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Determination of ^{16}O and ^{18}O sensitivity factors and charge-exchange processes in low-energy ion scattering

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Quantitative analysis in low-energy ion scattering (LEIS) requires an understanding of the charge-exchange processes to estimate the elemental sensitivity factors. In this work, the neutralization of He^+ scattered by ^{18}O-exchanged silica at energies between 0.6 and 7 keV was studied. The process is dominated by Auger neutralization for $E_i < 0.8$ keV. An additional mechanism starts above the reionization threshold. This collision-induced neutralization becomes the dominant mechanism for $E_i > 2$ keV. The ion fractions P^+ were determined for Si and O using the characteristic velocity method to quantify the surface density. The ^{18}O/^{16}O sensitivity ratio indicates an 18% higher sensitivity for the heavier O isotope. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4758699]

Low-energy ion scattering (LEIS) is a very powerful tool for the analysis of the elemental composition of the surface of a wide range of materials including insulators and conducting samples. It has been applied for the study of different processes in which the outermost atomic layer drastically affects the material functionality, such as catalysts, semiconductors, electronics, and solid oxide fuel cells.[1–5] The capability of LEIS to selectively probe the first monoatomic surface relies on the very effective neutralization of the noble gas ions being scattered from inner layers, which assures that the signal originates from the outermost surface since only scattered ions are detected.[6] This surface sensitivity represents the main advantage of LEIS over other surface analysis techniques (e.g., secondary ion mass spectrometry (SIMS), x-ray photoelectron spectroscopy (XPS), or Auger electron spectroscopy (AES)) where the information comes from the first 3 to 20 atomic layers (depth of about 1–10 nm).

In LEIS measurements noble gas ions (e.g., He^+, Ne^+, and Ar^+) are directed onto the sample surface with energies ranging from 0.5 to 10 keV, being scattered by the surface atoms in a binary collision process. The backscattered ions are analyzed providing isotope resolved information of the surface composition. The yield of ions scattered over a given scattering angle θ for an element i is a measure of the atomic surface concentration N_i and can be expressed as[6]

$$S_i = \frac{I_p}{e} \times t \times \xi \times R \times \eta_i \times N_i, \quad (1)$$

where I_p is the primary ion beam current, e is the elementary charge, t is the acquisition time, ξ is the instrumental factor depending on the analyzer transmission and the detector efficiency, R is the roughness factor, N_i is the surface density of the element i (atoms/cm^2), and η_i is the elemental sensitivity factor, given by

$$\eta_i = P_i^+ \times \frac{d\sigma_i}{d\Omega}, \quad (2)$$

where P_i^+ is the ion fraction of the backscattered noble gas ions and $(d\sigma_i/d\Omega)$ is the differential scattering cross-section, which can be calculated for the LEIS regime with a screened Coulomb potential using the Molière approximation to the Thomas-Fermi potential (TFM) or the "universal" potential (ZBL).[7]

The ion fraction P_i^+ represents both the survival and the reionization probabilities of the scattered ion after the collision with the surface and is dependent on the charge-exchange processes taking place during the ion-atom interaction. Unfortunately, the charge-exchange processes are not fully understood making the prediction of P^+ very difficult.[6] Several mechanisms can lead to the primary ion neutralization, namely, Auger neutralization (AN), resonant neutralization (RN), and collision-induced neutralization (CIN). Additionally, the neutralized ion can be reionized during the close encounter (via electron promotion, which is the reverse process of CIN) or during the outgoing trajectory via resonant ionization (the reverse process of RN).[6,8,9] While AN is often assumed to be the predominant mechanism at low energies (E_i in the order of a few eV),[10] additional processes may contribute to the ion neutralization/reionization at higher energies (e.g., RN becomes the predominant neutralization mechanism for low work function surfaces).[9,11,12] Since several processes may occur during the scattering event, a quantitative prediction of the neutralization behaviour (e.g., P^+ dependence on the primary ion energy) is required for the selection of the optimal experimental parameters to perform a reliable quantitative LEIS analysis while avoiding time-consuming calibrations.[6,13,14]

In this work, we used the characteristic velocity method in order to study the neutralization behaviour of $^4He^+$ scattered from ^{16}O and ^{18}O and to determine the elemental sensitivity factors. A silica sample has been chosen as a reference material since the preferential sputtering can be neglected at the low ion doses used for the analysis.[15]

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Si samples (Dynamit Nobel Silicon, Ltd) were subjected to different annealing treatments in dry ($^{18}O_2$) and wet ($H_2{}^{18}O$) atmospheres in order to grow a thick SiO_2 layer (around 2 μm) with different ^{18}O isotopic concentrations. A detailed description of the annealing methodology can be found elsewhere.[16] The samples were analyzed by ToF-SIMS (ION-TOF GmbH, Germany) in order to check the isotopic composition, confirming the 3% and 97% ^{18}O enrichment of the grown SiO_2 layers.

