The relation between the electron energy loss spectra of hafnia and its dielectric function

Maarten Vos,⁎, Pedro Luis Grande

A. Atomic and Molecular Physics Laboratories, Research School of Physics and Engineering, The Australian National University, Canberra 0200, Australia
B. Electronic Materials Engineering Department, Research School of Physics and Engineering, The Australian National University, Canberra 0200, Australia
C. Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil

A R T I C L E   I N F O

Article history:
Received 13 April 2014
Accepted 11 June 2014
Available online 20 June 2014

Keywords:
Reflection electron energy loss spectroscopy
Dielectric function
HfO₂

A B S T R A C T

Recently two papers have been published deriving the dielectric function from hafnia from electron energy loss data (Jin et al. Applied Physics Letters 100 083713 (2006), Behar et al. Phys. Rev A 80 062901 (2009)). The obtained dielectric functions are compared in their optical limit and differ considerably. Here we try to clarify the situation by presenting new experimental data and reviewing the analysis procedure used in the earlier work. We conclude that the discrepancy is most likely caused by a shortcoming in the way that the momentum-dependence of the dielectric function is modelled.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The dielectric function \( \epsilon(\mathbf{k}, \omega) \) describes the response of a material to an electric field. One cause of a time-dependent electric field is a charged particle (here an electron) penetrating matter. Knowledge of the dielectric function makes it possible to calculate the probability that an energetic charged particle creates an electronic excitation with energy \( \omega \) and momentum \( \mathbf{k} \) (we use atomic units in this paper). From the dielectric function one can calculate the inelastic mean free path (IMFP) of electrons, or the electronic stopping power for ions.

The electron energy loss spectrum is proportional to

\[
\int \text{Im}[\frac{1}{\epsilon(\mathbf{k}, \omega)}] d\mathbf{k}
\]

where the extent of the integration over momentum space depends on the experimental setup. It is impossible to derive the dielectric function \( \epsilon \), depending both on \( \omega \) and \( \mathbf{k} \), from a single measured electron energy loss spectrum without further assumptions. Extracting the dielectric function has been attempted by many researchers as the dielectric function plays an essential role in many parts of physics. It is used in many-body physics where it affects the electron–electron interaction, in photo-emission where it determines both the IMFP as well as the extrinsic satellites due to energy losses, and in X-ray physics. Generally one assumes a certain momentum-dependence of the dielectric function. Examples here are the Drude–Lindhard and Mermin approximations. Once a momentum-dependence is assumed one can fit a dielectric function to the experimental data. The assumed momentum dependence can then be tested if a measurement can be done that probes a different part of momentum space.

The first estimates of the dielectric function by electron spectroscopy were done in a transmission mode at typical energies between 20 and 200 keV and these experiments are referred to as (Transmission) Electron Energy Loss Spectroscopy ((T)EELS) [1]. Here one requires thin samples. When one positions the detector at 0° one measures the dielectric function for very small \( k \) values i.e. close to the ‘optical limit’. By moving the detector away from 0° one can monitor the dispersion and determine the dielectric function for specific \( k \) values, as was done, for example, in the case of aluminium [2].

More recently attention has switched to reflection measurements using lower primary energies, where no sample thinning is required and nm-thick layers can be measured. These lower energy measurements are partly motivated by a desire to understand photo-emission spectra fully quantitatively as photo-emission usually involves (sub-) keV electrons. At lower energies surface excitations are stronger and multiple scattering is always present in thick samples. Modelling these processes properly is a first requirement for the extraction of the dielectric function in a reflection geometry, and the mathematical tools to do this have been established over the last decades [3–6]. Recently claims were made that Reflection EELS (REELS) is a competitive way of determining the dielectric function of a material [7].

In the case of the dielectric function determination by REELS most attention has so far been directed to elemental solids, and the determination by REELS of the dielectric function of binary compounds is still in its infancy. One case that has been studied by REELS is HfO₂. Sanz et al. studied the oxidation of Hf metal [8], Jin et al. used REELS to study thin films (3 nm thick) of HfO₂ deposited on Si [4–9], see also

⁎ Corresponding author.
E-mail address: maarten.vos@anu.edu.au (M. Vos).
[10]). These authors used measurements at a primary energy $E_0$ of 300 and 500 eV to derive a description of its dielectric function based on 6 Drude–Lindhard oscillators with no dispersion.

More recently Behar et al. [11] derived the dielectric function from the same compound using experimental data, obtained in a transmission geometry with $E_0 = 20$ keV, by Frandon et al. [12]. The spectra obtained by Frandon et al. have a similar shape as the 200 keV transmission measurements of more recent date [13–15]. Behar et al. also derived a description of the dielectric function but they used a set of oscillators with Mermin-type dispersion [16]. The Drude–Lindhard and Mermin approach to the description of the dielectric function differ in how they model the $k$-dependence but the models coincide for $k = 0$.

