An analytical energy-loss line shape for high depth resolution in ion-beam analysis

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(Dated: July 30, 2006)

Abstract

The knowledge of the energy-loss distribution in a single ion-atom collision is a prerequisite for subnanometric resolution in depth-profiling techniques such as Nuclear Reaction Analysis (NRA) and Medium Energy Ion-Scattering (MEIS). The usual Gaussian approximation specified by the stopping power and energy straggling is not valid for near surface regions of solids, where subnanometric or monolayer resolution can be achieved. In this work we propose an analytical formula for the line shape to replace the usual Gaussian distribution widely used in low-resolution ion-beam analysis. Furthermore, we provide a simple physical method to derive the corresponding shape parameters. We also present a comparison with full coupled-channel calculations as well as with experimental data at nearly single collision conditions.

PACS numbers: 34.50.Bw , 61.85.+p, 34.50. Fa, 79.20.Rf.

I. INTRODUCTION

Research of advanced materials as for example new gate oxides in metal-oxide-semiconductor (MOS) structures requires characterization tools in the subnanometer scale. Medium energy ion scattering (MEIS) and narrow nuclear resonant reaction profiling (NRP) are well established ion-beam characterization techniques with subnanometric depth resolution capabilities. In connection with ultra high vacuum conditions they allow for surface and near-surface investigations [1] and give complementary characterization to the results obtained by techniques using electrons or photons as incident particles.

During the last years the improved experimental conditions have allowed for energy-resolved spectra that can lead close to monolayer resolution, using medium energy ion scattering (MEIS) [2], Rutherford backscattering (RBS) [3] and also recoil detection analysis (ERDA) [4]. The fundamentals for monolayer resolution analytics using the energy loss of ionic projectiles is, besides the high energy filter resolution, grazing incidence or detection conditions (only few degrees with respect to the surface), because the ratio of the energy loss straggling to the mean energy loss decreases for increasing projectile pathlength. Recently, individual atom layers [5] (adatom and adlayers as well [6]) have been observed by backscattered measurements. In these experiments the interpretation of energy spectra is still an open question because this requires a detailed knowledge on the energy-transfer distribution, which cannot be simply approximated by a Gaussian distribution.

The differential excitation/ionization probability for each subshell in a single collision is the important quantity in this case, since generally only few collisions are involved. Thus, standard energy-loss theories or semi-empirical methods based on Gaussian energy-loss distributions cannot be used successfully. Instead, an atomistic description of the electronic excitation process and its impact parameter dependence have to be taken into account in a stochastic approach which leads, in general, to an asymmetric line shape.

In most used ion-beam techniques (RBS, MEIS, ERDA, NRA,..) [7], the energy scale has to be converted to depth and the measured yield to elemental concentration. In this way, the accurate knowledge of the projectile energy-loss distribution and charge-states are of fundamental importance. Not only the stopping forces are needed but also the energy straggling (Gaussian or non-Gaussian) as a function the projectile charge-state have to be accurate, at a few % level, for some applications, as for example the ones involving ion therapy [8]. Furthermore, the accurate

knowledge of the instrumental function as well as the Doppler effect due to target thermal vibrations are of ultimate importance to understand the asymmetric energy-loss distributions in future ultra-high resolution experiments.

In this work, using ab-initio calculations of the electronic energy-loss [9, 10] as a benchmark, we will propose a simplified model for the asymmetric energy-loss distribution found in high-resolution ion-beam experiments. As it will be shown, the understanding of this asymmetry and its correct modeling is crucial to put forward the ion-beam analysis into subnanometric regions near the surface.

II. CURRENT ENERGY-LOSS DISTRIBUTIONS

The use of Gaussian distributions for the electronic energy loss in IBA has been widely used in the literature not only because its simplicity but also because after some collisions the energy-loss distribution does tend to be a normal distribution according to the central limit theorem (for additional conditions see ref[11]).

