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# Electronic interactions of medium-energy ions: Some recent results and their implications for high-resolution depth profiling



Daniel Primetzhofer – Uppsala University

# Acknowledgements:



Karim Kantre  
Valentina Paneta  
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Strategic Research



Swedish Research  
Council



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Foundation

# Ion Physics in Uppsala



Anders  
Ångström

Tandemaccelerator

Ion-Implanter + MEIS

# High resolution depth profiling: Ion energies: keV/amu

## Possible complications:

- Contribution from nuclear energy loss along trajectories becomes relevant
- Low ion energy  $\leftrightarrow$  low energy transfer to electrons
- Excitation of valence and conduction electrons  $\leftrightarrow$  chemical effects
- Ion velocity comparable to electron velocity  $\leftrightarrow$  response of system
- Increased weight of surface (contaminations, deviations from bulk stoichiometry)

# Outline

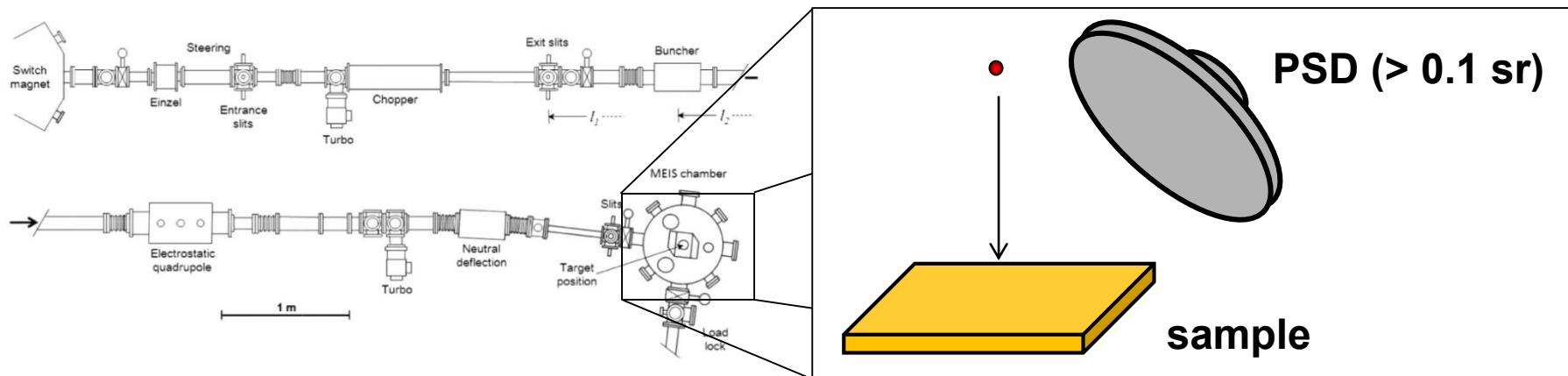


- Motivation: Stopping power research at keV energies
- Stopping power experiments by TOF-techniques
  - Heavy ions (Ne, I) in noble metals (Au, Ag, Pt)
  - Light ions in hafniumdioxide  $\text{HfO}_2$
- Conclusions/Summary



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# The Uppsala TOF-MEIS: an ideal tool



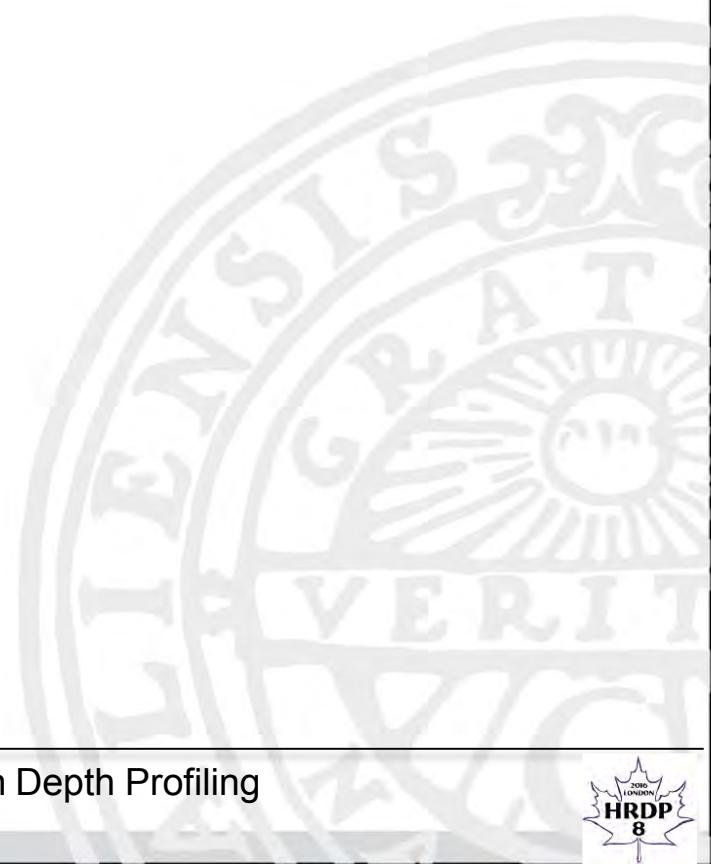
*M. Linnarsson et al., Rev. Sci. Instr. (2012)*

- Almost any ion, 20-350 kV acceleration voltage
- Microchannelplate detector + TOF: No problem with charge states
- Large solid angle: Extremely low dose!



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# Heavy ions... Ne!



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8<sup>th</sup> International Workshop on High-Resolution Depth Profiling  
(HRDP8)

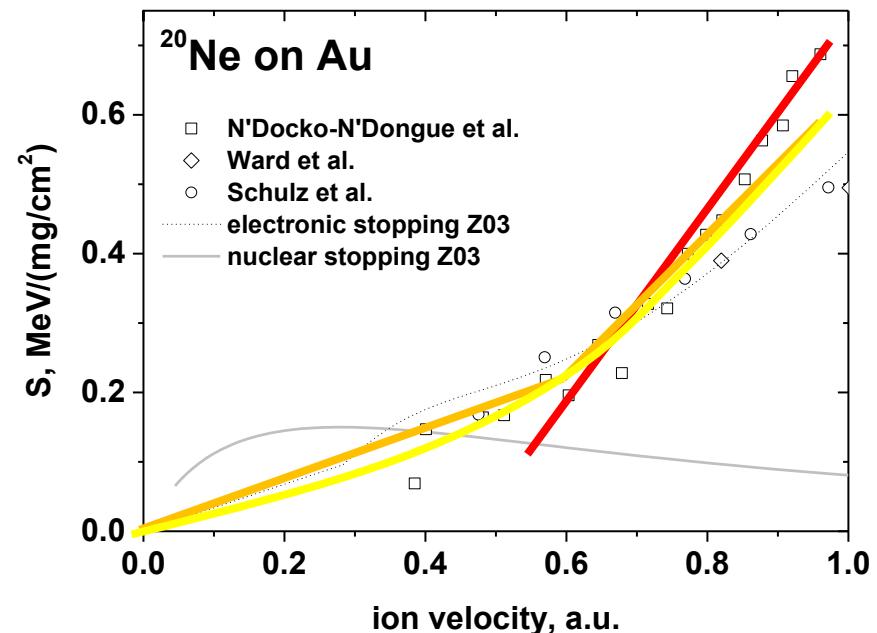
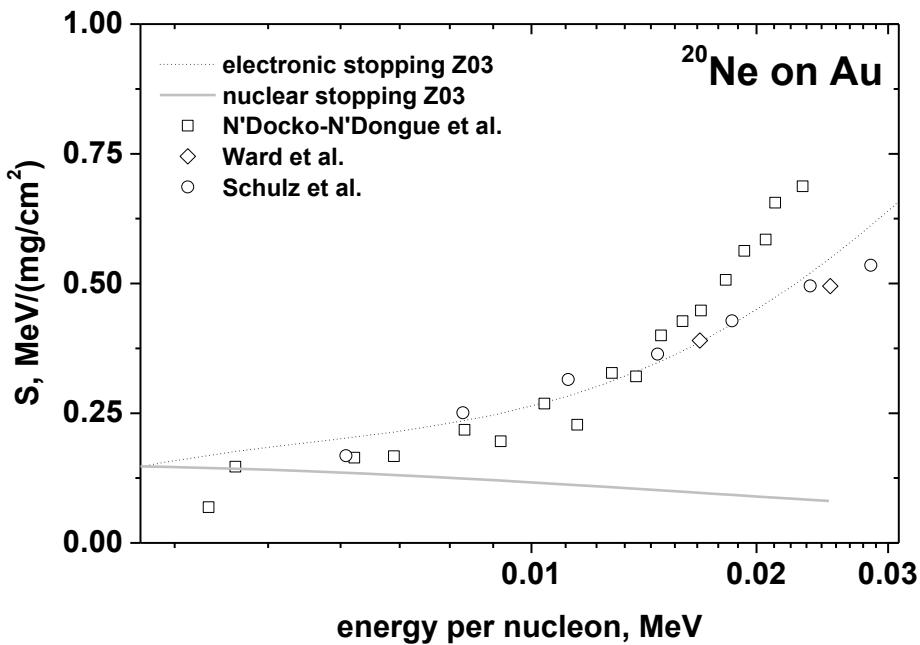




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# Heavy ions... Ne!

At low energies (< 1MeV):



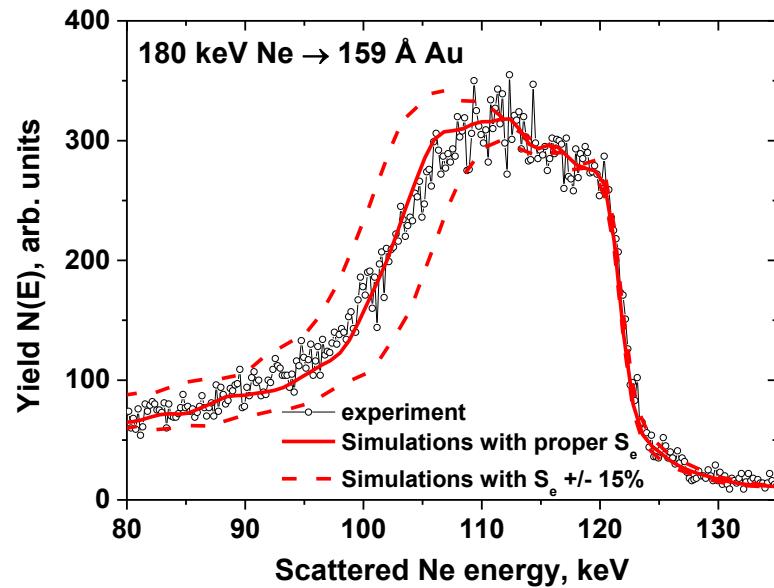
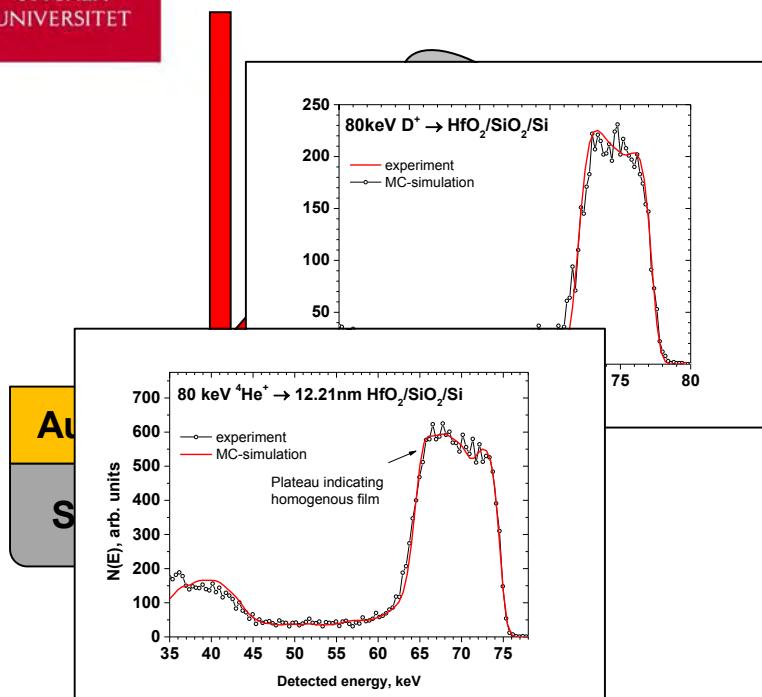
- Set of 3 transmission experiments from the literature
- Data shows a clear non-linear velocity dependence

N'Docko-N'Dongue et al.  
Ward et al.  
Schulz et al.  
electronic stopping Z03  
nuclear stopping Z03



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# Backscattering of Ne: dE/dx



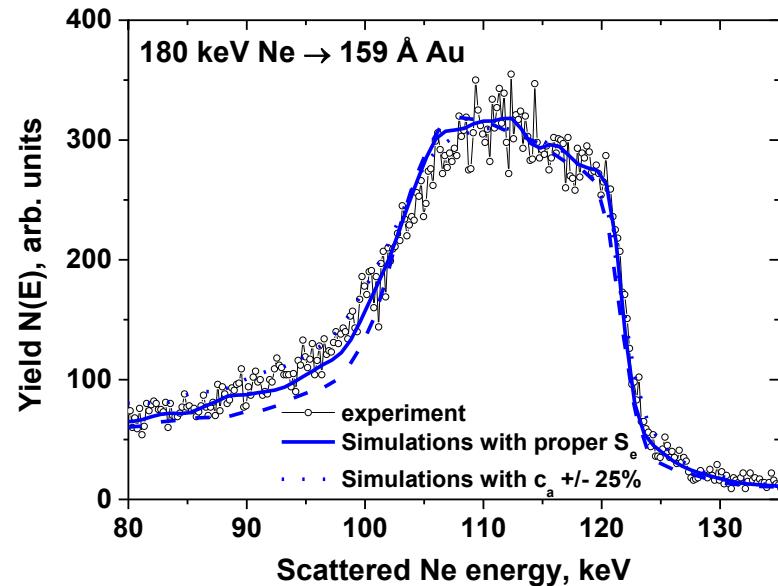
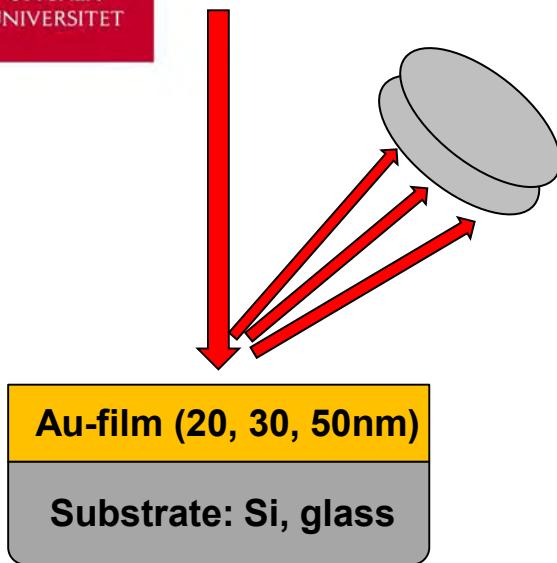
D. Primetzhofer, Nucl. Instr. Meth. B (2013)

- Electronic stopping can be obtained with high precision
- Multiple scattering affects low-energy edge of spectrum



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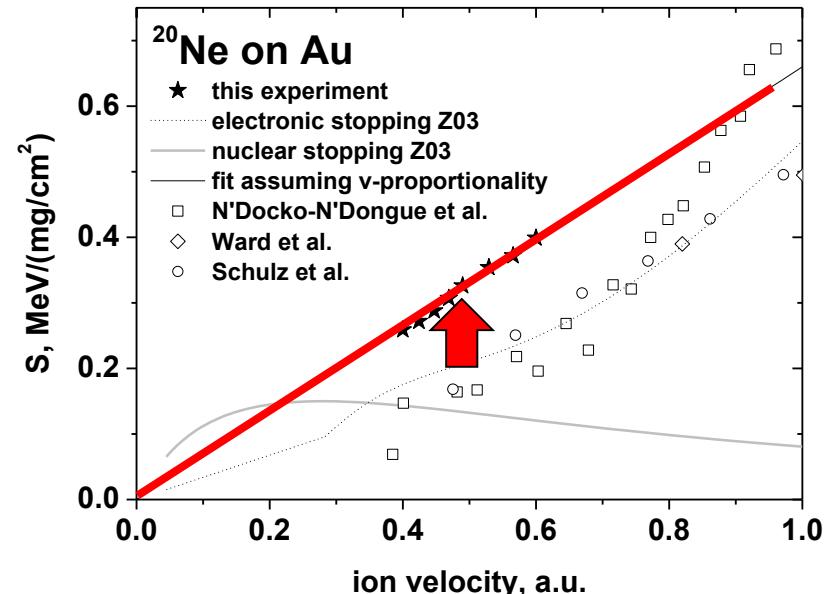
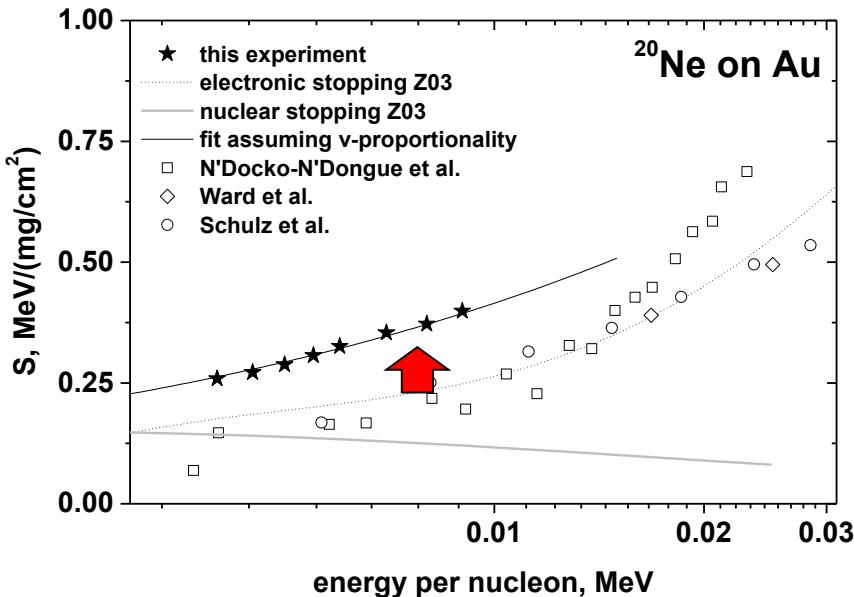
# Backscattering of Ne: $d\sigma/d\Omega$



*D. Primetzhofer, Nucl. Instr. Meth. B (2013)*

- Electronic stopping can be obtained with high precision
- Multiple scattering affects low-energy edge of spectrum
- Spectrum width unaffected by change in potential strength

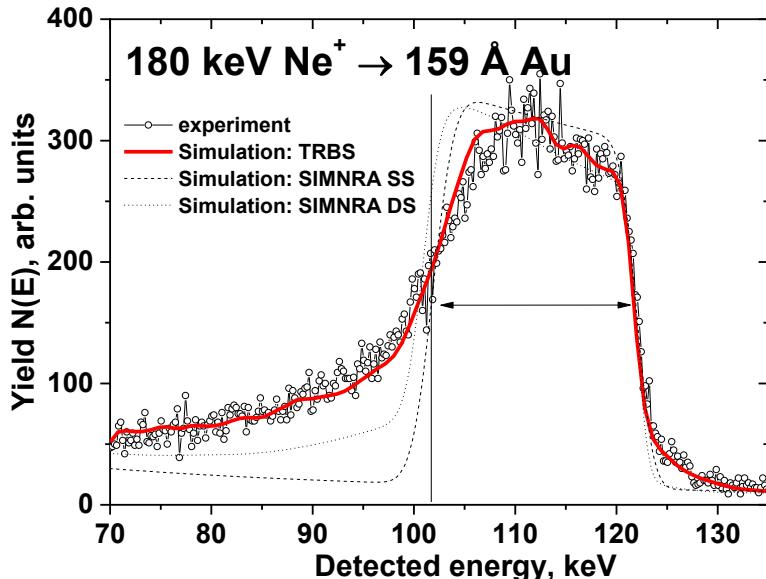
# Experimental stopping powers for $^{20}\text{Ne}$ :



D. Primetzhofer, Nucl. Instr. Meth. B (2013)

- Values deduced in backscattering are exceeding values in transmission
- Velocity proportionality of stopping cross sections

# Evaluation by different models:



- Single scattering model by SIMNRA
- Dual scattering model by SIMNRA
- Hands-on evaluation (Warter's method)
- MC-simulation by TRBS

→ Almost equivalent results!

