Surface exciton polariton in monoclinic HfO$_2$: an electron energy-loss spectroscopy study

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New Journal of Physics 11 (2009) 103009 (11pp)
Received 22 April 2009
Published 2 October 2009
Online at http://www.njp.org/
doi:10.1088/1367-2630/11/10/103009

Abstract. Surface exciton polaritons (SEPs) were mostly expected in materials displaying sharp excitonic absorptions. Using electron energy-loss spectroscopy with a spatial resolution of 0.2–2 nm and associated calculations, we demonstrated SEPs upon rather weak excitonic oscillator strengths (broad interband transitions) in insulating, monoclinic HfO$_2$ above its optical band gap. Broad interband transitions exist in many semiconductors and insulators above the band gap, and our work could stimulate future explorations of SEPs in a wide spectrum of materials and corresponding applications in optics.

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1. Introduction

Surface exciton polaritons (SEPs) are collective oscillations of delocalized excitons at the surface of materials [1]–[6]. Conventional knowledge of SEPs requires their existence in the sharp excitonic spectral regime, where the imaginary part of the complex dielectric function of materials ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) is much larger than the real part, $\varepsilon_2 \gg |\varepsilon_1| \geq 0$, manifested as a prominent peak in $\varepsilon_2$ [7]–[9]. The sharp excitonic oscillator strength at $\varepsilon_2$ could lead to the formation of delocalized Wannier-type excitons in the interior of certain materials, readily setting up SEPs at the surface [1]–[9]. A larger excitonic absorption $\varepsilon_2$ gives rise to a narrower SEP spectral feature and the sign of $\varepsilon_1$ does not affect the excitations of SEPs [7]–[9], both at odds with the well-known surface plasmon polaritons (SPPs) that rest upon negligible $\varepsilon_2$ and negative $\varepsilon_1$ [10]–[12]. Moreover, a thorough understanding of SEPs requires the consideration of a complex wavevector parallel to the surface ($k = k_r + ik_i$), of which the imaginary part results in attenuations of SEPs along the surface [7]–[9]. Despite all these intriguing characteristics, SEPs drew little attention in the past, probably because of the unconventional complex $k$ and the rather counterintuitive condition of $\varepsilon_2 \gg |\varepsilon_1| \geq 0$ [13]. The satisfaction of $\varepsilon_2 \gg |\varepsilon_1| \geq 0$ with the corresponding formation of delocalized excitons, which can be achieved in only a handful of semiconductors, should also account for the few experimental reports on SEPs previously [3]–[6].

We have recently revisited the conventional understanding in SEPs and established their excitations also in materials displaying an otherwise weak excitonic oscillator strength ($\varepsilon_2 > \varepsilon_1 > 0$), though broad [13]. The existence of SEPs is thus not limited to materials with a sharp excitonic absorption, and the collective nature of SEPs in $\varepsilon_2 > \varepsilon_1 > 0$ originates from oscillations of loosely defined delocalized excitons that are correlated with broad interband transitions in materials [13]. Most importantly, the relaxed condition of $\varepsilon_2 > \varepsilon_1 > 0$ and the associated interband transitions can be observed in many semiconductors and insulators above the band gap [13], suggesting the possible existence of SEPs in the materials.