Differently from other ion-beam techniques, the nuclear reaction profiling technique (NRP) does not assume Gaussian energy-loss distributions. Instead many self-convolutions are determined numerically for an approximate single collision spectrum. The nuclear-reaction probability is then obtained by considering Poisson statistics of collisions, the resonant-reaction cross-section, the beam spread and Doppler effect. Then, the experimental excitation curves are fitted using trial concentration profiles. In this way, highly accurate depth profiles of light isotopes have been obtained with remarkable depth resolution [12], though the electronic excitations for the ion-nucleus nuclear reaction is also important for an improved depth resolution in ultra-thin films [13].

The asymmetry in the energy-loss distribution may arise from the statistics of collisions, which are uncorrelated in amorphous materials and correlated in crystals. On the other hand, collisions with very small impact parameters, as the backscattering collision, may be responsible for very large energy-loss asymmetries, since inner-shells are likely to be ionized [9]. This is of high importance for the cases where there are collisions with high inner-shell ionization probability and large binding energy. Moreover, the inner-shell binding energy has to exceed the projectile energy straggling due to soft collisions, while the experimental resolution must have a FWHM smaller than (or comparable to) the inner-shell binding energy. This scenario is realized, for instance, in surface and near-surface investigations using typically protons of a few hundred keV or helium in

MEIS experiments [6]. In the following, we will first describe a simple physical ansatz for the determination of the energy-loss shape parameters (moments) and afterwards we will use these results within a simple mathematical description of the final energy-loss distribution.

III. SIMPLE MODEL FOR A NON-GAUSSIAN ENERGY-LOSS DISTRIBUTION

A. Determination of shape parameters

The first ingredient of a description of the electronic energy-loss distribution is the mean energy-loss value as a function of the impact parameter $Q(b)$. In recent works [14, 15] we have proposed a simple formula for $Q(b)$ (called Perturbative Convolution Approximation- PCA and Unitary Convolution Approximation - UCA) realized by the CasP Program [16]. This formula reproduces first-order Born results for all impact parameters for bare and also for screened projectiles (in the PCA mode) and contains some higher-order terms, reproducing the Bloch formula [17] at high velocities (in the UCA mode). The UCA model can also be seen as the impact-parameter realization of the Bloch formula and resembles the Binary model of Sigmund and Schinner [18]. The following simple formula (in atomic units)

$$Q(b) = \int d^2 r_T \, \mathcal{K}(\vec{b} - \vec{r}_T) \int dz \, \rho(\vec{r}_T, z) \tag{1}$$

with

$$\mathcal{K}(b) = \frac{2Z^2}{v^2 b^2} \times h(2vb/\eta) \times \sum_i f_i \, g(\frac{\omega_i b}{v}) \tag{2}$$

joins smoothly all regions of impact parameters b for which two-body ion-electron (small b) and dipole (large b) approximations are valid.

The function $h(2vb)$ (see ref.[14]) approaches zero for $b \ll 1/v$ (relative impact parameter smaller than the electron de Broglie wavelength in the projectile frame) and it reaches 1 for large values of b. The first two product terms in Eq.(2) resemble the classical energy transfer to a statistical distribution of electrons at rest and describe violent binary collisions. The last term, involving the g function (see ref.[14]) and the oscillator strengths f_i, accounts for the long ranged dipole transitions. With the parameter η equal to one, this formula mimics the first-order Born approximation very well [14] and it is denoted *PCA* (perturbative convolution approximation). For increasing projectile-charge first order calculations (on which PCA is based) break down. They do not take into account, for instance, that each electron transition gives rise to an increased final-state population and a corresponding reduction of the initial state population. It is clear that the

ionization probability cannot increase indefinitely with the strength of the perturbation (leading to the so-called saturation effect). Since these ionization processes come mostly from small impact parameters, we have introduced in ref. [15], a scaling parameter η in the function h that enforces unitarity in accordance with the Bloch model [17]. However, the UCA model, as most other stopping-power models [19, 20], determines the mean electronic energy loss only.