The spectra obtained by Jin et al. are quite different from those obtained in high-energy TEELS experiments, as is to be expected as the reflection measurements at 300–500 eV have much larger surface excitation probabilities and the multiple scattering effects are totally different in a reflection geometry compared to a transmission one. The analysis incorporates these surface excitation and multiple scattering effect and finally a model dielectric function based on the Drude–Lindhard oscillators is derived.

It is thus of interest to compare the loss function of Jin et al. and Behar et al. in the optical limit. This is done in Fig. 1. Somewhat surprisingly the two obtained loss functions for HfO$_2$ are quite different in the optical limit. The loss function obtained by Jin et al. is peaked near 16 eV and its intensity here is more than 3 times larger than the intensity of the peak near 46.5 eV. The loss function of Behar et al. has a peak near 15 eV, followed by a broader and slightly more intense one near 26 eV, but the feature near 46 eV has the largest intensity. These dielectric functions were used to determine the inelastic mean free path (IMFP). Surprisingly there is quite a good agreement between the IMFP obtained by Behar et al. and Jin et al. for 300 eV and 500 eV [11].

This situation is unsatisfactory. Not only does it put in doubt the proper description of the dielectric function of HfO$_2$, but it also questions the validity of the analysis procedures of the REELS spectra. Here we want to investigate these issues by electron energy loss studies of HfO$_2$ using a reflection geometry, but $E_0$ values between 5 keV and 40 keV [17], of the same order as those typically used in TEELS experiments.

2. Experimental details

The HfO$_2$ layers were grown by atomic layer deposition on a SiO$_2$ substrate. The thickness was 75 nm, the surface roughness of these films was measured by an atomic force microscope and was less than 1 nm [18]. The films deposited were amorphous, as no HfO$_2$ related diffraction peaks were seen in grazing incidence X-ray diffraction. Some samples were annealed at temperatures of 500 °C resulting in a monoclinc HfO$_2$ layer but this did not cause a noticeable change in shape of the REELS spectra. Rutherford backscattering spectra of HfO$_2$ layers grown on carbon did not show other elements than Hf, O and C (from the substrate) [19]. At 40 keV these electron scattering measurements resolve the Hf and O peaks and the observed intensity of the Hf and O peak and film thickness were as expected for the nominal stoichiometry and film thickness [20,18]. No changes were detected in the sample as a consequence of the electron beam irradiation, in either the intensity ratio of the Hf and O elastic peak or the shape of the loss spectra.

The REELS spectra were taken for the as-inserted samples, without further surface preparation and are shown in Fig. 2. The ANU spectrometer was described elsewhere [21], but has been modified since, such that the scattering angle is 135° and incoming and outgoing electrons and the surface normal are aligned in the same plane. It was operating at either 5 keV or 40 keV with an energy resolution of ≈0.3 eV. Two different geometries were used. One has the incoming beam directed along the surface normal and the outgoing beam 45° away from the surface normal. In the second geometry the sample is rotated over 35° in such a way that the outgoing trajectories are rather glancing making an angle of 80° with the surface normal (the geometries are sketched in Fig. 3).

The resulting spectra contained typically $2 \times 10^6$ counts in the elastic peak and extended up to 100 eV energy loss. The maximum of the elastic peak was aligned with 0 eV energy loss. The spectra plotted in Fig. 2 have elastic peak normalised to unit area.

The 5 keV spectra are typical REELS spectra with the energy loss contributions starting for energies larger than the band gap ($\approx 5.6$ eV). For this incoming energy the elastic peak intensity drops off very quickly to zero. Non-stoichiometric films have a tail extending at the low-energy side of the elastic peak due to excitation from 5d electrons from occupied orbitals to unoccupied orbitals. We see these tails for sputter-deposited HfO$_2$ films (unpublished) of Ta$_2$O$_5$ films [22] but never for films deposited by atomic layer deposition.

The 40 keV spectra have an additional feature near 4.4 eV energy loss. This feature is not related to electronic excitations, but is the elastic peak of electrons scattered from oxygen. The recoil energy for scattering from O over 135° at 40 keV is 4.4 eV larger than the recoil energy of electrons scattering from Hf (which forms the main elastic peak). The intensity of the O elastic peak is two orders of magnitude less than the Hf elastic peak, and the Hf:O intensity ratio is within 10% of the one.

Fig. 1. The loss function in the optical limit as derived from transmission measurements using 20 keV (full line) electrons [11] and a reflection experiment using 300–500 eV electrons (dashed line) [9]. The dotted line is the result of the present work obtained as described later in the paper.