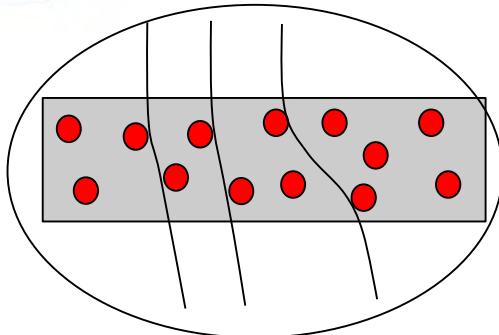
THUS:

- Nuclear stopping contribution to this experiment is apparently small!
- Contribution in transmission is expected to be even smaller!

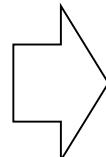
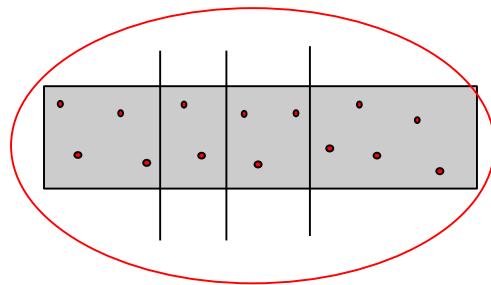
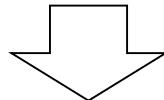


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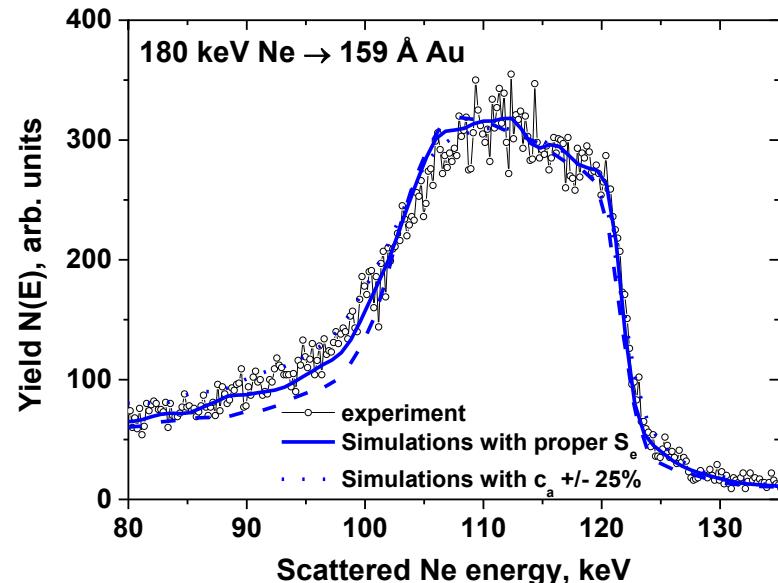
# Monte-Carlo: nuclear stopping?



"Realistic" interaction potential +/- 25%



Reducing/turning off  
the interaction potential



D. Primetzhofer, Nucl. Instr. Meth. B (2013)

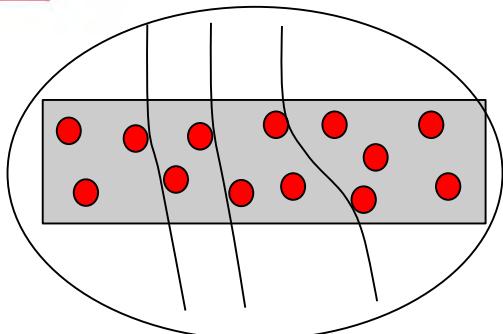
Electronic stopping exclusively...



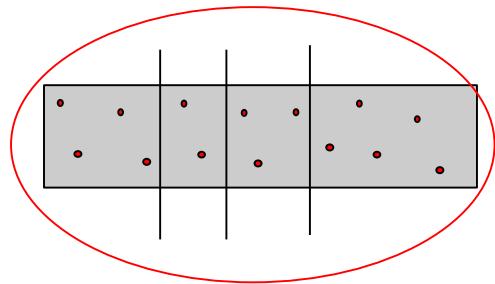
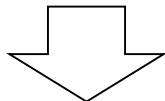
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# Monte-Carlo: nuclear stopping?

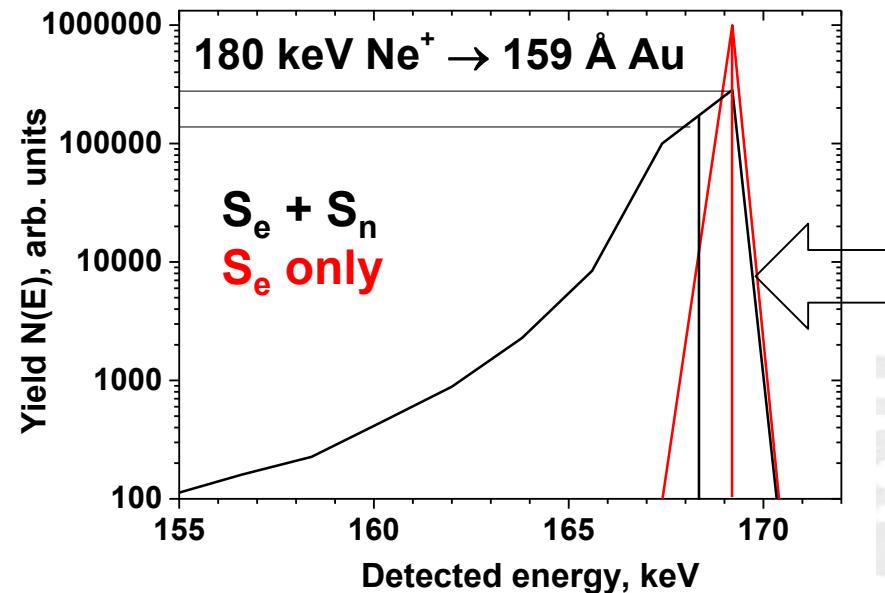
In transmission:



"Realistic" interaction potential +/- 25%



Reducing/turning off  
the interaction potential

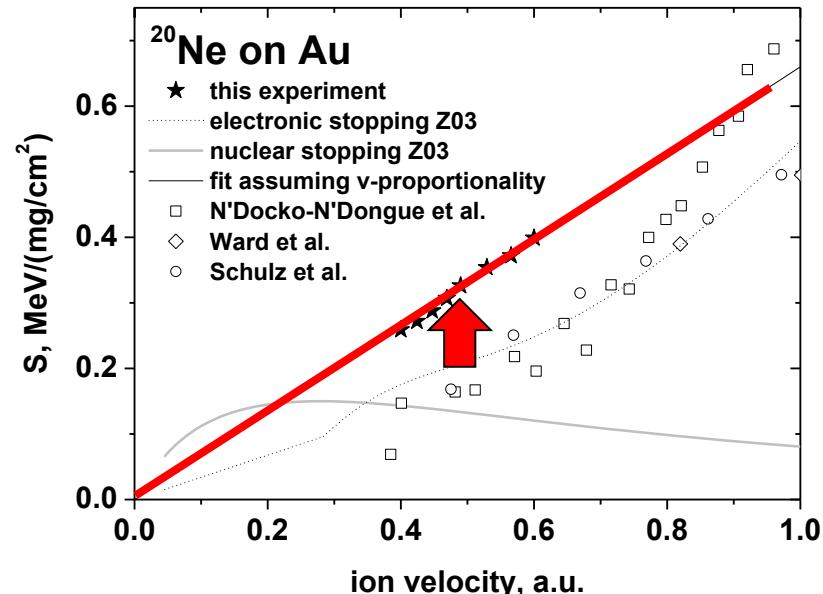
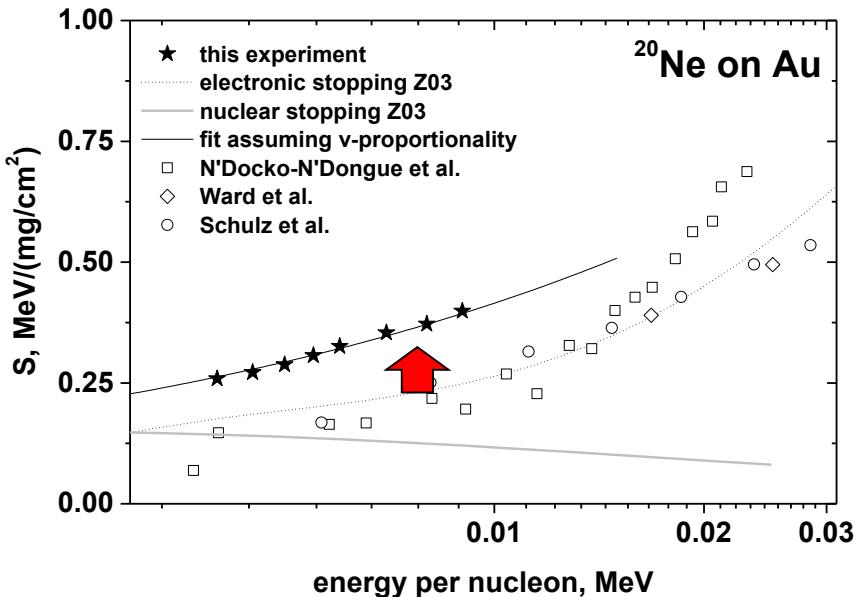


- Electronic stopping shifts spectrum
- Broadening due to nuclear stopping

BUT: only minor shift of median

$$S_{\text{nucl}} < S_{\text{elec}}/10$$

# Experimental stopping powers for $^{20}\text{Ne}$ :



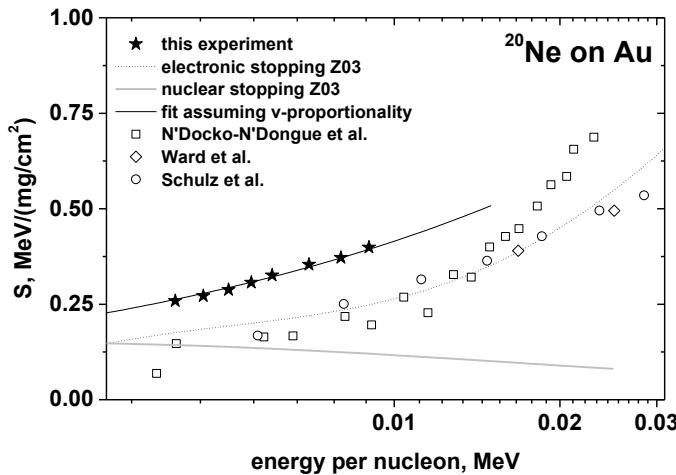
D. Primetzhofer, Nucl. Instr. Meth. B (2013)

- Values deduced in backscattering are exceeding values in transmission
- Velocity proportionality of stopping cross sections

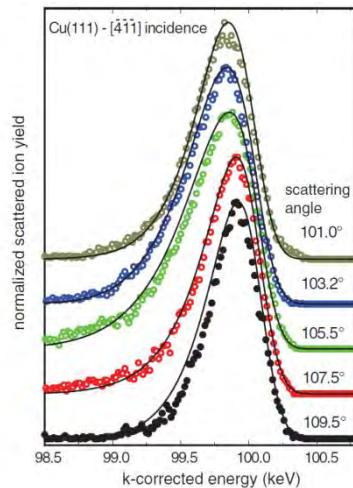


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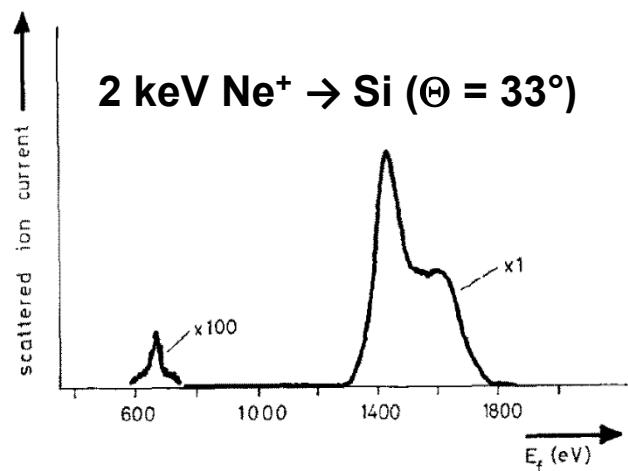
# Experimental data - revisited:



D. Primetzhofer, *Nucl. Instr. Meth. B* (2013)



A. Hentz et al., *PRL* (2009)



H.H. Brongersma et al., *Surf. Sci.* (1973)

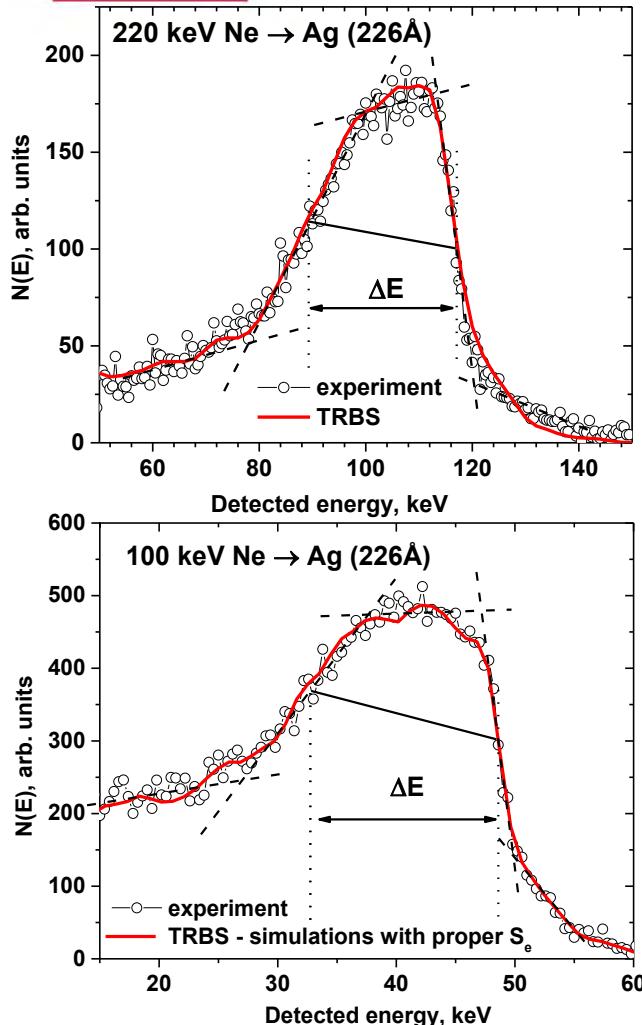
## Enhanced electronic stopping:

- Different impact parameters: backscattering vs. transmission
- Different charge state distribution: backscattering vs. transmission

# Other systems: Pt, Ag

- **Platinum results compare well with Au  
similar electronic structure – similar kinematics**
- **Silver: very different scattering kinematics**

# Ne: Evaluating $S_n$ for Ag in backscattering

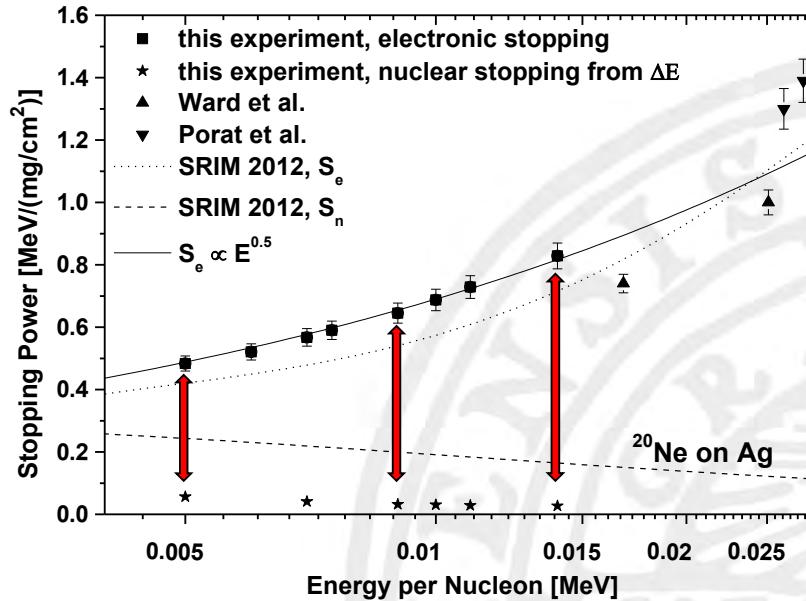


**Assumption 1: MC works correct**

$$\Delta E = \Delta E_{elec.(TRBS)} + \Delta E_{nuclear}$$

**Assumption 2:  $S_n$  scales as in SRIM**

$$\Delta E_{nuclear} = k \cdot x \cdot S_n^{in} + \frac{x}{\cos \theta} \cdot (c \cdot S_n^{in})$$

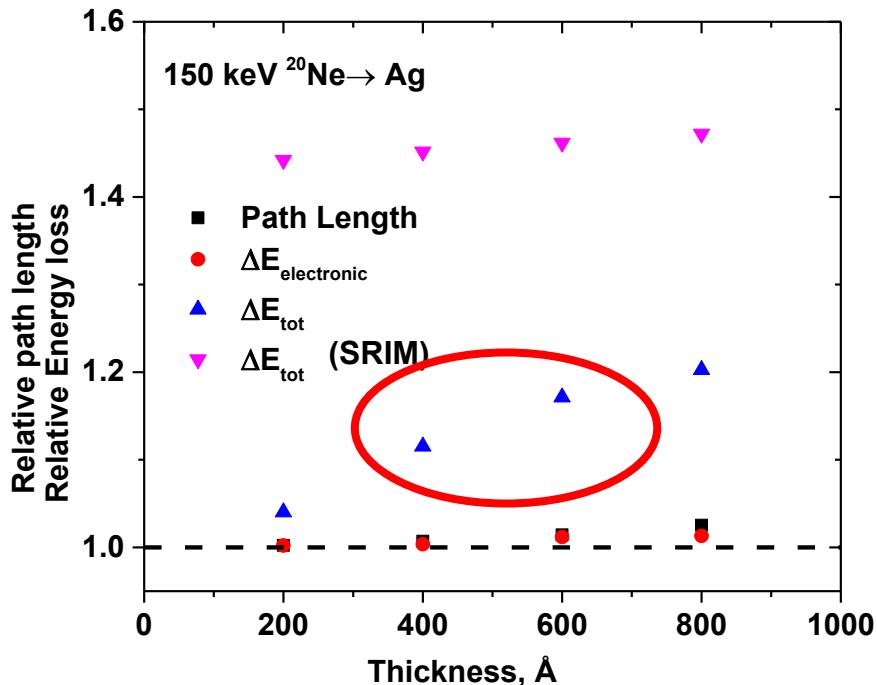


*Naqvi et al. Nucl.Instr. Meth. B (2016)*

$S_n$  is only about 15% of  $S_e$  in this experiment

# Comparing with transmission (MC)

TRIM: Transmission - exit angle 0 – 2 deg.