Using the mean energy loss $Q(b)$ calculated from the UCA model, we can determine the moments of the energy-loss distribution by assuming the following model.

In the framework of the independent electron model, the energy-loss distribution per electron has two parts. A no-loss part, represented by a delta function at zero energy transfer, and a loss part (f_{loss}), separated from the no-loss part by an energy gap corresponding about to the binding energy,

$$\frac{dP}{d\Delta E} = (1-a)\delta(\Delta E) + a f_{loss}(\Delta E). \tag{3}$$

For given loss part, the coefficient a is determined as a function of the impact parameters from the mean energy loss $Q(b)$ per electron from the UCA model. The second and the third moments of the distribution from Eq.(3), related to the standard deviation and skewness respectively, are then given by assuming a $f_{loss} \approx 1/\Delta E^2$ power law, starting from the sub-shell binding energy value I_b (excitations below the vacuum level are of minor importance) up to the maximum classical energy transfer for a electron at rest $2mv^2$ (m is the electron mass and v the projectile velocity). Deviations from the $1/\Delta E^2$ power law are well known and are attributed to the contribution of long-range dipole transitions as well as to the Compton profile.

This procedure is used as long as a single electron is concerned. Within the framework of the independent-particle model, the final energy-loss distribution is given by the convolution of all single-electron energy-loss distributions. Thus, the effect of all electrons is determined by adding the moments (relative to the 1st moment) according to the additivity rule found in convolutions of probability distributions.

Fig.(1) displays the results of this simple model for the standard deviation (σ_0) of the electronic energy loss spectrum as a function of the atomic number of the target, for impinging 100 keV protons at an impact parameter close to zero (near central collision). The results are compared to coupled-channel results [9, 10, 21]. In general the agreement is very good despite the crudeness of the present model. However, for the skewness parameter γ_0 (related to the third moment of the energy-loss distribution, see figure caption), the results of the present model, depicted as a solid line in Fig.(2), underestimate the coupled-channel ones in most cases (mainly for K). By

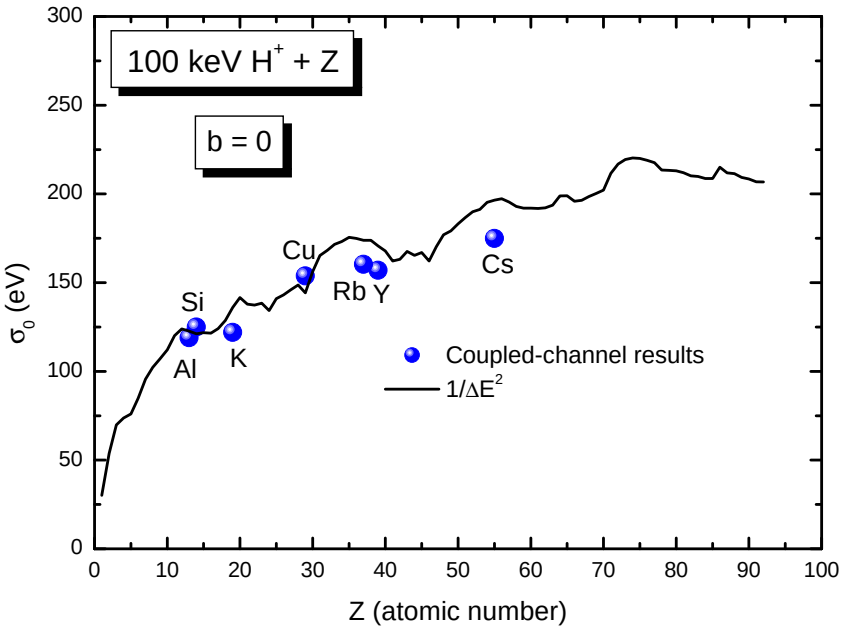

FIG. 1: Standard deviation σ_0 for the electronic energy-loss distribution in a single collision for impinging protons at 100 keV and $b = 0$ as a function of the atomic number of the target. The model indicated by a solid line is discussed in the text.

using somewhat more advanced loss part functions (including the effect of dipole transitions) we have observed the well-known sensitivity of the skewness parameter, but without any significant improvement over the simple power law $1/\Delta E^2$. Thus, we simply rely on this simple loss part function that should be sufficiently accurate to be used in MEIS or other ion-beam technique as a step forward to avoid Gaussian distributions. The parameters σ_0 and γ_0 are available at [16] for any element and ion energy.

