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Optical properties of SiO_2 determined by reflection electron energy loss spectroscopy

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Abstract

Reflection electron energy loss spectra (REELS) recorded with a 1 keV electron beam have been used to characterize the surface of amorphous SiO_2 compound and to obtain its complex dielectric function in the energy loss range 0–50 eV by their treatment numerically. The optical data have been derived from the energy loss function $\mathrm{Im}\left[-1/\varepsilon\right]$ using the Kramers–Krönig analysis. The obtained results are very interesting and agree well with the published values obtained by other methods.

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1. Introduction

The interest of silica SiO_2 compound in the industrial domain is due to its various qualities (electrical, optical, chemical and thermal properties). It is used in optical and electronic applications (opto-electronic devices, optic fibres, etc.) [1,2]. The crystal structure of silicon dioxide (SiO_2) has attracted the attention of many researchers [3–5] because it is one of the most fundamental oxide systems. Also, the determination of its dielectric function over a wide range of energy is indispensable for many applications. Typically, optical properties are determined using optical techniques such as reflectance and optical spectroscopy (ellipsometry) [6,7]. They are well-suited techniques to investigate the optical response of semi-conductors and dielectrics. But they present some experimental limitations due to a high sensitivity to surface roughness and cleanliness, which is sometimes questionable as a consequence of the influence of the atmospheric environment.

The treatment of electron energy loss spectroscopy both in the transmission (TEELS) and in the reflection (REELS) mode may be an excellent technique for the determination of optical properties [7–11]. REELS presents several advantages with respect to TEELS, like the use of incident electron beam energies lower than 3 keV which allow to carry out measurements in conventional ultra-high-vacuum systems used for photoemission and Auger spectroscopy [12]. Futhermore, the constraint of sample thickness does not exist allowing the study of any solid sample [13].

In addition to the experimental advantages associated to REELS, it is often combined to Auger electron spectroscopy for surface studies; the aim of the present work is to perform a numerical treatment of REELS' spectra in the frame of the dielectric theory [14] and derive the optical properties of the examined material.

2. Theory

When the incident beam interacts with the solid, the transfer of energy E and momentum q of incident electrons to the solid electrons is related to the complex dielectric function of the solid $\varepsilon = \varepsilon_1 + \mathrm{i}\varepsilon_2$ through its imaginary parts $\mathrm{Im}\left[-1/\varepsilon\right]$, which represents the energy loss function. Moreover, the intensity damping, due to the propagation in the dielectric medium, is proportional to ε_2. Therefore, the energy loss could be described by the function

$$\frac{\varepsilon_2}{|\varepsilon|^2} = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} = \mathrm{Im}\left[-\frac{1}{\varepsilon}\right] \tag{1}$$

The interpretation is based on the assumption that within the range of validity of the dielectric theory, the momentum transfer of the incoming electrons is negligible $q \to 0$. This means to work in the optical limit in which the energy loss function $\mathrm{Im}[-1/\varepsilon(q, E)]$, commonly defined as a

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function of both energy and momentum, is only represented by a function of the energy $\mathrm{Im}[-1/\varepsilon(E)]$ [13,14]. Thus, the application of the Kramers–Krönig analysis is possible to determine the optical data.

Before to begin the REELS analysis, we assume that, the loss signal is a linear superposition of both bulk and surface contributions as indicated by the following relation obtained from Refs. [9,15,16]:

$$N(E) \approx R\,\mathrm{Im}\left[-\frac{1}{\varepsilon(E)}\right] + S\,\mathrm{Im}\left[-\frac{1}{1+\varepsilon(E)}\right] \qquad (2)$$

where R and S are the coefficients that mainly depend on the primary beam energy E_p, its angle of incidence on the surface α and the inelastic mean free path λ:

$$R = \int_d^\infty \mathrm{d}z\,\exp\left(-\frac{2z}{\lambda\cos\alpha}\right) = \frac{\lambda\cos\alpha}{2}\exp\left(-\frac{2d}{\lambda\cos\alpha}\right),$$

$$S = \int_0^d \mathrm{d}z\,\exp\left(-\frac{2z}{\lambda\cos\alpha}\right) = \frac{\lambda\cos\alpha}{2}\left[1-\exp\left(-\frac{2d}{\lambda\cos\alpha}\right)\right] \qquad (3)$$

where z is the depth coordinate perpendicular to the sample surface and d is a phenomenological parameter which represents the thickness of that sample region where the surface scattering dominates and whose value is of the same order of magnitude of the primary electrons wavelength. If the scattering centre is located at a depth z below the sample surface, then $2z/\cos\alpha$ is the effective length of electrons in the material.