- Path length grows only slightly relative to thickness x.
- Electronic energy loss grows in accordance with path length
- Total energy loss shows increasing nuclear contribution.

Naqvi et al. Nucl.Instr. Meth. B (2016)

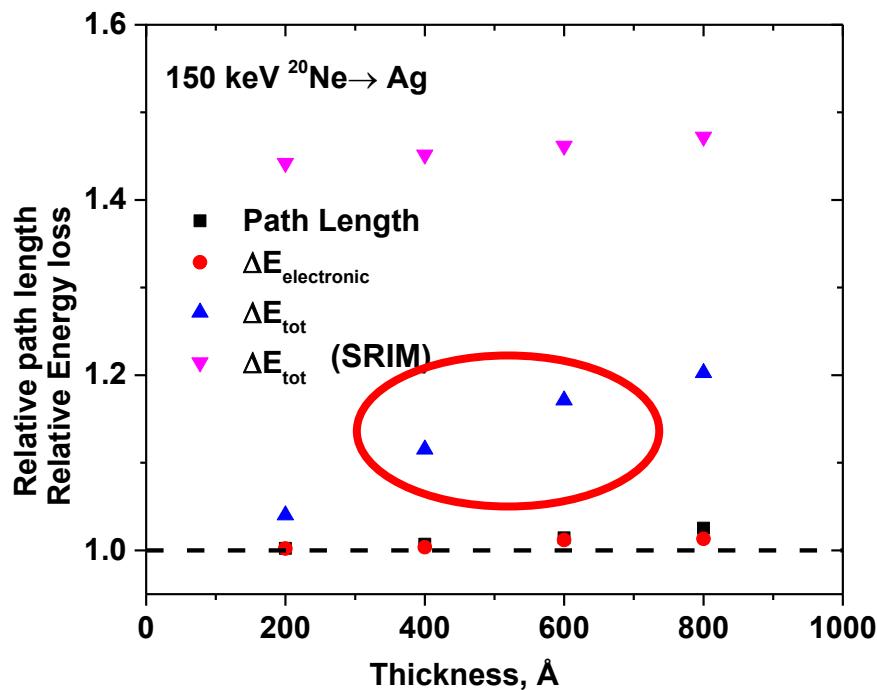
Almost identical nuclear contribution of about 10-15% for relevant thickness



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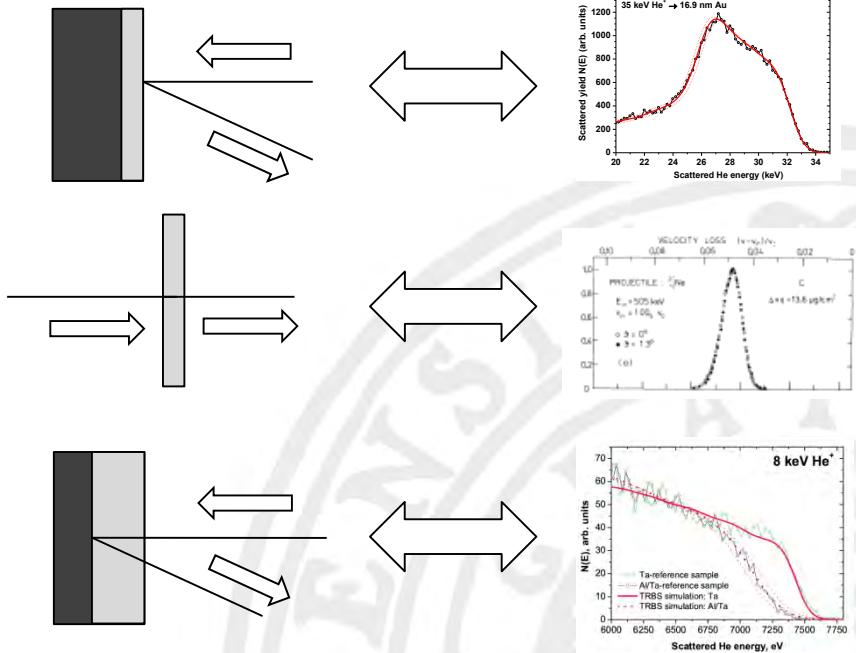
# Comparing with transmission (MC)

## TRIM - Transmission



Naqvi et al. Nucl.Instr. Meth. B (2016)

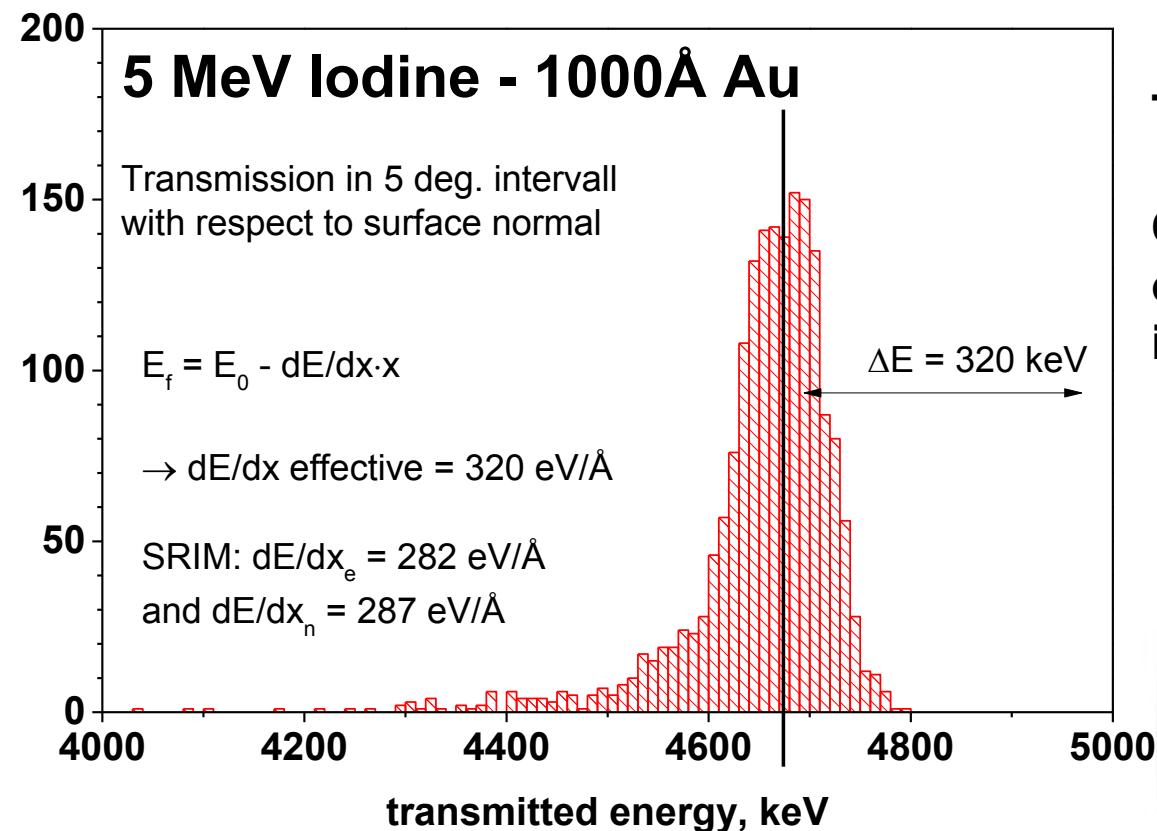
Any experiment is trajectory selective...



...when looking on characteristic spectral features!

# Applicable for even heavier ions?

- MeV ions like Bromine, Iodine employed in ERD

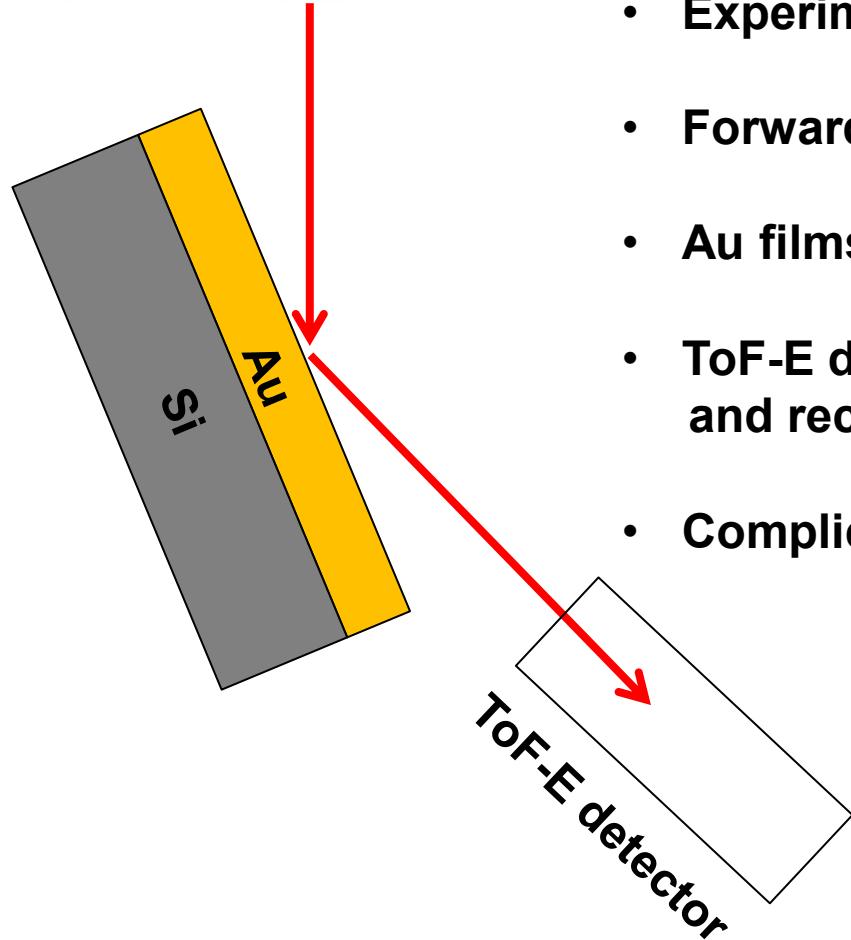


TRIM-simulations:

Only very minor contribution  
of  $dE/dx_n$  for films  
in transmission

What do we see  
experimentally?

# Forward scattering of Iodine

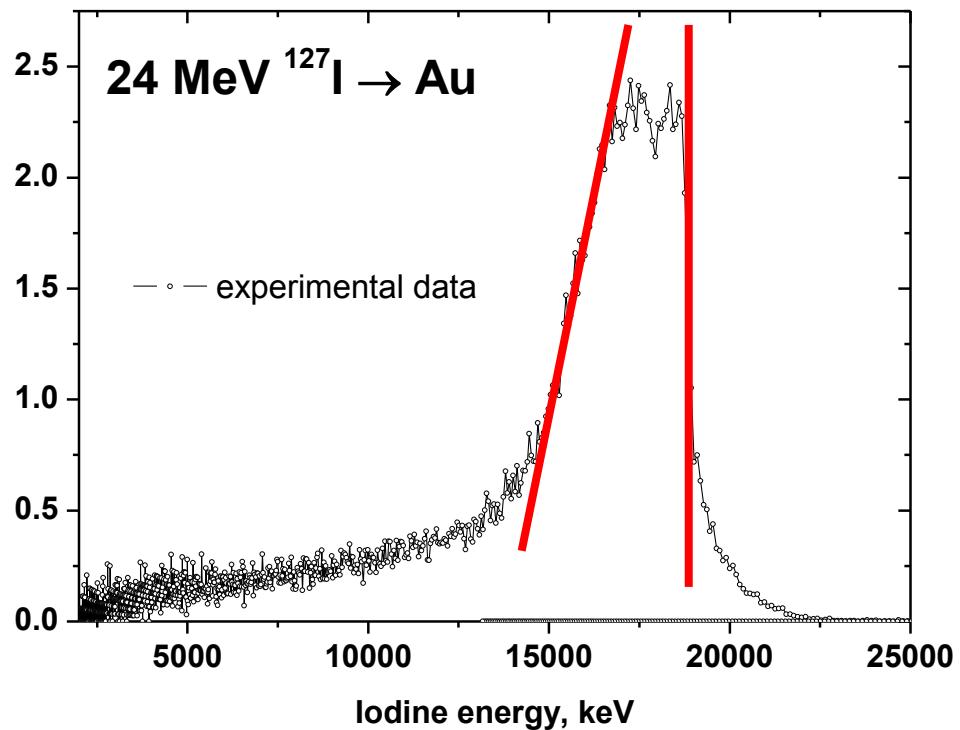


- Experiment performed with 5 MV NEC Tandem
- Forward scattering under 45 degrees
- Au films of up to 50 nm thickness
- ToF-E detector for discrimination of scattered and recoiling particles
- Complication: no  $2\pi$ -symmetry (simulations)



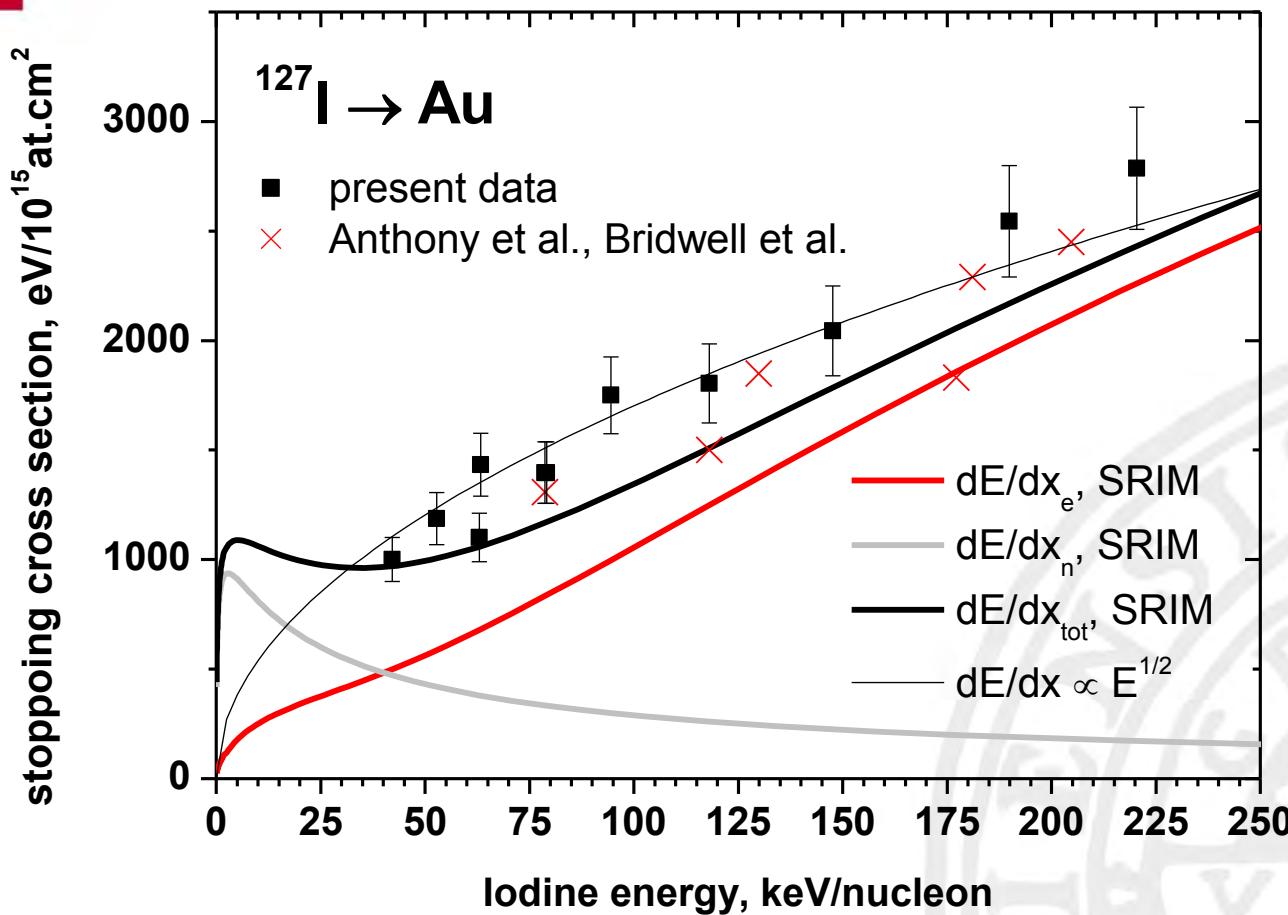
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# Forward scattering of Iodine: spectra



