

Electron energy loss spectroscopy of TiC, ZrC and HfC

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Abstract

The dielectric properties of commercial TiC, ZrC and HfC powders were determined by analyzing the low loss region of the EELS spectrum in a transmission electron microscope. From these data, the optical joint density of states (OJDS) were obtained by Kramers–Kronig analysis. As maxima observed in the OJDS spectra are assigned to interband transitions across the energy gap, these spectra can be interpreted on the basis of existing energy-band calculations. Comparison between experimental results and theory shows good agreement.

Keywords: EELS; Dielectric function, TiC, ZrC, HfC; Electronic band structure

Introduction

The electronic structure of transition metal carbides has been studied for more than two decades, TiC being the most extensively reported [1–6]. These compounds form a class of very hard materials and they often crystallize in the rock salt structure. They show metallic as well as covalent and ionic properties, which make them interesting for both technical applications and fundamental research. While they exhibit a number of unusual properties, most applications of the transition-metal carbides rely upon their extreme hardness, which are typically found for covalent crystals [7]. It is interesting that properties associated with covalent bonding are found in compounds which display a crystal structure normally associated with ionic bonding.

Electron energy-loss spectroscopy (EELS) is a powerful analytical technique that can be utilized to obtain information on the structure, bonding and electronic properties

of a material [8–14]. The interactions of fast electrons with the specimen result in excitations of electrons into unoccupied energy levels in the conduction band. When a spectrum is obtained by analyzing the energy lost by the incident electrons, the region up to an energy loss of ~50 eV is dominated by collective excitations of valence electrons (plasmon) and by interband transitions. At higher energy losses ionization edges occur due to excitation of core electrons into the conduction band.

To our knowledge, EELS has not been used for studies of ZrC and HfC crystals yet. In the present work we have conducted low-energy EELS on commercial TiC, ZrC and HfC powders obtaining the complex dielectric function and the optical joint density of states by Kramers–Kronig analysis. A comparison is made with theoretical results based on energy-band structure calculations.

Dielectric theory

The low loss region in an energy loss spectrum (<50 eV) contains information about excitations of outer shell electrons and the electronic structure of the material which determines its optical properties. The excitations of valence electrons are dominated by collective excitations (plasmon) and single electron interband transitions. Interband transitions originate from the excitation of electrons in the valence bands to empty states in the conduction bands, so these can be identified as transitions across the energy gap in a band structure model. The plasmon peak position is shifted upward due to excitations below the plasma frequency and downward due to higher energy excitations.

From the dielectric theory, it is possible to relate the experimental single scattering distribution $S(E)$, to the energy loss function $\text{Im}(-1/\epsilon)$, by [15-18]:

$$S(E) = \frac{I_0 t}{\pi a_0 m_0 v^2} \operatorname{Im} \left[-\frac{1}{\varepsilon(q, E)} \right] \ln[1 + (\beta/\theta_E)^2] \quad (1)$$

Where $\varepsilon(q, E) = \varepsilon_1 + i\varepsilon_2$ is the complex dielectric function at energy loss E and momentum transfer q , a_0 the Bohr radius, m_0 the electron rest mass, v the electron beam velocity, n_a the number of atoms per unit volume, $\theta_E = E / \text{unit volume}$, θ the scattering angle, γ is the relativistic factor, I_0 ins the zero loss intensity, t is the specimen thickness and β ins the collection semiangle.

For small q , $\varepsilon(q, E)$ varies very slowly with q , so that it can be replaced by $\varepsilon(E)$ which can, in principle, be directly compared with optical measurements.

The real and imaginary parts of the dielectric function can be obtained from the energy loss function $\operatorname{Im}(-1/\varepsilon)$, through Kramers-Kronig analysis [8,16,17]

$$\operatorname{Re} \left[\frac{1}{\varepsilon(E)} \right] = 1 - \frac{2}{\pi} P \int_0^{\infty} \operatorname{Im} \left[-\frac{1}{\varepsilon(E')} \right] \frac{E' dE'}{E'^2 - E^2} \quad (2)$$

Where P stands for the principal value of the integral.