Fig. 2. The REELS spectra as obtained at 5 keV and 40 keV, with either the incoming beam along the surface normal or rotated by 35° in such a way that the outgoing beam makes an angle of 80° with the surface normal.
calculated for HfO₂, see ref. [20]. Thus neither the high-energy REELS measurement nor the 5 keV measurement show any indication of the presence of non-stoichiometric films. For this paper the O elastic peak at 300 eV and 500 eV as published by Jin et al. [9] as well as the ones derived in this work at 5 keV (surface-sensitive geometry) and 40 keV (bulk-sensitive geometry). The lower sketches illustrate the geometry of Jin (left), and our surface-sensitive (central) and bulk-sensitive geometry (right).

3. Analysis

There are two well-published approaches for extracting the dielectric function from a REELS measurement. One was developed by Tougaard and co-workers [23–26] and one by Werner [5,6]. We will first consider the method of Tougaard and coworkers.

This method does not separate the loss function into surface and bulk losses. It considers the electric field of an electron approaching and penetrating a surface and this time-varying electric field causes electronic excitations in the solid. The outgoing losses are affected by the electronic excitations created by the incoming trajectory, but this effect becomes very small at high energies [24]. For this approach we used the QUEELS program which is available commercially.

The first step is to determine the normalised inelastic cross section, following the procedure of Tougaard–Chorkendorff [23] and implemented in the commercially available QUASES-XS-REELS programme. The results are given in Fig. 3 for the most surface sensitive and the most bulk-sensitive measurement done in this study, as well as the corresponding loss functions of Jin et al. [9] taken at much lower energies. There is a systematic evolution of the shape of these spectra with E₀: the intensity near 16 eV decreasing with increasing E₀, whereas the structures near 40–50 eV increase in intensity.

At large depth, where surface effects can be neglected, there is a simple relation between the observed normalised inelastic cross section and the dielectric function. The inelastic cross section is in the absence of surface effects, often called the differential inelastic inverse mean free path (DIIMFP) Wₙ and can be expressed in terms of the dielectric constant ε(k, ω) (see e.g. ref. [27]):

\[
W_n(\omega, E_0) = \frac{1}{\pi E_0^2} \int_{k, -\infty}^{k, \infty} \frac{dk}{k} \text{Im} \left[ -\frac{1}{\varepsilon(k, \omega)} \right].
\]

(1)

Here E₀ is the incoming energy, ω the energy loss, and k is the difference between the momentum of the probing electron before and after the collision: k = p₁ − p₀. The integral is over all possible values of k, but the main contributions (due to the 1/k factor in Eq. (1)) are from small k values. The smallest k values one can reach is in the forward direction, but this lower limit is not zero as, due to the energy loss, |p₁| < |p₀|. For a given ω value this lower limit of the integration is simply (neglecting relativistic corrections): \(\sqrt{2mE_0 - \sqrt{2m(E_0 - \omega)}}\) with m the electron mass. Thus for ω = 40 eV the lower cut-off k is 0.32 a.u. for E₀ = 300 eV electrons but 0.03 a.u. for E₀ = 40 keV. For smaller energy losses the lower cut-off is closer to 0.

At smaller depth, surface excitations are important and the probability of bulk excitations is reduced. These effects are modelled in the QUEELS program that considers a dielectric function and calculates the loss probability as a function of depth, taking into account the surface effects.

The second step is to calculate, using the QUEELS program and an assumed dielectric function, the loss function. The dielectric function is then varied until a good agreement with the shape of the experimentally obtained normalised inelastic cross section is found. The dielectric function is then finally put on an absolute scale using a Kramer–Kronig sum rule [28]:

\[
1 - \frac{1}{n^2} = \frac{2}{\pi} \int_0^\infty \text{Im} \left[ \frac{-1}{\varepsilon(0, E)} \right] \frac{dE}{E},
\]

(2)

with n the static refractive index of the material. For hafnia we used n = 1.89. In QUEELS the dielectric function is modelled as a sum of i Drude–Lindhard oscillators with energy ωᵢ, intensity Aᵢ, and width γᵢ:

\[
\text{Im} \left[ -\frac{1}{\varepsilon(k, \omega)} \right] = A_i \gamma_i \omega_i \times \sum_{i=1}^{n} \left( \frac{\omega_i - \text{Egap}}{\omega_i - \text{Egap} + \alpha_i k^2 / 2m} - \frac{\omega_i}{\omega_i - \text{Egap} + \alpha_i k^2 / 2m} \right)^2 + \frac{\omega_i^2 \gamma_i^2}{\omega_i - \text{Egap} + \alpha_i k^2 / 2m},
\]

(3)

where αᵢ models the dispersion and \(\theta(\omega - \text{Egap})\) is the step function ensuring that no excitations occur with energies less than the band gap.