The LEIS experiments were performed in a Qtac[100] instrument (ION-TOF GmbH) at a base pressure of $\sim 3 \times 10^{-10}$ mbar (which increases to the 10^{-8} mbar range during the analysis due to the flux of noble gas). The instrument is fitted with a double toroidal energy analyzer (DTA) which collects the scattered ions at a scattering angle of 145° from all azimuth angles. This large solid angle of acceptance combined with parallel energy detection allows a reduction in the surface damage due to the improved sensitivity compared to conventional LEIS instruments.[1,17] The samples were analyzed using a He^+ primary ion beam directed perpendicularly to the target surface at energies ranging from 0.6 to 7 keV at two different analyzer pass energies E_p (1 keV and 3 keV).

The samples were successively cleaned in acetone and methanol for 10 min each in an ultrasonic bath. Once the samples were introduced to the UHV chamber, low-energy sputtering was performed by 2 keV Ar^+ bombardment at 59° to remove any further surface contamination.

The sensitivity and separation of the ^{18}O and ^{16}O peaks is strongly affected by the initial energy of the primary ions and the scattering angle. The separation between the final energies (E_f) for scattering by ^{18}O and ^{16}O atoms decreases linearly with the initial energy (E_i). At lower E_i the relative peak width (width divided by E_i) increases, since the importance of inelastic processes increases. The experimental peak broadening has been reduced by using a lower E_p (1 keV instead of 3 keV) for low E_i, which gives a better separation of the ^{18}O and ^{16}O peaks (Fig. 1).

The ^{18}O and ^{16}O scattering yields for 100%-enriched SiO_2 samples at the different E_i were determined by extrapolation of the straight line obtained when plotting ^{18}O versus ^{16}O ion yields for the 97% and 3% ^{18}O-exchanged SiO_2 samples. As observed in Fig. 2, the higher yields are obtained when reducing the He^+ initial energy ($E_i \leq 800$ eV). In addition, the $^{18}O/^{16}O$ sensitivity ratios show 18% higher sensitivity for ^{18}O compared to ^{16}O atoms (slope in Fig. 2). The higher ^{18}O sensitivity is due to the higher ^{18}O scattering cross-sections, which are between 3.1 and 4.2% higher than for ^{16}O as E_i decreases from 7 to 0.6 keV, and the different ion fractions P^+.

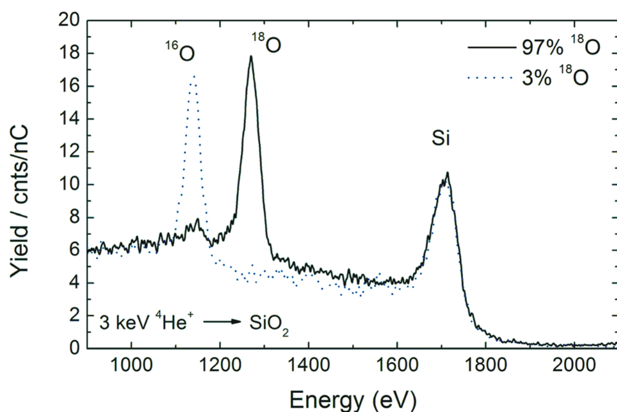

FIG. 1. Energy spectra for 3 keV He^+ scattered over 145° by an exchanged SiO_2 sample (^{18}O concentrations of 97% and 3%) using an E_p of 1 keV.

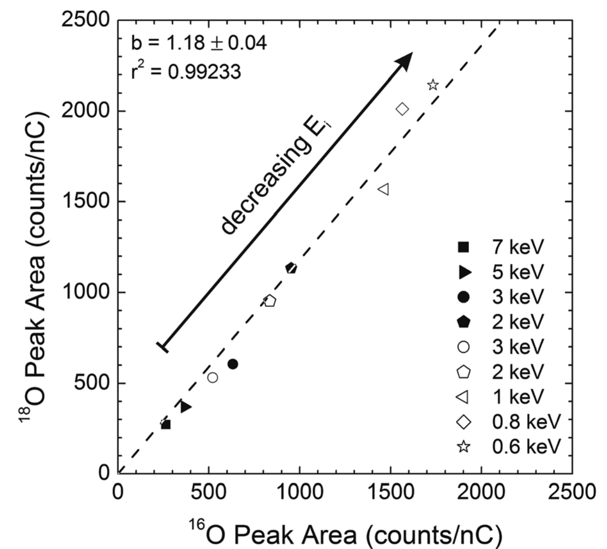

FIG. 2. Scattered ion yields for ^{16}O and ^{18}O isotopes in SiO_2 samples with 100% isotopic enrichment at different E_i. Closed symbols correspond to an E_p of 3 keV, open symbols correspond to an E_p of 1 keV.

