Electronic energy loss of H_3^+ ion clusters in SiO_2 films

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In this paper, we present results on the energy loss of H_3 molecules in SiO_2 films with thickness ranging from 2.5 to 50 nm. For this purpose, we have used the resonant $^{18}O(p,\alpha)^{15}N$ nuclear reaction at 151.2 keV with atomic and molecular H_3 beams. This reaction is particularly suitable in the present study, since the width of the resonance peak is only 50 eV. The experimental results show the maximum values of interference effects so far observed: $R \approx 1.8-2.1$ for the lowest thickness range of 2.5–7.0 nm. Calculations based on the *dielectric formalism* are in good agreement with the experimental data.

I. INTRODUCTION

In the velocity range where the energy loss of charged particles in the matter is dominated by the electronic stopping power regime, the energy loss per ion in solids is known to be significantly different for molecular projectiles, as compared with independent ions at the same velocity [1–5]. This difference has been interpreted as originated from the so-called *vicinage effect*, which can be obtained either from a dielectric or atomic description of the energy loss in solids [6–10]. The vicinage effect was theoretically explained as a result of the excitation of target electrons by the simultaneous interactions of two or more ions moving in a correlated way at short interior distances through the solid. It was also demonstrated that this interference effect could be constructive or destructive, according to the velocity of the molecular projectile and the interion distance. When the molecule enters the solid, the ions from the cluster will lose their electrons in the first few atomic layers of the target, remaining as an aggregate of positively charged ions. Then, due to the Coulomb repulsion, the molecule will explode, the ions begin to separate, and the interference effect will start to smear out, disappearing after a certain characteristic distance.

The vicinage effect has been intensively studied in the last 25 years. In their pioneer work, Brandt *et al.* [1,2] have shown that, for short dwell times τ of the ions in C and Au foils, the measured stopping ratio *R*—the energy loss of the molecule divided by the sum of that of its constituents—could be as high as 1.2 for H_2 and 1.5 for H_3. The accompanying theory [1,2] fitted the data quite well, and also predicted that, for $\tau \to 0$, $R_{H_2} \to 1.5$, and $R_{H_3} \to 2.0$. The same results can be derived in an approximate but simple way by using the equipartition rule of stopping power [1].

Since then, an intense experimental as well as theoretical activity related to this subject has been developed, particularly with protons diclusters [9,10]. A summary of these results can be found in Fig. 3 of Ref. [10]. There, several interesting features can be observed. First, there is a signifi-

cant increase of interference effects for energies larger than 40 keV/amu. Second, there is a large dispersion in the experimental data, which goes typically from $R \approx 1.0$ up to $R \approx 1.2$. Third, none of the experimental values reaches the asymptotic theoretical value $R \approx 1.5$. It should be mentioned that all the above quoted experiments were done via the transmission technique using carbon foils with thickness between about 10 and 25 nm.

Regarding H_3 cluster ions, the experimental data are scarce, but the general features are the same as those related to H_2 molecules. That is: first, the experiments were done using the transmission technique with self-supported thin films; second, there is a large dispersion in the results; and third, the experimental values never reached the maximum predicted value ($R \approx 2.0$).

Several arguments were raised, in order to justify the lack of consistency of the experimental results. The most quoted among them are the degradation of the carbon films due to the ion bombardment, and carbon deposit during the experiments [5]. On the other hand, the difficulty of producing ultrathin self-supported films should be quoted as the main restriction to the experimental confirmation of the maximum enhancement predicted for the energy loss. In fact, as the target thickness increases, information on the vicinage effect smears out, giving rise to experimental *R* values smaller than the maximum predicted one.

In order to overcome these problems, we decided to take a different experimental approach. Instead of using the transmission technique, we employed the nuclear resonant analysis to determine the energy profile of very thin $Si^{18}O_2$ films grown by thermal oxidation on Si wafers. We have determined the nuclear reaction analysis (NRA) spectra with H and H_3 beams. We may regard the stopping ratio *R* as roughly related to the ratio between the widths of the spectra obtained with H_3 and protons. We have also compared the experimental results with calculations performed through the dielectric function formalism using the Linhard's dielectric constant [11]. It will be shown that, not only a good agreement between theory and experiment has been achieved, but

also, for the first time, the experimental results reproduce the maximum predicted R value.