Fig. 3. The inelastic cross section \(\kappa_\omega\) at 300 eV and 500 eV as published by Jin et al. [9] as well as the ones derived in this work at 5 keV (surface-sensitive geometry) and 40 keV (bulk-sensitive geometry). The lower sketches illustrate the geometry of Jin (left), and our surface-sensitive (central) and bulk-sensitive geometry (right).

Fig. 4. A comparison of the loss function as measured at 40 keV in a bulk-sensitive geometry and a measurement at 5 keV (offset vertically by 0.01 eV⁻¹ for clarity) in a surface sensitive geometry (both full lines) with a calculation using a model dielectric function. The model dielectric function was obtained by the QUEELS software by optimising the dielectric function for the description of the 40 keV measurement. The changes in the spectrum between the two measurements are qualitatively reproduced by the theory, but quantitatively the 5 keV description is not as good.
For free electron materials $\alpha = 1$ for the outer valence region but for ionic compounds and deeper layers much less dispersion is expected. Here we assumed a value of 0.1 for all $\alpha$, but for large $E_0$ values very similar results are obtained for $\alpha = 0$.

We first considered our most bulk-sensitive measurement (40 keV, incoming beam along surface normal). Due to the structure-rich shape of the spectrum we had to use 9 Drude–Lindhard oscillators to obtain a good fit. This fit is shown in Fig. 4 and the corresponding parameters for the Drude–Lindhard oscillators are given in Table 1. In order to test if the fit obtained really describes the material we also calculated the normalised loss function for our most surface-sensitive measurement: the case of $E_0 = 5$ keV and the sample rotated over 35°. Ideally the QUEELS software would describe this spectrum using the same dielectric function with a similar accuracy. This result is shown in Fig. 4 as well. The peak near 15 eV increases in intensity in both calculation and experiment, but the width of this peak is now slightly larger in the experiment compared to theory. Also the structures near 40–50 eV are for $E_0 = 5$ keV somewhat less intense in the experiment compared to theory. Thus even within our own data we already find some indication that the dielectric function of the form given in Eq. (3) cannot describe experiments taken at all energies. As we will see later this tendency is enhanced if we consider the loss functions of Jin et al. [9], at even lower energies with the same dielectric function.

Here we analyse the same data using the partial intensity method of Werner. Here one considers the spectrum as a consequence of surface and bulk losses. The surface losses are the additional loss processes due to the presence of a surface [29]. By measuring spectra under two conditions where the contribution of surface losses are rather different and bulk losses. These are obtained by Monte Carlo simulations, and are reproduced in Table 2 as well. The output of the procedure is a normalised DSEP and (combined incoming and outgoing) normalised DSEF. It turns out that only for one value of $a$ the obtained normalised DSEP has unit area. We take this as an experimental estimate of $a$.

The 5 measurement combinations with different $\nu(E, \theta)$ values all provided consistent results for the normalised DIMP as is shown in Fig. 5. The normalisation of the ‘normalised DIMFP’ was generally not 1 but between 0.8 and 0.85. These values are obtained by integrating the ‘normalised DIMP’ from 0 to 100 eV. Very similar values for the area were obtained when applying QUASES-XS-REELS to calculate the normalised cross section in the Tougaard–Yubero approach. The deviation from unit area may have the same origin and be an indication that 15–20% of the loss function is at energies exceeding 100 eV.

Note that at high incoming energies the sharp minima in the differential elastic cross sections disappear and their shapes become rather similar. It is at lower energies where the differential elastic cross section can have a very intricate shape which results in large variations of the

**Table 1**

<table>
<thead>
<tr>
<th>$i$</th>
<th>$\omega_i$ (eV)</th>
<th>$\alpha_i^2$ (eV$^2$)</th>
<th>$\alpha_i$</th>
<th>$\gamma_i$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.0</td>
<td>3.9</td>
<td>0.039</td>
<td>4.5</td>
</tr>
<tr>
<td>2</td>
<td>15.6</td>
<td>38.0</td>
<td>0.156</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>21.5</td>
<td>105.4</td>
<td>0.228</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>27.7</td>
<td>140.0</td>
<td>0.182</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>35.7</td>
<td>22.4</td>
<td>0.0176</td>
<td>2.8</td>
</tr>
<tr>
<td>6</td>
<td>38.2</td>
<td>20.9</td>
<td>0.0143</td>
<td>2.0</td>
</tr>
<tr>
<td>7</td>
<td>42.5</td>
<td>14.0</td>
<td>0.0077</td>
<td>2.4</td>
</tr>
<tr>
<td>8</td>
<td>47.3</td>
<td>225.2</td>
<td>0.101</td>
<td>7</td>
</tr>
<tr>
<td>9</td>
<td>58</td>
<td>148.7</td>
<td>0.0442</td>
<td>35</td>
</tr>
</tbody>
</table>

The QUEELS program allows only for 9 oscillators, and this fit underestimates the loss function at high energy losses. QUEELS and SEFINPAC use somewhat different definitions of the Drude–Lindhard amplitudes. Both values are given here for convenience ($\alpha_i^2$ and $\alpha_i$) but they are related as $\alpha_i = \omega_i^2 \alpha_i$.

