A theoretical-experimental straggling study
of H ions into HfO$_2$ films

Raúl Fadanelli$^1$, Moni Behar$^1$, Néstor R. Arista$^2$, Rafael Garcia-Molina$^3$, Cristian D. Denton$^4$ and Isabel Abril$^4$

$^1$Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brasil
$^2$División Colisiones Atómicas, Centro Atómico Bariloche, RA-8400 San Carlos de Bariloche, Argentina
$^3$Departamento de Física – CIOyN, Universidad de Murcia, Apartado 4021, E-30080 Murcia, Spain
$^4$Departament de Física Aplicada, Universitat d’Alacant, Apartat 99, E-03080 Alacant, Spain

Abstract

We present an experimental study of the energy-loss straggling of protons into HfO$_2$ films, as well as a comparison with the theoretical predictions of the MELF-GOS model.

The experiments were performed using a H beam provided by a 3 MV Tandetron accelerator in an energy range between 40 and 2000 keV. The targets were HfO$_2$ films with thicknesses of 40, 60, 80, 100 and 150 nm. We have used nuclear reaction analysis (NRA) and Rutherford backscattering (RBS) techniques with a Si barrier detector, having a resolution of 7 keV. By comparing the front and back edge of the RBS spectra we extract the corresponding energy loss straggling values for each one of the energies we have studied.

The calculations were done in the framework of the dielectric formalism, paying especial attention to a proper description of the Energy Loss Function (ELF) of the HfO$_2$ targets, which accounts for the electronic excitations produced in the material by the passage of a charged projectile.

The experimental data and the theoretical results of the energy-loss straggling of swift H beams in HfO$_2$ films show a very good agreement.

I.- EXPERIMENTAL PROCEDURE [1]

The films of HfO$_2$ were deposited on Si wafers, with different thickness that varied between 40 and 150 nm.

Proton beam (between 40 and 2000 keV) provided by the 3 MV Tandetron accelerator, with an overall resolution better than 7 keV.

RBS technique at high proton energies (above 400 keV) was employed using a Si detector with the samples oriented at different angles with respect to the beam.

At low proton energies Nuclear reaction analysis (NRA) was used. The resonant reaction $^{18}$O(p,$\alpha$)$^{15}$N at 151.2 keV, with a narrow resonance $\Gamma$ = 50 eV, provides an excellent depth resolution; $\alpha$ particles emitted in the reaction were detected by a large Si surface barrier detector.

The NRA excitation curve comprises: (a) width of the nuclear resonance, (b) Doppler broadening caused by atomic vibrations in the target, (c) energy spread of the analysing beam and (d) energy-loss straggling.
By comparing the front and back edges of the NRA or RBS spectra the corresponding energy-loss straggling was extracted for each beam energy.

II.- ENERGY LOSS OF SWIFT PROJECTILES IN THE DIELECTRIC FORMALISM [2,3]

The stopping power $S_p$ and the energy-loss straggling $\Omega^2$ of a projectile with charge $Z_1$ and velocity $v$ are calculated as a weighted sum of the partial stopping power $S_{p,q}$ and straggling $\Omega^2_q$ for the different charge states $q$ that the projectile can acquire during its travel through the target,

$$S_p = \sum_{q=0}^{Z_1} \phi_q S_{p,q},$$  \hspace{1cm} (1)  

$$\Omega^2 = \sum_{q=0}^{Z_1} \phi_q \Omega^2_q.$$  \hspace{1cm} (2)

We use the dielectric formalism to obtain $S_{p,q}$ and $\Omega^2_q$:

$$S_{p,q} = \frac{2e^2}{\pi v^2} \left[ \frac{d}{dk} \frac{Z_1 - \rho(k)}{k} \right]^2 \frac{d\omega}{\omega} \omega \text{Im} \left[ \frac{-1}{\varepsilon(k, \omega)} \right],$$  \hspace{1cm} (3)  

$$\Omega^2_q = \frac{2e^2 h}{\pi v^2} \left[ \frac{d}{dk} \frac{Z_1 - \rho(k)}{k} \right]^2 \frac{d\omega}{\omega} \omega^2 \text{Im} \left[ \frac{-1}{\varepsilon(k, \omega)} \right].$$  \hspace{1cm} (4)

$\phi_q$ represents the probability of finding the projectile in a given charge state $q$, and $\rho(k)$ is the Fourier transform of the projectile electronic charge.
III.- MELF-GOS MODEL FOR THE ENERGY-LOSS FUNCTION (ELF) OF HfO$_2$ [2,3]

The energy loss function (ELF) of a material accounts for its excitation spectrum (with momentum and energy $\hbar k$ and $\hbar \omega$, respectively). We model the target ELF as two contributions. On the one hand we have the contribution due to outer electrons, described by a sum of Mermin-type ELF fitted to experimental ELF in the optical limit ($k=0$)

$$\text{Im} \left[-\frac{1}{\varepsilon(k = 0, \omega)}\right]_{\text{outer}} = \sum_i A_i \text{Im} \left[-\frac{1}{\varepsilon_M(\omega_i, \gamma_i; k = 0, \omega)}\right],$$  \hspace{1cm} (5)

$A_i$, $\omega_i$, and $\gamma_i$ are fitting parameters related to the intensity, position and width, respectively, of the ELF; $\varepsilon_M$ is a Mermin type dielectric function.