At first we have to eliminate the elastic peak then to remove the background signal, which is proportional to the elastic peak intensity. Sometimes multiple scattering are presents in the REELS experimental signal, there presence depend on the materials qualities. In this case, they must be also subtracted. Thus, in order to obtain the dielectric function, the volume contribution of energy loss function $\mathrm{Im}[-1/\varepsilon(E)]$ has to be isolated from the experimental spectrum.

The aim of this paper is to develop a method permitting to determine the dielectric function of SiO_2 using REELS measurements in the energy range 0–50 eV. At first, the method consists to extract the energy loss function $\mathrm{Im}[-1/\varepsilon]$ from the experimental REELS spectrum. Secondly, we calculate the optical constants using the Kramers–Krönig analysis. The dielectric function determined for SiO_2 will be presented and compared with what is found in the literature.

3. Experimental

The acquisition of experimental REELS curves was performed in a UHV chamber with a base pressure of about 10^{-7} Pa. The samples were amorphous SiO_2 films; they were submitted to a primary electron beam of 1 keV at an incidence angle of 20°. Before introducing the samples into the spectrometer, usual ex situ chemical cleaning procedure was performed. Once into the chamber, the sample was flash-heated in order to eliminate the residual contamination. The cleanliness of the studied surfaces was controlled by Auger electron specroscopy using a hemispherical analyser operating in the constant pass energy mode with an energy resolution of $\Delta E = 0.4$ eV. The acceptance semiangle angle β of the analyser was about 0.1°. The REELS spectra were recorded in the direct mode $N(E)$ and explored in 0–100 eV energy range.

4. Data analysis

In order to extract the optical function from REELS spectra, both the elastic peak and the background must be removed to isolate the differential inelastic electron scattering cross section $K(E)$. The subtraction of the elastic peak is facilitated by the existence of a band gap ~9 eV and may be performed by a fit to its gaussian line shape, while the elimination of the background due to multiple scattering is more complicated. As suggested by Tougaard and Kraaer [10], a self-consistent method based on a model for the transport of electrons in a solid is used and given by the following relation:

$$\frac{\lambda L}{\lambda+L}K(E) = \frac{1}{C}\left[j_1(E) - \int_0^E \frac{\lambda L}{\lambda+L}K(E'-E)\,j_1(E')\,\mathrm{d}E'\right] \qquad (4)$$

where $K(E)$ is the differential inelastic cross section for an energy loss E of the measured REELS spectrum without the elastic peak, $j_1(E)$ the measured energy distribution of backscattered electrons, λ the inelastic mean free path of the electrons, L the attenuation length of the reflected electrons due to elastic scattering and C is the related to the intensity of the elastic peak but here it will be used as a scaling parameter [17,18].

Once the elastic peak and background have been eliminated, the next step is to isolate the bulk electron loss function. If surface contributions can be assumed negligible [13,19] (i.e. Eq. (2)), $K(E)$ is given by

$$K(E) = \tau\,\mathrm{Im}\left[-\frac{1}{\varepsilon}\right]\pi\log\left[1+\frac{\beta^2}{\theta_E^2}\right] = \mathrm{cste}\,\mathrm{Im}\left[-\frac{1}{\varepsilon}\right] \qquad (5)$$

where cste = 54.054, $\theta_E = \Delta E/2E_p$ (E_p is the energy of the primary electron beam and ΔE is the energy loss), τ is an equivalent sample thickness which represents the effective path length of the electron inside the sample. The Kramers–Kröning transform is then used to deduce the real part of $1/\varepsilon$:

$$\mathrm{Re}\left[-1/\varepsilon(E)\right] = 1 - \frac{2}{\pi}P\int_0^\infty A\,\mathrm{Im}\left[-\frac{1}{\varepsilon(E')}\right]\frac{E'}{E'^2-E^2}\mathrm{d}E' \qquad (6)$$

where P denotes the principal Cauchy parts of the integral and A is a constant deduced from the value of the dielectric constant at zero energy:

$$A = \frac{\pi}{2}\frac{\left[1 - \mathrm{Re}\left[-1/\varepsilon(0)\right]\right]}{\int_0^{\infty}\mathrm{Im}[-1/\varepsilon(E)](1/E')\mathrm{d}E'} \tag{7}$$

In the case of semi-conductors or insulators $\mathrm{Re}\left[-1/\varepsilon(0)\right]$ is equal to $\varepsilon_1(0)^{-1}$, $\varepsilon_1(0) = 2.13$ for the case of SiO_2 [3].