**Table 2**

The first two partial intensities $P_{1,2}$ and the surface excitation probability (SEP) for energies $E_0$ and incoming angle $\theta_i$ as indicated.

<table>
<thead>
<tr>
<th>$E_0$ (keV)</th>
<th>$\theta_i$ (deg)</th>
<th>$P_{1}$</th>
<th>$P_{2}$</th>
<th>$\nu(E_0, \theta_i)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0</td>
<td>1.04</td>
<td>1.03</td>
<td>0.034</td>
</tr>
<tr>
<td>40</td>
<td>35</td>
<td>0.98</td>
<td>0.95</td>
<td>0.094</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>1.00</td>
<td>0.99</td>
<td>0.094</td>
</tr>
<tr>
<td>5</td>
<td>35</td>
<td>0.91</td>
<td>0.82</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The outgoing angle is $\theta_1 + 45$. The combined SEP $\nu$ was calculated using Eq. (5) with $a = 2$.

We follow the procedure as described in the appendix of ref. [6]. One assumes that the SEP is the same for an incoming and outgoing trajectory and only depends on $\theta$ and $E_0$ and hence for the combined SEP we get $\nu(E, \theta)$:

$$\nu(E, \theta) = P_{1}(E_0, \theta_{in}) + P_{2}(E_0, \theta_{out})$$  \hspace{1cm} (5)

The values for $\nu(E_0, \theta)$ are reproduced in Table 2, assuming $a = 2$. Note that the surface-sensitive 40 keV measurement has the same $\nu(E_0, \theta)$ value as the bulk-sensitive 5 keV measurement. This measurement combination can thus not be used for this deconvolution procedure. There are 5 remaining combinations of measurements that we can analyse. The method also requires as input the partial intensities for bulk losses. The first (second) partial intensity is the ratio of the number of trajectories with one (two) bulk loss(es) and the number of trajectories without bulk losses. These are obtained by Monte Carlo simulations, and are reproduced in Table 2 as well. The output of the procedure is a normalised DIMFP and (combined incoming and outgoing) normalised DSEP. It turns out that only for one value of $a$ the obtained normalised DSEP has unit area. We take this as an experimental estimate of $a$.

The 5 measurement combinations with different $\nu(E, \theta)$ values all provided consistent results for the normalised DIMFP as is shown in Fig. 5. The normalisation of the ‘normalised DIMFP’ was generally not 1 but between 0.8 and 0.85. These values are obtained by integrating the ‘normalised DIMP’ from 0 to 100 eV. Very similar values for the area were obtained when applying QUASES-XS-REELS to calculate the normalised cross section in the Tougaard–Yubero approach. The deviation from unit area may have the same origin and be an indication that 15–20% of the loss function is at energies exceeding 100 eV.

Note that at high incoming energies the sharp minima in the differential elastic cross sections disappear and their shapes become rather similar. It is at lower energies where the differential elastic cross section can have a very intricate shape which results in large variations of the

![Fig. 5](image-url)
partial intensities. Within the Tougaard–Yubero framework this gives large variations of \( L \) (for the definition see ref. [23]) which can be either negative or positive depending on the structure in the elastic cross section [26] and this is, in their model, the cause of areas deviating from unity. This should be a small correction under our conditions.

The intensity of the DIIMFP is not strictly 0 for large losses. Integrating the DIIMFP using SESINPAC indicates that for the model loss function of Table 1 5% of the intensity of the DIIMFP is at energy losses exceeding 100 eV, and taking this into account, there is a 10% deficit in the area of the normalised DIIMFP. Using the dielectric function of Behar et al. [11], which has oscillators near 100 eV and 400 eV, we find that 20% of the DIIMFP is for energy losses over 100 eV, which compares well with the 15–20% found experimentally. Thus we consider the values obtained here reasonable and an indication that the loss function indeed extends beyond 100 eV energy loss.

The \( a \) values of Eq. (4) for which obtained DSEP had indeed a normalisation of 1 ranged between 1.6 and 2.7, which are reasonable values according to Pauyl et al. [32] for insulators with a large band gap. The internal consistency for the DIIMFP is excellent, for the DSEP there exist some spread and the curves are more affected by noise, but all DSEP curves peak at the same energy loss. The larger variations in the DSEP are to be expected, as the surface excitation probabilities are relatively small under these conditions and the DSEP is thus extracted from the small difference in shape of the input data.

