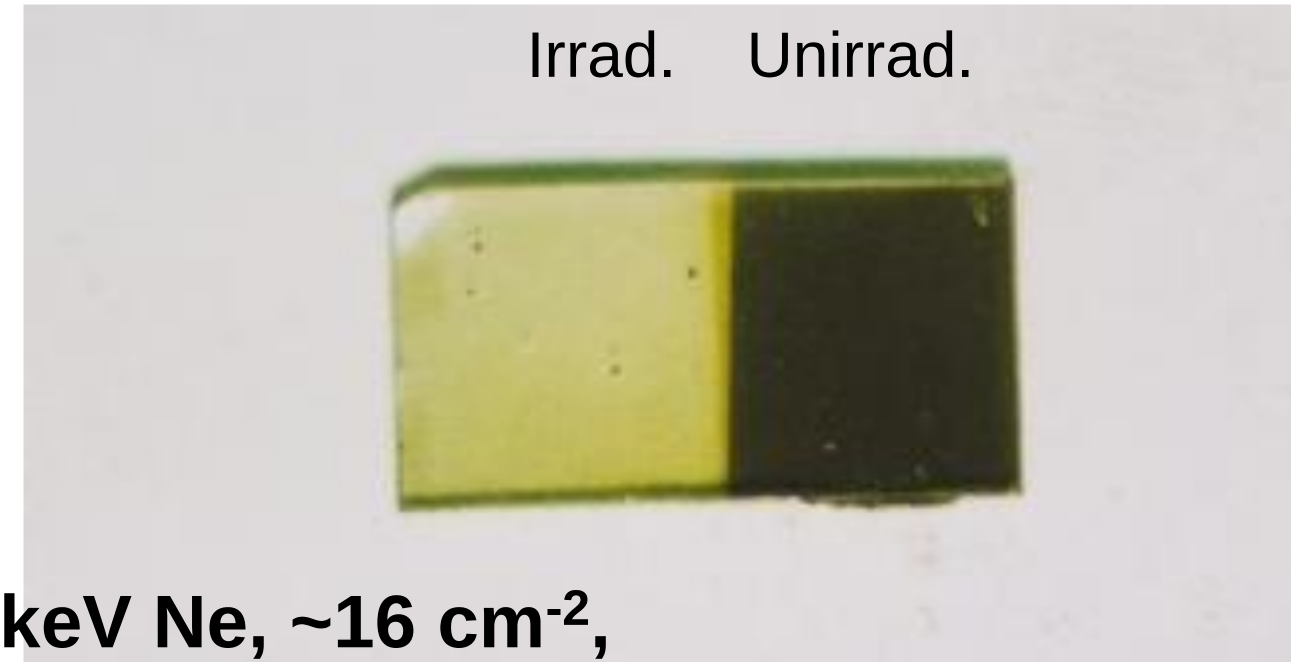
Matsunami, Hosono, Appl. Phys. Lett. 63 (1993)2050.

RESISTIVITY MODIFICATION of High Tc Cu oxide superconductors by ion impact



unpublished

Low energy ion irradiation effects on HTc spuerconductor (YBaCuO-1237, BiSrCaCuO-222310)



unpublished

5 keV Ne, ~16 cm^{-2},

Projected range ~7 nm << film thickness ~100 nm

<u>How ion irradiation effects beyond the projected range?</u>

Low energy ions (<10 eV) in solids ?

略歴　　　　　松波紀明　2013.3.6

1967(S42)	名古屋大学工学部原子核工学科入学
1971(S46)	同上卒業
1971(S46)	名古屋大学大学院工学研究科原子核専攻入学
1976(S51)	同上終了、工学博士 学位論文：Uses of channeling technique for determination of defect concentration and structures in crystals
1976(S51)	名古屋大学工学助手
1976~1978	Solid State Branch, Chalk River Nuclear Laboratory, Atomic Energy Canada Limited (AECL)
1986(S61)	名古屋大学工学講師
1992(H4)	名古屋大学工学助教授
2003(H15)	名古屋大学理工総研助教授
2005(H17)~	名古屋大学エコトピア科学研究所准教授

共同研究(学外)等

産総研 (2002 ~)

核融合科学研究所（1980頃~）

原研東海 (1999 ~)

＊産学連携重点研究（2007~ ）(代表:2007~2012）

「高速重イオンによる電子励起効果と物性改質」

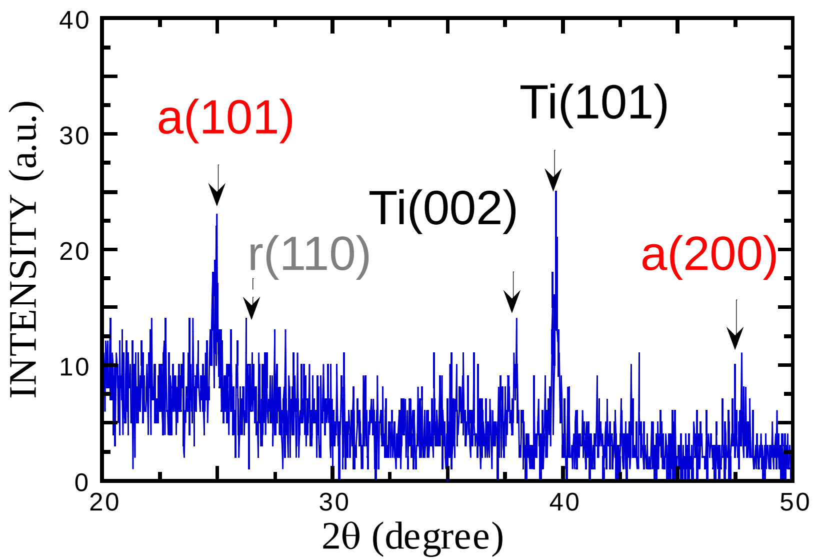
＊プラズマ壁相互作用に関する調査:

炭素材の化学スパッタリング（2007~2010）

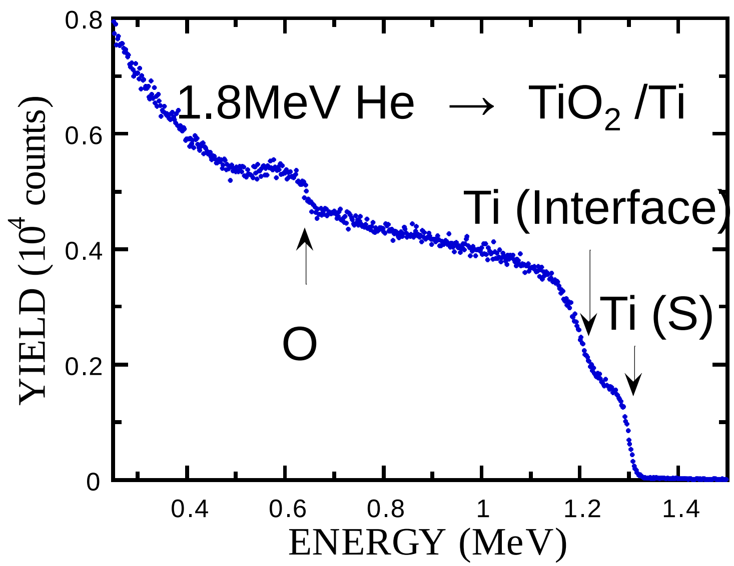
Ion irradiation effects on catalytic activity of TiO_2