Theoretically, by measuring the absolute cross-section and the thickness of the sample, we can obtain the value of the energy loss function. However, this approach is usually not practically feasible. In order to obtain the absolute value of the energy loss function, the optical dielectric function at one point is needed to normalize the energy loss spectrum. This can be achieved by using the Kramers-Kronig relations, Eq. (2). In the limit $E \rightarrow 0$, we can obtain the normalization condition for the energy loss spectrum as

$$\operatorname{Re} \left[\frac{1}{\varepsilon(0)} \right] = 1 - \frac{2}{\pi} P \int_0^{\infty} \operatorname{Im} \left[-\frac{1}{\varepsilon(E')} \right] \frac{dE'}{E'} \quad (3)$$

Solving for $\operatorname{Im}(-1/\varepsilon)$ in Eq. (1) and integrating gives

$$\int_0^{\infty} \frac{S(E)}{E \ln[1 + (\beta/\theta_E)^2]} dE = K \int_0^{\infty} \frac{\operatorname{Im}[-1/\varepsilon(E)]}{E} dE \quad (4)$$

Here we have defined the normalization factor K , as

$$K = \frac{I_0 t}{\pi a_0 m v^2} \quad (5)$$

Which can be obtained from experiment.

Replacing the right hand side in Eq. (4) by the expression in Eq. (3) and solving for K , allows us to write

$$K = \frac{2}{\pi \{1 - \operatorname{Re}[1/\varepsilon(0)]\}} \int_0^{\infty} \frac{S(E)}{E \ln[1 + (\beta/\theta_E)^2]} dE \quad (6)$$

For metals, $\operatorname{Re}[1/\varepsilon(0)]=0$, since ε_2 become very large for $E \rightarrow 0$. For semiconductors ε is real below the band gap and can be obtained from the refractive index by the relation $\varepsilon_1=n^2$. Finally, by substituting Eq. (6) in Eq- (1) and solving for $\operatorname{Im}[-1/(\varepsilon)]$ gives

$$\operatorname{Im} \left[-\frac{1}{\varepsilon(E)} \right] = \frac{S(E)}{K \ln[1 + (\beta/\theta_E)^2]} \quad (7)$$

Another useful relation, used to check consistency of the data, is the f -sum rule

$$\int_0^{\infty} E \varepsilon_2(E) dE = \frac{\pi}{2} E_p^2 \quad (8)$$

Where E_p ins the free electron plasmon energy (Drude Model), defined as

$$E_p^2 = \frac{\hbar^2 n e^2}{\varepsilon_0 m} \quad (9)$$

Here n ins the total charge density, e the electron charge, m the mass of the electron and ε_0 the permittivity of vacuum. Thus, the total integral of $E \varepsilon_2$ is proportional to the number of electrons involved in the transition processes. By integrating Eq. (8) from 0 to E we obtain the effective number of electrons per molecule n_{eff} contributing to absorption (ε_2) below energy E as:

$$n_{\text{eff}}(E) = \frac{2 \varepsilon_0 m}{\pi \hbar^2 e^2 n_a} \int_0^E E' \varepsilon_2(E') dE' \quad (10)$$

Where n_a is the number of atoms (or molecules) per unit volume for the sample.

To compare the experimental results from EELS with the density of states (DOS) obtained from band theory calculations, we can define the optical joint density of states (OJDS) as [3, 19]

$$J_1(E) = \frac{2E \varepsilon_2(E)}{\pi E_p^2} \quad (11)$$

Where E_p is the plasmon energy in Drude model.

Experimental

In this work the complex dielectric function of commercial TiC, ZrC and HfC powders (99 %pure) were obtained using a Gatan Parallel Electron Energy Loss

spectrometer (PEELS model 766) attached to the Philips CM-200 transmission electron microscope (TEM). Thin specimens suitable for electron microscopy were prepared by placing clean, dry crushed powders onto commercial holey carbon coated copper grids.

Spectra were taken in diffraction mode with 0.1 eV/ch dispersion an aperture of 3 mm and a collection semi-angle of 4.9 mrad. As the scattering angle in an EELS experiment can involve momentum transfer, we acquired the spectra using a small collector aperture and a camera length of 360 mm, to measure predominantly optical transitions.