In fact, the use of the Kramers–Kröning transformation needs in principle infinite integration ranges for the determination of $\mathrm{Re}\left[-1/\varepsilon(E)\right]$. This is possible, thanks to the extension of the energy loss measurements, which allow to perform the calculations over a wide energy range. The complex dielectric function $\varepsilon(E)$ is then easily obtained from both $\mathrm{Re}\left[-1/\varepsilon(E)\right]$ and $\mathrm{Im}\left[-1/\varepsilon(E)\right]$ as

$$\varepsilon_1(E) = \frac{\mathrm{Re}\left[-1/\varepsilon(E)\right]}{\left[\mathrm{Re}\left[-1/\varepsilon(E)\right]\right]^2 + \left[\mathrm{Im}\left[-1/\varepsilon(E)\right]\right]^2},$$

$$\varepsilon_2(E) = \frac{\mathrm{Im}[-1/\varepsilon(E)]}{\left[\mathrm{Re}\left[-1/\varepsilon(E)\right]\right]^2 + \left[\mathrm{Im}[-1/\varepsilon(E)]\right]^2} \tag{8}$$

The above treatment becomes easier owing to the fact that there are no surface contributions in our REELS spectrum checked at 1000 eV.

5. Results and discussion

Fig. 1 shows the REELS spectra of the silicon oxide (SiO_2), where the elastic peak and the bulk plasmon peak appearing at 22.2 eV can be easily identified.

The application of the deconvolution procedure described in Section 4 has allowed the obtention of the background subtraction in terms of Eq. (4), which is reported in Fig. 2 for three different values of C (i.e. $C = 13I_0$, $22I_0$ and $33I_0$, where I_0 is the intensity of elastic peak). This figure shows the experimental REELS spectrum without the elastic peak of intensity I_0, the background calculated spectra corresponding to the three values of C and the three $N(E)$ curves obtained by subtraction of the background spectra from the $j_1(E)$ spectrum. The separation of the elastic peak does not lead to information loss, because of the large band gap at low losses. The background is eliminated in varying arbitrary the C parameter between $13I_0$ and $33I_0$. Below $13I_0$, the loss function presents negative values between 29.5 and 70 eV. These negative $\mathrm{Im}\left[-1/\varepsilon(E)\right]$ values are obviously not physically real.

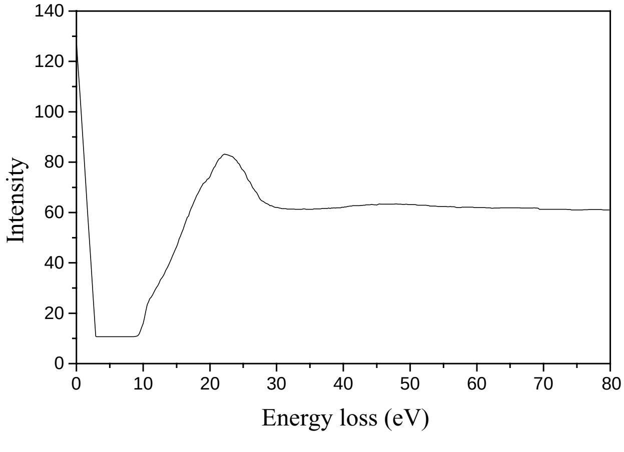

Fig. 1. Experimental REELS spectra of SiO_2.

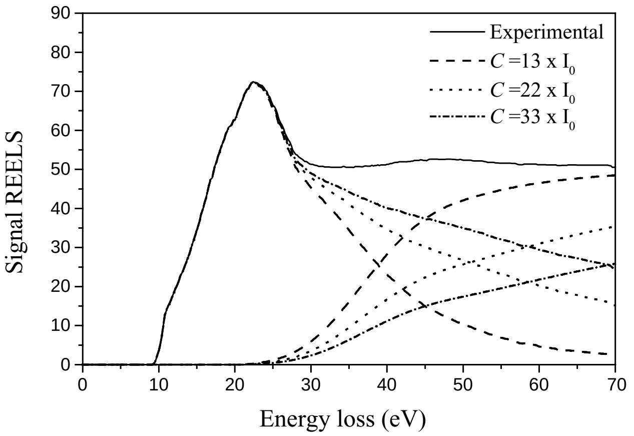

Fig. 2. Experimental SiO_2 REELS spectrum without the elastic peak $j_1(E)$ and after background subtraction $N(E)$ for three differents C values. Also are shown the corresponding $N(E)$ background signals.

As indicated in Fig. 3, the comparison between the different curves representing the pure bulk loss function after their isolation from the experimental spectrum shows that the best fit correspond to $C = 13I_0$, which presents a good agreement with the corresponding electron loss function found by the optical method [20]. A noticeable broad volume plasmon peak centered at 22.4 eV is observed in the bulk loss function.