TiO_2 Film Characterization

X-ray diffraction



Rutherford backscattering spectroscopy (RBS)



Structure

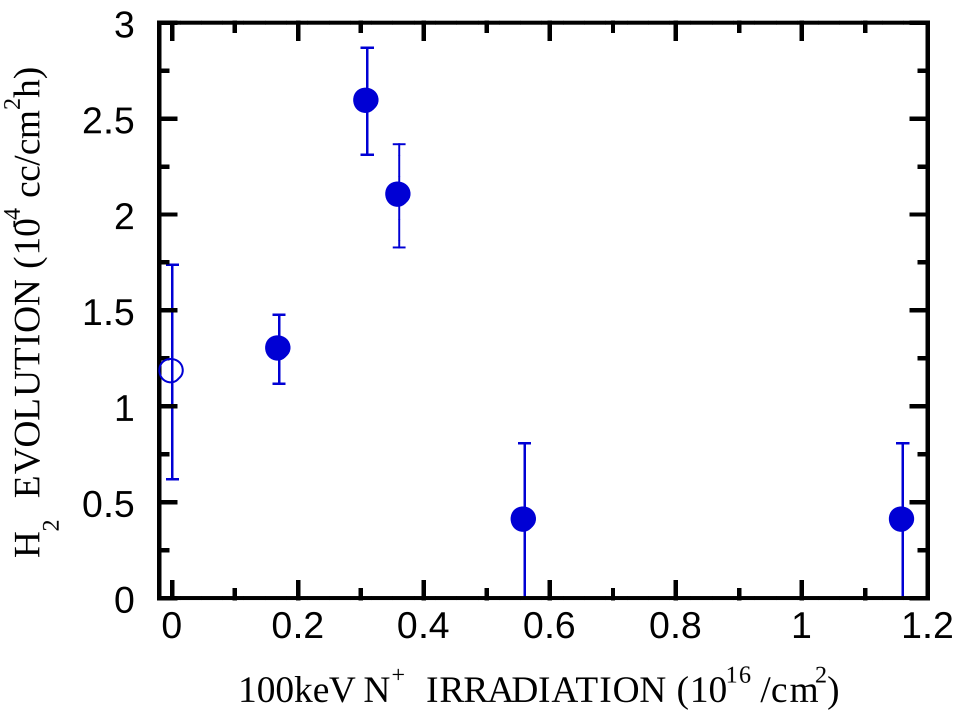
a : Anatase,

r : Rutile was not observed.

Thickness 120 nm

Composition O/Ti=2.0±0.1

Enhancement of photocatalytic activity of anatase-TiO_2 by N ion irradiation



H_2 evolution vs N ion fluence

100 keV N ion irradiation=> enhancement by 2

Factors of enhancement

- Valency modification (Ti^{+4} -> Ti^{+3})
- Problems
  Area modification?
  Carbon contamination

Matsunami, Uebayashi, Hirooka, Shimura, Tazawa, NIM B267 (2009)1654.

Similar enhancement (a factor of 1.5) was observed for Ni-loaded Rutile-TiO_2

Optimization of Ni concentration by N ion irradiation

Dopant replacement by ion impact: In-doped ZnO

6% In doped ZnO
Unirrad.：5~0.03 Ohmcm

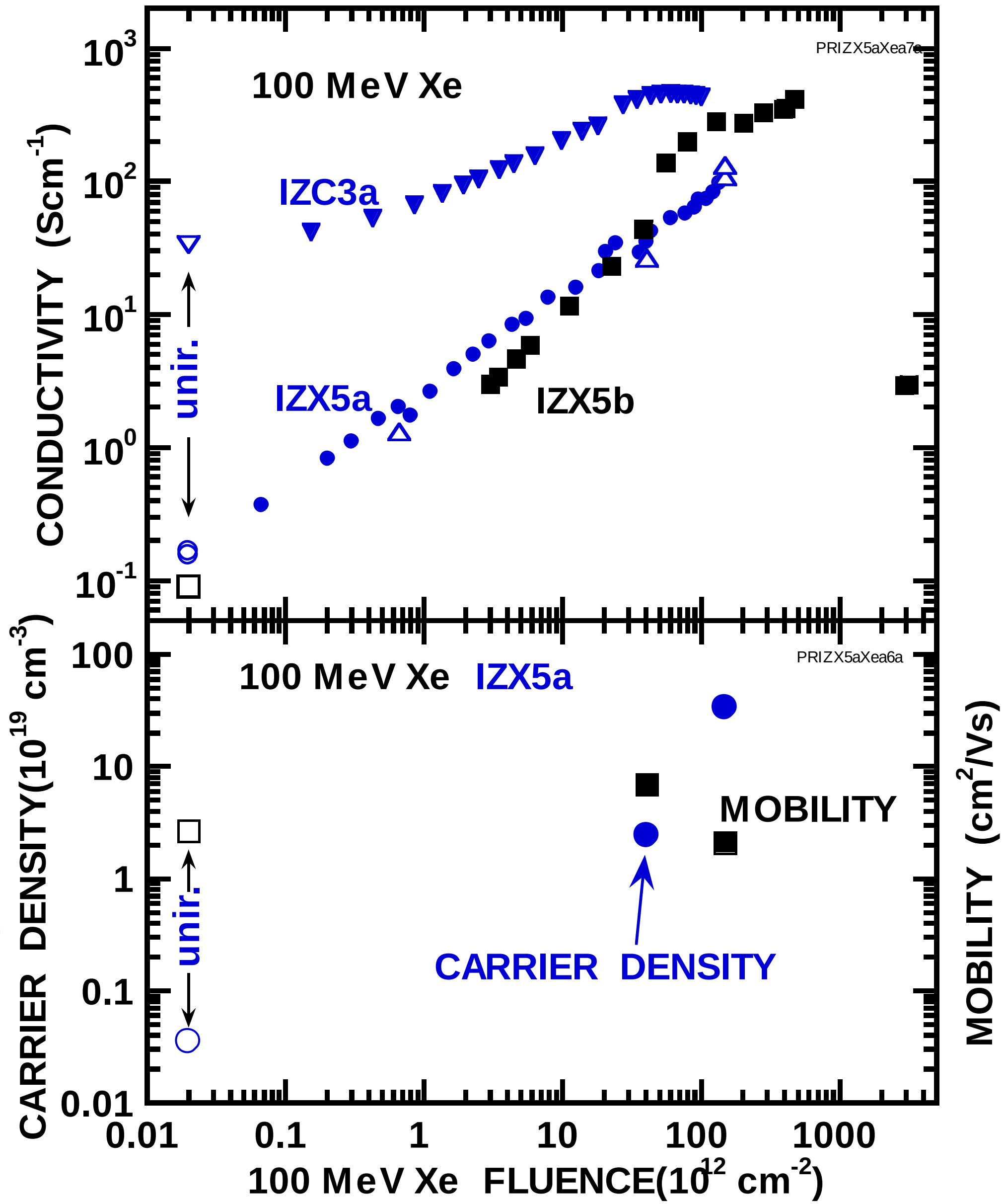
・**Conductivity：increase by 4 order of magnitude**

・Main factor is the carrier (electron) conc. increase due to **dopant replacement.**

In into Zn sites

Non-thermal effect

・**Direct evidence of dopant replacement?**



Matsunami, Fukushima, Sataka, Okayasu, Kakiuchida, NIM B268(2010)3071.