The resolution of the spectra was determined by measuring the full width at half-maximum (FWHM) of the zero-loss peak and this was typically close to 1.3 eV when the TEM was operated at 200kV.

The EELS spectra were corrected for dark current and readout noise. The channel to channel gain variation was minimized by normalizing the experimental spectrum with independently obtained gain spectrum of the spectrometer.

Results and discussion

Spectra acquired with the PEELS spectrometer were Fourier-Log deconvoluted to have the single scattering distributions $S(E)$, and then normalized with the method previously described to obtain the energy loss function $\text{Im}(21/\epsilon)$. The real and imaginary parts of the dielectric function were obtained, after removing surface loss effects, by Kramers–Kronig Analysis, as described by Egerton [8].

The single scattering distribution spectra obtained with Gatan EL/P software present a steep increase at an energy loss $\sim 2\text{--}3$ eV that could be attributed to the energy gap, but due to our finite energy resolution (1.3 eV), data below 3 eV are not

reliable, so we extrapolated an exponential curve between 0 and 3 eV. As is well known, this is a crucial step, for minor changes in the low loss spectrum produce noticeable variations on ϵ_1 and ϵ_2 , although the energy loss function and optical joint density of states remain almost unaltered.

As is required for normalization, we need the value of ϵ_1 at low energies (optical frequencies) for TiC, ZrC and HfC. However, as we adjusted spectra from zero energy loss in the lower part of the spectrum (0–3 eV), we used $\text{Re}[1/\epsilon(0)]=0$, valid for conductors. We have analyzed TiC, whose optical properties have already been determined by optical methods and by electron energy loss spectroscopy [3], to check consistency of our analysis.

The energy loss function and the real and imaginary parts of the dielectric function for TiC, ZrC and HfC are shown in Fig. 1a–c. The dominant feature in all energy loss spectra is the volume plasmon at 22.9, 21.4 and 22.2 eV for TiC, ZrC and HfC, respectively. We may compare these values to the corresponding free-electron plasma energies calculated from Eq. (9). Taking eight electrons as participating in plasma oscillations in all three compounds (metal 3d and 4s orbitals and nonmetal 2s and 2p orbitals) we obtain 23.4, 20.8 and 20.6 eV calculated for TiC, ZrC and HfC, which agree reasonably well with experimental results.

The ϵ_1 spectra show zero upward crossing at 21.2, 19.4 and 20.6 eV for TiC, ZrC and HfC, respectively, indicating that the dominant peak in the energy loss spectrum is a well-defined plasmon. The absence of any other zero crossing implies that there are no free electrons in these compounds and the peaks appearing at energies below the plasmon peak are effectively due to interband transitions, supporting the analysis made

by Pflüger et al. [3,4] for TiC. Similar results are expected for ZrC and HfC as these compounds belong to the same transition metal carbides group, all having fcc (NaCl) structure.

