Influence of surface oxidation on the valence electron energy-loss spectrum of wurtzite aluminum nitride

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The influence of surface oxidation on the low-loss spectrum of aluminum nitride (AlN) is investigated in electron energy-loss spectroscopy with scanning transmission electron microscopy. Contrary to intrinsic bulk AlN, oxidized AlN exhibits considerable spectral broadening both in the full width at half maximum of bulk plasmon and the subsidiary features. The modification in the low-loss lineshapes due to oxidation significantly complicates the determination of the dielectric function intrinsic to AlN. Simulations based on dielectric theory qualitatively consist with the experimental results while incorporating thick overlayers, further suggesting that the surface oxide of AlN can be rough and porous in nature. © 2013 American Institute of Physics.

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Wurtzite aluminum nitride (AlN), with a wide direct bandgap up to 6.2 eV, has recently attracted considerable attention, because of its promising optoelectronic applications, especially in energy related fields such as high-brightness light-emitting diodes and full spectrum solar cells when alloyed with other III-V nitride semiconductors.¹ To further enhance the functionality of this material, comprehensive understanding of the fundamental electronic structures is required. Access to the electronic structures can be achieved by examining the corresponding dielectric function (DF), which essentially determines the response to external electromagnetic perturbations such as light or electrons. Compared to conventional optical methods, electron energy-loss spectroscopy (EELS) with scanning transmission electron microscopy (STEM) can alternatively provide spectral information over a significantly wider frequency range accompanied by excellent spatial resolution, which substantially facilitates the exploration for nanomaterials.^{2,3} Therefore, extensive studies on AlN dielectric properties have been made accordingly.^{4,5} However, the majority of earlier works in the literature do not appear to represent the intrinsic properties of bulk AlN accurately, since the influence of surface oxidation was not adequately verified.

Owing to the strong chemical affinity of AlN for oxygen, AlN is easily prone to oxidation, forming an amorphous Al₂O₃ (a-Al₂O₃) surface layer by reactions with moisture or oxygen even at room temperature,^{6–8} despite the superior stability that is generally regarded. The current results are thus argued to be more consistent with the oxidized material.^{7–9} The available examinations into oxidation with EELS were concentrated, however, primarily on the variation of the core-loss features such as Al-L_{2,3} and N-K edges.^{6,8} None were dedicated to the low-loss regime, which is essential for subsequent dielectric property investigation. Furthermore, certain electronic excita-

tions, designated to originate from Al vacancies or localized states,^{9,10} were commonly observed below the fundamental bandgap, further revealing their defective crystallinity. In addition, concerning the calculations of the DF of AlN using EELS, the relativistic effects such as retardation and Čerenkov radiation (ČR), which can potentially induce spectral artifacts near the bandgap especially for semiconductors,^{11,12} were largely ignored.^{4,5} Thus previous derivations of DFs from the low-loss spectrum remain unreliable and must be reexamined.

In this study, the low-loss spectrum of bulk AlN is clearly demonstrated to be significantly modified by oxygen incorporation, which subsequently complicates the accurate determination of the DF through the Kramers-Kronig analysis (KKA). With careful consideration for both surface oxidation and retardation effects, the corresponding complex DF, closely representative of the intrinsic and oxygen-free bulk AlN, is proposed. Theoretical simulations have also been made in support of the experimental observations.

Commercial AlN nanoparticles (NPs) with well established chemical compositions and a crystallographic structure (wurtzite) were employed in this study. For obtaining the low-loss spectrum representative of intrinsic bulk AlN, considerable attention has been paid to minimizing the surface oxidation. Samples were prepared by dispersing AlN powders directly on Cu grids with a lacy carbon network without any aqueous process,⁷ followed by plasma cleaning to remove carbon contamination, and were then loaded into TEM with minimal exposure to the atmosphere. Spectroscopic analysis was performed in STEM mode with a probe size of approximately 0.1–0.12 nm, in a probe-Cs-corrected TEM JEOL 2100F system operated at 200 kV, equipped with a Gatan ENFINA spectrometer. Throughout the STEM-EELS acquisition, the energy resolution was optimized to be 0.6 eV along with respective convergence and collection semi-angles of 13 and 7.4 mrad.