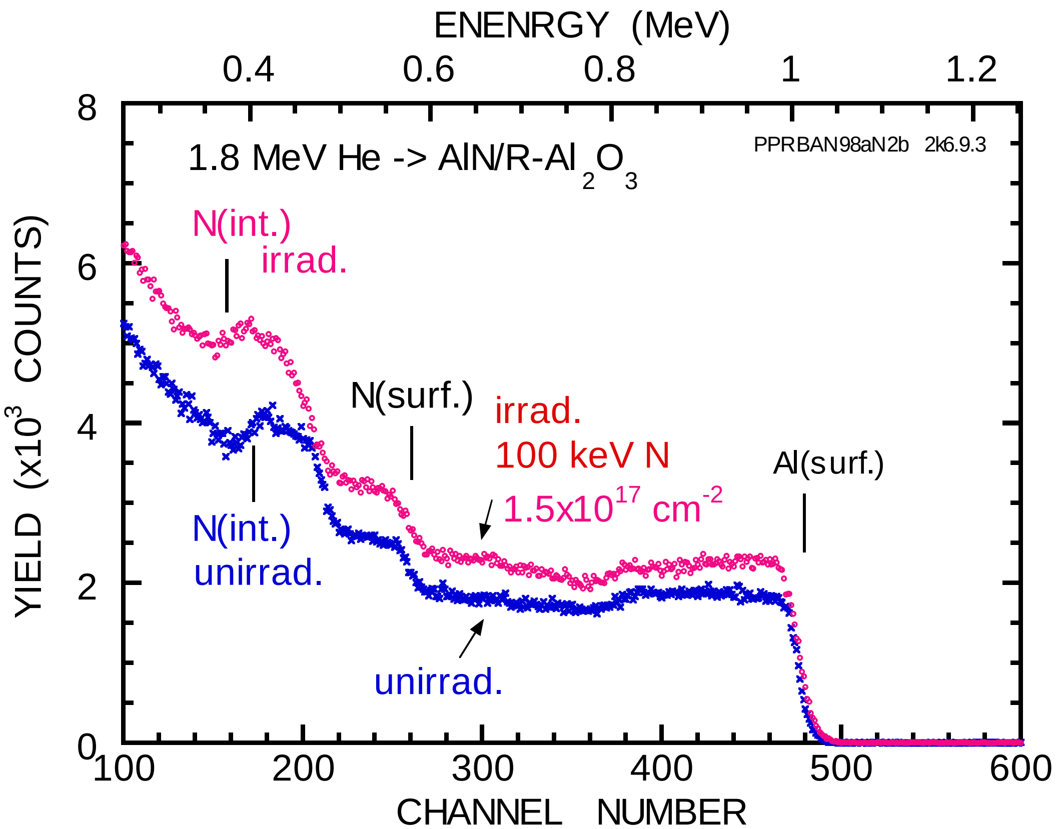
Similarly dopant-replacement induced by ion impact, i.e., conductivity increase was observed for Al-doped ZnO, Mn-doped ZnO.

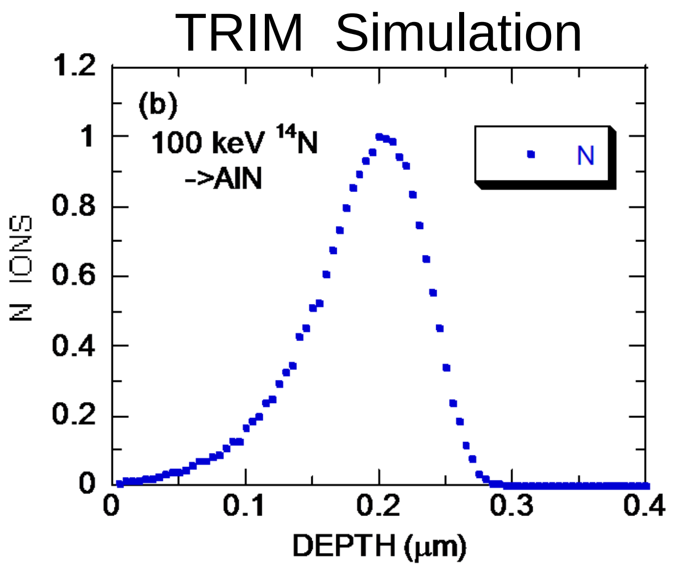
***Direct evidence of dopant-displacement by ion impact**

XEAFS

Reaction of N ions with nitride films near film to substrate interface (Interface reaction)

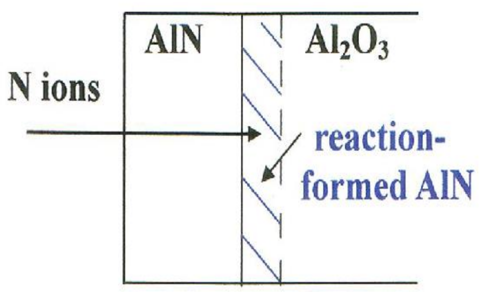
Interface reaction: non-thermal (AlN/Al_2O_3)



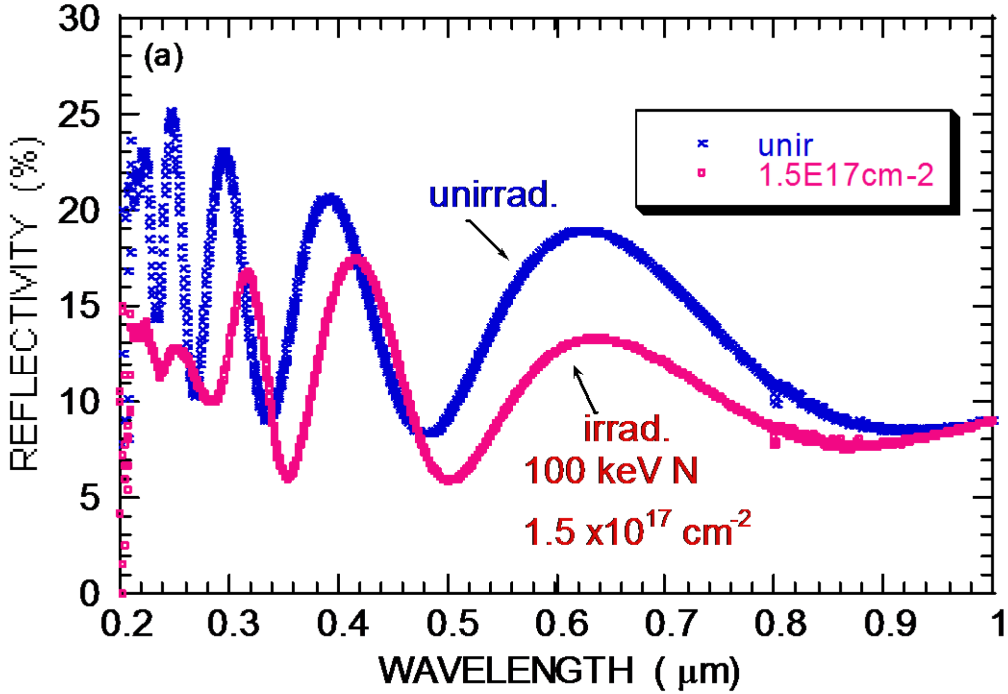


- Increase of film thickness by 100 keV N ion irradiation
- Optical reflectivity also shows film thickness increase
- N-Al(Al_2O_3) reaction, growth of AlN layer