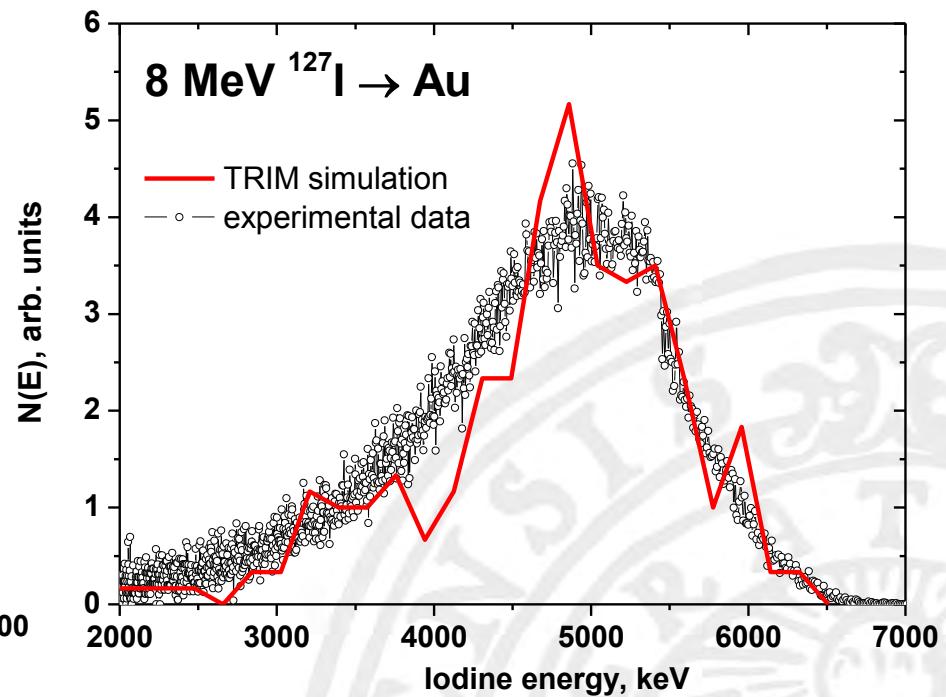
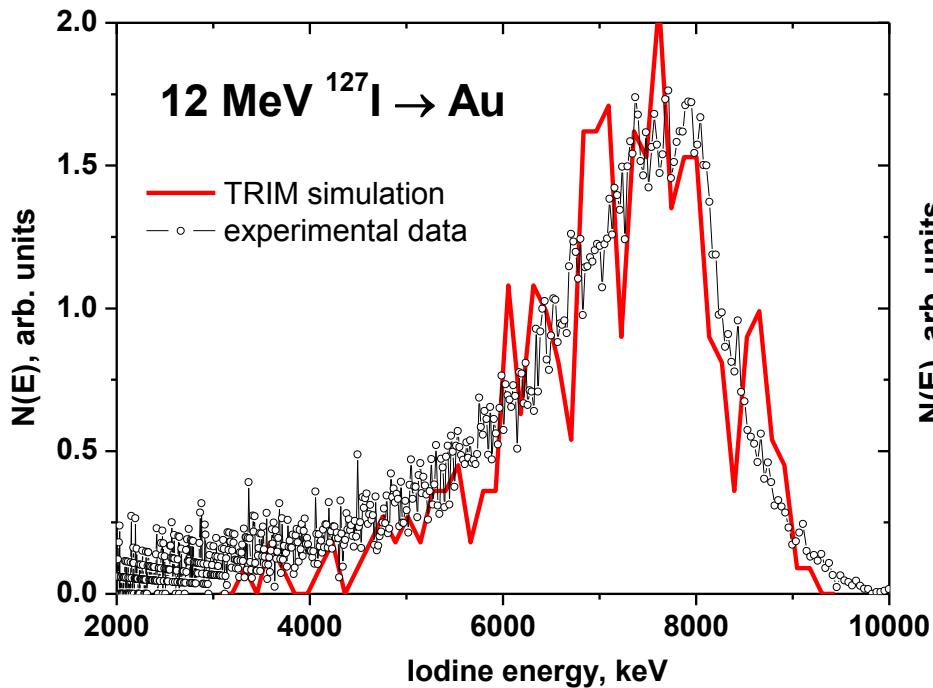
- Spectra resemble RBS-spectra for thin films
- Reasonable definition of  $\Delta E$
- Stopping power evaluation performed as for Ne

# Total stopping power deduced for I in Au



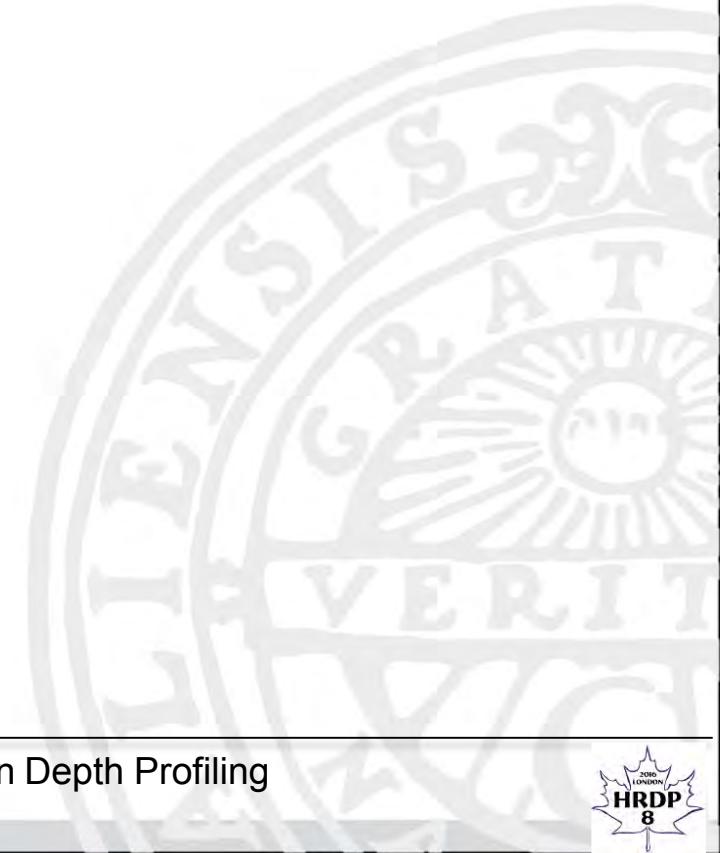
- High absolute total stopping power with reasonable v/E scaling

# Future steps: simulation by TRIM and evaluation of the relative contributions



1. Simulation by TRIM
2. Characterization of trajectories: separate  $dE/dx_e$  and  $dE/dx_n$

# Energy loss of light ions: H and He

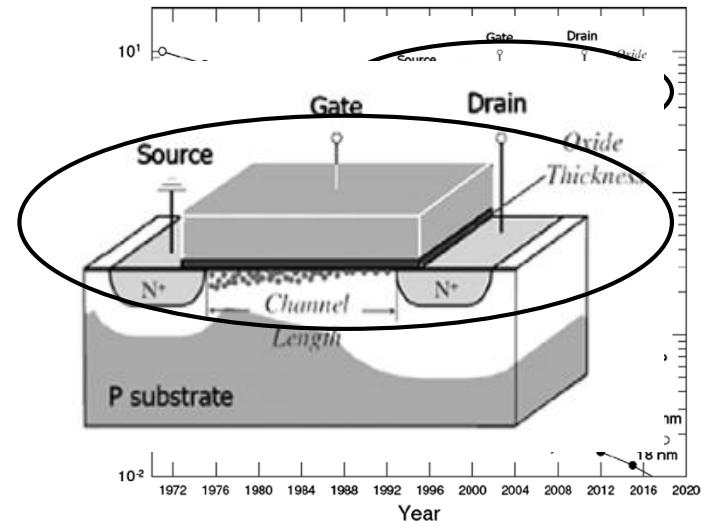
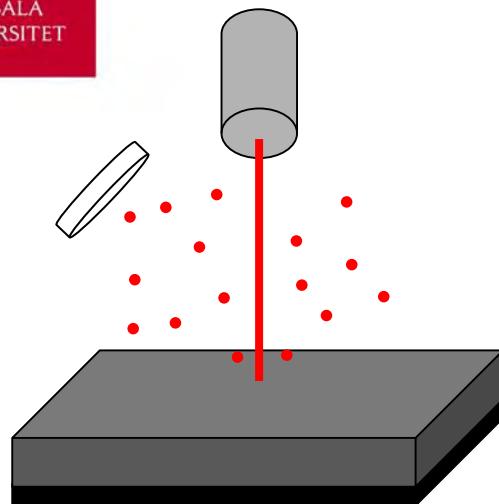


# Energy loss of light ions: H and He in $\text{HfO}_2$



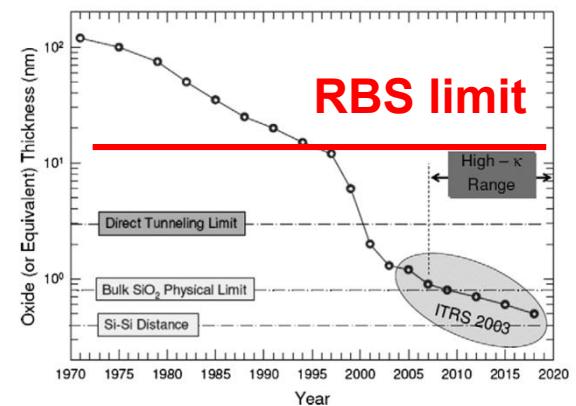
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# Why HfO<sub>2</sub> at keV energies?



H. Wong, H. Iwei, Microelec. Eng. (2006)

- Ion scattering for depth profiling
- Thin films from e.g. electronics (gate-stacks)
- 90's: Ongoing miniaturization: Film thickness below resolution limits for "conventional" RBS
- Last decade: high-k materials – good scatterers
- Higher  $\Delta E/E$ : → development of MEIS





# Characterization of high-k dielectrics...

Cross characterization of ultrathin interlayers in  $\text{HfO}_2$  high-k stacks by angle resolved x-ray photoelectron spectroscopy, medium energy ion scattering, and grazing incidence extreme ultraviolet reflectometry

Matus Baranyai<sup>a,b</sup> and Larsena, Asachenko  
a) WZL Aachen University, Chair for Technology of Optical Systems, Steinbachstr. 15, 52074 Aachen,  
Germany and b) Fundamentals of Future Information Technology, Research Center Jülich 52425,  
Germany

Eric Bersch, Daniel Franca, Michael Lierh, and Alain Diebold  
College of Nanoscale Science and Engineering (CNSE), 255 Fuller Rd., Albany, New York, 12203

(Received 29 July 2011; accepted 26 April 2012; published 21 May 2012)

In order to miniaturize metal oxide semiconductor field effect transistors even further and improve their performances, channel lengths and gate dielectric thicknesses must be decreased. Tradition

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Nuclear Instruments and Methods in Physics Research B 283 (2011) 146–155



Appl. Surface Science 263–264 (2009) 414–422



and high-resolution RBS analysis of

High resolution medium energy ion scattering analysis for the quantitative depth profiling of ultrathin high-k layers

M. A. Reading<sup>a</sup>, J. A. van den Berg<sup>b</sup>, P. C. Zalm<sup>b</sup>, and D. G. Armour<sup>c</sup>  
Institute for Materials Research, University of Salford, Salford M3 4WT, United Kingdom

P. Bailey and T. C. O. Noakes  
STFC Daresbury Laboratory, Daresbury, WA4 4AD, United Kingdom

se Bologna, Via Göbbetti, 40129 Bologna, Italy

J. S. De Gendt<sup>a</sup>  
et al., Leuven, Belgium  
June 2009; accepted 21 September 2009; published 1 March 2010

layers such as hafnium oxide ( $\text{HfO}_2$ ) in combination with a subnanometer  $\text{SiO}_2$  or  $\text{Si}$  emerged as Si compatible gate dielectric materials. Medium energy ion scattering has been carried out on a range of such metal oxide dielectric films of thickness between 1 and 2 nm on

High-resolution depth profiling of ultrathin gate oxides by medium-energy ion scattering

T. Gustafsson<sup>a</sup>, H.-C. Lu<sup>a</sup>, B.-W. Busch<sup>a</sup>, W.H. Schlueter<sup>a</sup>, E. Gaertner<sup>a</sup>,  
Departments of Phys. & Chemistry, and Laboratory for Surface Modification, Rutgers State University  
Frelinghuysen Road, P.O. Box 848, Piscataway, NJ 08854-8019, USA

Received 31 October 2009



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journal homepage: www.elsevier.com/locate/apsusc



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30 SEPTEMBER 2003

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Characterization and control of the  $\text{HfO}_2/\text{Si}(001)$  interfaces

Y. Hosono and Y. Kiddo<sup>a</sup>  
Department of Physics, Ritsumeikan University, Kusatsu, Shiga-ken 525-8577, Japan

K. Yamamoto, S. Hayashi, and M. Niwa  
Matsushita Electric Industrial Co., Ltd., Nishiohno-Kasugacho, Minami-ku, Kyoto 601-8413, Japan  
(Received 14 June 2002; accepted 6 August 2003)

The  $\text{HfO}_2/\text{Si}(001)$  interfaces formed by reactive dc sputter deposition of  $\text{Hf}$  buffer layer followed by  $\text{HfO}_2$  stacking were analyzed by high-resolution transmission electron microscopy, medium energy ion scattering (MEIS), and photoelectron spectroscopy using synchrotron-radiation lights. The present MEIS analysis determined the elemental depth profiles and revealed that at  $\text{Hf}$  buffer layer region, the oxygen concentration at the interface was higher than that in the  $\text{HfO}_2$  layer due to the formation of  $\text{Si}-\text{rich}-\text{oxide-like}-\text{interlayer}$ . The bonding environment of  $\text{SiO}_4$  in the  $\text{HfO}_2$  layer and the chemical bonds of the interfacial layers and confirmed the formation of  $\text{SiO}_4$  (in buffer layer) and silicate layers (presence of the buffer layer) at the interfaces. The  $\text{Hf}$ -buffer layer suppresses the O diffusion toward the interface and thus the thicker the  $\text{Hf}$  buffer layer, the thinner the  $\text{Hf}$ -silicate interlayer. The deposition condition of  $\text{HfO}_2$  (1.3 nm)/ $\text{Hf}$  (1.3 nm) has achieved the highest permittivity of 28. Copyright © 2002 American Institute of Physics [DOI: 10.1063/1.1510941]

High-k dielectric metal oxide films have attracted much attention as promising candidates for the forthcoming gate dielectric material of metal–oxide–silicon field-effect transistors in place of  $\text{SiO}_2$ . The main requirements are high dielectric constant  $k$  and a stable and sharp interface. So far, many efforts have been made to suppress the interfacial layer of  $\text{SiO}_2$  and/or silicates.<sup>1–4</sup> Unfortunately, however, how to control the high-k film/Si(001) interface is still unknown.

$\text{HfO}_2$  is one of the most suitable materials, because it has a high- $k$  value of about 25 and expected to be stable in

precise analysis of the chemical bonding of the interlayers, we prepared thin thermal oxides of  $\text{SiO}_2$ ,  $\text{HfO}_2$ , Hf silicates, and Hf silicides ( $\text{HfSiO}$  and  $\text{HfSi}$ ) as the standards for PES analysis. All the above thin films were grown on  $\text{Si}(001)$  substrates. Their elemental compositions and absolute thickness were determined by Rutherford backscattering (RBS) using  $400 \text{ keV}$   $\text{He}^+$  beams and these RBS data calibrated the MEIS spectra.

The surfaces of on-axis  $p$ -type  $\text{Si}(001)$  substrates were chemically treated with an  $\text{HF}$  solution and then annealed at  $400^\circ\text{C}$  for 20 min in  $\text{N}_2\text{H}_4$  ambient. The results in terms

## Research

Received 18 Aug.  
(www.interscience

A col-  
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**Hf-b**

## 1. Introduction

Medium-energy ion scattering (MEIS) is a complicated and extensive analysis method. It

Ultra-thin high-k layers based on  $\text{HfO}_2$ , or  $\text{HfSiO}$ , in combination with a  $\text{SiO}_2$ -containing gate dielectric, XPS has been applied over a range before and after deionized plasma nitration (DPN) at 1073 K. The individual layer thicknesses of the multilayer stack taking into account the procedure adhered to the prescriptions of ISO18118:2004(E) for its elastic scattering theorem, using the measured properties, like the scattering was taken throughout the respective MEIS spectra versus a (RSF) was used. The XPS-derived thicknesses were compared with cor scattering (MEIS) measurements on the same series of specimens in cor quantitative layer normalizations sub-nanometer resolution. The XPS deduced layer structures within the respective experimental total layer parameters of the high-k nanofilms. Copyright © 2010 John Wiley

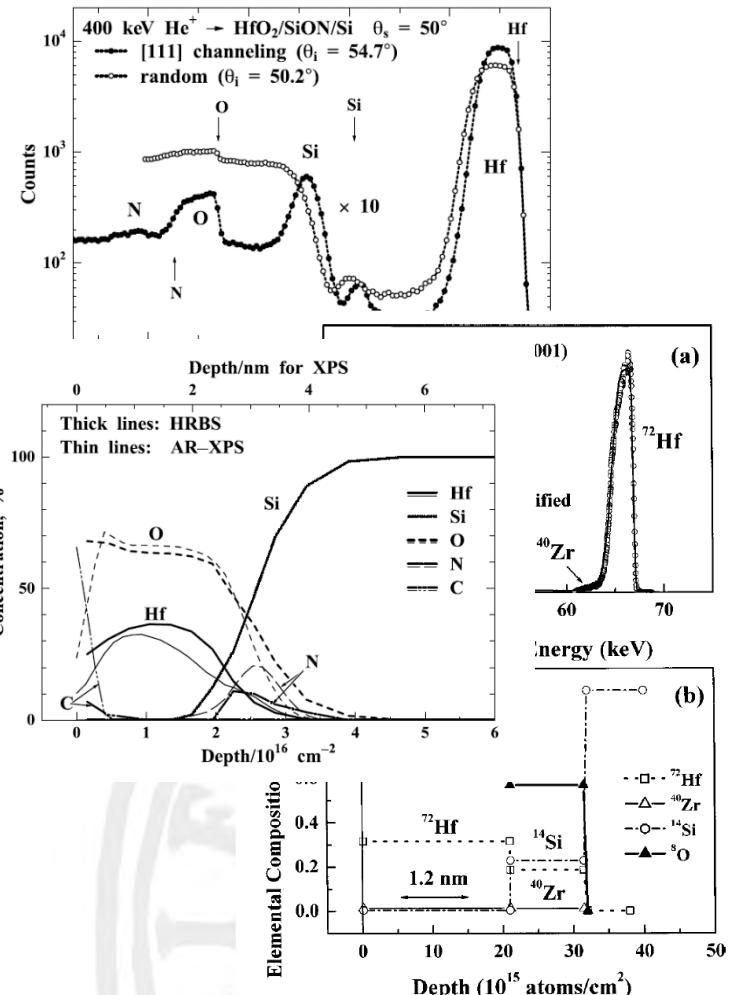
Keywords: high-k nanofilm;  $\text{HfO}_2$ ; hafnium silicate; XPS; MEIS; layer thickness