Here, we demonstrate the excitation of SEP in insulating HfO$_2$ bulk ceramics (monoclinic) above the optical band gap using electron energy-loss spectroscopy (EELS) in conjunction with scanning transmission electron microscopy (STEM) with a 0.2–2 nm electron probe, i.e. the combined technique of STEM–EELS [13, 14]. Theoretical simulations of the STEM–EELS results supportive of SEP excitations were also carried out. The nanometer-scale electron probe provides an ultimate spatial resolution to our spectroscopic investigation [13, 14], and Kramers–Krönig analysis (KKA) [15] of the STEM–EELS results unraveled an interband-transition absorption ($\sim 6.2$ eV) above the derived band gap ($\sim 5.1$ eV) [16]. The broad
spectral feature of the interband-transition excitation overwhelms the weak SEP excitation at \( \sim 7.5 \text{ eV} \). The unambiguous observation of SEP in bulk HfO\(_2\) can only be accomplished at a grazing incidence of the electron probe along the specimen edge just outside the bulk, so-called aloof geometry [13, 14, 17, 18]. In such a probe-sample geometry, volume electronic excitations (e.g. interband-transition excitation here) can be much reduced, propitious for the predominant observations of surface excitations such as SEPs [13, 14, 17, 18]. Spatially resolved STEM–EELS investigations were also performed on monoclinic HfO\(_2\) films (5 nm) grown on GaAs(001) [19], showing good agreement with the corresponding calculations. Monoclinic HfO\(_2\) with its high static dielectric constant is a technically important material for high-\(\kappa\) dielectrics applications [19]–[24], and interests in spatially resolved investigations of its electronic excitations have been strong [20]–[22]. Excitations of SEP in monoclinic HfO\(_2\) have, however, never been documented or discussed in previous reports [20]–[22].

2. Experiment

Two types of stoichiometric, monoclinic HfO\(_2\) materials were investigated by STEM–EELS in this work, HfO\(_2\) bulk ceramics and HfO\(_2\) films (5 nm) grown on GaAs(001) substrates. The material synthesis details were published elsewhere [19, 25]. The study of bulk ceramics is to tackle the intrinsic electronic excitations of HfO\(_2\), and HfO\(_2\)/GaAs(001) provides a more practical sample geometry to perform the aloof STEM–EELS for further unveiling the SEP physics in HfO\(_2\).

Specimens for STEM–EELS investigations were prepared by standard tripod polishing, followed by a quick ion milling at 3 kV for a few tens of seconds. The specimens were then subjected to careful plasma cleanings in order to remove carbon contaminations before STEM–EELS experiments. All STEM–EELS spectra were acquired on an FEI field-emission STEM/TEM, Tecnai F20, operated at 200 kV and equipped with an electron monochromator. Throughout the STEM–EELS experiments, respective spectrum collection and probe convergence semi-angles of 4.9 and 13 mrad were used. Both the deconvolution of single scattering STEM–EELS spectra from raw results and the subsequent KKA were conducted on the DigitalMicrograph EELS package written on the basis of [15].

3. Results and discussion

Figure 1(a) shows the STEM–EELS spectra acquired on bulk HfO\(_2\) with the incident electron probe moved from the material interior to vacuum by a 2-nm probe step and normalized among each other with reference to the zero-loss peak (ZLP) intensity. Using an electron monochromator, the probe size is 2 nm and the energy resolution is 0.22 eV. The black curve indicated by the solid arrow (figure 1(a)) exhibits the spectrum taken in vacuum and right at the grazing incidence to the sample edge.

Positioning the electron probe in the bulk (blue, figure 1(a)), the distinct spectral feature at 15.9 eV is characterized as the volume-plasmon excitation in HfO\(_2\), and this observed value is in good agreement with the literature (\(\sim 15.7–16 \text{ eV} \)) [20, 26]. The two small peaks above the volume plasmon, 18 and 19.8 eV, arise from high-energy interband transitions [20], whereas the origin for the broad intensity maximum from \(\sim 7\) to \(\sim 11 \text{ eV} \) was not clearly documented [20, 26]. Considering that the macroscopic physics of STEM–EELS can be understood in the framework of the dielectric response of materials [10], we thus derived
Figure 1. (a) STEM–EELS spectra acquired on bulk HfO$_2$ with the electron probe positioned at various locations of the material (inset; probe step, 2 nm). The intensities of the spectra were normalized to each other with reference to ZLP. The color circles (inset) denote probe locations and the corresponding spectra are shown by the same colors. Solid arrow, the spectrum acquired in grazing incidence to the sample edge. Dashed arrow, the intensity decrease of broad interband-transition excitation at $\sim 7$–$11$ eV as a function of probe positions toward vacuum. (b) The complex dielectric function of HfO$_2$ derived from the blue spectrum in (a). The black, dark gray and gray spectra are the blow-ups of those in (a) with ZLP tail intensities below $\sim 5$ eV being ignored for clarity.