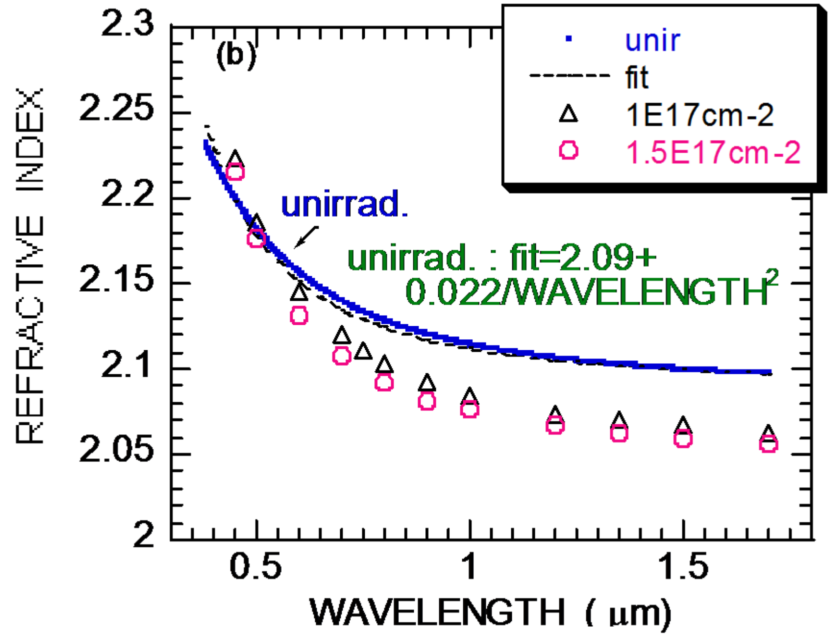
Interface reaction was also observed for Si_3N_4 (amorphous, ~0.2 μm) /SiO_2.

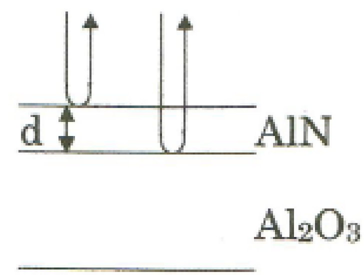


Optical reflectivity



Refractive index



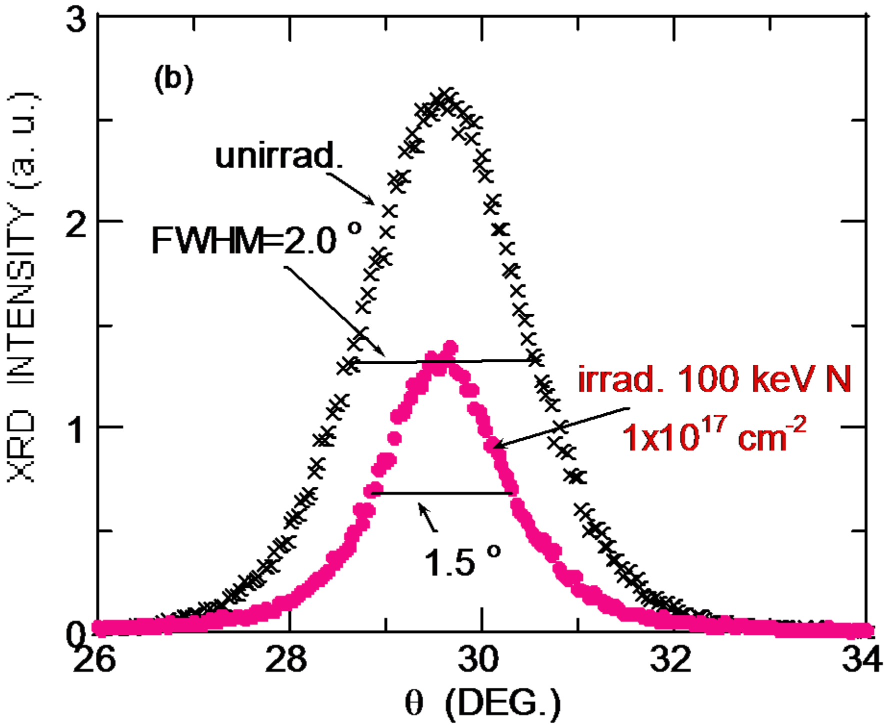


Oscillations: Interference of photon beams between directly reflected and reflected from AlN-Al_2O_3 well-defined interface

The shift of the wavelength l_m at which the reflectivity takes their maxima & minima towards longer wavelength, with the measured refractive index => increase of film thickness

λ_m =4dn/j; reflectivity minima with even integer j, maxima with odd integer j, for n(AlN) > n(Al_2O_3)~1.8
d : film thickness
n : refractive index

X-ray diffraction



FWHM of XRD rocking curve decreases by N ion irradiation => alignment of grain-orientation

Under ion irradiation,

- **Degradation of XRD intensity, does not become amorphous but disordered state**
- **Decrease of a-axis parameter**
- **No diffraction peak other than AlN & Al_2O_3**

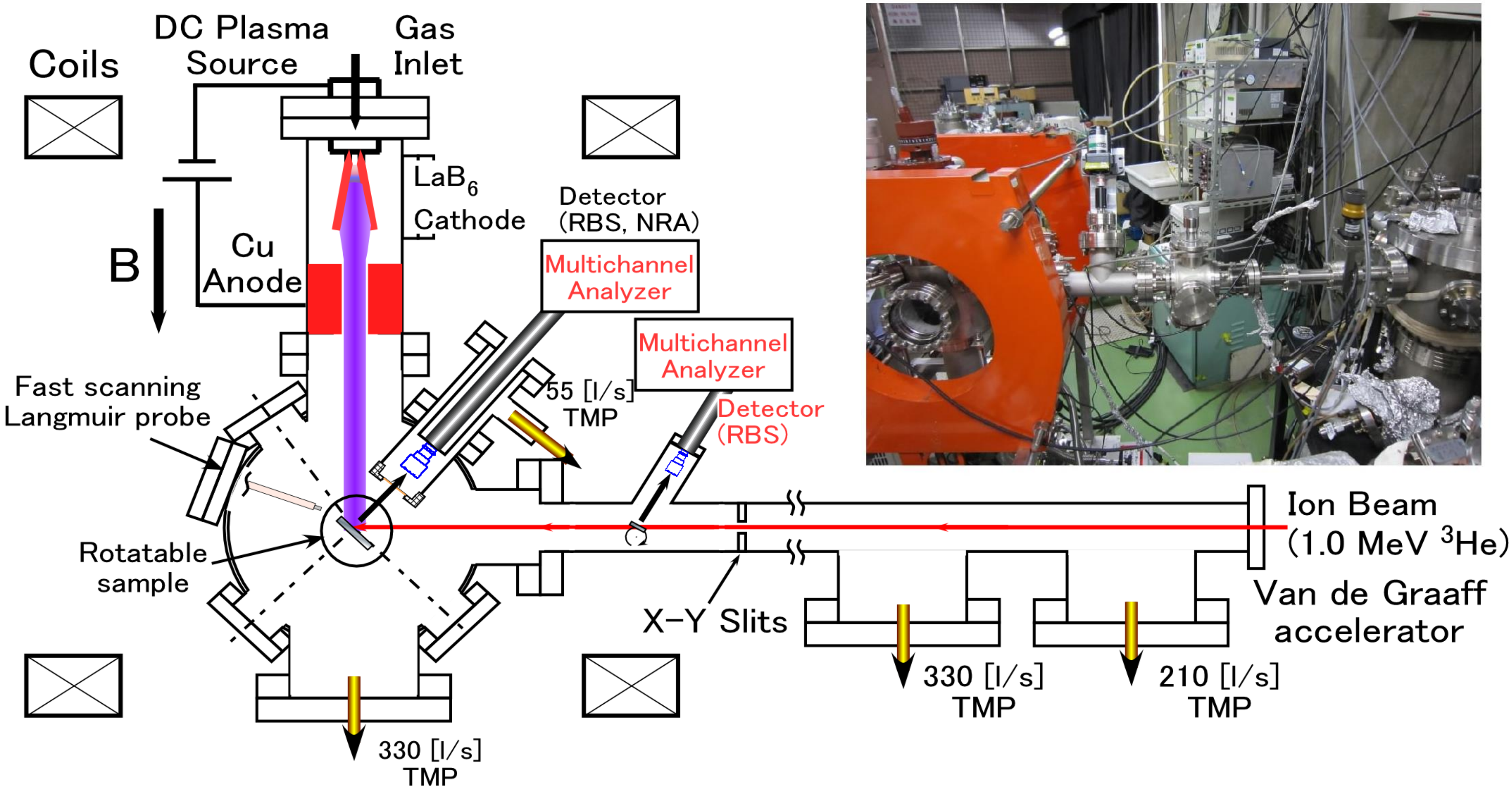
Matsunami et al, NIM B257(2007)433.