On the other hand, excitations of inner-shell electrons are incorporated to the ELF by means of the Generalized Oscillator Strength (GOS) of the target atom inner shells, because these electrons are not sensitive to aggregation effects in the compound target:

$$\text{Im} \left[-\frac{1}{\varepsilon(k, \omega)}\right]_{\text{inner}} = \frac{2\pi N}{\omega} \sum_j \sum_{nl} \frac{d^2 f_n^j(k, \omega)}{d\omega},$$  \hspace{1cm} (6)

$N$ is the molecular density of the target, $d^2 f_n^j(k, \omega)/d\omega$ is the GOS of the $(n,l)$ subshell of the $j$-th element.

**Fig.1.-** Energy loss function of HfO$_2$ as a function of the transfer energy at the optical limit, $k=0$. The dark line represents experimental data from Frandom et al. [4], and the red line is the corresponding fitting proposed through the MELF-GOS model, eq.(5).
Fig.2.- Energy loss function of HfO$_2$ as a function of the transfer energy at the optical limit ($k=0$). The dark crosses correspond to experimental data from Frandom et al. [4], the green crosses correspond to experimental data from Henke et al. [5], and the red line represents the fitting obtained by the MELF-GOS model, eqs.(5) and (6).

Besides a proper fitting to experimental values, the model ELF must satisfy physical constrains, such as the $f$-sum rule:

$$N_{\text{eff}}(\omega) = \frac{1}{2\pi^2} \int_{0}^{\omega} d\omega' \omega' \text{Im} \left[ \frac{-1}{\varepsilon(k,\omega')} \right],$$

(7)

where $N_{\text{eff}}(\omega)$ is the effective number of electrons that participate in excitations up to an energy $\hbar \omega$. Obviously, for very large excitation energies, $N_{\text{eff}}$ should tend to 88, i.e., the total number of electrons of HfO$_2$.

For stopping power calculations, an important magnitude is the mean ionization energy, $I$, which can be obtained as

$$\ln I = \int_{0}^{\omega} d\omega \omega \ln(\omega) \text{Im} \left[ \frac{-1}{\varepsilon(k=0,\omega)} \right] + \int_{0}^{\omega} d\omega \omega \text{Im} \left[ \frac{-1}{\varepsilon(k=0,\omega')} \right],$$

(9)

After doing the calculation, we obtain the following value $I$(HfO$_2$) = 363.6 eV, which can be compared to $I$(HfO2) = 552 eV derived by interpolation in ICRU [6].
Fig. 3.- The dark line represents the effective number of electrons, $N_{\text{eff}}$, of HfO$_2$ as a function of the transfer energy, eq.(7). The contribution of the outer electrons, and the electrons from the inner shells are also shown in different colours (see inset).

IV.- ENERGY LOSS OF H IN HfO$_2$

The following figures show the comparison between our experimental measurements and our calculated values for the energy loss of protons in hafnium oxide, as a function of the projectile energy.

As no experimental data are available for the stopping power, we compare our calculations to SRIM semiempirical predictions, which are always lower than our results.

Fig. 4.- Stopping power of H beam in HfO$_2$ as a function of the incident projectile energy. Results from the MELF-GOS model are given by a red line, while the dark line represents the values obtained by the SRIM 2008 code [7].
The comparison between experimental and calculated energy-loss straggling shows an excellent agreement for a broad energy range.

![Energy-loss straggling graph](image)

**Fig. 5.** Energy-loss straggling of H beam in HfO$_2$ as a function of the incident projectile energy. We represent in blue squares our experimental data and by a red line the results obtained by the MELF-GOS model. The dark line corresponds to the Bohr energy-loss straggling, which is obtained applying the additivity rule.

Bohr energy-loss straggling is

$$\Omega_B^2 = 4mnZ_1^2Z_2^2,$$  \hspace{1cm} (10)

where $n$ is the target atomic density, and $Z_1$ and $Z_2$ are, respectively, the projectile and target atomic numbers.

Applying the additivity rule for the Bohr energy-loss straggling of the compound HfO$_2$, gives

$$\Omega_B^2 (\text{HfO}_2) = \Omega_B^2 (\text{Hf}) + 2\Omega_B^2 (\text{O})$$  \hspace{1cm} (11)

**V.** CONCLUSIONS

We present, by the first time, the experimental energy-loss straggling of proton beams in HfO$_2$ films as a function of the incident energy, for a broad energy range. The experimental data were obtained by nuclear reaction analysis (NRA) and Rutherford backscattering (RBS) techniques. Also, a theoretical calculation based in the dielectric formalism, where the ELF of the HfO$_2$ was fitted to contain their main electronic properties is presented. We obtain that the mean ionization energy of HfO$_2$ is $I = 363.6$ eV, much less than the result provided by interpolation in ICRU [6]. The calculated stopping power of H in HfO2 is bigger than the semiempirical predictions obtained from the SRIM code [7]. The calculated and experimental energy-loss straggling agrees very well.
REFERENCES

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