As mentioned previously, P^+ is characteristic of each ion-atom combination and will depend on the different charge exchange processes that are involved during the ion-target interaction. The energy dependency of the neutralization must be known in order to determine the elemental sensitivity factors, η_i. In this work, we use the characteristic velocity method based on Hagstrum's model to determine the neutralization rate. In this model, the neutralization rate is assumed to be dependent only on the distance between the ion and the target surface.[10]

According to this method, the ion fraction is given by

$$P^+ = \exp\left(-V_c\left(\frac{1}{v_i} + \frac{1}{v_f}\right)\right), \tag{3}$$

where $\left({}^1/_{v_i} + {}^1/_{v_f}\right)$ is the sum of the reciprocal velocities of the incoming and outgoing primary ion, respectively, and V_c is the characteristic velocity which is a measure of the neutralization probability. Both the characteristic velocity and the definition of the reciprocal velocity depend on the neutralization mechanism involved during the ion-target interaction.[6]

By combining Eqs. (1)–(3) and taking natural logarithms it can be found that

$$\ln \frac{S_i}{(d\sigma_i/d\Omega)} = \ln(c') + \ln(N_i) - V_c\left(\frac{1}{v_i} + \frac{1}{v_f}\right). \tag{4}$$

A straight line is expected when plotting the logarithm of the LEIS signal (corrected for the scattering cross-section estimated using the TFM potential approximation) as a function of the reciprocal velocities, as long as one single neutralization mechanism dominates the process. The slope of the line is the

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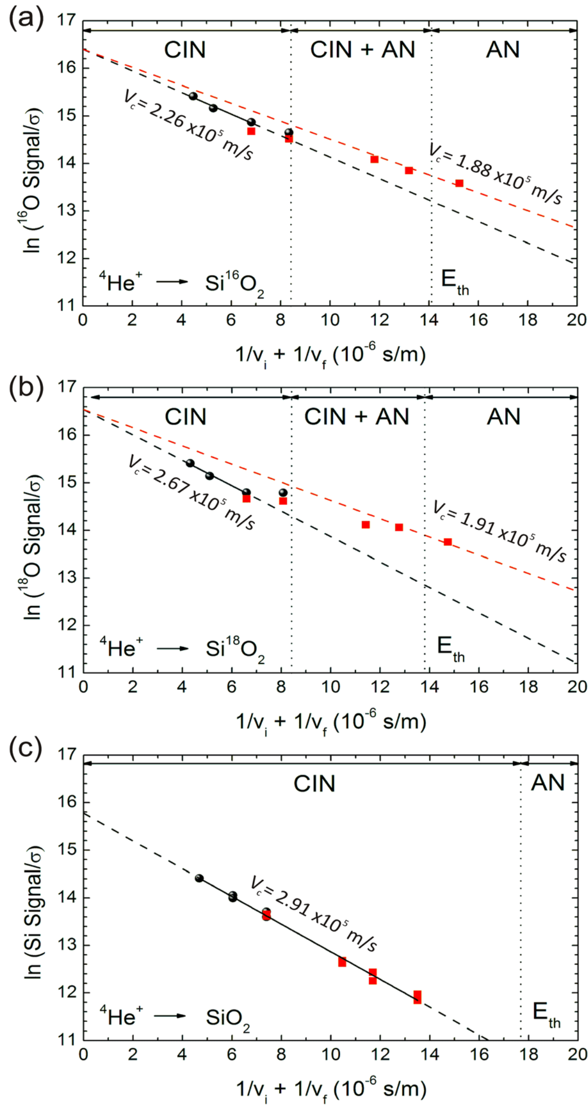

FIG. 3. Natural logarithm of the LEIS signal (peak areas) corrected for the differential cross-sections (σ) versus the sum of the reciprocal velocities before and after scattering for He^+ scattered by SiO_2. The yields were extrapolated to 100% O isotopic composition in the different samples. (a) ^{16}O in 100%-enriched $Si^{16}O_2$, (b) ^{18}O in 100%-enriched $Si^{18}O_2$, and (c) Si in both SiO_2 samples. Circles: E_p 3 keV; squares: E_p 1 keV.