Plasma Surface Dynamics with Ion Beam Analysis for study of dynamic retention of H isotopes under plasma exposure

PS-DIBAを用いたプラズマ照射下における水素同位体吸蔵のその場計測

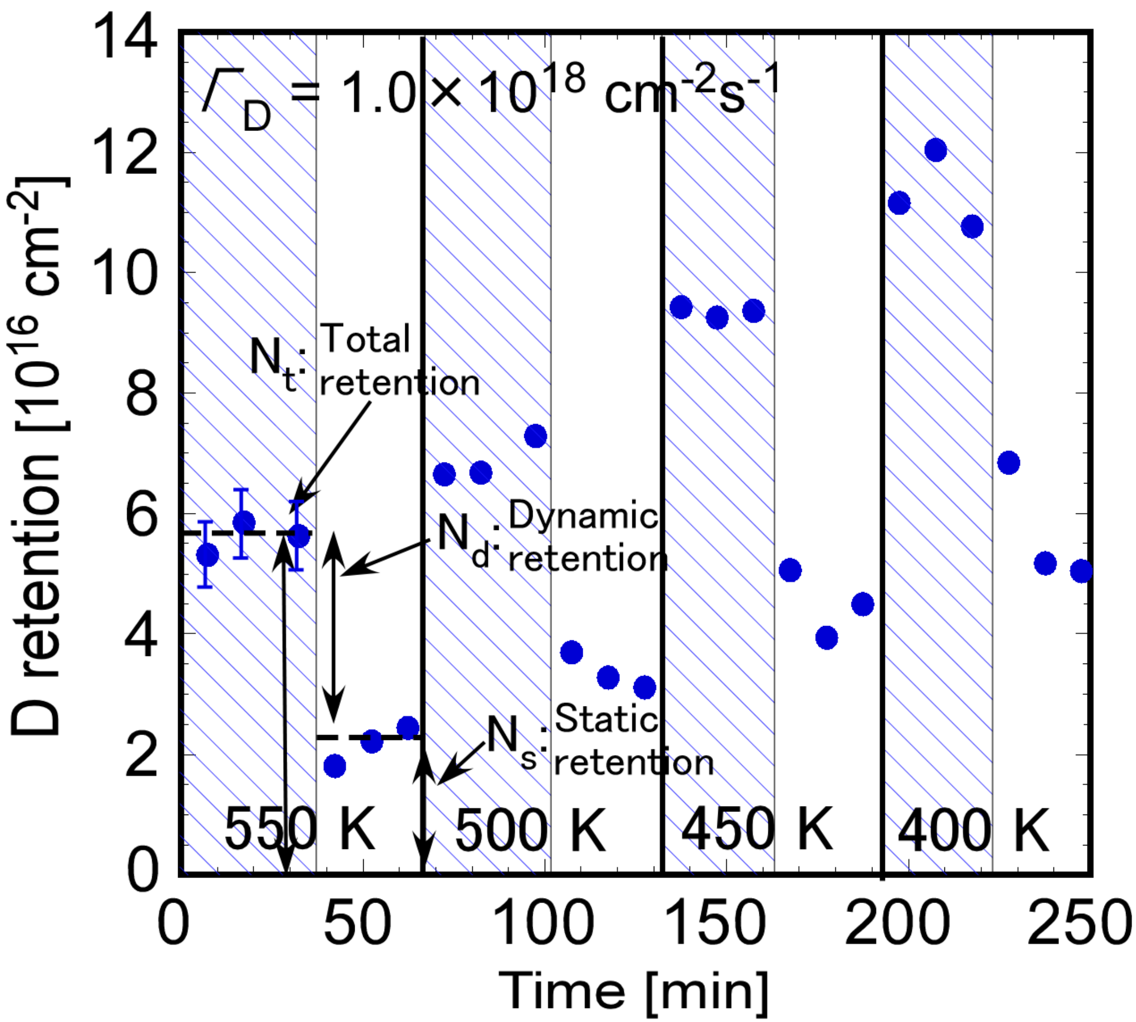
Yamagiwa, Nakamura, Matsunami, Ohno, Kajita, Takagi, Tokitani, Masuzaki, Sagara, Nishimura, Phys. Scr. T145(2011)014042.

Plasma Surface Dynamics with Ion Beam Analysis (PS-DIBA)



i) 高密度プラズマ照射下でのイオンビーム計測が可能
ii) 差動排気によってイオンビーム検出器とVan de Graaff加速器を保護
iii) プラズマ照射下でビーム照射量をモニタリング
iv) 試料台の空冷によって試料温度制御

等方性黒鉛を用いた重水素吸蔵量その場計測



フラックスΓ_D一定で重水素プラズマ照射及びNRA計測開始（斜線部）

試料温度を制御しながら、試料への重水素イオン照射を停止

試料温度を550Kから空冷により50K毎に温度を下げて吸蔵量計測

プラズマ照射中

吸蔵量　5.7×10[16] Dcm[-2]

・・・合計の吸蔵量N_t

プラズマ照射停止後

吸蔵量　1.8×10[16] Dcm[-2]

・・・静的吸蔵量N_s

劇的な減少

3.9×10[16] Dcm[-2]