## Introduction

Significant research effort has been recently directed toward replacing the conventional  $\text{SiO}_2$  nanofilms with ultra-thin high-k layers based on  $\text{HfO}_2$ , or  $\text{Hf}$ -silicates, in combination with sub-

as un-  
below,  
obtain-  
within the ANNA project on the same series of samples.<sup>26</sup>

- Investigations of stacks containing  $\text{HfO}_2$  are common





# ....a MEIS-success story...

Cross characterization of ultrathin interlayers in  $\text{HfO}_2$  high-k stacks by angle resolved x-ray photoelectron spectroscopy, medium energy ion scattering, and grazing incidence extreme ultraviolet reflectometry

Matus Baranyai<sup>a</sup> and Larsena Aachman<sup>b</sup>  
 a) WZL Aachen University, Chair for Technology of Optical Systems, Steinbachstr. 15, 52074 Aachen,  
 Germany and JARA—Fundamentals of Future Information Technology, Research Center, Jülich 52425,  
 Germany

Eric Bersch, Daniel Franca, Michael Lierh, and Alain Diebold<sup>c</sup>  
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 (Received 29 July 2011; accepted 26 April 2012; published 21 May 2012)

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and high-resolution RBS analysis of  
 High resolution medium energy ion scattering analysis for the quantitative depth profiling of ultrathin high-k layers

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 June 2009; accepted 21 September 2009; published 1 March 2010

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High-resolution depth profiling of ultrathin gate oxides by medium-energy ion scattering

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 Received 31 October 2009



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Characterization and control of the  $\text{HfO}_2/\text{Si}(001)$  interfaces

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 K. Yamamoto, S. Hayashi, and M. Niwa  
 Matsushita Electric Industrial Co., Ltd., Nishio-kaa-gaoka, Minami-ku, Kyoto 601-8413, Japan  
 (Received 14 June 2002; accepted 6 August 2003)

The  $\text{HfO}_2/\text{Si}(001)$  interfaces formed by reactive dc sputter deposition of  $\text{Hf}$  buffer layer followed by  $\text{HfO}_2$  stacking were analyzed by high-resolution transmission electron microscopy, medium energy ion scattering (MEIS), and photoelectron spectroscopy using synchrotron-radiation lights. The present MEIS analysis determined the elemental depth profiles and revealed that at  $\text{Hf}$  buffer layer region, the oxygen concentration at the interface was low in the presence of the  $\text{Hf}$  layer led to the formation of  $\text{Si}_3\text{N}_4$ -like structure. The bonding environment of  $\text{Si}$  atoms was confirmed and the chemical bonds of the interfacial layers and confirmed the formation of  $\text{SiO}_2$  (as buffer layer) and silicate layers (presence of the buffer layer) at the interfaces. The  $\text{Hf}$ -buffer layer suppresses the O diffusion toward the interface and thus the thicker the  $\text{Hf}$  buffer layer, the thinner the  $\text{Hf}$ -silicate interlayer. The deposition condition of  $\text{HfO}_2$  (1.3 nm)/ $\text{Hf}$  (1.3 nm) has achieved the highest permittivity of 28. Copyright © 2003 American Institute of Physics [DOI: 10.1063/1.1510941]

High-k dielectric metal oxide films have attracted much attention as promising candidates for the forthcoming gate dielectric material of metal–oxide–silicon field-effect transistors, in place of  $\text{SiO}_2$ . The main requirements are high dielectric constant  $k$  and a stable and sharp interface. So far, many efforts have been made to suppress the interfacial layer of  $\text{SiO}_2$  and/or silicates.<sup>1–4</sup> Unfortunately, however, how to control the high-k film/Si(001) interface is still unknown.

$\text{HfO}_2$  is one of the most suitable materials, because it has a high- $k$  value of about 25 and expected to be stable in the annealing process within the temperature range of 400–600 °C.

precise analysis of the chemical bonding of the interlayers, we prepared thin thermal oxides of  $\text{SiO}_2$ ,  $\text{HfO}_2$ , Hf silicates, and Hf silicides ( $\text{HfSiO}$  and  $\text{HfSi}$ ) as the standards for PES analysis. All the above thin films were grown on  $\text{Si}(001)$  substrates. Their elemental compositions and absolute thickness were determined by Rutherford backscattering (RBS) using  $400 \text{ keV}$   $\text{He}^+$  beams and these RBS data calibrated the MEIS spectra.

The surfaces of on-axis  $p$ -type  $\text{Si}(001)$  substrates were chemically treated with an  $\text{HF}$  solution and then annealed at  $400^\circ\text{C}$  for 20 min in  $\text{N}_2\text{H}_4$  ambient. The results in terms

## Research

Received 18 Aug.  
 (www.interscience

A collection of spec  
 ifications for Hf-b  
 b.

## 1. Introduction

Medium-energy ion scattering (MEIS) is a complicated and extensive analysis method. It

Ultra-thin high-k layers based on  $\text{HfO}_2$ , or  $\text{Hf}$ -silicates in combination with a Si-compatible gate dielectric, XPS has been applied in a range before and after plasma nitridation (DPN) at 1073 K. True individual layer thicknesses of the multilayer stack taking into account the procedure adhered to the prescriptions of ISO18118:2004(E) for its elastic constants thereof, using the measured properties, like  $E_{\text{eff}}$  were taken throughout all the respective MEIS spectra as a (RSP) was used. The XPS-derived thicknesses were compared with cor scattering (MEIS) measurements on the same series of specimens in cor quantitative layer normalizations sub-nanometer resolution. The XPS deduced layer structures within the respective experimental total layer parameters of the high-k nanofilms. Copyright © 2010 John Wiley & Sons, Ltd.

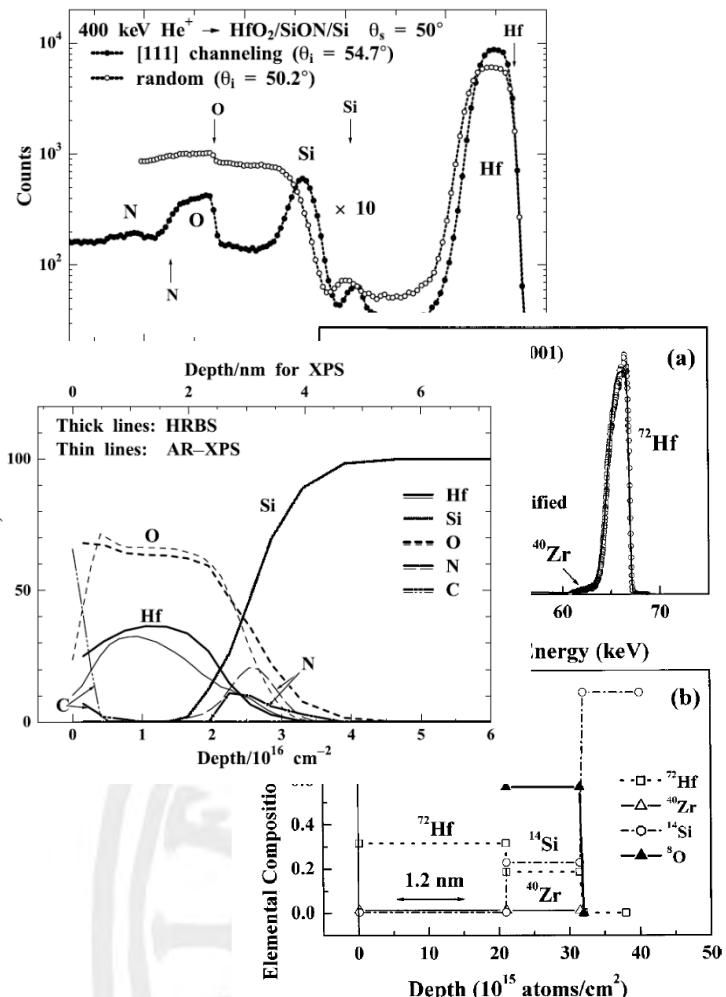
Keywords: high-k nanofilm;  $\text{HfO}_2$ ; hafnium silicate; XPS; MEIS; layer thickness

## Introduction

Significant research effort has been recently directed toward replacing the conventional  $\text{SiO}_2$  nanofilms with ultra-thin high-k layers based on  $\text{HfO}_2$ , or  $\text{Hf}$ -silicates, in combination with sub-

as thick as 1 nm below, obtainable within the ANNA project on the same series of samples.<sup>26</sup>

- Investigations of stacks containing  $\text{HfO}_2$  are common



# ...with open questions.



Cross characterization of ultrathin interlayers in  $\text{HfO}_2$  high-k stacks by angle resolved x-ray photoelectron spectroscopy, medium energy ion scattering, and grazing incidence extreme ultraviolet reflectometry

Matus Baranyai<sup>a</sup> and Larsisa Lascu<sup>b</sup>  
 a) *WZL Aachen University, Chair for Technology of Optical Systems, Steinbachstrasse 15, 52074 Aachen, Germany* and *JARA—Fundamentals of Future Information Technology, Research Center Jülich 52425, Germany*

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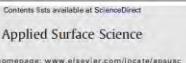
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Characterization and control of the  $\text{HfO}_2/\text{Si}(001)$  interfaces

Y. Hoshino and Y. Kiddo<sup>a</sup>  
*Department of Physics, Ritsumeikan University, Kusatsu, Shiga-ken 525-8577, Japan*

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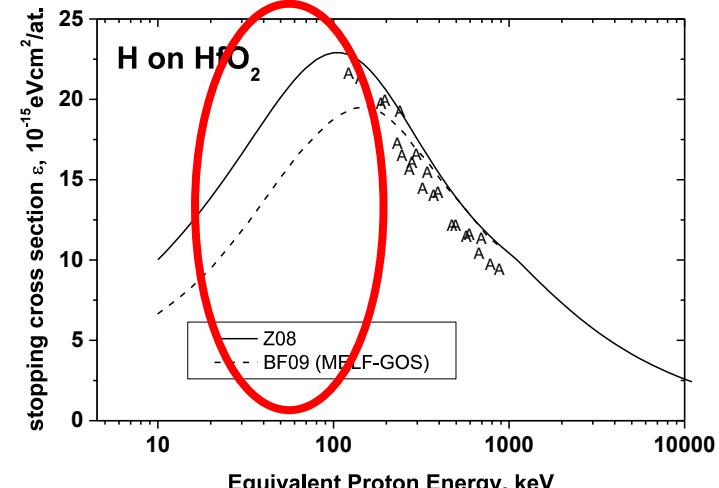
The  $\text{HfO}_2/\text{Si}(001)$  interfaces formed by reactive dc sputter deposition of  $\text{HfF}$  buffer layer followed by  $\text{HfO}_2$  stacking were analyzed by high-resolution transmission electron microscopy, medium energy ion scattering (MEIS), and photoelectron spectroscopy using synchrotron-radiation lights. The present MEIS analyses determined the elemental depth profiles and revealed that the  $\text{Hf}$  buffer layer remained at the interface even in the presence of the  $\text{Hf}$  layer led to the formation of  $\text{Si}-\text{rich silicate-like structure}$ . The binding energies of  $\text{Si}$  and  $\text{O}$  were measured and the chemical bonds of the interfacial layers and confirmed the formation of  $\text{SiO}_4$  (in buffer layer) and silicate layers (presence of the buffer layer) at the interfaces. The  $\text{Hf}$ -buffer layer suppresses the O diffusion toward the interface and thus the thicker the  $\text{Hf}$  buffer layer, the thinner the  $\text{Hf}$ -silicate interlayer. The deposition condition of  $\text{HfO}_2$  (1.3 nm)/ $\text{Hf}$  (1.3 nm) has achieved the highest permittivity of  $\text{HfO}_2$  (3.6 nm) and 8 for the silicate layer (1.7 nm). © 2002 American Institute of Physics [DOI: 10.1063/1.1510941]

High-k dielectric metal oxide films have attracted much attention as promising candidates for the forthcoming gate dielectric material of metal–silicon field-effect transistors, in place of  $\text{SiO}_2$  film. The main advantage requires a high dielectric constant  $k$  and a stable and sharp interface. So far, many efforts have been made to suppress the interfacial layer of  $\text{SiO}_2$  and/or silicates.<sup>1–4</sup> Unfortunately, however, how to control the high-k film/Si(001) interface is still unknown.

$\text{HfO}_2$  is one of the most suitable materials, because it has a high-k value of about 25 and expected to be used within the ANNA project on the same series of samples.<sup>5</sup>

precise analysis of the chemical bonding of the interlayers, we prepared thin thermal oxides of  $\text{SiO}_2$ ,  $\text{HfO}_2$ ,  $\text{Hf}$  silicates, and  $\text{HfSiO}_4$  (HSi) as the standards for PES analysis. All the above thin films were grown on  $\text{Si}(001)$  substrates. Their elemental compositions and absolute thickness were determined by Rutherford backscattering (RBS) using  $1.5 \text{ MeV}$   $\text{He}^+$  beams and these RBS data calibrated the MEIS spectra.

The surfaces of  $\text{Si}(001)$  w-type  $\text{Si}(001)$  substrates were chemically treated with an HF solution and then annealed at  $400^\circ\text{C}$  for 20 min in  $\text{N}_2\text{H}_4$  ambient. This resulted in



from H. Pauls stopping collection:  
[www-nds.iaea.org/stoppinggraphs/](http://www-nds.iaea.org/stoppinggraphs/)

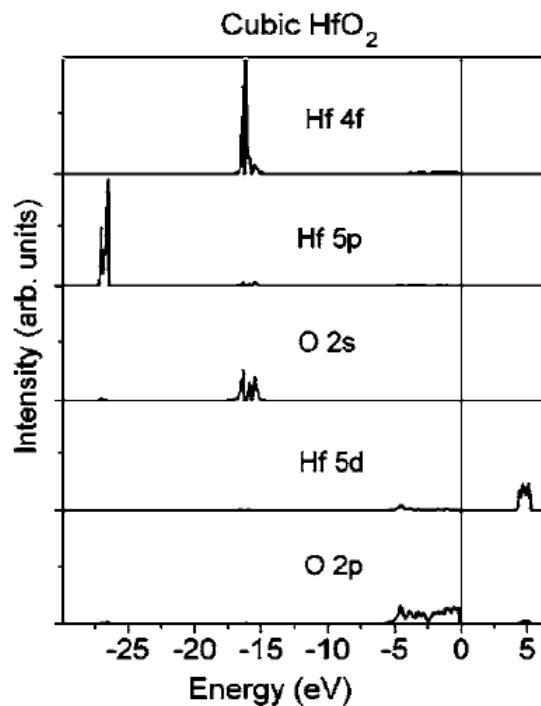
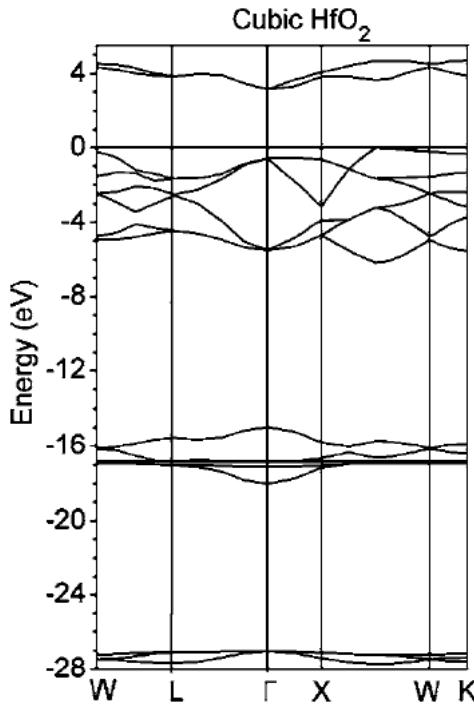
- **Experimental stopping data is scarce**

- **Investigations of stacks containing  $\text{HfO}_2$  are common**

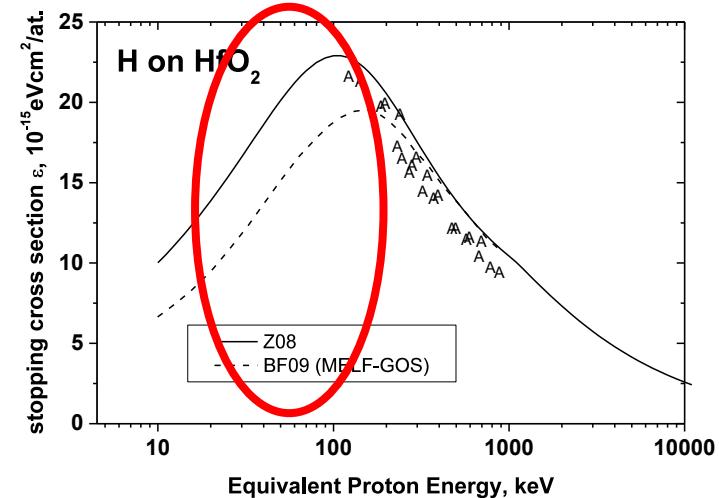


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# ...with open fundamental questions.