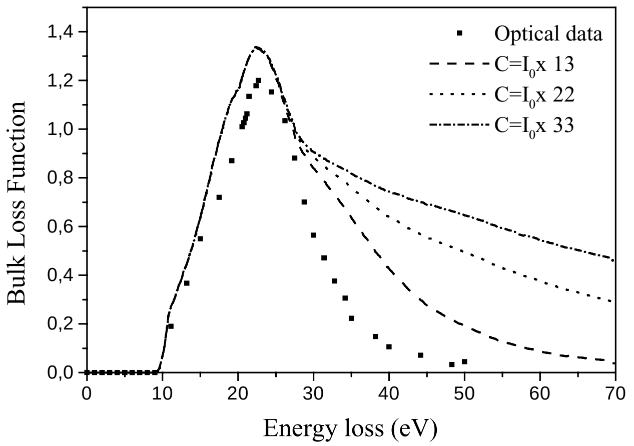

Fig. 3. SiO_2 bulk loss functions determined from Fig. 2 after background subtraction for $C = 13\ I_0$, $C = 22\ I_0$ and $C = 33\ I_0$. The loss function determined by optical measurements [20] is also shown.

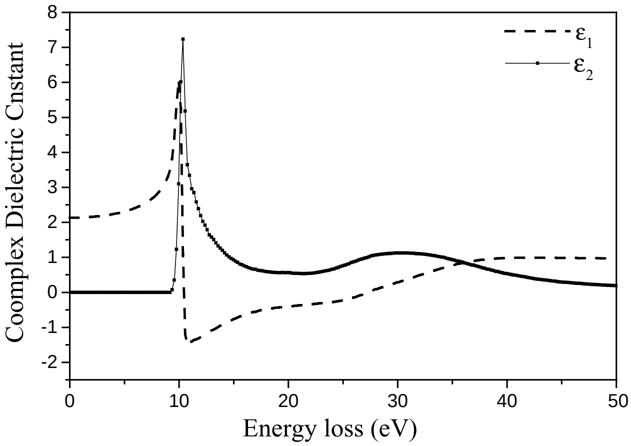

Fig. 4. Complex dielectric constant of SiO_2 as deduced from REELS data.

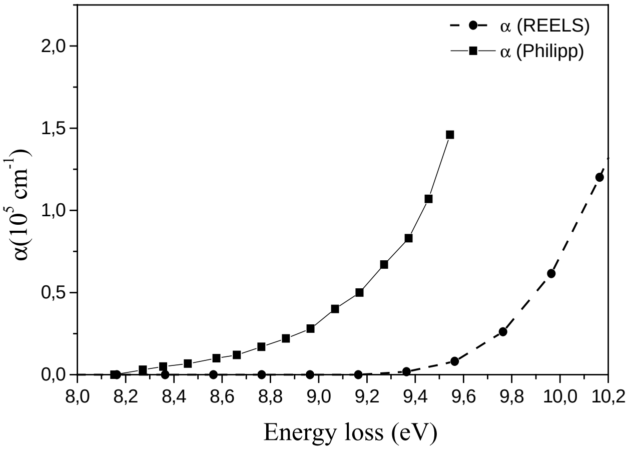

Fig. 5. Absorption coefficient of SiO_2 deduced from REELS. A curve obtained from reflectance data is added for comparison.

In Fig. 4 are shown the real and imaginary parts of the dielectric constants ε_1 and ε_2, calculated from Eq. (8). The variations of ε_1 and ε_2 show well the insulating behavior. ε_2 has a maximum at 10.53 eV which represents the resonance energy, at this energy $\varepsilon_1 = 0$.

To reinforce the validity of our method, we have extended the calculus to the determination of the absorption coefficient. The morphology of the curves agrees and its variation agrees well with optical results given by Phillip [3], where the SiO_2 band gap was about ∼8.28 eV, whereas the SiO_2 used in our study was about $E_g = 9$ eV. This is shown in Fig. 5.

6. Conclusion

Optical constants for SiO_2 have been determined from REELS spectra obtained at a primary beam energy of 1 keV and the data treatment of REELS spectra has been described in detail. Based on the results presented here, the use of a primary beam energy equal or higher than 1 keV mostly favours only the bulk contribution and minimizes the surface effects. The Kramers–Kröning analysis has been used to derive the real part from $\mathrm{Im}\left[-1/\varepsilon(E)\right]$. The plot of ε_1 and ε_2 shows that REELS spectroscopy is an interesting method for the determination of optical properties. We think to develop it to extend its application on other materials as semiconductors or metals.

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