The shape of the DIIMFP as obtained by the method of Werner is now compared with the DSEP calculated by SESINPAC for the dielectric function obtained from QUEELS (i.e. the dielectric function of Table 1) This is done in Fig. 6. The agreement is very good. Using SESINPAC we can also calculate the shape of the DSEP, based on the formula given by Tung et al. The agreement is somewhat less good, as the experimentally measured DSEP extends to somewhat larger energy losses compared to the calculated one, but the position of the maximum of the calculated DSEP is the same as derived from Werner’s analysis.

Overall the agreement between the analysis by QUEELS and the method of Werner is good. The dielectric function derived by QUEELS described the DIIMFP obtained by the Werner analysis very well and a reasonable agreement is found between the DSEP as calculated from this dielectric function and the one obtained from the Werner analysis. Thus in summary at these high incoming energies the analysis by both methods results in very similar dielectric functions.

The optical limit of the dielectric function obtained by QUEELS for the 40 keV measurements is plotted as well in Fig. 1. It is rather different from the one published by Jin et al. [9]. The agreement with the one given by Behar et al. [11] is somewhat better, the main discrepancy is the strength of the peak near 16 eV.

4. Discussion

The present measurements appear to have a good internal consistency. At high incoming energies the loss function is dominated by collisions with extremely small momentum transfer, hence the similarity in shape of the measured normalised DIIMFP and \( \text{Im}[-1/\epsilon(k = 0, \omega)] \). Additional support for the DIIMFP obtained here can be found in recent TEELS measurements and calculations of Shivaraman et al. [15]. Their results are compared with the present one in Fig. 7. Their experimental results are in good agreement with the DIIMFP obtained here. Their calculated loss function in the optical limit agrees very well with experiment up to 30 eV, at larger energy loss there is a significant difference between the width and position of the loss features. As far as the position of the peak at the largest energy loss is concerned this was attributed to the choice of exchange-correlation potential used in the calculation.

Note that the dielectric function was obtained here by fitting the 40 keV measurement using QUEELS. The 5 keV measurement was reasonably but not perfectly well described by this dielectric function (see Fig. 4). A close inspection of Fig. 2 of Jin et al. in ref. [9] shows that their fit was optimised for the 300 eV spectrum, and for the 500 eV spectrum the observed reduction in width of the main peak is not, or only poorly mimicked by theory. As is clear in Eq. (1) the volume of momentum space probed changes with \( E_0 \). Thus the problems encountered here could be an indication that the \( k \)-dependence of the dielectric function deviates significantly from that of the Drude–Lindhard model i.e. Eq. (3).

We think that both our measurements and Jin’s measurements show a different dependence in theory and experiment on the width and intensity of the loss peaks as a function of \( E_0 \). If one changes \( E_0 \) from 40 keV down to 300 eV then the failure of the theory to describe the experiment becomes much more dramatic. In Fig. 8 we compare the loss function at 300 eV, as calculated with the parameters of Table 1, and the experimental one. The differences are substantial, and agreement cannot be obtained by simply changing the dispersion parameters \( \alpha \).

One possible cause of the problem could be the extraction of a single loss distribution from the experimentally obtained spectra. It has been argued that the normalised inelastic cross section obtained by the deconvolution procedure of Tougaard–Chorkendorff [23] is not a pure single-scattering distribution, but differs by a term proportional to a
convolution of the bulk and surface loss function [5]. At high-energies, when the probability of excitation surface losses is small, this should be a minor contribution. Indeed in the work of Novak [34] and Went et al. [21] it was shown that this effect decreases with incoming energy, and is only a minor correction at 40 keV. However, neither the discrepancy seen in Fig. 8 nor the smaller one for the 5 keV measurement in Fig. 4 resemble in shape the convolution of the surface and bulk loss function, which is in our case a broad distribution with the main intensity between 25 and 80 eV. Hence it seems unlikely that the cause of the problem is the deviation of the distribution obtained by the Tougaard-Chorkendorff method from a pure single scattering contribution.

Similar problems in the interpretation of REELS spectra were encountered by Pauly et al. in a study of indium [35]. Indium is a free electron metal, and as a consequence its dielectric function can be described by a single Drude–Lindhard oscillator. By varying $E_0$ between 200 eV and 2 keV they found that the width of the In REELS spectrum cannot be reproduced by assuming a single $\gamma$ value independent of $k$, but it was found that $\gamma$ changed from 2.8 eV at $E_0 = 200$ eV to 1 eV at $E_0 = 2$ keV. Such a change in $\gamma$ could be explained if $\gamma$ increases sharply with $k$. Then the spectra taken at lower $E_0$ values should be broader as in that case small $k$ values are excluded from contributing to the loss spectrum. Different dispersion relations were also considered recently by Abril et al. in the case of water and DNA [36] and by Calliari et al. in the case of Si [37].