T.V. Perevalov et al., J. Appl. Phys. (2007)



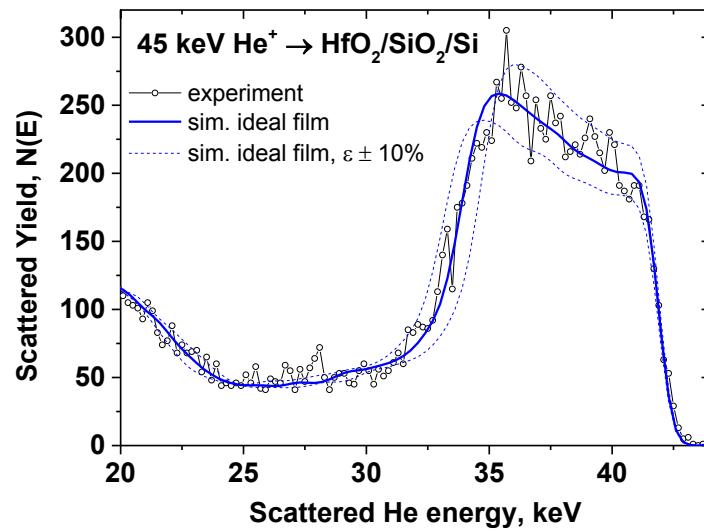
from H. Pauls stopping collection:  
[www-nds.iaea.org/stoppinggraphs/](http://www-nds.iaea.org/stoppinggraphs/)

- Experimental stopping data is scarce
- Insulator with ~ 5-6 eV gap

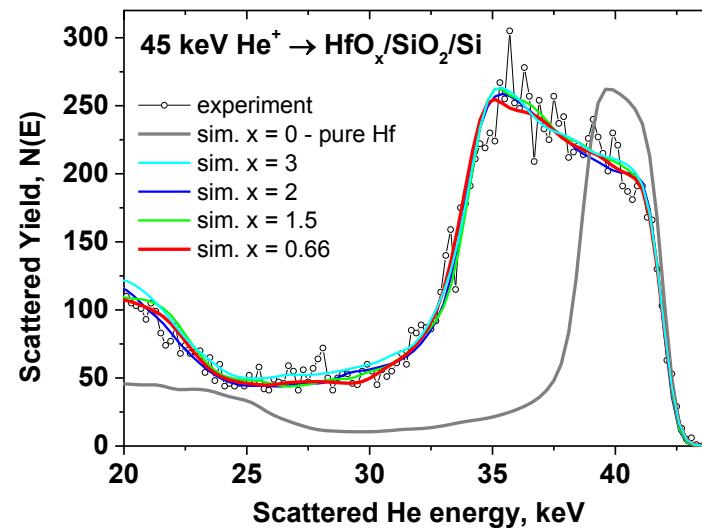
# Relevance for analysis of thin films

## Potential complications:

- Energy loss in the thin film      ↔      Thickness calibration in MEIS
- Entanglement of compositional information and energy loss

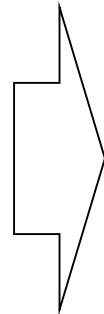
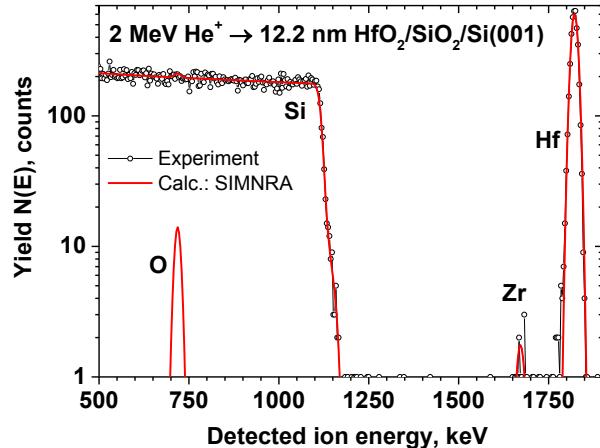


D. Primetzhofer et al., Nucl. Instr. Meth. B 332 (2014)

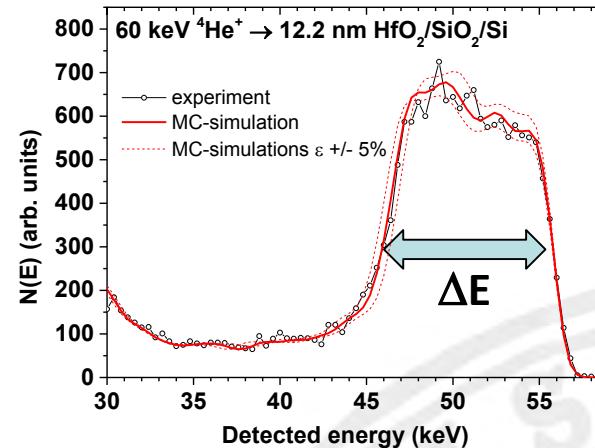




# Analysis of electronic energy loss in $\text{HfO}_2$



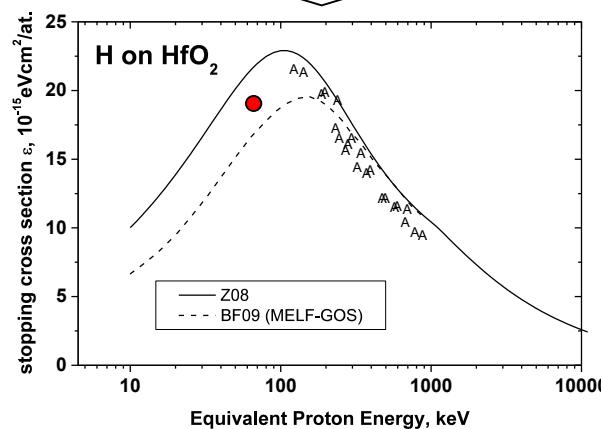
- Fit width of ToF-MEIS energy spectra



- Determine Hf content from RBS

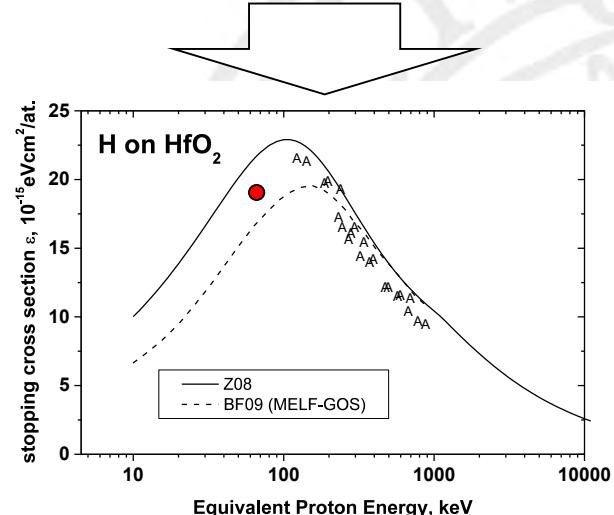
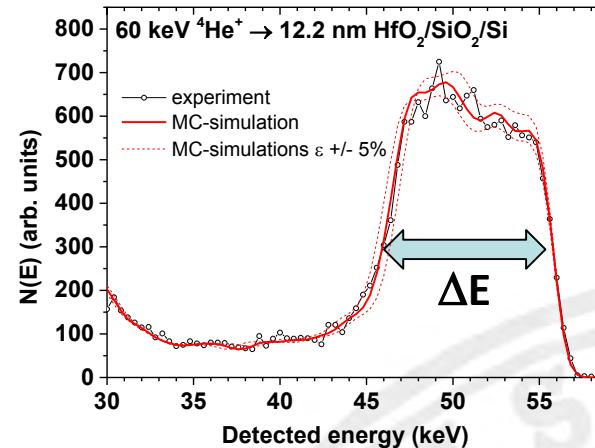
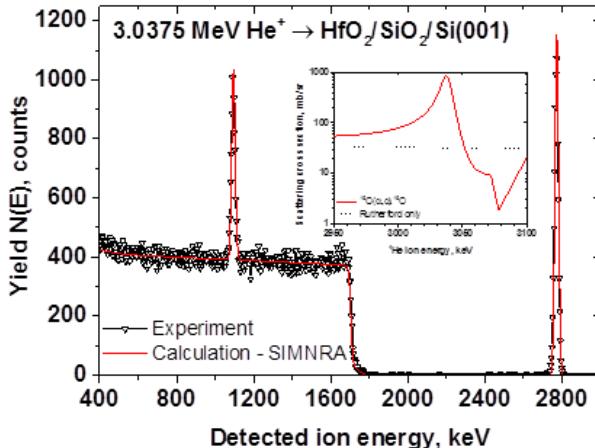
**Uncertainty from:**

- **Statistics**
- **Thickness calibration**
- **Composition**



# Analysis of electronic energy loss in $\text{HfO}_2$

- Fit width of ToF-MEIS energy spectra



C.J. Zoller, *Nucl. Instr. Meth. B* 347 (2015)

- Determine Hf content from RBS (check oxygen by e.g. EBS, channeling,...)

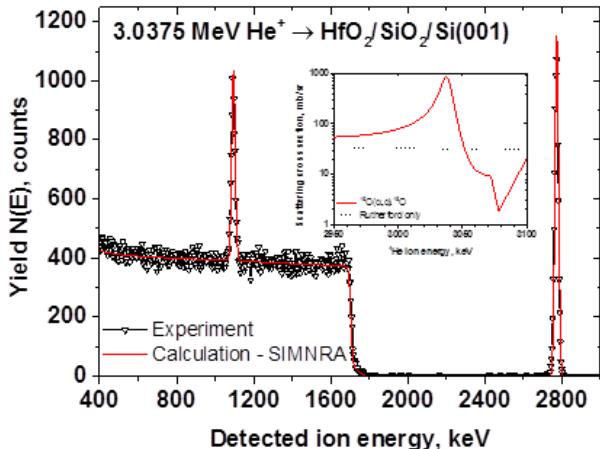
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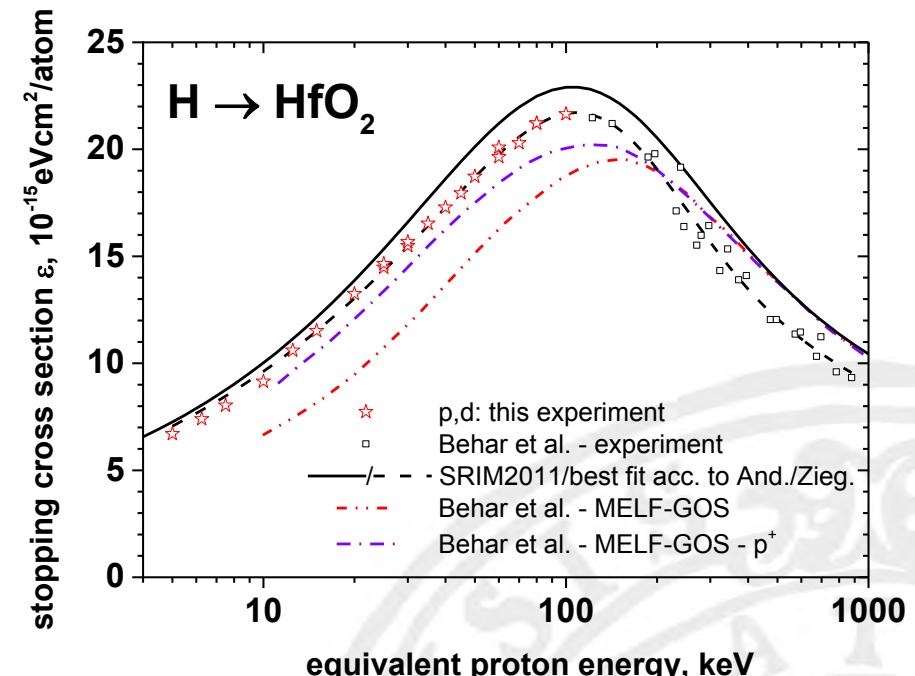
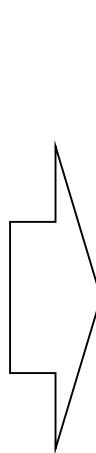


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# Analysis of electronic energy loss in $\text{HfO}_2$



C.J. Zoller, *Nucl. Instr. Meth. B* 347 (2015)



D. Primetzhofer, *Nucl., Instr. Meth. B* 320 (2014)

Uncertainty from:

- Statistics
- Thickness calibration
- ~~Composition~~

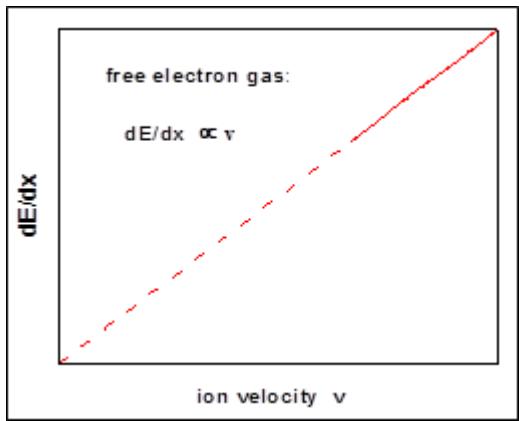
- Very good agreement with data of Behar et al.
  - $S \propto E^{1/2}$  down to 5keV/u.



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# Analysis of electronic energy loss in $\text{HfO}_2$

## Theory:



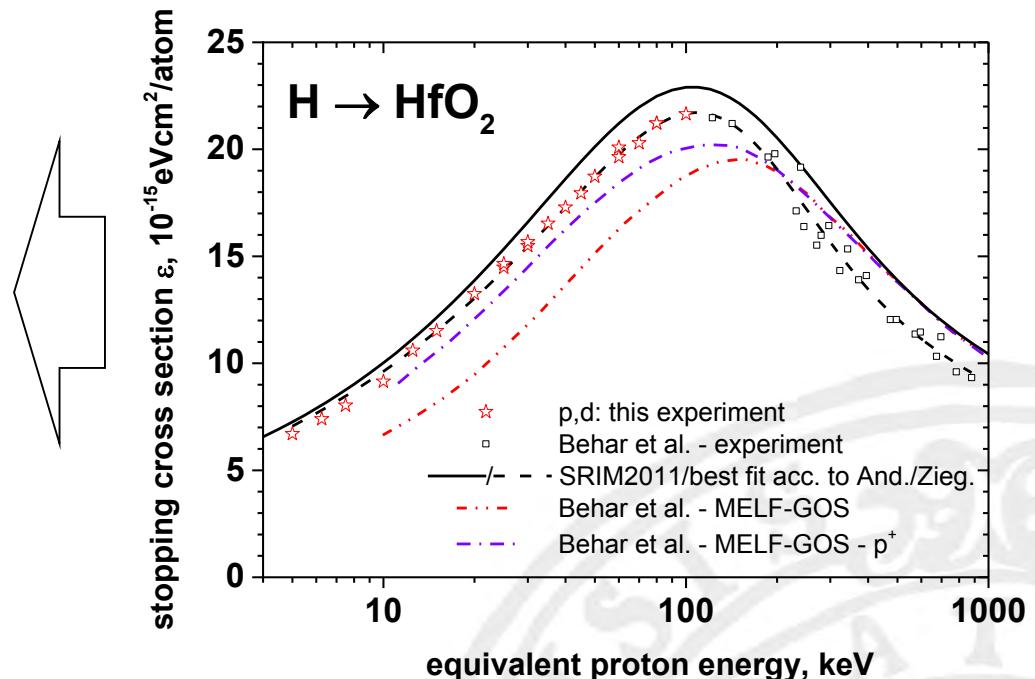
Fermi et al. Phys. Rev. (1947)

$$dE/dx = Q(r_s, \dots) \cdot v$$

$$\Delta E_{\max} \leq 2 \cdot m_e \cdot v \cdot v_F$$

## Maximum energy transfer + Excitation limits

## Effects on stopping



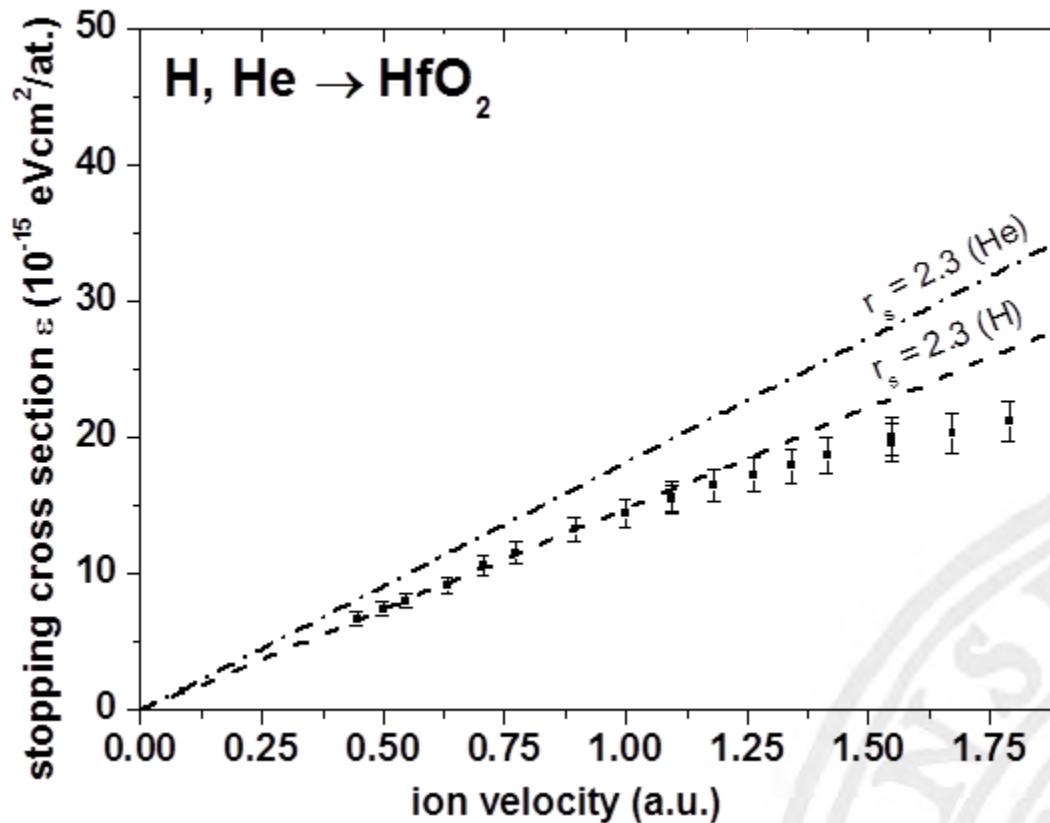
D. Primetzhofer, Nucl., Instr. Meth. B 320 (2014)

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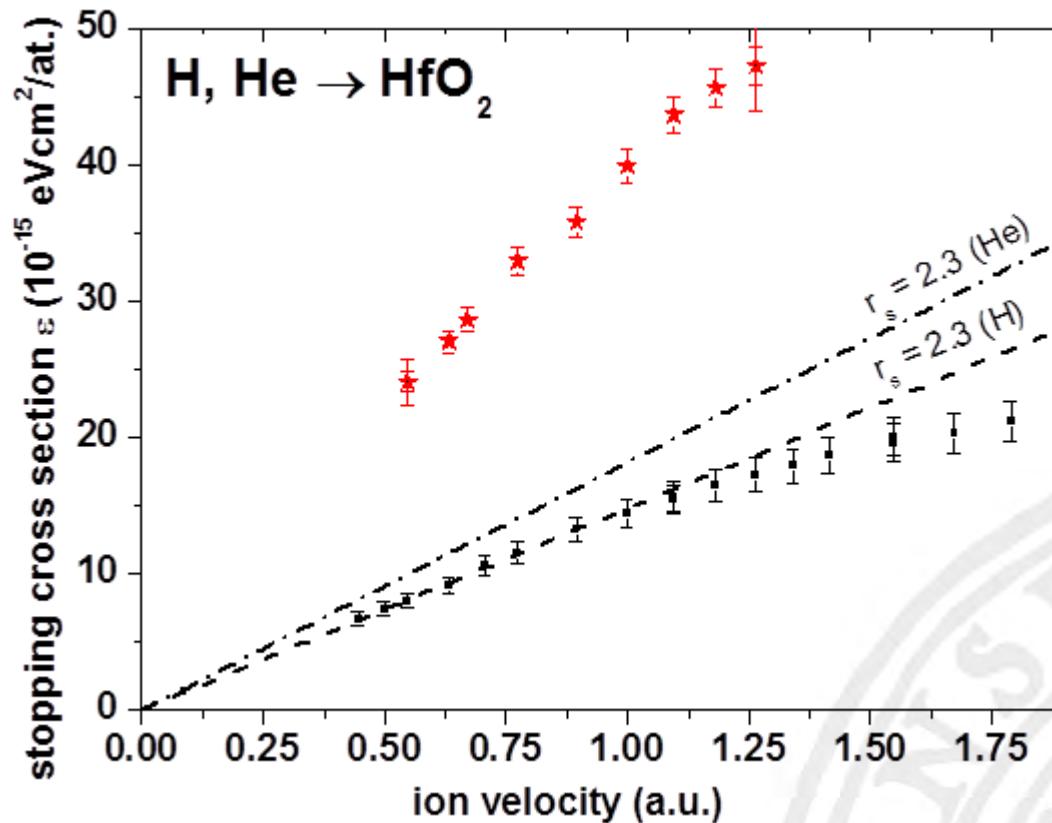
# Electronic stopping in $\text{HfO}_2$ : He