characteristic velocity, which can be later used to calculate P_i^+ according to Eq. (3). However, when more than a single neutralization/ionization mechanism is involved, this linear relationship no longer holds. Fig. 3 shows these plots for He^+ scattering by ^{16}O, ^{18}O, and Si in the energy range of 0.6-7 keV for SiO_2, correcting the ion yields for 100%-enriched $Si^{16}O_2$ and $Si^{18}O_2$. The characteristic velocities (V_c) and the intercepts (a) for the different E ranges found for the different atoms involved are summarized in Table I.

Each neutralization mechanism occurs at a specific interaction distance, and, hence, it is possible to predict the charge-exchange process involved by taking into account the distance of the closest approach (R_{min}). For this study, we only consider AN and CIN mechanisms, since RN will be predominant for noble gas ion scattering on low work function surfaces, usually in the order of 2 eV.[9,18] AN requires a close overlap of the ion and target orbitals for the effective transfer of a valence electron of the surface atom to the K-shell of the He^+ ion[10] and will take place at a distance of about 1-2 Å.[19] Conversely, CIN occurs during the close encounter at shorter distances (~0.5 Å), involving the interaction of the ion ground state and the core levels of the target atom.[20,21]

As observed in Fig. 3, the expected linear relationship according to Eq. (4) is held for the Si atoms, indicating that a single neutralization/reionization process is taking place throughout the whole E range. As reported by Mikhailov *et al.* for the scattering of He^+ on Si,[12] the dominant charge exchange process at E_i of 1-3.5 keV is CIN, with high V_c values compared to those elements showing AN. For a head-on collision at $E_{th} = 300$ eV (corresponding to the reionization of He^0 scattering by Si atoms[6]) the R_{min} is 0.34 Å. At higher E_i and shorter R_{min} the channel for reionization is open, which implies that also the reverse process (CIN) is possible. Since CIN is much more effective than reionization, this leads to a net decrease in the LEIS signal (higher V_c). For oxygen there is more than one charge-exchange process, as indicated by the slope change at $E_i \geq 1$ keV ($(1/v_i + 1/v_f) \leq 12 \times 10^6$ m/s). For $E_i < 800$ eV, AN is the only neutralization process for He^+ scattered by O atoms. In a head-on collision, R_{min} at the E_{th} (700 eV for ^{16}O and 684 eV for ^{18}O atoms, respectively[6]) corresponds to 0.18 Å. Above the E_{th}, CIN starts to take place which leads to a decrease in the LEIS signal. CIN becomes the dominant charge-exchange process for $E_i > 2$ keV ($(1/v_i + 1/v_f) \leq 8 \times 10^6$ m/s), with a neutralization rate defined by the slope of the straight line (black dashed line). At intermediate E_i (1–2 keV), both charge-exchange processes occur simultaneously, and a deviation of the linear relationship for AN mechanism (red dashed line) is noticed.

Additionally, the characteristic velocity method can be applied to estimate the relative surface density of the species

TABLE I. Characteristic velocities (V_c) and intercepts (a) as estimated from the linear fittings of the corrected scattering yields versus the sum of the reciprocal velocities of the He^+ ions scattered by SiO_2, extrapolated for 100% O isotopic composition. The straight lines for AN in O isotopes was defined by the intercept value (a) and the corrected scattering yield at $E_i = 600$–800 eV, assuming that CIN contribution at these E can be neglected.

Mechanism	Atom	E_i range (keV)	a	V_c ($\times 10^5$ m/s)	r^2	$(N_O/N_{Si})_{Surf}$
CIN	Si	$E_i \leq 7.0$	15.78 (±0.06)	2.91 (± 0.06)	0.99404	
	^{16}O	$E_i > 2.0$	16.40 (± 0.16)	2.26 (± 0.29)	0.96737	1.86 (± 0.19)
	^{18}O	$E_i > 2.0$	16.54 (± 0.15)	2.67 (± 0.28)	0.97880	2.14 (± 0.19)
	O (mean)	$E_i > 2.0$	16.47 (± 0.16)	2.47 (± 0.28)	···	2.00 (± 0.19)
AN	^{16}O	$E_i < 0.8$	16.40 (± 0.16)	1.88 (± 0.03)	0.99998	···
	^{18}O	$E_i < 0.8$	16.54 (± 0.15)	1.91 (± 0.02)	0.99999	···
	O (mean)	$E_i < 0.8$	16.47 (± 0.16)	1.90 (± 0.02)	···	···