Fig. 1(a) shows the spectrum acquired from a nearly oxygen-free region, where no oxygen K-edge signal can be

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FIG. 1. (a) Low-loss spectrum of AlN acquired from a nearly oxygen free region. (b) Comparison of the spectra from intrinsic AlN (blue), atmosphere (green), and O₂ (red) annealed samples, with zero-loss peaks and plural scattering deconvoluted. The inset shows a TEM bright-field image of a-Al₂O₃ overlayers at the edge of an oxidized NP.

detected, indicating rather low oxygen content below the EELS detection limit, typically within few atomic percent. It consists of a dominant bulk plasmon (BP) peak located at 20.4 eV with a narrow full width at half maximum (FWHM) of about 4.4 eV, along with some subsidiary interband transitions at 10, 13, 15–16, 26–28, and 37–44 eV. Specifically, no features are found below the fundamental bandgap, where no excitations should be expected for perfect crystallinity. This low-loss spectrum thereby is believed to represent the intrinsic AlN bulk property. To further illustrate the influence of oxidation on the spectral features, the low-loss spectrum of intrinsic AlN (Fig. 1(a)) is then compared to the results obtained from purposely oxidized samples, annealed at 200 °C in the atmosphere (green line) and in O₂ (red line) for 2 h, respectively (Fig. 1(b)). More serious oxidation was confirmed in the O₂-annealed sample than in the air-annealed one through measuring the intensity of the oxygen K-edge. The surface oxide remains amorphous according to the TEM bright-field image and electron diffraction (inset in Fig. 1(b)). For clarity, these spectra were collected from regions of similar thicknesses and deconvoluted with both zero-loss peaks and plural scattering removed, accompanied by normalization to the intensity maxima.

Fig. 1(b) reveals that with increasing oxidation the spectrum is characterized by a gradual increase in the FWHM of the BP, from about 4.4 eV for the intrinsic case (blue) to over 6.4 eV for the oxidized AlN (red), together with prominent broadening on both tails of the plasmon peak. The BP maximum additionally shows a systematic shift toward the

higher energy side with oxidation. Actually, a majority of the as-received NPs exhibit similar spectral features as the oxidized cases with only few resembling intrinsic AlN as shown in Fig. 1(a), which experimentally supports the high oxidation affinity of AlN even handled with caution at room temperature. Note that most of the earlier EELS works on AlN coincides with the results of the oxidized AlN obtained here (green and red lines in Fig. 1(b)), especially in the spectral width, which strongly suggests the possible oxidation of these samples.^{4,5}

For understanding the inherent physics of the low-loss spectra, the energy-dependent complex DF ($\epsilon = \epsilon_1 + i\epsilon_2$) is thus derived. To accurately extract the dielectric information, the KKA has been performed accordingly with careful consideration for relativistic contributions by evaluating sample thicknesses. The solid lines in Fig. 2(a) show the calculated DF of intrinsic AlN according to the blue curve in Fig. 1(b). Compared with the reported optical data^{7,9} determined from a single-crystalline AlN film with oxygen content controlled and mitigated (Fig. 2(b)), qualitative consistence can be achieved either in the profile shape or the relative intensity between ϵ_1 and ϵ_2 . Distinctively the absence of an additional absorption hump in ϵ_2 below the bandgap further verifies the reliability of the extracted DF. The remaining difference in the DF structure might result from both the limited energy resolution in the EELS and the angular-integrated signals under the converged illumination STEM mode, which can cause some momentum-dependent or anisotropy-related features in the spectra as well as in the DF to be smeared.

With surface oxidation incorporated, the corresponding DF (dashed lines in Fig. 2(a)), however, exhibits a considerable modification in the lineshape together with an appreciable

FIG. 2. (a) Experimentally derived complex DFs ($\epsilon = \epsilon_1 + i\epsilon_2$) of intrinsic (solid line) and oxidized (dashed line) AlN. (b) Computed DF according to the optically determined refractive index and extinction coefficient in Refs. 7 and 9.

shift toward the lower energy side, particularly below 20 eV. Meanwhile, the maximum magnitudes of the real and imaginary parts of the DF are reversed ($\epsilon_{1\max.} > \epsilon_{2\max.}$), in stark contrast to the results of both the intrinsic AlN (solid lines in Fig. 2(a)) and the optical reference (Fig. 2(b)). Moreover, examination of another well-recognized EELS work shows that the behavior of the proposed DF⁵ is more analogous to the oxidized case, rather than to intrinsic AlN. Thus a more profound influence of surface oxidation on the DF determination is clearly demonstrated.