B. Simple line shape

The coupled-channel calculations have also been used to search for simple analytical formulas for an approximate description of the electronic energy-loss distribution, thereby replacing the Gaussian distribution for the cases, where the asymmetry cannot be neglected.

In Fig.(3) two analytical formulas for the energy-loss distribution are compared with coupled-channel results for 100 keV protons colliding with an Y atom at $b = 0$. These analytical de-

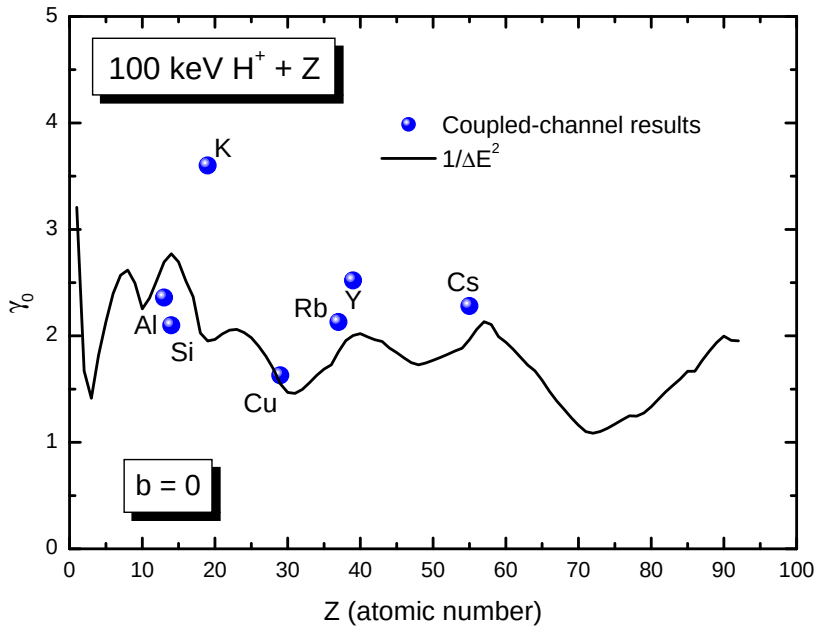

FIG. 2: The same as in Fig.1 but for the third moment of the distribution $\gamma_0 =< \Delta E - < \Delta E >>^3 /\sigma_0^3$

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scriptions are the asymmetric Gaussian (two Gaussian functions linked at the same point - the absolute maximum - with different standard deviations below and above this common point), used to analyze some MEIS experiments[22, 23] and the more realistic basic lineshape, proposed here

$$\begin{aligned} f(\Delta E) &= \alpha \exp(-\alpha \Delta E)\Theta(\Delta E) * \text{gauss}(\Delta E, \sigma) \\ &= \frac{\alpha}{2} \exp\left(-\frac{\alpha}{2}(2\Delta E - \sigma^2\alpha)\right)\left(1 + \text{erf}\left(\frac{\Delta E - \sigma^2\alpha}{\sqrt{2}\sigma}\right)\right), \end{aligned} \tag{4}$$

where $*$ stands for the convolution operation, σ is the experimental resolution ($\sigma = FWHM/2.355$) and $\alpha = 1/\sigma_0$ (σ_0 from Fig.(1)) quantifies the effect of the single collision contribution. In Fig.(3) all curves have the same standard deviation, but only the proposed curve (the basic line shape) has a good overall agreement with coupled-channel calculations. We have also tested other simple analytical curves but no other was yielding a reasonable agreement with the coupled-channel results for Y as well as for some other targets [9, 10, 21].