Within the Mermin model of the dielectric function the width of the peak increases with $k$. To get some insight on how this affects the spectra we calculated the DIIMFP for the present loss function, assuming either a Drude–Lindhard and a Mermin behaviour using the SESINIPAC program. This is done in Fig. 9, where we also varied $\alpha$ for the Drude–Lindhard model. At 40 keV the spectra are close to the optical limit and both models give very similar results, but at 300 eV the differences are more substantial. Only the calculation with $\alpha = 0.1$ gives the energy position for the peak at highest energy loss (47 eV) in agreement with the experiment. Both the Drude–Lindhard calculation with $\alpha = 1$ and the Mermin calculation has this peak at too large an energy loss. The peak near 47 eV becomes less pronounced especially for the Mermin-type dispersion. Unfortunately calculating the normalised cross section at 300 eV (i.e. including surface effects) with a Mermin-type dispersion is not possible with the QUEELS program.

It is worthwhile to point out that the $k$-dependence of the dielectric function can be measured directly in a transmission geometry, as was demonstrated by Batson and Silcox in the case of aluminium as early as 1983 [2] and more recently reviewed for a large range of solids by Fink et al. [38]. These measurements reveal a complex dependence of the intensity and peak position as a function of momentum transfer and a failure of the simple approaches explored here should not come as a surprise.

Recently full calculations of $\text{Im}[-1/\epsilon(k, \omega)]$ have become available for noble metals [39]. The shape of the loss function is quite complex, with dipole-allowed transitions dominating for $k \approx 0$ (i.e. excitation from d levels to p and f levels) and significant non-dipole contributions away from $k = 0$ which leads to a broadening of the features. Approximations like Eq. (3) apply only to plasmon-like excitations, not to most interband transitions. The evolution of the intensity of the various interband transitions is rather varied. Especially for Ag and Au some interband transitions decrease in intensity with increasing $k$ values, whereas others are more constant. Thus equations such as Eq. (3) (or modified versions as suggested by Abril et al. [36] or Calliari et al. [37]) for the calculation of the DIIMFP cannot be expected to be very accurate as they do not describe such an intricate behaviour. Assuming that similar observations hold for HfO2 then it is less surprising that it is difficult to extract the loss function in the optical limit from low-energy REELS measurements. It will be interesting to see if, when they become available, first-principle calculations of $\text{Im}[-1/\epsilon(k, \omega)]$ can describe both low and high energy REELS data well.

High-energy REELS measurements are thus suitable for the study of the dielectric function near $k = 0$. If one wants to study e.g. the inelastic mean free path of low energy electrons, then one has to know the dielectric function away from $k = 0$. For this reason it could be argued that the dielectric function derived from low energy REELS measurements is more appropriate for the calculation of the IMFP than a dielectric function derived from high-energy REELS measurement, even if the former is in the optical limit only a poor approximation of the true

![Fig. 8. A comparison of the inelastic cross section at 300 eV, as calculated using QUEELS-eps-REELS based on the dielectric function derived from our measurements for both $\alpha = 0.1$ or $\alpha = 1$ with the measurement of Jin et al. [9].](image)

![Fig. 9. A comparison of the normalised bulk inelastic cross section at 40 keV (offset vertically by 0.01 eV⁻¹ for clarity) and 300 eV for $\text{Im}[-1/\epsilon(k, \omega)]$ shown in Fig. 1 as ‘this work’ when one assumed a Mermin-type dispersion or Drude–Lindhard (D–L) type dispersion with $\alpha = 0.1$ or $\alpha = 1$.](image)

<table>
<thead>
<tr>
<th>$E_1$ (keV)</th>
<th>$\theta_1$ (deg)</th>
<th>$E_2$ (keV)</th>
<th>$\theta_2$ (deg)</th>
<th>$\alpha$</th>
<th>Area DSEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0</td>
<td>40</td>
<td>35</td>
<td>2.35</td>
<td>0.82</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>5</td>
<td>35</td>
<td>2.2</td>
<td>0.81</td>
</tr>
<tr>
<td>40</td>
<td>5</td>
<td>0</td>
<td>35</td>
<td>1.6</td>
<td>0.81</td>
</tr>
<tr>
<td>40</td>
<td>35</td>
<td>5</td>
<td>35</td>
<td>2.2</td>
<td>0.81</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>5</td>
<td>35</td>
<td>2.7</td>
<td>0.83</td>
</tr>
</tbody>
</table>

The value of $\alpha$ (see Eq. (5)) required for the normalised DSEP to have unit area is given as well. The last column is the area of the obtained normalised DIIMFP for integration up to 100 eV energy loss.
dielectric function. The ground for this would be that collisions with \( k \approx 0 \) do not contribute to energy loss of low-energy electrons. In the QUEELS framework the dielectric function in the optical limit is used in Eq. (2) and hence essential for the determination of the IMFP. We summarise the IMFP as obtained for the different dielectric functions at relevant energies for this work in Table 4.