II. EXPERIMENTAL PROCEDURE

The measurements of H_3 and H stopping powers have been carried out by a simple procedure based on the determination of the nuclear reaction profile of very thin $Si^{18}O_2$ films. This was done alternately with H_3 and H beams by using the NRA technique. With this aim, we have used a set of $Si^{18}O_2$ films produced by thermal oxidation on Si wafers. Their thickness, which ranged from 2.5 up to 17 nm, were determined through the $^{18}O(p,\alpha)^{15}N$ nuclear reaction at 730 keV (where the nuclear cross-section has a plateau) along with a $Ta^{18}O_2$ sample used as a standard. The uncertainty in the areal atomic density of the standard was about 1%, resulting in a maximum error of 5–10% in the thickness of the $Si^{18}O_2$ films. In addition, we have implanted 25 keV of ^{18}O into a $Si^{16}O_2$ film with a fluence of $\Phi = 2 \times 10^{16}$ ions/cm². In this way, we have produced an ^{18}O marker at a depth of 54 nm in the $Si^{16}O_2$ film. The projected range of the ^{18}O implanted ions was also measured through the resonant $^{18}O(p,\alpha)^{15}N$ reaction at 151.2 keV, resulting in an uncertainty of about 5% [12]. This marker was also used in the determination of the ratio between the molecular and atomic stopping power, by measuring its position (in energy) with both H_3 and H beams.

In order to determine the ratio R between the molecular and the atomic stopping power, we have used the resonant $^{18}O(p,\alpha)^{15}N$ reaction at 151.2 keV. This reaction has one of the narrowest resonances ($\Gamma = 50$ eV) among the resonant nuclear reactions, which makes it very suitable for the present experiment. At the resonance energy, the projectiles, for both atomic and molecular beams, have a speed of 2.4 a.u., so that, after traversing a few atomic layers of the target, it can be assumed that the ions are completely stripped.

The ion beams were provided by the 500-kV ion implanter of the Instituto de Física, Universidade Federal Rio Grande do Sul, Brazil. The α particles emitted in the reaction were detected by a large Si surface barrier detector (300 mm²) placed at 30 mm from the target. The vacuum system
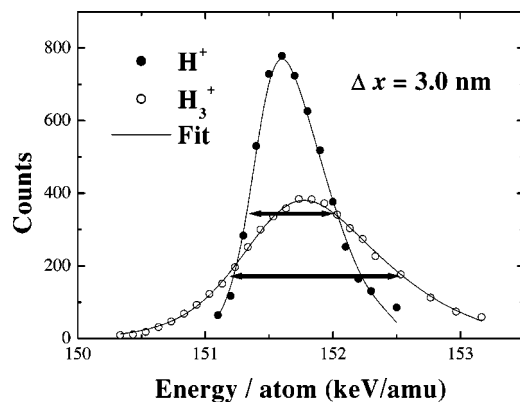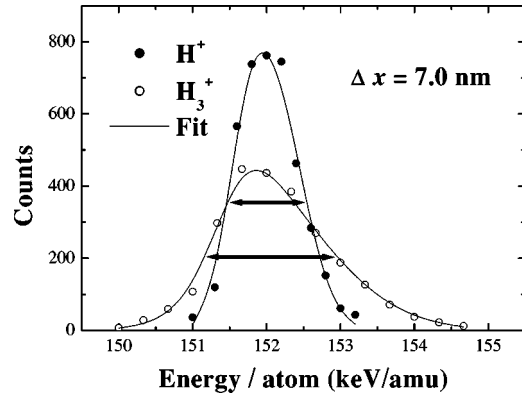

FIG. 2. The same as Fig. 1, but for a target of 7.0 nm.

of the analyzing chamber consisted of an oil-free turbo-molecular drag pump with a liquid-nitrogen trap, capable of reaching a final pressure of about 10^{-7} mbar.

In order to control the possible carbon deposition on the samples surface, for each sample, a $H-H_3-H$ sequence of profile measurements has been performed. This is a very stringent condition, since the nuclear reaction used in the present experiment has a very narrow resonance, being, thereby, very sensitive to any surface modification.

As noted above, H_3 and H ions will suffer different energy losses when penetrating through the $Si^{18}O_2$ films. Therefore, a difference in the widths of the NRA spectra obtained with the molecular and atomic beams, implies a ratio R different from one.