The frequency($\omega$)-dependent dielectric function of HfO$_2$ (figure 1(b)) by performing KKA on the blue spectrum in figure 1(a) with $\varepsilon(\omega)$ normalized to the refractive index of 2.1 at $\omega \rightarrow 0$ [20]. It should be noted that each experimental spectrum in figure 1(a) integrates electronic contributions from a large number of reciprocal-space vectors due to the noticeable probe convergence semi-angle of 13 mrad. This STEM–EELS convergence semi-angle results in transmission/reflection discs of 13 mrad in radius, and covers many Bragg reflections in HfO$_2$ (for example, $\sim 4.6$/ $\sim 9.6$ mrad for low-index, symmetry-allowed (100)/(002) reflections, respectively). Specific anisotropic electronic contributions ascribed to the monoclinic symmetry of HfO$_2$ would then be averaged out throughout all spectra in figure 1(a). The thus-determined $\varepsilon(\omega)$ in figure 1(b) could be empirically regarded as an isotropic counterpart and is essential for

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Figure 2. (a, b) Thickness \(d\)-dependent characteristics of \(k_r\) and \(k_i\) of the respective symmetric (black, \(L^+\)) and antisymmetric (red, \(L^-\)) SEP modes in HfO\(_2\) at 7.5 eV \((\varepsilon = 0.95 + i6.28)\) with reference to \(k_r\infty\) and \(k_i\infty\) for an infinitely thick material. Gray dot-dash line in (a), the light line \(k_0\) (\(=\omega/c\)). Inset in (b), the loss function for the \(L^-\)-mode (red) at the given \(k_r\) and \(k_i\) of HfO\(_2\) (thickness, 30 nm) and that for an infinitely thick HfO\(_2\) in the large-\(k\) limit (green) with featureless characteristics instead. The loss probability of the infinitely thick HfO\(_2\) was normalized to that of the \(L^-\)-mode at the lower energy end in the inset.

following theoretical derivations of SEPs and STEM–EELS excitations (figures 2–4), both of which are on the basis of isotropic considerations [13, 27].

In figure 1(b), \(\varepsilon_1\) passes through zero at \(\sim 15.9\) eV accompanied by a decrease in \(\varepsilon_2\), leading to a maximum in the volume loss function \(\propto \text{Im}\left\{-1/\varepsilon(\omega)\right\}\) at the given energy. Such a feature is characteristic of volume-plasmon excitations [10], and the derived \(\varepsilon_1\) and \(\varepsilon_2\) (figure 1(b)) thus faithfully capture the electronic characteristics of HfO\(_2\). Further inspection of the absorption features in figure 1(b) \((\varepsilon_2)\) indicates an interband transition \((\sim 6.2\) eV) right above the band gap onset \((\sim 5.1\) eV) [16] and a weaker transverse oscillator strength at \(\sim 11\) eV. The broad STEM–EELS feature from \(\sim 7\) to \(\sim 11\) eV (blue, figure 1(a)) is then taken as a result of the interband-transition excitation.

Moving the electron probe from the bulk (blue, figure 1(a)) to the grazing incidence near the edge (black, figure 1(a)), the predominant spectral weight at 15.9 eV (volume plasmon) gradually red-shifts to SPP at \(\sim 13.4\) eV [20] \((\varepsilon = -0.83 + i1.74,\) figure 1(b)) and the intensities of interband-transition excitations \((\sim 7–11, 18\) and 19.8 eV) also weaken accordingly. Eventually SPP becomes the predominant feature with a broad shoulder from \(\sim 7.5\) eV, which is shown more clearly in figure 1(b) (black; ignoring intensities ascribed to the ZLP tail below \(\sim 5\) eV). The intensity decrease of interband-transition excitation at \(\sim 7–11\) eV is most visible for the 10-eV hump (dashed arrow, figure 1(a)). It is noted that the evanescent wave fields of surface excitations are well extended into vacuum, while the volume excitations are relatively more confined within the bulk of materials [13, 14, 17, 18]. With the probe positioned toward the vacuum (figure 1(a)), the electromagnetic field coupling between the probe and the material thus favors SPP, leading to diminished contributions from the volume-related electronic excitations.