Finally we want to draw attention on a problem specific for low-energy measurements from high-Z materials. In Fig. 10 we show the elastic differential cross section for electrons scattering from Hf at the energies of relevance as calculated using ELSEPA [41]. The angular dependence becomes more feature-rich with decreasing energy. In particular near 300 eV the dependence of the elastic cross section on the precise energy is large. A strong dependence of the differential cross section is observed not just near the minima but over a wide range of \( \theta \) values. For \( \theta = 125^\circ \) (the scattering angle of Jin’s experiment) there is a 50% reduction in the DCS when going from 300 eV to 250 eV (see Fig. 10, lower panel). The assumption made in almost all REELS analyses, that the elastic scattering probability does not depend on the precise energy of the electron is not justified here. If the electron loses 50 eV along the incoming trajectory (the more likely scenario, as it is longer), then, for v-shaped trajectories the probability of being backscattered into the detector is halved. This is an additional reason for a reduced intensity in the observed loss function near 50 eV energy loss for \( E_0 = 300 \) eV. It does however, not explain the deviations which are also present for \( E_0 = 500 \) eV where this effect is minor.

5. Conclusions

From the analysis of the present REELS data the following picture appears. Interpretation of the data is possible using either the QUEELS program or the partial intensity method and with either method the obtained results are consistent with the same dielectric function. At these high energies the obtained inelastic cross section is quite close to the loss function in the optical limit \( \text{Im}[\epsilon(0, \omega)] \), and we are not very sensitive to the k-dependence of the dielectric function. This changes at lower incoming energies where we probe larger k-values. The most likely explanation for the difference in the dielectric function obtained at the low \( E_0 \) values used by Jin et al. [9] and the one derived from the measurements of Frandon et al. at higher \( E_0 \) values [12] is thus a deviation of the k-dependence from either a Drude–Lindhard or Mermin model. Limited validity in application of these models for HfO\(_2\) should not be too surprising as this wide gap insulator is far removed from the free-electron gas assumption on which these dielectric functions are based.

Finally we want to point out that there are indications that the problems encountered for HfO\(_2\) are also encountered in other materials. Fuentes et al. studied TiO\(_2\) using energies between 500 eV and 1500 eV [42,43]. The changes in the intensity of the peak near 12 eV with \( E_0 \) are again not well reproduced by the calculations. Frandon’s transmission measurement at 20 keV shows again considerably less intensity near 12 eV, and our own reflection measurements at \( E_0 = 40 \) keV (unpublished) are in line with those of Frandon [44]. Understanding the problems sketched in this paper may have thus broader ramifications for the interpretation of the REELS data of oxides.

Acknowledgements

This work was made possible by a grant from the Australian Research Council. P.L.G. acknowledges the Brazilian agency CAPES (proc. 102209/12-3) for the financial support. The authors want to thank Erich Weigold and Tatsuya Nagao for a critically reading of the manuscript and Dinesh Venkatachalam for growing the HfO\(_2\) layers and also the XRD analysis.

References


Table 4
The inelastic mean free path as calculated using the formula of Tanuma, Powell and Penn (TPP) [40], the dielectric function of Jin et al. [9], Behar et al. [11] and the dielectric function of Table 1.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>TPP (Å)</th>
<th>Jin et al. (Å)</th>
<th>Behar et al. (Å)</th>
<th>This work (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>7.5</td>
<td>6.9</td>
<td>7.9</td>
<td>5.7</td>
</tr>
<tr>
<td>500</td>
<td>10.4</td>
<td>10.1</td>
<td>11.1</td>
<td>8.5</td>
</tr>
<tr>
<td>5</td>
<td>60.4</td>
<td>65.9</td>
<td>67.4</td>
<td>61</td>
</tr>
<tr>
<td>40 keV</td>
<td>354</td>
<td>402.2</td>
<td>408</td>
<td>394</td>
</tr>
</tbody>
</table>

![Fig. 10.](image-url) The elastic scattering cross section as calculated using ELSEPA for scattering from Hf at the energies indicated. The dark and light dashed lines are the nominal scattering angles of the present experiment and Jin’s experiment. The strong dependence of this cross section on energy near 300 eV is emphasized in the lower panel.