III. DATA ANALYSIS AND EXPERIMENTAL RESULTS

In Figs. 1 and 2, we display the NRA spectra obtained with protons and H_3 beams from 3.0 and 7.0 nm-$Si^{18}O_2$ films, respectively. In both figures, one can clearly observe a difference in the widths of the NRA profiles measured with atomic and molecular beams. This effect is basically due to the difference between the proton and the H_3 stopping powers per atom. In Fig. 3, we show the NRA spectra measured with atomic and molecular beams corresponding to the 25-keV ^{18}O implants into a $Si^{16}O_2$ film, and we still can see a shift in the position of the maximum of the ^{18}O distribution.

FIG. 1. The NRA spectra obtained with protons and H_3 cluster beams for a target of 3.0 nm. The results of the fitting procedure are also shown.
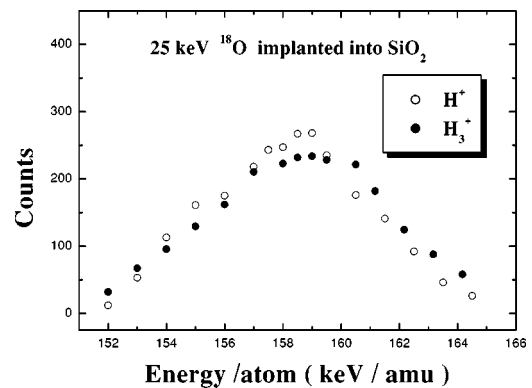

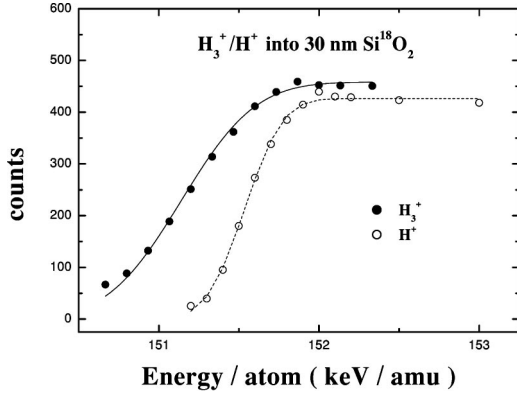FIG. 3. NRA spectra corresponding to the 25 keV ^{18}O implants into a $Si^{16}O_2$ film.

FIG. 4. Front edge of the NRA spectra from a 30 nm-$Si^{18}O_2$ film measured with protons and H_3 cluster beams.

FIG. 5. Experimental (points) and theoretical (lines) results for the averaged ratio R as a function of the target thickness. r_s is the Wigner-Seitz radius.

In order to obtain the energy loss in the $Si^{18}O_2$ films, the following effects have to be taken into account: (a) the width of the nuclear resonance ($\Gamma = 50$ eV), (b) the Doppler broadening caused by atomic vibrations, both in the target and in the H_3 molecule, (c) the energy spread of the analyzing beam, and, finally (d) the energy straggling. The latter arises from two different processes, namely (i) the projectile slowing-down, and (ii) the Coulomb explosion (when corresponds). With this aim, we have developed an algorithm, that performs a numerical convolution of the above effects, leaving the contribution of the Coulomb explosion to the energy straggling and the stopping power as the only free parameters.

The contributions of the effects (a), (b), and (c) to the NRA spectra were experimentally determined by measuring the front edge of a thick $Si^{18}O_2$ film with both types of beams—see Fig. 4. From the edge position, we can calibrate the energy of the machine, whereas its width is composed by the convolution of the resonance width the Doppler broadening, and the energy spread of the analyzing beam. All these effects together yield a full width at half maximum (FWHM) of about 250 and 500 eV, for protons and H_3 beams, respectively. A few layers of native $Si^{16}O_2$ on top of the $Si^{18}O_2$ film can change these values, but the ratio R is approximately insensitive to this effect. The FWHM values have entered the fitting program as inputs. The energy straggling of H in the SiO_2 films was calculated according to the Bohr model [13]. Finally, it should be noted that the contribution of the resonance width to the total FWHM is negligible [$\Gamma = 50$ eV $\ll 250$ eV$=$FWHM(H)].