With further increases in distances from the probe to the sample edge (e.g. dark gray, gray, etc; figures 1(a) and (b)), significant intensity decreases at \(\sim 13.4\) eV can be observed that are characteristic of the exponential decay of SPP wave fields from the material surface [13, 14].
Figure 3. (a) STEM–EELS spectra acquired on 5-nm HfO$_2$ films grown on GaAs(100) with the electron probe positioned at various locations of the film (inset). These green, red, orange and purple spectra were aligned and normalized to ZLP, then deconvoluting ZLP and vertically shifted for clarity. The blue spectrum was taken from that in figure 1(a) for the convenience of comparison. The purple spectrum was acquired at grazing incidence, and the green one was taken at the center of the film. The red and orange spectra were recorded at $\sim$0.6 and $\sim$1.2 nm from the green electron probe position (center of the film), respectively. (b) Theoretical counterparts of (a) with the probe–sample geometry used for calculations depicted in the inset, which is the schematic side view of that in (a). Inset, the red electron trajectory giving the red calculated spectrum. A, SPP in HfO$_2$; B, interface plasmon; C, interband-transition excitations in GaAs and HfO$_2$; D, CR from GaAs (see also figure 4).

It is, however, surprising that the broad shoulder at $\sim$7.5–10.5 eV (figure 1(b)) persists and evolves into a prominent spectral onset at $\sim$7.5 eV ($\varepsilon = 0.95 + i6.28$; dark gray and gray in figure 1(b)). This clearly indicates the nature of evanescent surface wave fields around $\sim$7.5 eV, which has not been documented before [20]–[22]. Compared to SPP ($\sim$13.4 eV, figure 1(b)), the slower intensity decays at $\sim$7.5 eV are consistent with the smaller wave-field decay constant,

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Figure 4. (a)–(c) Energy-loss probability maps (logarithmic scale; minimum to maximum, 4 orders of magnitudes in difference) calculated for a bare HfO$_2$ film (5 nm) symmetrically bound by vacuum, the realistic system investigated in figure 3(a) (associated with the purple spectrum in figure 3(b)), and the GaAs substrate alone, respectively. The electron probe position exploited for the calculations is depicted in each corresponding inset. (d) The STEM–EELS spectra integrated upon $k$ ranges of 0–0.1 (blue) and 0–0.2 nm$^{-1}$ (red) in (a). The spectra have been shifted vertically for clarity. A, SPP in HfO$_2$; B, interface plasmon; C, interband-transition excitations in GaAs and HfO$_2$; D, CR from GaAs; E, interband-transition excitations in GaAs; F, SEP in HfO$_2$.

$\sim \omega/\nu$ ($\nu$, the velocity of incident electrons; $\sim 0.7c$ at 200 kV; $c$, the speed of light) [13, 17, 18], characteristic of surface excitations with a lower eigen-frequency. Considering the circumstance of $\varepsilon_2 > \varepsilon_1 > 0$ at $\sim 7.5$ eV and the close correlation with the interband-transition absorption at $\sim 6.2$ eV (figure 1(b)), this spectral onset at $\sim 7.5$ eV raises a strong possibility that its physical origin is due to SEP [13], which is further exemplified in figure 2.