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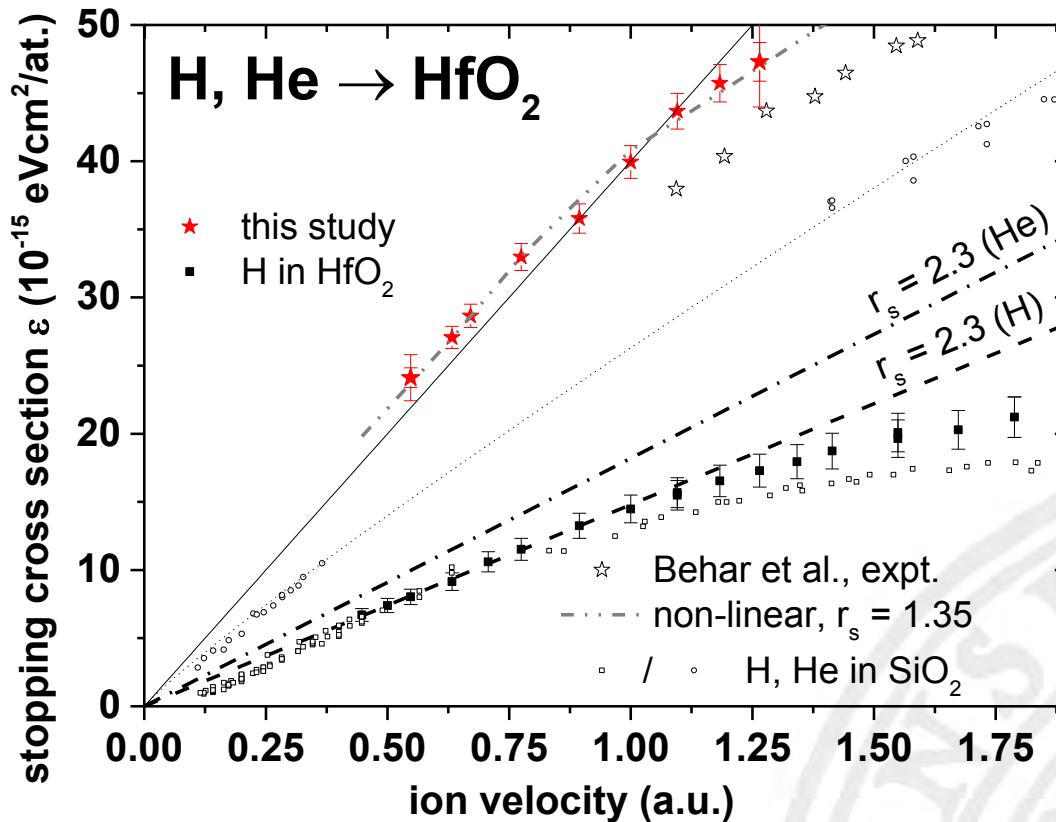
# Electronic stopping in $\text{HfO}_2$ : He



- Totally different electron density in DFT-models necessary



# Electronic stopping in $\text{HfO}_2$ : He



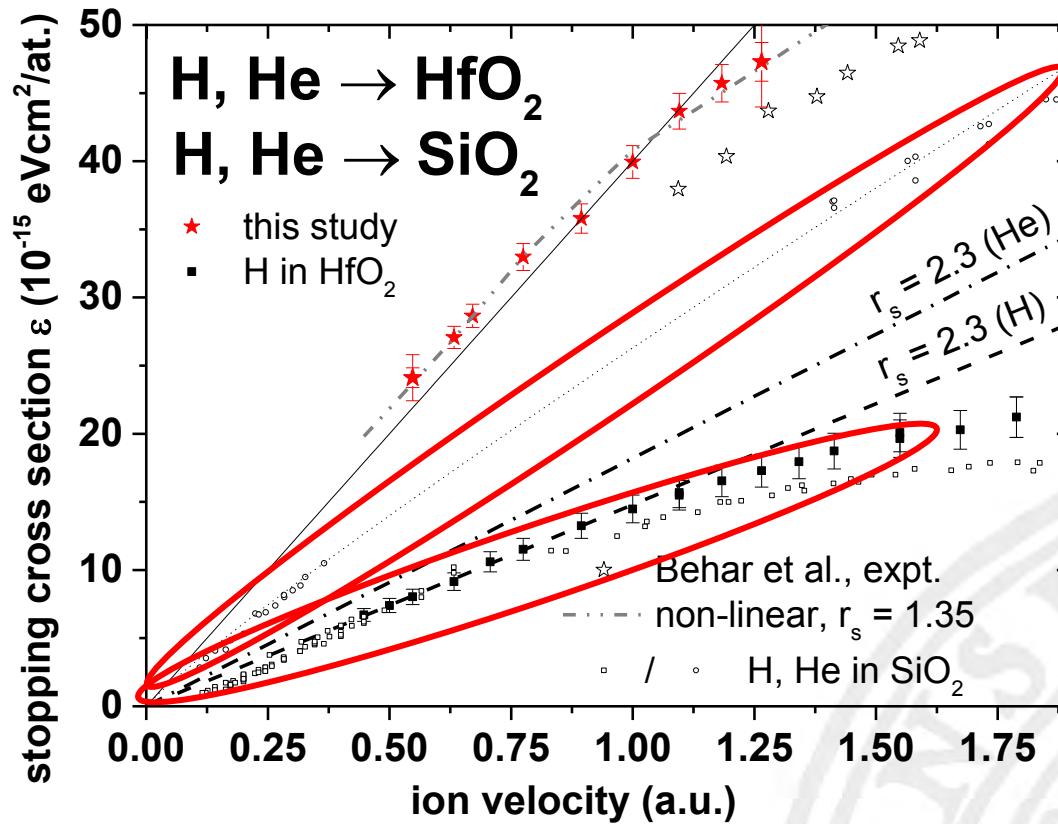
D. Primetzhofer, Phys. Rev A 89 (2014)

- Totally different electron density in DFT-models necessary
- Energy loss shows a non-linear behaviour!



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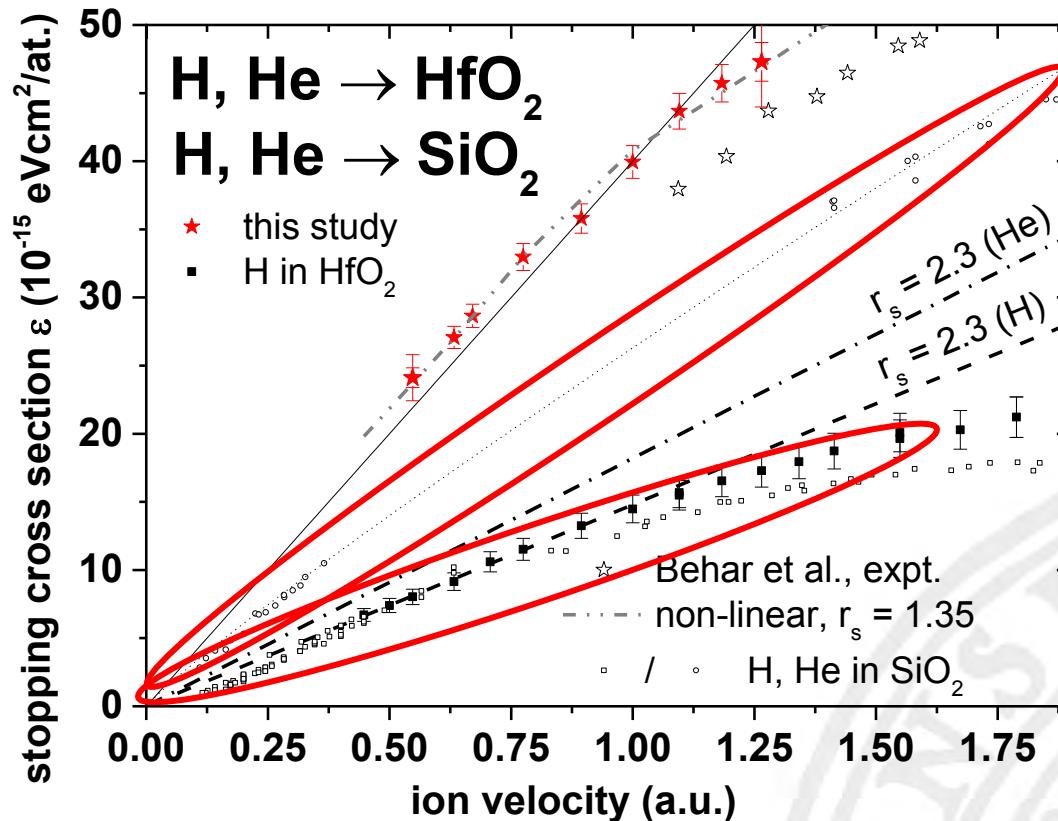
# Comparison: $\text{SiO}_2$ vs. $\text{HfO}_2$ : He



D. Primetzhofer, Phys. Rev A 89 (2014)



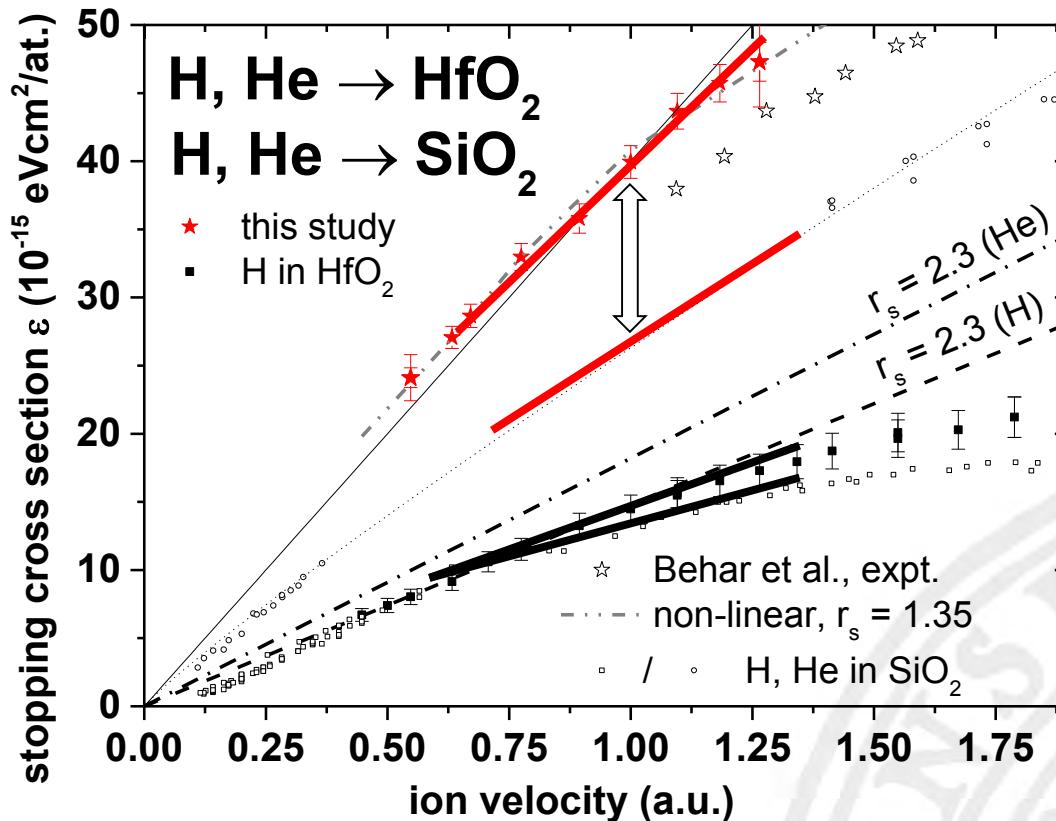
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D. Primetzhofer, Phys. Rev A 89 (2014)

- Protons show no large discrepancy – excitation of O-2p states!?
- He-stopping high in both materials

# Comparison: $\text{SiO}_2$ vs. $\text{HfO}_2$ : He



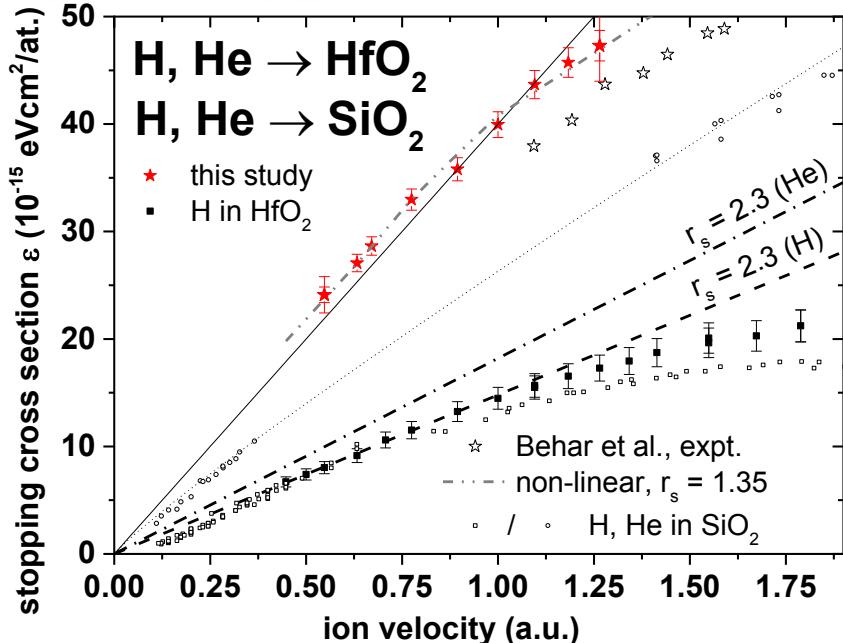
D. Primetzhofer, Phys. Rev A 89 (2014)

- Protons show no large discrepancy – excitation of O-2p states!?
- He-stopping high in both materials but much higher in  $\text{HfO}_2$



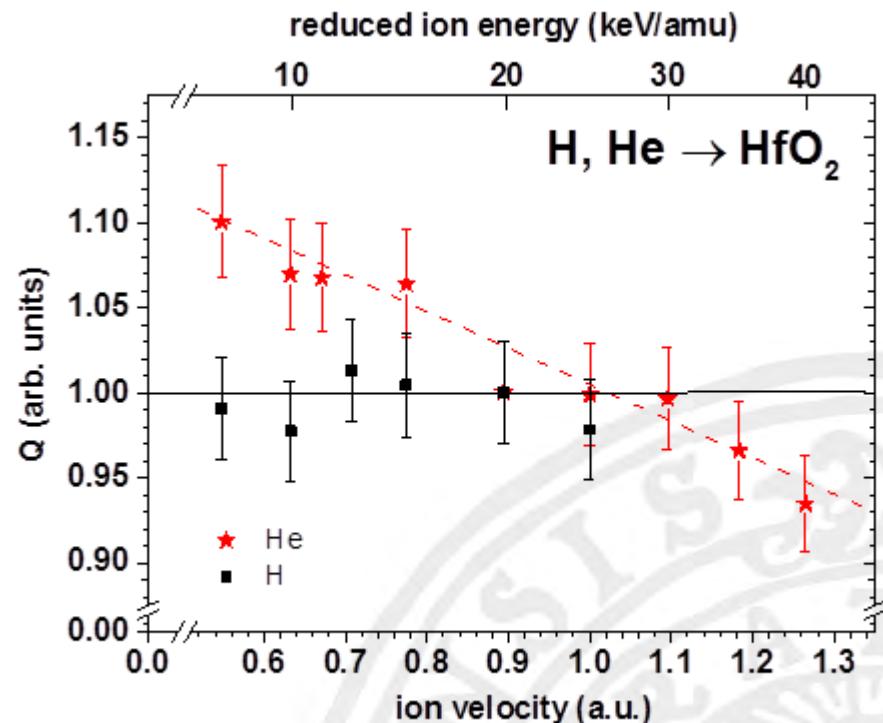
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D. Primetzhofer, Phys. Rev A 89 (2014)

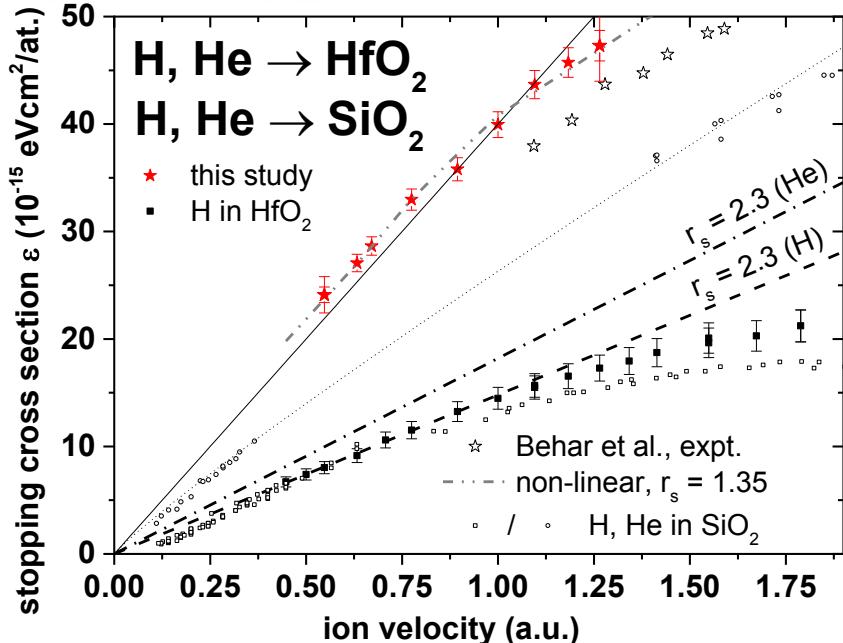
- Protons:  $dE/dx \propto E^{0.5}$   $\leftrightarrow$  He: non-linear velocity dependence
- Different electron density in DFT-models necessary
- Very high energy loss compared to  $\text{SiO}_2$  – different from protons