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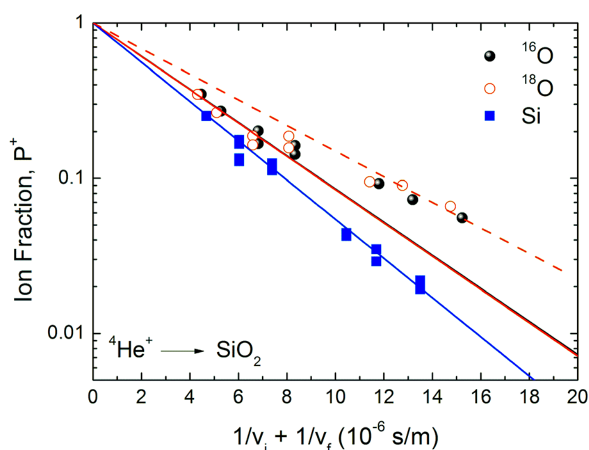

FIG. 4. Ion fractions for Si, ^{16}O and ^{18}O in 100%-enriched SiO_2. Dashed lines: AN mechanism; solid lines: CIN mechanism.

under investigation if V_c is constant over the energy range on which the extrapolation is based.[18] The relative surface density can be estimated by extrapolating Eq. (4) for $v \rightarrow \infty$, as for infinite velocities there is no time for neutralization and the ion fraction equals unity ($P_i^+ = 1$). The relative surface density of O and Si is given by

$$\ln\left(\frac{N_o}{N_{Si}}\right) = \ln\left(\frac{S_O / \sigma_O}{S_{Si} / \sigma_{Si}}\right)_{v\rightarrow\infty}. \quad (5)$$

According to Eq. (5), the surface density was found to be O:Si = 2.14 ± 0.19 and 1.86 ± 0.19 in 100% enriched $Si^{18}O_2$ and $Si^{16}O_2$, respectively. These results confirm that any preferential sputtering of O during the initial cleaning stage of the sample surfaces can be neglected (within 10% of experimental error). By assuming a silica density of 2.32 g/cm^3, the atomic surface densities in silica correspond to 0.81 and 1.60×10^{15} atoms/cm^2 for Si and O atoms, respectively.

Once the neutralization behaviour is known and characterized by the corresponding V_c values, the P^+ can be calculated for different E_i using Eq. (3), as shown in Fig. 4, and used to determine the ^{18}O and ^{16}O sensitivity factors (η_i).[13]

These values can be used as a reference to perform quantitative analysis on other ^{18}O-exchanged materials, provided that there are no matrix effects. Previous investigations of $^3He^+$ scattering by polydimethylsiloxane (PDMS) at energies from 800 eV to 5 keV showed a change in V_c for O atoms in the E range of 800-1800 eV indicating a change in the dominant neutralization mechanism,[22] in agreement with the present work. These results suggest that matrix effects can be ruled out for He^+ scattering by O atoms for $E_i > 2$ keV since CIN mechanism takes place at close distances (interaction with the core electrons) and does not involve the surrounding atoms in the surface.

In this study, the neutralization behaviour of He^+ scattering on ^{18}O-exchanged silica samples was found to be dependent on the different charge-exchange processes taking place in the energy range under study. The characteristic velocity method has been applied to determine the influence of the ion velocity on the He^+ ion fractions (P^+). For O atoms, the survival/reionization probability is dominated by Auger neutralization taking place at long ion-atom distances at low $E_i \leq 0.8$ keV. Conversely, collision-induced neutralization dominates the process at $E_i > 2$ keV. At intermediate E_i (1–2 keV), both charge-exchange processes occur simultaneously. Furthermore, the neutralization efficiency of the CIN mechanism was found to be higher than in AN, according to their V_c values. For Si, the charge-exchange process is based on a CIN mechanism for 0.6 keV < E_i < 7 keV. The elemental surface density of ^{18}O-exchanged SiO_2 samples could be estimated by the characteristic velocity method for $E_i > 2$ keV, confirming that there is no preferential sputtering of O at the low doses used during the analysis as previously reported by Pitts and Czanderna.[15] Since the CIN results from interaction with the core electrons of the oxygen atoms, no matrix effects are expected, and hence the ^{16}O and ^{18}O sensitivity factors at E_i from 2–7 keV can be used as a reference for the quantitative analysis of other ^{18}O-exchanged oxide materials. The $^{18}O/^{16}O$ sensitivity ratio shows a 18% higher sensitivity for the heavier O isotope.

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