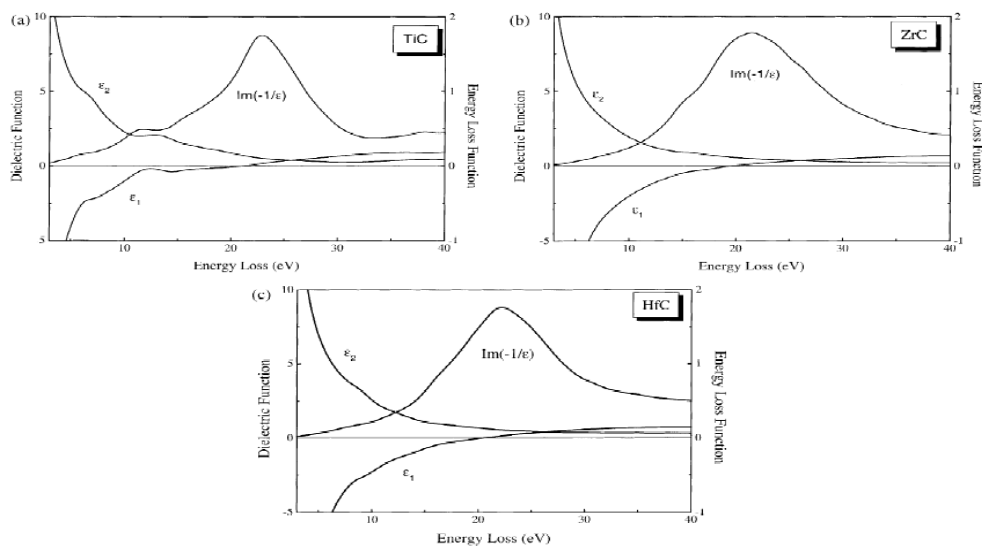


Fig. 1. (a–c) Energy loss function $\text{Im}(-1/\epsilon)$, and real and imaginary parts of the dielectric function ϵ_1 , ϵ_2 for TiC, ZrC and HfC.

As peak positions in the energy loss spectrum at low energy losses are strongly influenced by the volume plasmon and the positions of other excitation, the energy loss spectrum cannot be directly associated with interband transitions. However, the imaginary part of the dielectric function can be associated with interband transitions. In Fig. 1a, a shoulder at ~7 eV and a small peak at ~13 eV are clearly observed in ϵ_1 spectrum, for TiC; however, no such structure is seen in Fig. 1b,c for ZrC and HfC, respectively, at least at a first glance. However, this structure exists and it can be made evident as we will show below.

Fig. 2a–c shows the effective number of electrons per molecule participating in the oscillation up to an energy E , calculated from Eq. (10). From these curves, we should be able to identify the presence of interband transitions as small steps in n_{eff} as the energy loss increases. In order to make these transitions apparent, we take the

derivative of n_{eff} with respect to E , but from Eq. (10) it follows that this derivative is proportional to the optical joint density of states defined in Eq. (11). Fig. 3a-c show the optical joint density of states versus energy loss for TiC, ZrC and HfC, respectively. It is noted that the peaks associated with interband transitions have been enhanced. The results for TiC are in good agreement with those reported by Pflüger et al. [3].

As we mentioned above, the form of the single scattering distribution at low energies is critical for the calculation of \mathcal{E}_1 and \mathcal{E}_2 and we would expect this to be reflected in n_{eff} and hence in OJDS. However, we do not observe any appreciable changes in the optical joint density of states for energies above 3 eV, when we chose other curves to be adjusted in the range 0-3 (.g., a straight line fitting).

Taking the second derivative of $J_1(E)$ with respect to E , Peaks not visible in the $J_1(E)$ versus E plots are further enhanced, as is shown in the insets of Fig. 1a-c. The appearance and height of these peaks show clearly that they are not noise in character, showing instead more structure associated with interband transitions. For TiC, well defined peaks at 6.9, 9.0, 13.6 eV are observed; for ZrC the achieved data show several peaked features at 8.9, 9.8, 11.3, 13.0 16.1 eV; and for HfC the enhanced peaks appear at 6.5, 9.0, 12.6 and 17.0 eV. As maxima observed in the $J_1(E)$ versus E plots are assigned to interband transitions across the energy gap, these peaks can be interpreted on the basis of existing energy-band calculations [1,5,6,20,21]. Tables 1-3 show a comparison of our EELS results with theoretical calculations based on the augmented plane wave (APW) method.