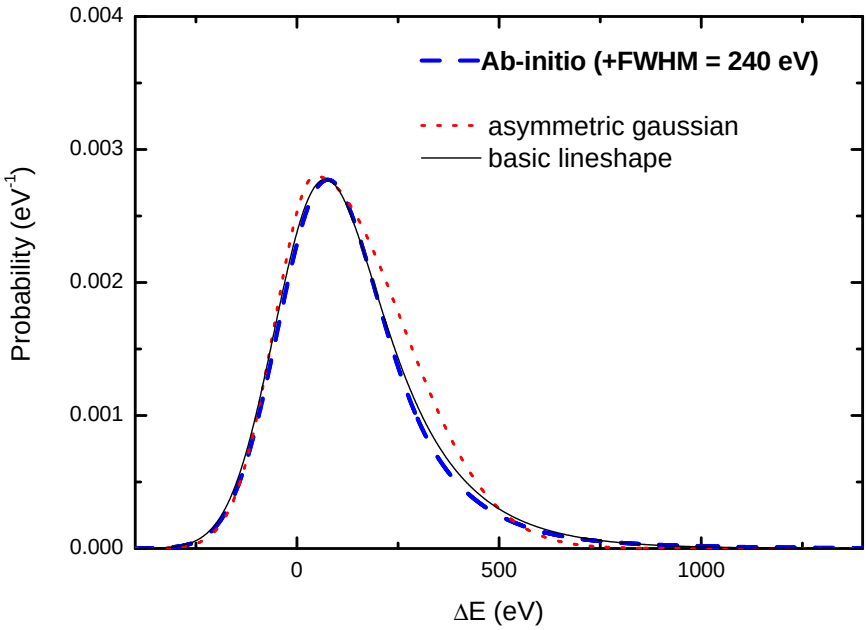

FIG. 3: Coupled-channel results for 100 keV protons colliding with Y at an impact-parameter close to zero in comparison with two analytical line shapes. All results have been convoluted with the experimental resolution of 240 eV

IV. EXAMPLE

A realistic energy loss model for a single collision is mandatory for investigations of surface and near-surface interfaces as will be seen in the following example.

In Fig.(4) we show MEIS results (the symbols) and the corresponding simulations (the solid lines) line for $Hf_{1.06}Zr_{0.1}O_2$ oxide with different thicknesses (see Fig.(4) caption) taken with 100 keV protons [24]. The total fluence of protons was about 10 μC for all recorded spectra. Here, the simulations, noted as standard ones, are based on a pure Gaussian-shape of the energy-loss distributions, with the mean energy-loss value from the SRIM code[25] and the straggling value from the Chu formula [26]. As can be observed from the upper panel in the figure, the agreement is very poor, if a homogenous oxide layer with the quoted thickness is assumed. Moreover, the simple Gaussian ansatz for the line shape yields results that are in severe contradiction with the integrated line intensities [24].

On the other hand, as can be observed in lower panel of Fig.(4) , if the energy-loss straggling