When measuring the spectra with H_3 beams, one has to consider the contribution of the Coulomb explosion to the energy straggling. However, according to Ref. [10], this contribution is only significant for depths larger than 10 nm. Thus, only in these cases, it was taken into account. Figs. 1 and 2 show the result of the fitting procedure applied to the NRA spectra. The experimental results for the averaged ratio R, as a function of the target thickness, are displayed in Fig. 5. Each point represents the average of two or three independent measurements, which were reproducible within ±5%. The main uncertainty in the energy loss comes from the fitting procedure, that is, we were able to fit a given NRA profile equally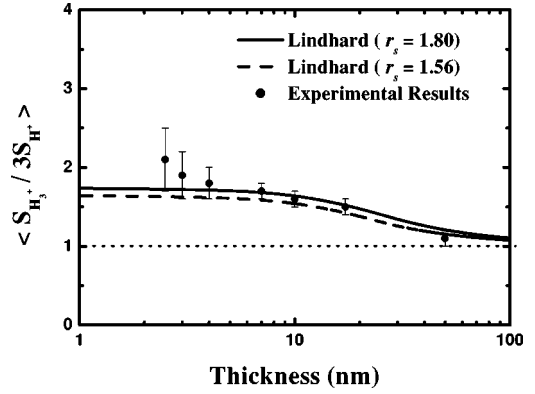 well by using a range of values of stopping power. We can see that the stopping-power ratio reaches the highest values $R \approx 1.8 - 2.1$ for thicknesses between 2.5 and 7.0 nm, and then decreases smoothly to unity. These are the highest values of vicinage effects so far observed using molecular ions.

IV. DISCUSSION

The molecular ions dissociate after they enter into the solid, so that what we actually calculate is the energy loss of the fragments (H^+ ions) moving at small distances through the solid. The correlated interaction of these ions with the target electrons produces the so-called *vicinage effect* in the energy loss.

We denote by $\vec{r}_i(t)$ (with $i=1,2,3$) the instantaneous position of each ion, and $\vec{v}_i(t)$ its instantaneous velocity. We assume that $\vec{v}_i(t) = \vec{v} + \vec{u}_i(t)$, with $\vec{v}=$ C.M. velocity and $\vec{u}_i(t) =$ small relative velocity of each ion, so that $|\vec{u}_i(t)| \ll v$. Initially $\vec{u}_i(t) \simeq 0$, since the molecule enters the solid as a single body, so that all the ions have the same initial velocity $\vec{v}$ (we neglect small differences that may be produced by vibrational states of the molecule).

The internuclear distances are given by $\vec{r}_{ij}(t) = \vec{r}_i(t) - \vec{r}_j(t)$, and they are assumed to be slowly changing quantities. For simplicity, we assume that the three protons form an equilateral triangle ($r_{12} = r_{23} = r_{31}$) whose size increases slowly with time (due to the Coulomb explosion). In order to calculate the stopping power, we separate the problem into three parts.

A. Instantaneous stopping power

We calculate the average energy loss for a given value of the internuclear distances r_{ij}, using a previous formulation based on the dielectric function formalism, where the energy loss of an ion cluster is given by [14]

$$S_3^{\text{inst}}(r) = \left[\sum_{i=1}^3 Z_i^2 + \sum_{i \neq j}^3 Z_i Z_j I(r_{ij}) \right] S_p. \quad (1)$$

In our case we set $Z_i = 1$ (protons).

In Eq. (1), S_p is the electronic stopping power for a single proton (at the same velocity v),

$$S_p = \frac{2}{\pi v^2} \int_0^\infty \frac{dk}{k} \int_0^{kv} d\omega \; \omega \; \text{Im}\left[\frac{-1}{\epsilon(k,\omega)}\right], \qquad (2)$$

and $I(r_{ij})$ is the "vicinage function" that incorporates the interference effects between the correlated protons (depending on the internuclear distance r_{ij}) [15]

$$I(r) = \frac{2}{\pi v^2 S_p} \int_0^\infty \frac{dk}{k} \frac{\sin kr}{kr} \int_0^{kv} d\omega \; \omega \; \text{Im}\left[\frac{-1}{\epsilon(k,\omega)}\right]. \quad (3)$$

We can also define the *instantaneous stopping power ratio*, normalizing the energy loss of the cluster to the energy loss of three independent (uncorrelated) protons, namely,

$$R_3(r_{ij}) = \frac{S_3^{\text{inst}}(r_{ij})}{3S_p}. \qquad (4)$$

In order to calculate these expressions, we have used Lindhard's dielectric function $\varepsilon(k,\omega)$ [11].