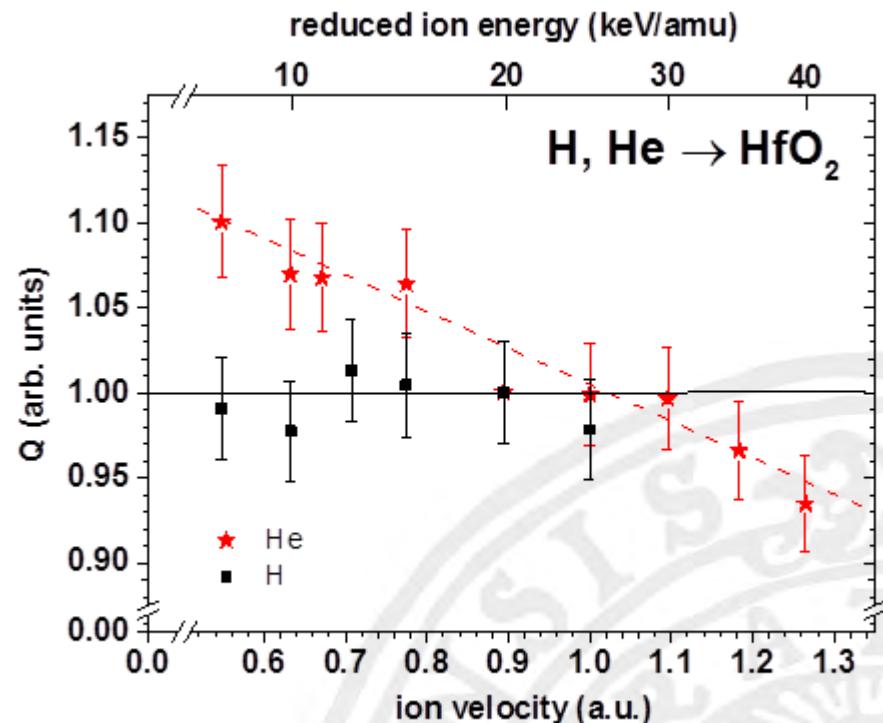
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D. Primetzhofer, Phys. Rev A 89 (2014)

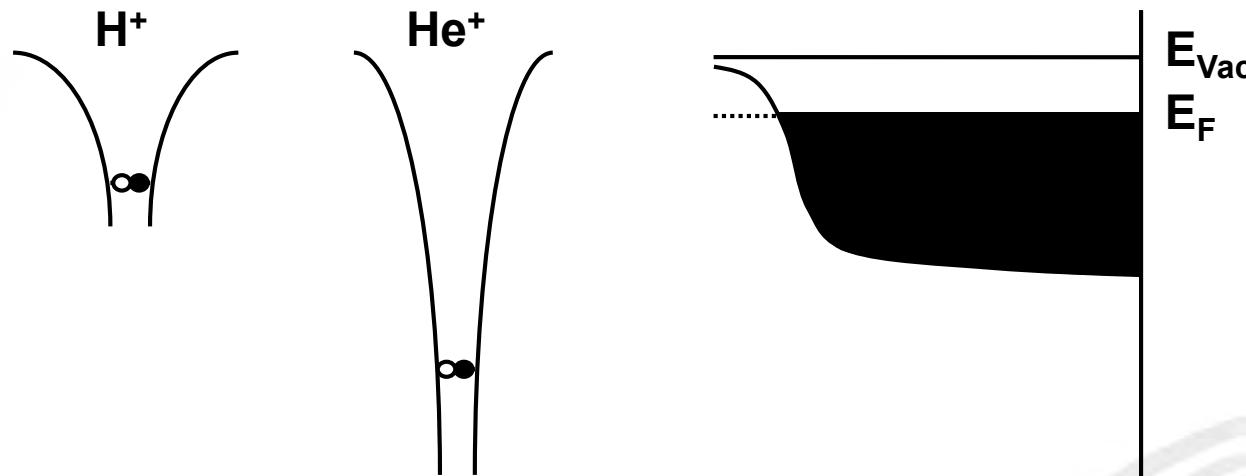
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# So why is He so much different?



Difference in position of unoccupied atomic level:

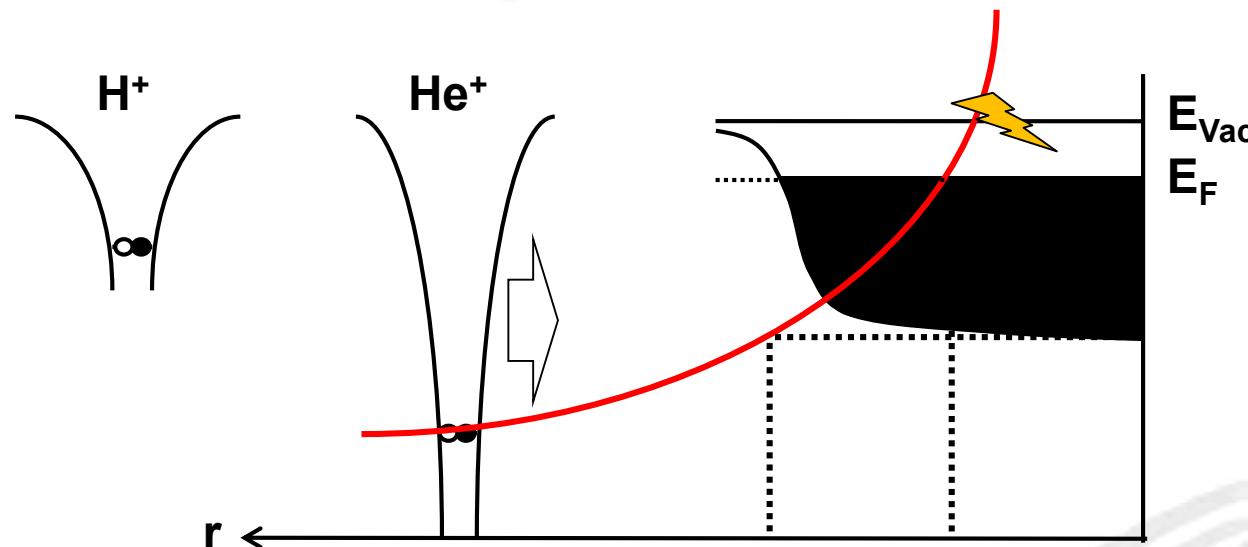
$$H(1s) = 13.6 \text{ eV} \quad \text{vs.} \quad He(1s) = 24.4 \text{ eV}$$

$H(1s)$  resonant with bands in solid  $\leftrightarrow$   $He(1s)$  below lower band edge



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$H(1s)$  resonant with bands in solid  $\leftrightarrow$   $He(1s)$  below lower band edge

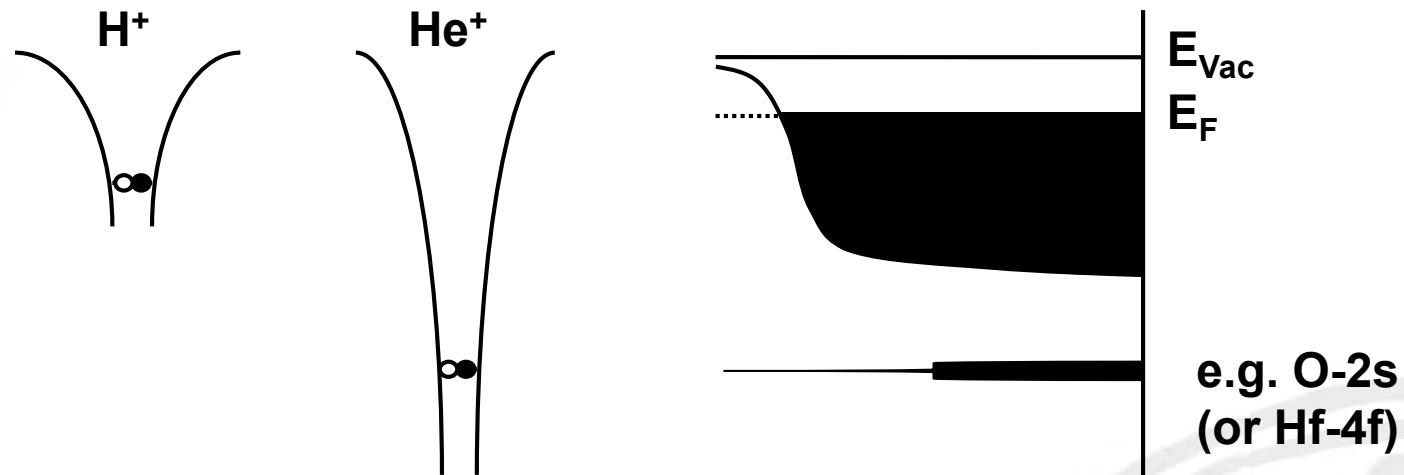
Levels are dynamic:  $E(r)$  with  $r$  = distance between nuclei

**He: Critical distance for resonant neutralization and reionization**



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# More possible differences:



Difference in position of unoccupied atomic level:

$$H(1s) = 13.6 \text{ eV} \quad \text{vs.} \quad He(1s) = 24.4 \text{ eV}$$

$H(1s)$  resonant with bands in solid  $\leftrightarrow$   $He(1s)$  below lower band edge

Levels are dynamic:  $E(r)$  with  $r$  = distance between nuclei

**He: Quasi-resonant levels influence charge states**



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# Reionization well known from LEIS

Thresholds for reionization:

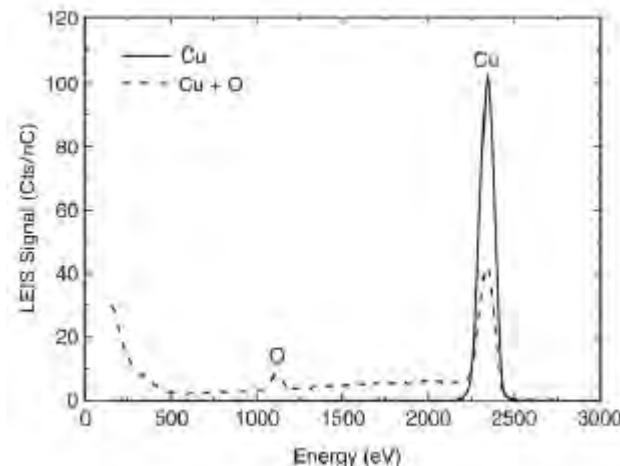
Table for reionization thresholds (see Section 6.3.3(b))

Element	Hc	Method 1	Method 2	Method 3
Ag		>2000 [113]	$\leq 1500$ [37]	
Al	300 [113]		$\leq 500$ [37]	400 [110]
Au			$\leq 1000$ [37]	
Ba	600 [114]			
C	200 [113]			
...				
Mo	400 [113]		$\leq 1000$ [37]	900 [5]
Na	$\leq 200$ [113]			
Ni	>2000 [113]		$\leq 1500$ [37]	2200 [5]
O				700 [91]
Pb	>2000 [113]			
Pt			$\leq 1000$ [37]	1100 [115]

O: 700 eV

Determined from reionization tails

→ even lower in backscattering

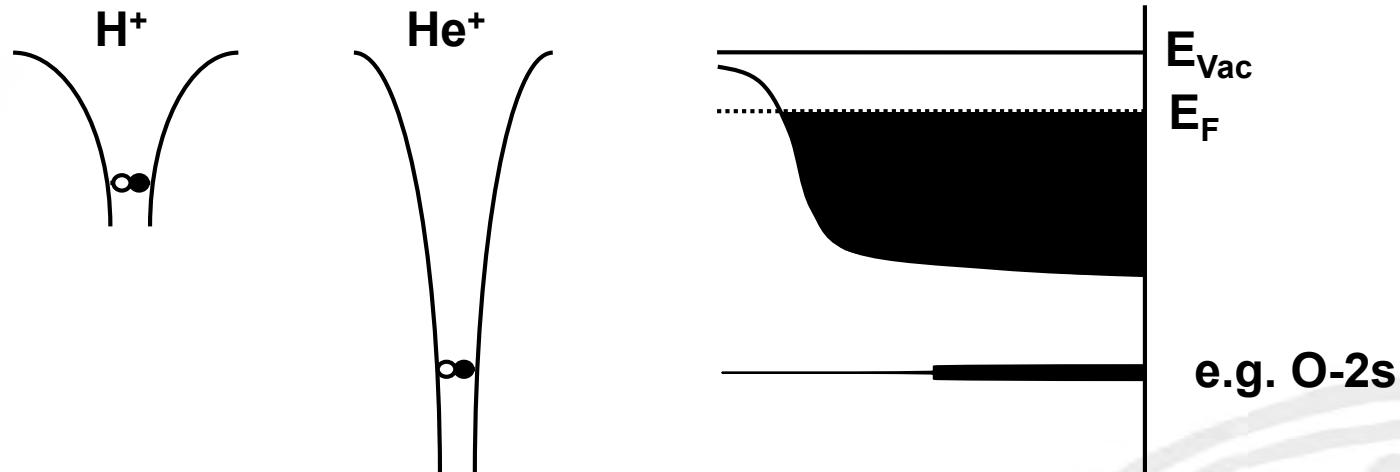


H.H. Brongersma et al., Surf. Sci. Rep. (2007)



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# More possible differences



Difference in position of unoccupied atomic level:

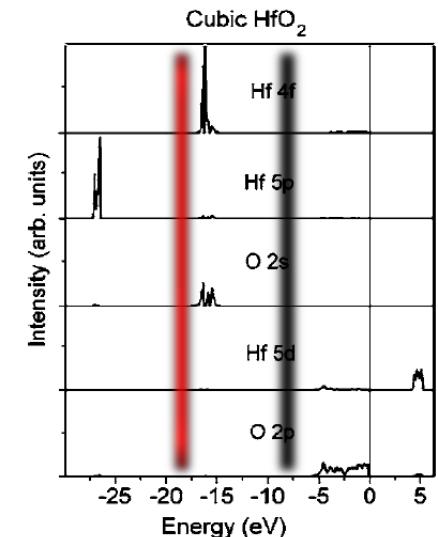
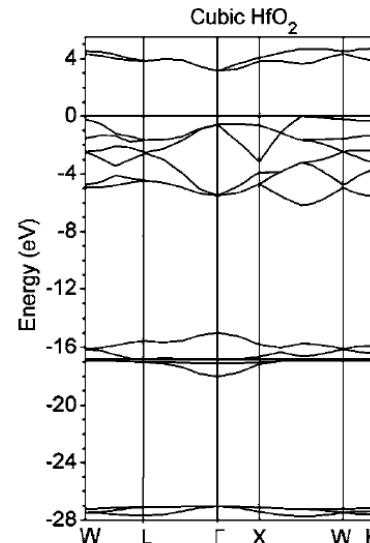
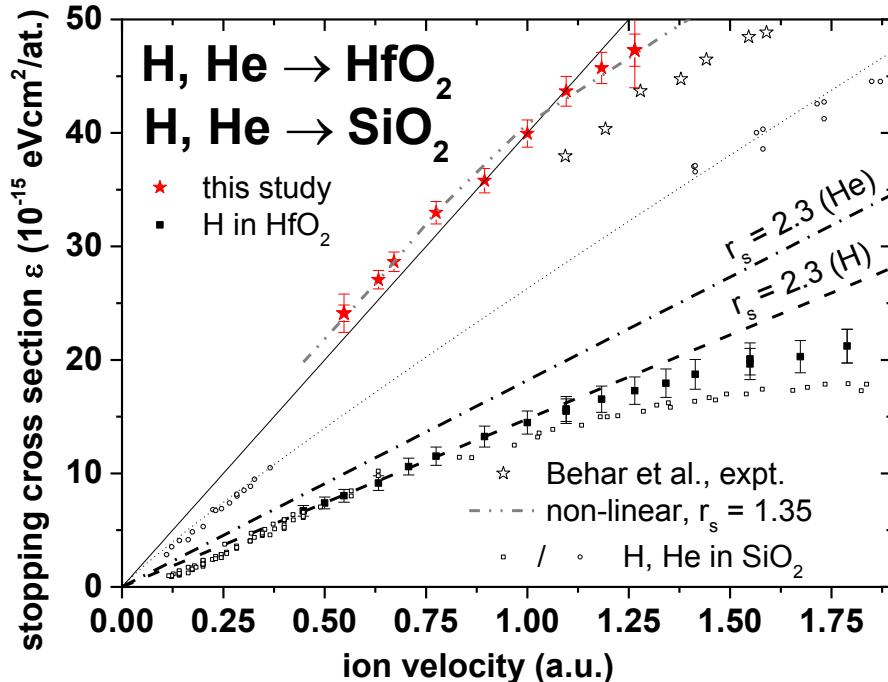
$$H(1s) = 13.6 \text{ eV} \quad \text{vs.} \quad He(1s) = 24.4 \text{ eV}$$

$H(1s)$  resonant with bands in solid  $\leftrightarrow$   $He(1s)$  below lower band edge

Levels are dynamic:  $E(r)$  with  $r$  = distance between nuclei

**He: Quasi-resonant levels influence charge state & dissipate energy**

# Analysis of electronic energy loss in $\text{HfO}_2$

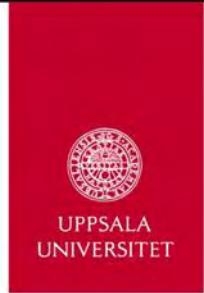


T.V. Perevalov et al., J. Appl. Phys. (2007)

- Interaction of He-1s with O-2s in both  $\text{HfO}_2$  and  $\text{SiO}_2$
- In  $\text{HfO}_2$  additional interaction with heavily populated 4f-states

# Conclusions (I):

- **(ToF-) MEIS offers an ideal tool for high-resolution thin film profiling.**
- **Energy loss at medium energies (quantification!) can be complex!**
- **Trajectory dependent loss in atomic collisions can be relevant (He, Ne).**



# Conclusions (II):

- (ToF-) MEIS offers an ideal tool for high-resolution thin film profiling.
- Energy loss at medium energies (quantification!) can be complex!
- Trajectory dependent loss in atomic collisions can be relevant (He, Ne)...
- **Heavier Ions: Nuclear stopping in backscattering experiments found low compared to SRIM (random trajectories).**
- **Inherent trajectory selectivity of each experiment affects energy loss.**
- **Selective mechanisms in backscattering almost as effective as in transmission.**
- **Monte Carlo calculations should be performed for relevant geometry.  
(Use TRIM not SRIM)**