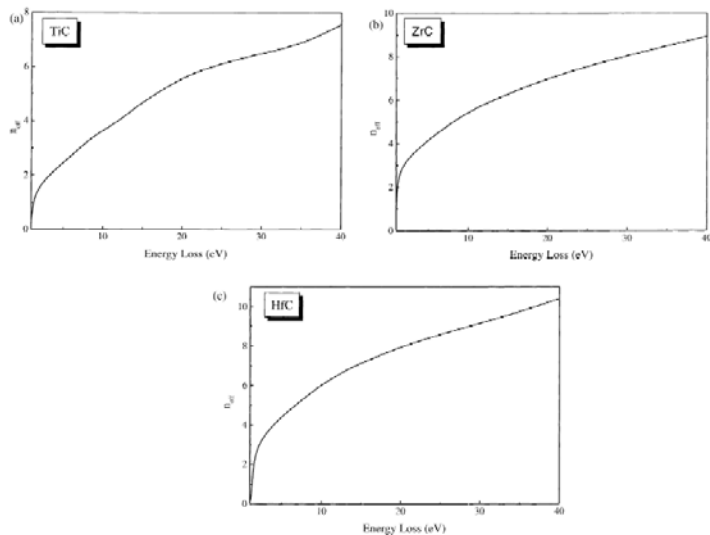


Fig. 2. (a-c) Effective number of electrons per molecule contributing to absorption up to energy E , as obtained from the partial sum rule, for TiC, ZrC and HfC.

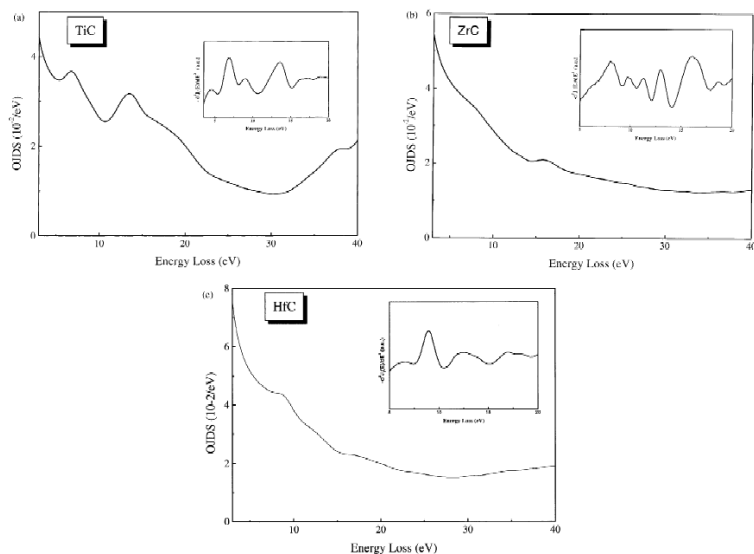


Fig. 3. (a-c) Kramers-Kronig derived optical joint density of states $J_1(E)$, for TiC, ZrC and HfC.

Table 1
Comparison between EELS and theoretical calculations for TiC

| EELS (present work) (eV) | Theoretical calculations [20] (eV) | Origin |
|--------------------------------|--|-------------------------|
| 6.9 | 6.8 | X_1-X_4' |
| 9.0 | 8.6 | X_1-X_3 |
| 13.6 | 13.4 | $\Gamma_1-\Gamma_{25'}$ |

Table 2
Comparison between EELS and theoretical calculations for ZrC

| EELS (present work) (eV) | Theoretical calculations [22] (eV) | Origin |
|--------------------------------|--|------------------------|
| 8.0 | 7.9 | X_1-X_3 |
| 9.8 | 9.9 | X_1-X_5 |
| 11.3 | 11.9 | $\Gamma_1-\Gamma_{15}$ |
| 13.0 | 13.2 | L_2-L_1 |
| 16.1 | 16.2 | $W_2'-W_2$ |

It must be recalled that, even though we have identified all the peaks in Fig. 3a–c with band structure calculations, for many of the structures a unique assignment cannot be made. For example, the peak at 6.9 eV in TiC, can arise from transitions of the type W_2, W_1 (.1 eV) and L_2, L_3 (6.3 eV) as well, because of our energy resolution, but in the tables we have chosen the transitions that best fit our experimental results. A more precise assignment could be obtained with experiments carried out with higher energy resolution.

Conclusions

Electronic structure of commercial TiC, ZrC, and HfC powder was studied by low-loss transmission electron energy loss spectroscopy. We obtained Kramers–Kronig derived complex dielectric function and optical joint density of states (OJDS) for the three compounds. Peaks in the OJDS were enhanced by taking the second derivative with respect to energy loss and compared with previously reported data for TiC and with theoretical predictions based on band-structure calculations for TiC, ZrC and HfC. Good agreement was found between our experimental results and those based on theoretical calculations.

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