In addition to the satisfaction of $\varepsilon_2 \gg |\varepsilon_1| > 0$ and $\varepsilon_2 > \varepsilon_1 > 0$, a specific requirement for SEPs excitations is the small magnitude of $k_i$, which decreases with decreasing material thickness ($d$) [13]. The excitations of SEPs thus also require a small material thickness that is ultimately determined by the respective magnitudes of $\varepsilon_1$ and $\varepsilon_2$ in materials [13]. Using $\varepsilon = 0.95 + i6.28$ at $\sim 7.5$ eV and the isotropic SEP theory [13], we have calculated $k_r$ and $k_i$ of SEP in HfO$_2$ as a function of $d$, figure 2, with reference to the asymptotic limits, $k_{r\infty}$ and $k_{i\infty}$,
for an infinitely thick HfO$_2$ ($k_{r\infty} = 0.98k_0$ with $k_0 = \omega/c$; $k_{i\infty} = \sim 10^{-1}k_{r\infty}$), where SEP is not favorable due to the large value of $k_{i\infty}$. For SEP excitations, $k_{i\infty}$ ($k_i$) needs to be at least of the order of $10^{-2}k_{r\infty}$ ($k_r$) [13] and smaller $k_{i\infty}$ ($k_i$) will result in more prominent SEP features [7, 8, 13]. The interpretation of the spectral onset at $\sim 7.5$ eV (figure 1) as SEP would then suggest a small thickness of the HfO$_2$ ceramics. A thickness estimation using EELS log-ratio analysis [15] on the blue spectrum in figure 1 yields a sample thickness of $\sim 30$ nm along the incident probe direction. At this small thickness, wave fields at both surfaces of the sample couple with each other, giving rise to symmetric ($L^+$) and antisymmetric ($L^-$) surface modes according to the charge–density symmetries across the material (figure 2) [7]–[13].

\[
L^+ : \varepsilon_0 a_0 + \varepsilon_0 \alpha \tanh \left( \frac{ad}{2} \right) = 0,
\]

\[
L^- : \varepsilon_0 a_0 + \varepsilon_0 \alpha \coth \left( \frac{ad}{2} \right) = 0,
\]

where $\varepsilon_0$ is the dielectric function of the surrounding free space (vacuum throughout this work, $\varepsilon_0 = 1$), and $a_0$ and $\alpha$ are the wave-field decay constants normal to the surface towards vacuum and HfO$_2$, respectively. In figure 2(a), calculated $k_r$, relative to $k_{r\infty}$, points out a given SEP mode being located to either the left or right of the light line $k_0$ (gray dot-dashed line) [7]–[9], [13]. The calculated $k_i$ in figure 2(b) further indicates whether the SEP mode can exist in thin HfO$_2$ (30 nm), where the existence of $L^-$-SEP mode is unambiguous ($k_i \sim 0.059k_{r\infty}$; see the profile of the corresponding loss function near $\sim 7.5$ eV, inset) and that of $L^+$-SEP is not possible because $k_i > k_{i\infty}$ (meaningless and featureless in the calculated loss function, and thus not shown). In figure 2(b) (inset, green), the featureless loss probability for an infinitely thick HfO$_2$ in the large-$k$ limit, $\sim \text{Im}\{\frac{-1}{\varepsilon(\omega)+1}\}$, in the spectral regime is, however, intentionally shown to demonstrate that the SEP excitation in HfO$_2$ does require a small material thickness. The spectral onset at $\sim 7.5$ eV in HfO$_2$ as a result of SEP excitation is hence conclusive and it cannot be observed clearly without positioning the electron probe away from the sample edge to disentangle contributions from the broad intensities of nearby interband-transition excitation ($\sim 7$–11 eV). Although the thin specimen of HfO$_2$ (figure 1) consists of SEP and SPP that might lead to spurious $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ structures upon KKA analyses [28], the very weak intensity of SEP (figure 1(b)) and the broad and relatively weak excitation of SPP (blue, figure 1(a)) actually produce little effect on $\varepsilon(\omega)$.