・・・動的吸蔵量$N_d = N_t - N_s$

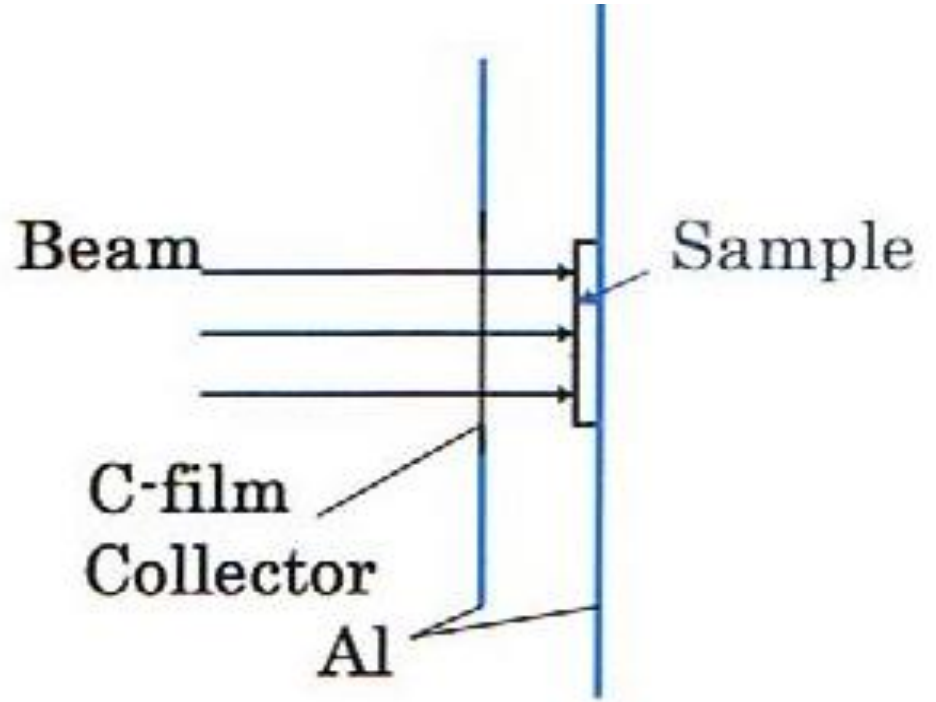
ELECTRONIC SPUTTERING

(in collaboration with JAEA)

High energy ions

^{136}**Xe** 200, 100 MeV
^{58}**Ni** 90MeV
^{40}**Ar** 60 MeV

(0.73 ~ 1.5 MeV/u)



Analysis of sputtered atoms: 1.8 MeV He RBS

Calibration of C-film Collection Efficiency

Samples: 15 Oxides & 3 Nitrides

a-SiO_2, c-SiO_2, ZnO, SCO, Y_2O_3, Al_2O_3, $MgAl_2O_3$, MgO, $SrTiO_3$, TiO_2, CeO_2, Cu_2O, CuO, WO_3, ZrO_2,

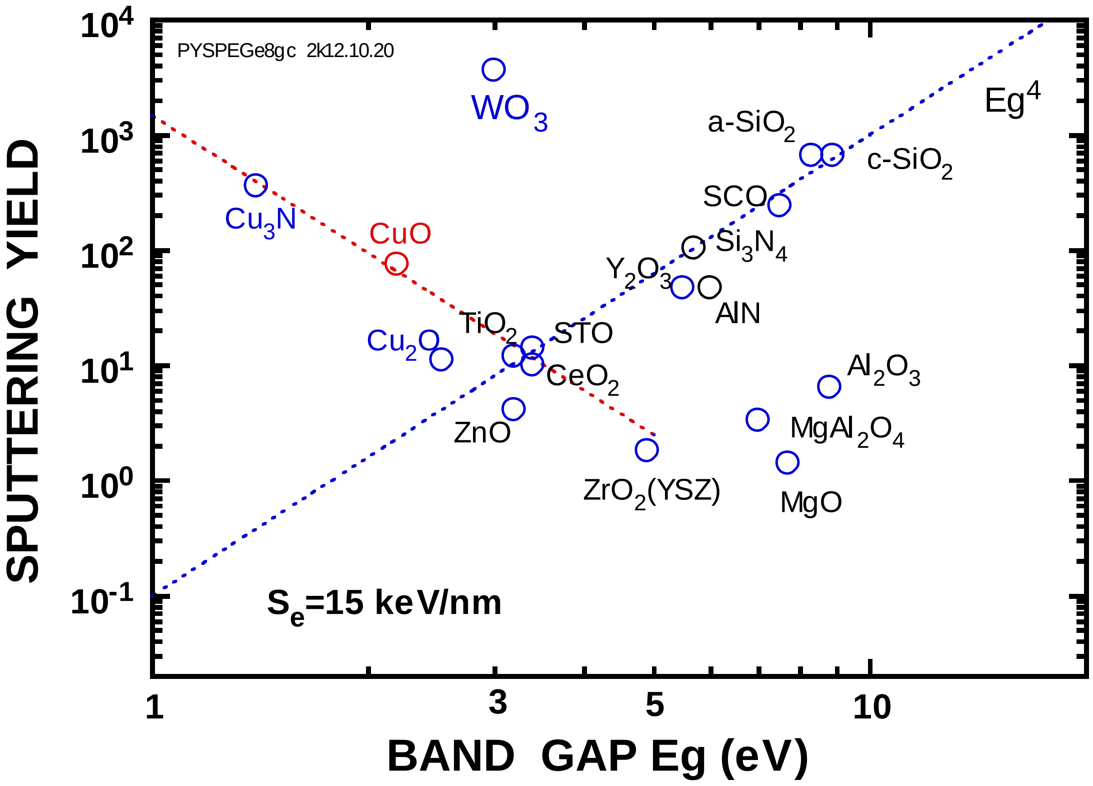
Cu_3N, AlN, Si_3N_4

- Nearly stiochiometric
- From the linear relationship between sputtered atoms in Carbon-foil and ion fluence with the collector efficiency, the sputtering yields are evaluated.
- Sputtering yields Y are non linear with the electronic stopping power; $Y \propto Se^n$ with $n>1$.

Electronic Sputtering Yield Y

(Electronic excitation effects)

CuO, WO_3 & Cu_3N,
The erosion yields are much larger than the suggested bandgap dependence.