To further assist the interpretation of the observed spectral variation with oxidation, simulations with dielectric theory have been conducted. The employed Bolton-Chen equations, describing the energy-loss probability of fast electrons transmitting a thin film, include bulk dielectric loss and contributions from surface, interface, and retardation as well.^{12–14} This calculation can also be applied to multilayer systems and, hence, is suitable for the present study. Here the modeled material structure consists of a 60-nm AlN slab, which can intrinsically reflect bulk characters and approximate the experimental magnitude, with the oxide overlayer of various thicknesses on each side. The input DF for AlN is experimentally derived, while that for the a-Al₂O₃ is adopted from the literature.¹⁵

Fig. 3(a) summarizes the calculated results with intensity normalized, in which the gray-shaded region represents the intrinsic AlN profile, whereas the influence of surface oxidation is illustrated by solid lines. With increasing oxide thickness, systematic broadening can be readily identified in both the BP and peripheral features, which satisfactorily agrees

with the experimental observations. It thus computationally proves that the surface oxidation can indeed cause the broadening of intrinsic AlN. Another noticeable point is that rather thick overlayers (>5 nm on each side) are required to cause such a change. In addition, despite the higher BP energy of a-Al₂O₃ at 23 eV, the predicted BP reveals merely a small blue-shift (<0.3 eV) even with much thicker oxide layers almost reaching 60% of the total thickness.

Further comparing the spectra of AlN and a-Al₂O₃ of the same 60 nm calculated separately (Fig. 3(b)), it is found that the AlN substantially dominates over the a-Al₂O₃, especially near the energy regime where its BP falls. This is also well revealed in the intensity magnitude, in which the AlN peaks at 0.03 eV^{-1} whereas the maximum of a-Al₂O₃ is only 0.01 eV^{-1} , implying that the AlN plasmon has higher excitation probability and thus can be naturally more pronounced. It is then clear that, because of the relatively weak excitations of a-Al₂O₃, the resultant low-loss spectra exhibit mainly broadened features along with a marginal shift of the corresponding BP instead of showing drastic interference in their lineshapes, even with a large amount of oxide incorporated. Another possible explanation for the highly estimated overlayer thickness can be associated with either non-stoichiometry or incomplete oxidation. The formed surface oxide can be composed of a-Al₂O₃ with partial AlN, forming Al-oxynitride, and the actual loss-probability profile may lie between the pure a-Al₂O₃ and AlN (Fig. 3(b)), which reduces the computational thickness necessary to conform to the experimental results.

Therefore, based upon the above analysis, it is concluded that the surface of AlN may not be as stable as intuitively recognized. Unlike the dense and self-limited SiO₂ grown on Si, typically <2 nm,¹⁶ the property of natural aluminum oxide can be rough and porous, which significantly facilitates continuous oxidation. The earlier proposed low-loss spectra of AlN,^{4,5} characterized by broad lineshapes with relatively large BP FWHM (>6 eV), could incorporate quite thick oxide layers on the surface already and thus do not represent the intrinsic characteristics of AlN. It should be mentioned that the simulations utilized in this study, with a simplified model considering the oxide overlayers on both sides, actually exclude the main oxygen impurities dissolved in AlN bulk lattices, especially at high temperature processes.^{6,17} Such compositional fluctuations, although uninvolved in the simulations here, are believed to have impacts on the low-loss features principally through the alteration of valence electron density¹⁸ and may account for the large discrepancy in the measured BP energy, ranging from 20 to over 21 eV.^{4,5,10,19} Moreover, some induced structural defects, such as stacking faults,²⁰ can also damp the BP resonance and decrease the relaxation time, further leading to the increase in the BP width as well. These factors, however, tangle interactively and are difficult to be experimentally differentiated.

In summary, the correlation between the variation in the low-loss features of bulk AlN and surface oxidation has been established using STEM-EELS. With the incorporation of oxide overlayers, a considerable spectral broadening both in the BP and in the subsidiary characteristics can be identified, which further complicates the DF determination of intrinsic AlN. The experimental observations in the low-loss regime

FIG. 3. (a) Simulated low-loss spectra of a 60-nm bulk AlN slab with various thicknesses of a-Al₂O₃ overlayer. The schematic representation of the multilayer model utilized is also shown in the inset. (b) Calculated loss-probabilities of the respective bulk AlN and a-Al₂O₃ of the same 60 nm.

can be well reproduced in theoretical simulations, which also imply the porous and rough properties of natural oxide formed on the AlN surface.

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