Now, we further investigate the SEP excitation in HfO$_2$ with a well-defined material lateral dimension perpendicular to the interface, 5 nm films grown on GaAs(100) substrates (inset, figure 3(a)) [19, 25]. The vanishing $k_i$ of $L^+$- and $L^-$-SEPs in a 5 nm HfO$_2$ slab (figure 2(b)) suggests favorable conditions for their excitations. However, no noticeable SEP excitations at $\sim 7.5$ eV can be observed by spatially resolved probing HfO$_2$/GaAs at the grazing incidence (purple, figure 3(a)) and positions further away from the HfO$_2$ surface (spectra similar to purple and weaker, and thus not shown) even using an electron probe with a better spatial resolution of 0.2 nm (energy resolution, 0.66 eV). Instead, broad intensities onset at $\sim 8$–10 eV (C) and new spectral features, B ($\sim 5.7$ eV) and D ($\sim 3.7$ eV) in figure 3(a), appear in addition to SPP in HfO$_2$ (A, $\sim 13.4$ eV). Probing HfO$_2$/GaAs from the HfO$_2$ film center (green, figure 3(a)) to grazing incidence (purple) leads to a predominance of SPP over volume excitations, as revealed in the bulk material (figure 1). Moreover, the volume- and surface-plasmon peak positions observed in HfO$_2$ films agree well with those observed in bulk (blue spectrum in figure 1(a) incorporated.
into figure 3(a) for comparison), indicating that the thin HfO$_2$ films grown on GaAs possess electronic properties similar to bulk. This similarity is crucial for further explorations of the origins for B, C and D and the absence of SEP on the basis of macroscopic dielectric theory for STEM–EELS excitations (figures 3(b) and 4) [27].

Figure 3(b) shows the STEM–EELS spectra calculated per unit path length along the electron trajectory, and the optical constants of GaAs were taken from [29]. The calculations were performed using probe-sample geometries identical to those in experiments (schematic inset, side view of that in figure 3(a)) and integrations of $k \approx k_r$ ($k_i$ vanishing in thin HfO$_2$, and thus ignored), out of the paper plane, from 0 to 1 nm$^{-1}$. Integrations up to larger $k$ make no visible changes to figure 3(b). The agreements between figures 3(b) and (a) are remarkably good, reproducing the experimentally observed SPP predominance (peak A, from green to purple probe positions), peak-B onset, the absence of SEP (∼7.5 eV) accompanied by intensities at C and the broad feature below the optical band gap (D). The calculated energy-loss probability maps in figures 4(a)–(c) visualize their respective origins.