Electronic excitation into atomic displacement

***Eg ~ Maximum available energy**

***Number of electron hole pairs ∝ 1/Eg**

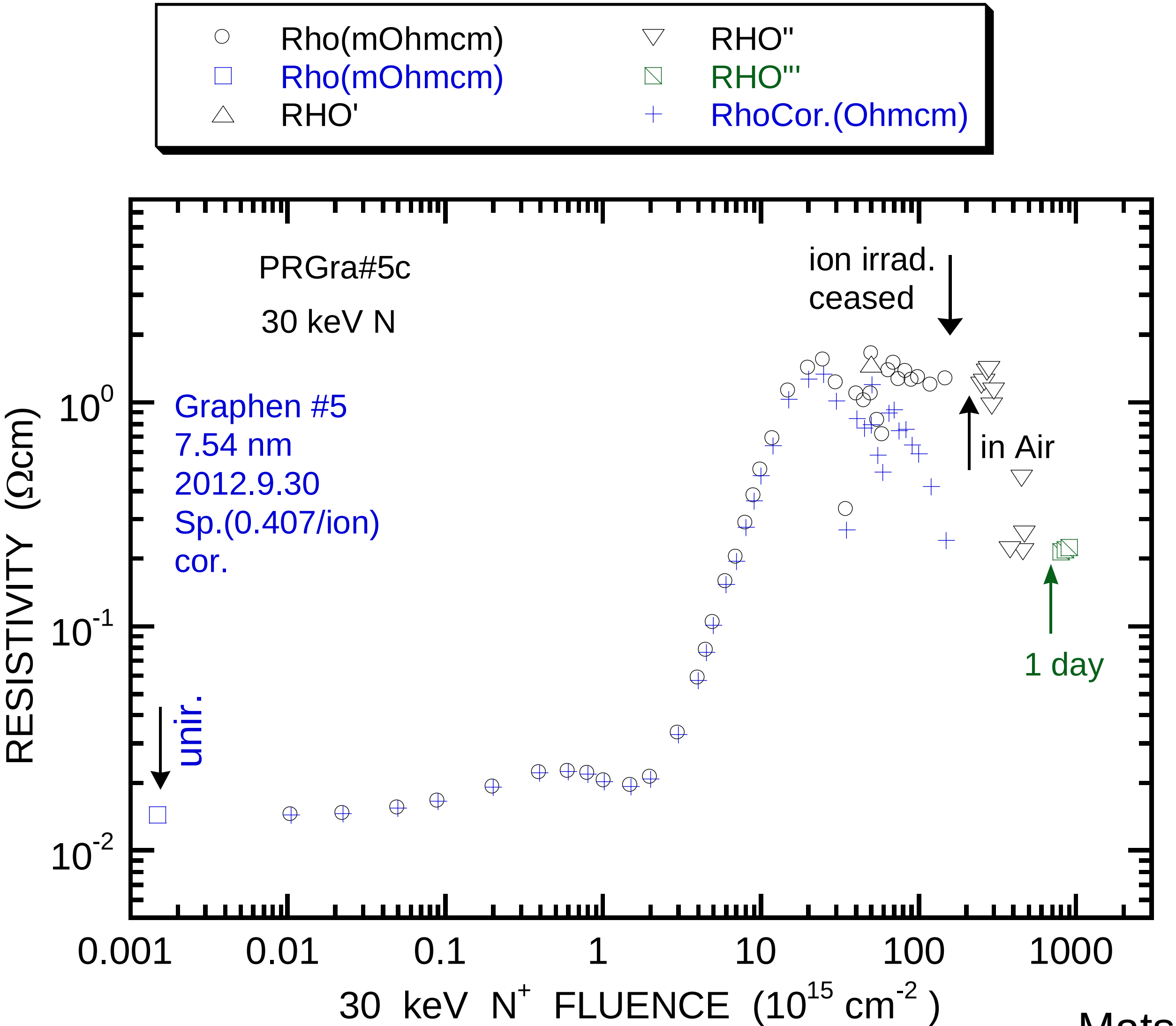
***Efficiency factor ?**

WO_3, NIM B268(2010)3167. Cu_3N, NIMB267 (2009) 2653. Cu_2O, NIM B266(2008)2986.

Mechanism of electronic sputtering?

Energy transfer from electronic system into atoms?

Ion impact effects on graphene

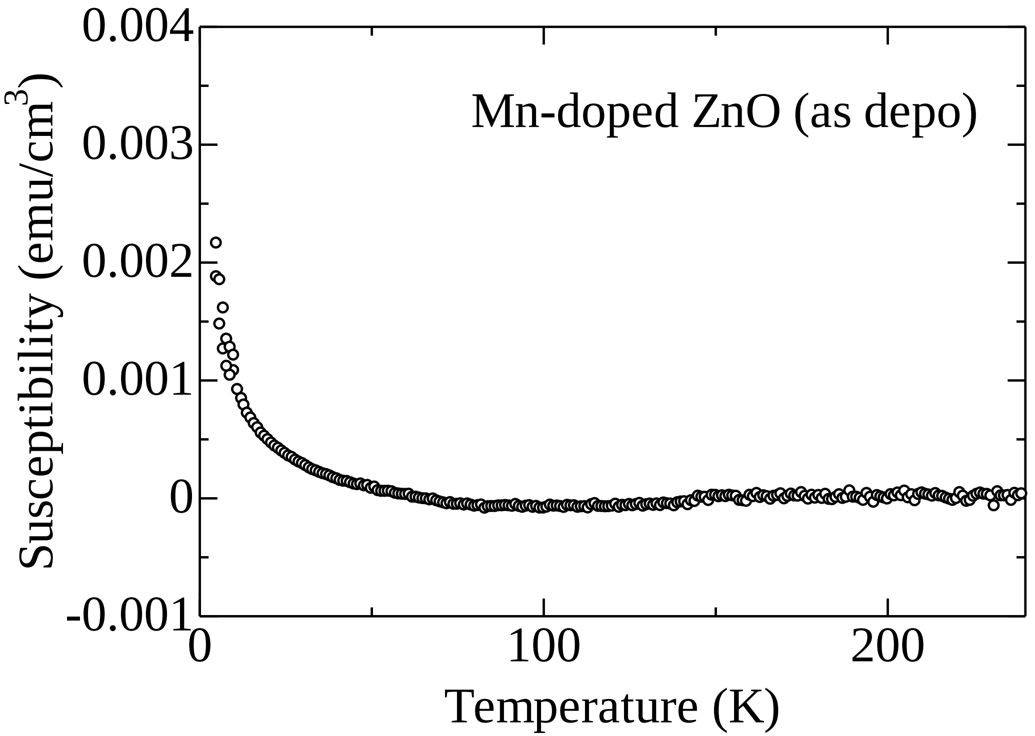


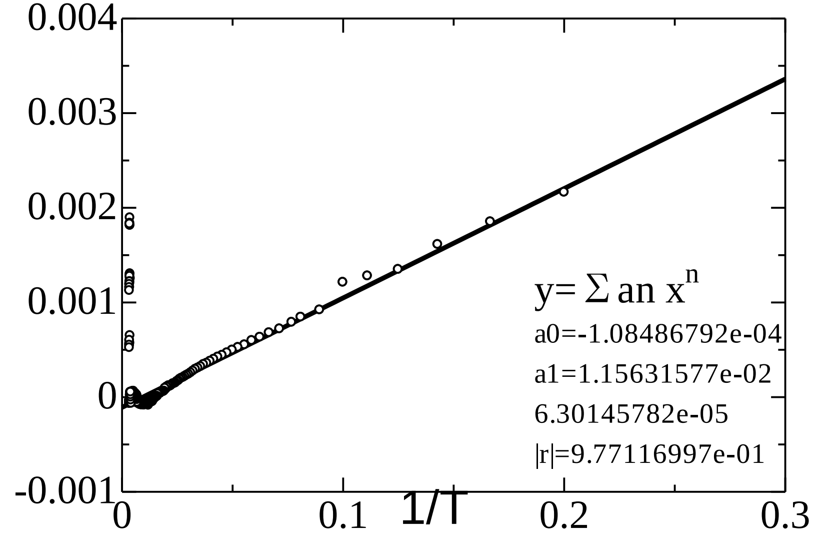
Matsunami, Tsuchiya, Mizuno, Bandoh, 2013