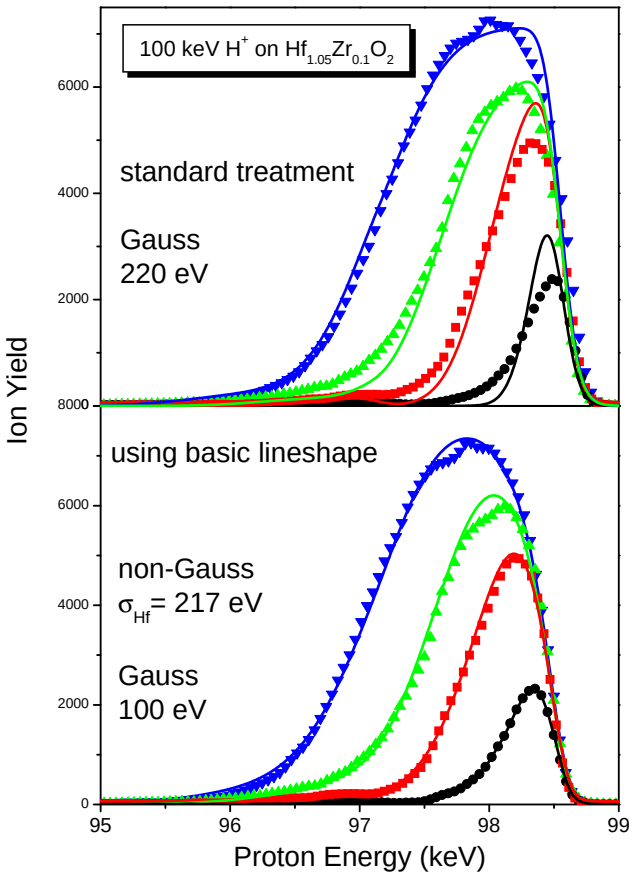

FIG. 4: MEIS spectra taken with 100 keV protons backscattered form Hf in thin films of HfO_2 (with small amount of Zr). The nominal thicknesses of the films are 0.2 (full circles), 0.5 (full squares), 1 (up triangles) and 2nm (down triangles). The solid curves are simulations using analytical line shapes (see text).

due to the backscattering collision is included, a very good agreement is obtained. The experimental oscillations for the thickest film may be attributed to instrumental effects in the conversion from angle and energy 2D spectrum to energy 1D spectrum [24]. Here we have used the basic lineshape from Eq.(4) to describe the energy-loss distribution in a single, violent collision, responsible for the backscattering. The exponential decay α was obtained from Fig. (1) for Hf, and amounts $1/217$ eV^{-1}. In this case the assumed experimental resolution of about 100 eV that

is much smaller than the one used in the upper panel of Fig.(4) because of the extra broadening arising from the backscattering collision. In addition, the total Hf quantity as a function of the film thickness is a linear function that crosses the origin [24].

V. CONCLUSIONS

We have proposed a simple model with physical boundary conditions for the energy-loss moments in a single violent collision. The results for the standard deviation σ_0 agree well with coupled-channel calculations for typical energies of MEIS and NRP experiments. However, higher deviations for the corresponding skewness parameter are observed. Furthermore, we have also used coupled-channel results as benchmarks for simple analytical line shapes for the energy-loss distribution. It was shown that a simple exponential function was able to successfully replace the standard Gaussian distribution. Thus, this so-called basic line shape can be considered as a step forward for near surface ion-beam analysis.

The energy loss in a single violent collision (as the backscattering collision in RBS or MEIS) leads to a broadening of the scattering spectra. In fact, the usually reported analyzer resolutions in high-resolution experiments are probably often smaller, due to the additional backscattering broadening that is usually neglected. In general, protons or He ions incident at a few hundred keV involve substantial additional broadening when scattered by heavy elements (RBS and MEIS), while this effect is not so important for techniques involving light elements, such as resonant nuclear reaction profiling.

Finally, as observed in the example given in sec. IV, the correct modeling of the energy-loss distribution has been shown as a mandatory requirement for reliable depth profiles near the sample surface, having central implications in several research areas, such as, characterization of advanced materials for future generation electronic devices. Thus, we hope that the proposed basic lineshape together with reasonable estimates for the moments of the energy-loss distribution can be useful to achieve clear and unequivocal subnanometric depth resolution in ion-beam analysis of solids based on measured energy-loss spectra.

Acknowledgments

This work was partially supported by CAPES -PROBRAL, by CNPq and by the Alexander-von-Humboldt foundation. Part of this work is a result of fruitful collaborations with D.P Woodruff (Warwick), T. Gustafsson (Rutgers), and M. Copel (IBM).

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