Figure 4(a) exhibits the map calculated for a bare 5-nm HfO$_2$ film, symmetrically bound by vacuum, with the electron probe passing along one of the two surfaces at grazing incidence. The null loss probability below the band gap has been ignored to enhance the figure contrasts. The null loss probability below the band gap has been ignored to enhance the figure contrasts. Otherwise, the dispersive spectral details (A and F, figure 4(a)) become obscure for their observations as a result of the associated change in logarithmic color scale. Figure 4(b) shows the map calculated for the actual material system investigated in figure 3(a), and figure 4(c) represents that for the pure GaAs substrate, i.e. equivalent to figure 4(b) without the HfO$_2$ layer as a control calculation set. Comparing figures 4(a)–(c), the sharp intensity at B unambiguously arises from the HfO$_2$/GaAs interface plasmon [20], which is absent in bare HfO$_2$ (figure 4(a)) and observed as an intensity dip at the given energy in GaAs (dashed arrow, figure 4(c)). The wave-field delocalization of peak B from the interface, estimated to $\sim \nu/\omega \approx 24$ nm [17, 18], gives rise to its excitation at a few nanometers from the interface (figure 3). Peak C excited at $\sim 8$–10 eV (figures 4(b) and 3) is primarily attributed to delocalized excitations of interband transitions [30, 31] in GaAs and HfO$_2$. In contrast, peak E at nearly the same energy in figure 4(c) shows mixed contributions from SPP and interband-transition excitations in GaAs [30]. Due to significant $\epsilon_1 \sim 14$ in GaAs ($\omega \rightarrow 0$) [29], the intense dispersive features below 4.4 eV (D, figures 4(b) and (c)) signify the Cherenkov radiation (CR) in GaAs, satisfied upon $(\nu/c)^2 \cdot \epsilon_1 > 1$ and proportional to the material lateral dimension perpendicular to the surface as a result of its volume excitation character [30, 32], and account for the broad maximum D in figure 3. It should also be mentioned that surface excitations actually have negative contributions to volume excitations when the material investigated is thin enough in its lateral dimension [18, 30]. The CR excitation in HfO$_2$ is, therefore, negligible here (though satisfied) due to the small material lateral dimension of 5 nm (infinity for GaAs, instead). Most importantly, the dispersion of peak F (dashed line, figure 4(a)), similar to that of SPP in bare HfO$_2$ (dashed line, peak A), is a strong signature for its surface character [10]–[12] due to the associated $L^+$- and $L^-$-SEP excitations that are otherwise energetically indistinguishable considering the broad feature of F (figure 4(a)). In the actual material system with GaAs (figure 4(b)), SEP in HfO$_2$ is, however, effectively damped out, as observed by an intensity dip at F (dashed arrow). It has been demonstrated that the presence of an asymmetrically bound absorbing material ($\epsilon_2 \neq 0$) deteriorates SEP resonances, leading to their negligible excitations [8]. GaAs is exactly characterized by $\epsilon_2 \neq 0$ throughout the spectral regime in this work [29].
Figure 4(d) shows the STEM–EELS spectra integrated upon $k$ ranges of 0–0.1 (blue) and 0–0.2 nm$^{-1}$ (red) in figure 4(a). The calculated large- ($k$) and small-$k$ (blue) spectra in figure 4(d) display SEP (F, $\sim$7.5 eV), SPP (A) and volume-plasmon ($\sim$15.9 eV) excitations in HfO$_2$ and obviously resemble to the experimental spectra acquired in bulk HfO$_2$ with the probe at grazing incidence (black, figure 1(b)) and several nanometers away from the bulk edge (dark gray and gray, figure 1(b)), respectively. This resemblance is not surprising, because a larger integrated $k$ corresponds to a smaller impact-parameter (the probe-to-sample distance) in real space for STEM–EELS probing [27]. The existence of SEP in HfO$_2$ upon interband-transition absorption, $\sim$6.2 eV, above the band gap with $\varepsilon_2 > \varepsilon_1 > 0$ is affirmative from all consistencies (figures 1–4).

4. Conclusions

Using STEM–EELS with an ultimate spatial resolution of 0.2–2 nm and corresponding spectral calculations, we have firmly established the existence of SEP ($\sim$7.5 eV) in insulating HfO$_2$ upon the weak excitonic absorption, $\sim$6.2 eV, above the optical band gap ($\sim$5.1 eV). The relaxed SEP-excitation condition of $\varepsilon_2 > \varepsilon_1 > 0$ is satisfied at $\sim$7.5 eV. Interband transitions along with $\varepsilon_2 > \varepsilon_1 > 0$ can be found in many semiconductors and insulators above the band gap, and this work could stimulate future interests in SEPs in various materials, where SEP excitations may find unexpected optics applications via manipulations of their surface wave fields analogous to SPPs for plasmonics [14]. More recently, we are becoming aware of some early STEM–EELS investigations in insulating MgO smoke cubes, where surface resonances closely correlated with interband-transition onsets ($\varepsilon_2 > \varepsilon_1 > 0$) have also been reported above its optical band gap [33]–[36]. Although the nature of these surface excitations in MgO was not clearly indicated then [33]–[36], they do bear strong resemblance to the SEPs elucidated here in monoclinic HfO$_2$. In addition to the optical potentials proposed above, SEPs represent fertile ground for revisiting surface excitations in a wide spectrum of materials.

Acknowledgments

This work was supported by the National Taiwan University Excellence Project and the National Science Council Taiwan.

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New Journal of Physics 11 (2009) 103009 (http://www.njp.org/)