magnetic property of 6%Mn-doped ZnO

Temperature dependence

Below150K : Curie's law -> Para-magnetic





y= Σ an x^n

a0=3.92928826e-05

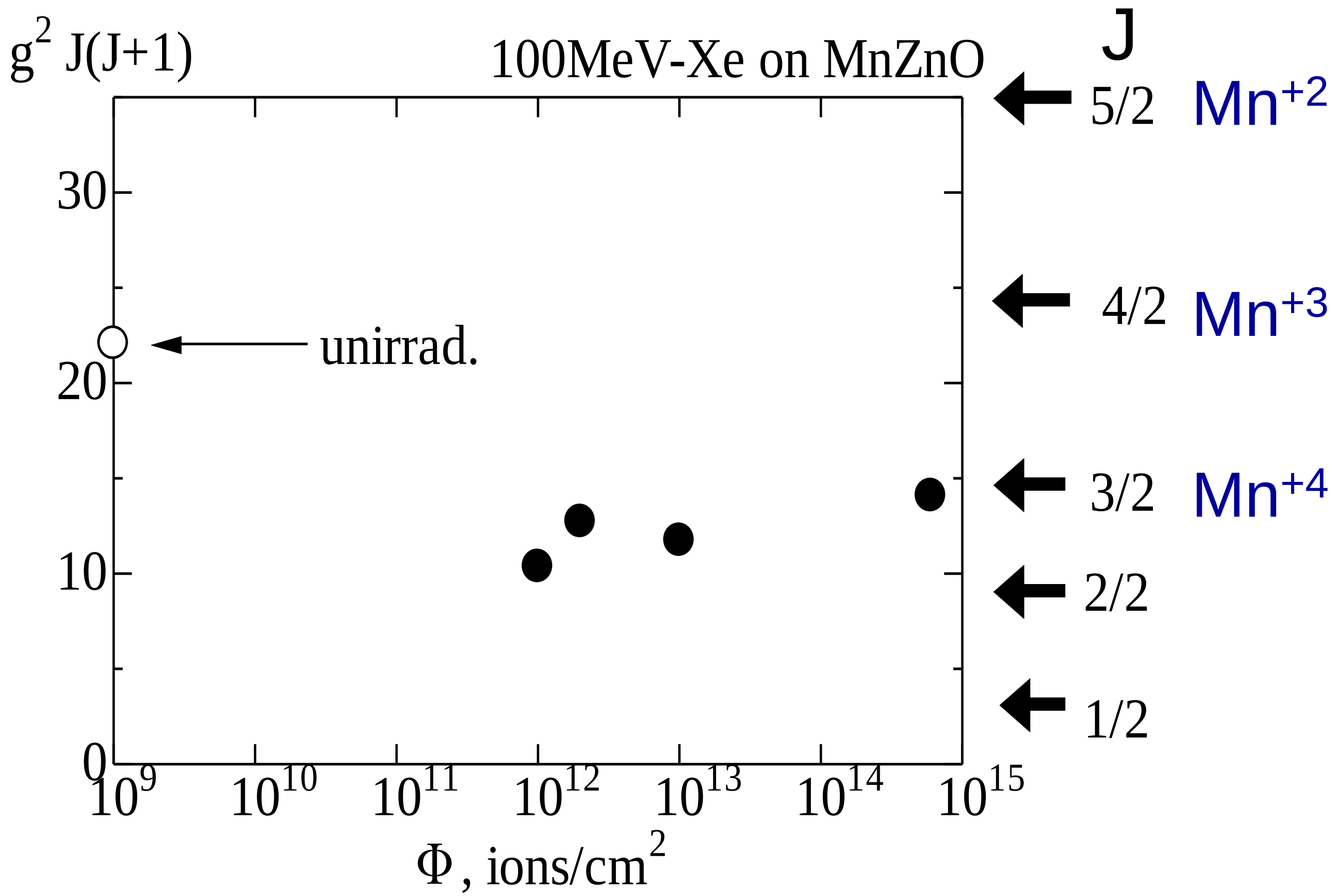
a1=9.28827931e-03

3.70429287e-04

|r|=5.04287536e-01

Ion impact effect on magnetic property of 6%Mn-doped ZnO, 100 MeV Xe

Susceptibility follows Curie law (para-magnetic)

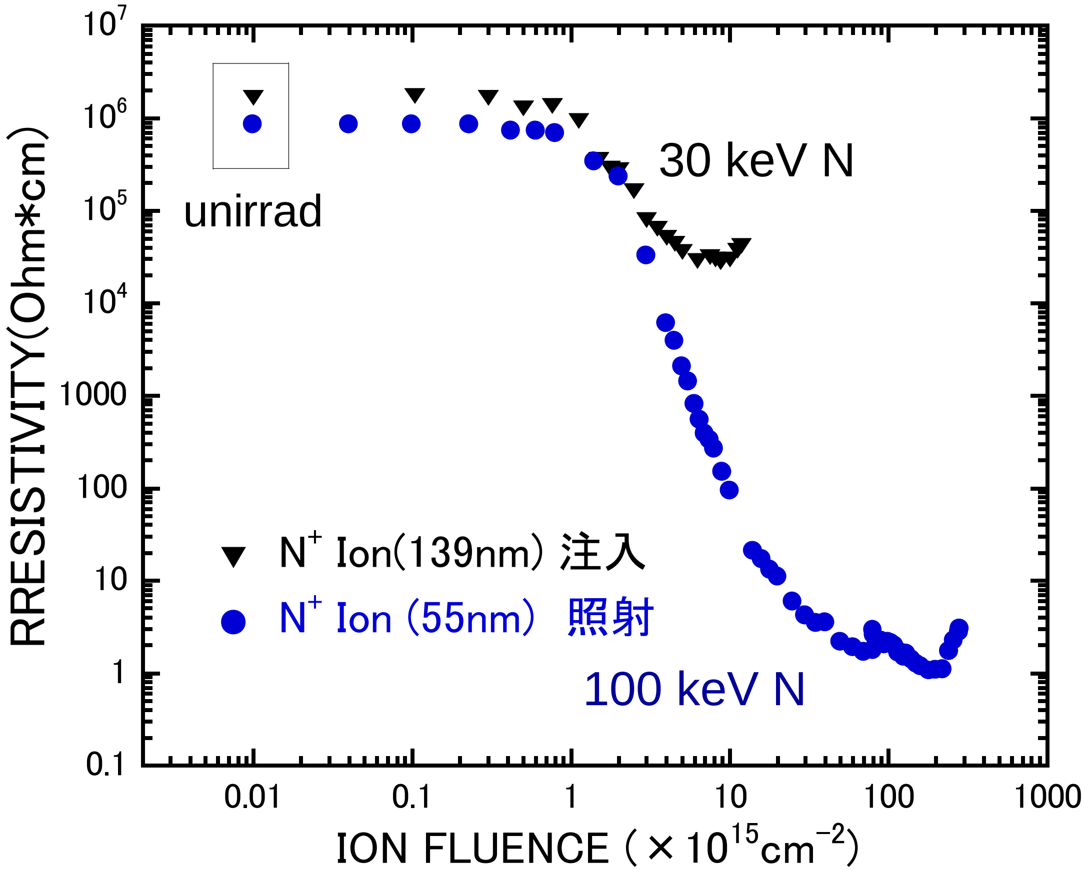


Matsunami, Okayasu, Sataka, et al. 2013

N ion energy deposition & implantation effects: Mn(6%)-doped ZnO

100 keV N
Rp=160nm >> film thickness 55 nm
energy deposition effect

30 keV N
Rp=47nm < film thickness 140 nm
N ion implantation effect



Itoh, Matsunami, 2013

Concluding remarks, future problems

- Challenge
- Valency modification by ions & its effects
- Ion implantation (inclusion) effects
- Displacement threshold energy for dpa
- Mechanism of electronic excitation into atomic displacement

Thank you for your attention!