Note that if effective charges $Z_i = Z^*$ were introduced in Eq. (1) to describe the state of the hydrogen ions, the result for the stopping power ratio will be the same, since in that case we should normalize Eq. (4) with the corresponding value $3Z^{*2}S_p$.

B. Screened Coulomb explosion

When the H_3^+ molecule penetrates the solid, the binding electrons are quickly stripped off (in the first atomic layers) leaving three protons that are screened by the valence electrons of the solid, so that the effective interaction potential may be approximated by

$$V(r_{ij}) = \frac{Z^2 e}{r_{ij}} \exp(-\alpha r_{ij}), \qquad (5)$$

where $\alpha \cong (\pi/2)\omega_P/v$ is the effective screening constant, which depends on the ion velocity v (dynamical screening) and plasma frequency ω_P.

Since this is a repulsive potential, the ions will tend to separate from each other. This gives place to the "Coulomb explosion" of the molecule. However, since the mass of the ions is much larger than the electron mass, this explosion is "slow" in terms of the reaction time for the electrons (so that we can use the instantaneous stopping power values), but it is comparable to the usual dwell times of the ions in the solid (explosion times of the order of some femtoseconds, 1 fs $= 10^{-15}$ s, or of the order of 100 a.u. of time).

We simulate the screened Coulomb explosion by solving the Newton equations for the relative motion of the ions, subject to the repulsive potential $V(r_{ij})$. This gives us the values of $r_{ij}(t)$, in the range of interest: $0 < t < \tau$ ($\tau = \Delta x/u$, is the dwell time Δx is the penetration distance).

C. Integration of the stopping for finite penetration distances

First we calculate the instantaneous stopping power ratio, for a given distance $r(t) = r_{ij}(t)$ between the ions, as described before, namely,

$$R_3(r(t)) = \frac{S_3(r(t))}{3S_p}. \qquad (6)$$

Then we calculate the accumulated effect, for $0 < t < \tau$, by integrating over the time

$$\bar{R}_3 = \frac{1}{\tau} \int_0^\tau dt \; R_3(r(t)). \qquad (7)$$

The time dependence $r(t)$ in this integration is the one obtained from the previous study of the Coulomb explosion. This is the value that we may compare with the experiments.

In the calculation of the Lindhard's dielectric constant [11] for the SiO$_2$ matrix, two different values of the Wigner-Seitz radius have been adopted, namely, $r_s = 1.56$ and $r_s = 1.8$. The first value ($r_s = 1.56$) corresponds to the observed plasma frequency $\omega_P = 24$ eV of SiO$_2$, whereas the second value ($r_s = 1.8$) corresponds to the total number of valence electrons, $N_v = 12$ (taking into account the four $2p$ electrons of each O atom and the four valence electrons of Si). The results of the calculations described above, are shown in Fig. 3, along with the experimental values. The comparison reveals a good agreement between theory and experiment.

V. CONCLUSIONS

In the present paper, we have used a new technique based on the 151.2 keV resonance of the ^{18}O$(p,\alpha)^{15}$N ($\Gamma = 50$ eV) nuclear reaction to study the energy loss of H$_3$ clusters in Si^{18}O$_2$ films. This approach enabled us to work with target thickness from 2.5 up to 50 nm. For depths between 2.5 and 7.0 nm the ratio R reaches values between 1.8 and 2.1. The maximum effect observed with the thinnest film is $R = 2.1 \pm 0.4$. This is the first time that the maximum predicted value for R is experimentally attained. On the other hand, such a high enhancement factor allows an improved depth resolution, which is very important in the thickness determination of ultrathin films. The experimental results also show that, for thicknesses above 50 nm ($\tau \gtrsim 9.3$ fs or 390 a.u. of time), H$_3$ molecules lose energy at the same rate of a cluster of three independent protons. Finally, the results of theoretical calculations based on the *dielectric formalism* and using Lindhard's dielectric constant are in good agreement with the experimental values.

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