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Investigations the Electronic Structure in Monoclinic phase Gadolinium Sesquioxides by Electron Energy Loss Spectroscopy

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Gadolinium sesquioxide (Gd_2O_3) has various applications in magnetic resonance imaging and optical coating material. Due to its high dielectric constant (κ~ 14), large band gap (5.4 eV), and high refractive index of 1.8 ~ 2, it has become a potential candidate material for metal-oxide semiconductor field-effect transistors (MOSFETs) [1]. It has been reported that two crystalline Gd_2O_3 phases, cubic phase (space group Ia3) and monoclinic phase (space group of C2/m), exist at ambient temperature and pressure [2], while cubic Gd_2O_3 has applied in most of the applications. In addition, monoclinic phase Gd_2O_3 (denoted as m- Gd_2O_3) can usually obtain during the fabrication process [3]. Here, we study an electronic structure of m- Gd_2O_3 performed by electron energy loss spectroscopy (EELS) in conjunction with scanning transmission electron microscopy (STEM) mode (STEM-EELS) and momentum (q)-dependence EELS (q-EELS).

TEM samples of m- Gd_2O_3 powders, were synthesized through the process in ref. [3], were prepared by suspending m- Gd_2O_3 powders in ethanol solvent, sonicating, and then drop onto a holey C-coated Cu grid. STEM- and q-EELS were examined using a Thermo Fisher Themis 300 (scanning) transmission electron microscope [(S)TEM] equipped with electron monochromator and Gatan Image Filter (GIF, model Quantum 965), operating at 300 kV. The energy resolution with electron monochromator is 0.2 eV throughout the STEM-EELS experiments. Real-space spectrum-imaging (SI) in energy-filtered TEM (EFTEM) mode with a tunable energy-selection slit was conducted on the same microscope. The single scattering EELS spectra were deconvoluted from raw data, and the subsequent Kramers-Krönig analysis (KKA) was conducted on the DigitalMicrograph EELS package, which is described elsewhere [4]. The q-EELS experiments were carried out under diffraction mode with q resolution of 0.03 Å-1.

Figure 1(a) shows the STEM-EELS spectra acquired on m- Gd_2O_3 with the incident electron probe positioned at various locations of the material as indicated in the HRTEM image [inset in Fig. 1(a)]. The blue curve in Fig. 1(a) reveals several spectral features at the energies of ~7.5, ~10, ~15, ~17.8, ~27.5, ~31.5, and ~36 eV, respectively. Combining the ε1= 0 at ~14.5 eV in the frequency (ω)-dependent dielectric function [$\varepsilon(\omega)= \varepsilon1(\omega)+ i\varepsilon2(\omega)$] of Gd_2O_3 in Fig. 1(b) and the maximum intensity localized in the bulk interior in EFTEM-SI [see Fig. 1(e)], the spectral feature at ~15 eV can be interpreted as volume plasmons (VPs). Positioning the electron probe at the sample edge as indicated as a green circle and green curve in Fig. 1(a), the spectral intensity of the VP peak significantly decreases, and following up with visibly enhanced the peak at ~13.6 eV. This result indicates the existence of surface-related excitation, surface plasmons (SPs), due to negative ε1 in Fig. 1(b). This result is also consistent with the calculated relativistic E-k map (E, energy loss; k, momentum transfer) for the 10-nm thick Gd_2O_3 films inset in Fig. 1(b) exhibiting the peak maximum at ~13.6 eV. By moving the incident electron probe further from the sample edge into vacuum [e.g., red and black curves in Fig. 1(a) with probe step of 2 nm], the broad shoulder at ~7 and ~ 9.5 eV persists. Meanwhile, the spectral feature at ~7 eV bears a strong surface excitation character with evanescent wave field decaying into vacuum revealing by EFTEM-SI intensity map [Fig. 1(d)]. Combining with both STEM-EELS spectra and EFTEM-SI intensity maps, the spectral

feature at ~7 eV peak can be considered as a surface resonance associated with excitonic onsets understood as surface exciton-polaritons (SEPs) [4]. In contrast to VP at 15 eV, the spectral intensity at 36 eV peak decreases when position electron probe from the material interior to the specimen edge, and then vanished when the electron probe is positioned at 2 nm away from the material surface as shown in Fig. 1(a). Furthermore, the spectral feature at 36 eV also exhibits maximum intensity localized in the bulk interior in EFTEM-SI [see Fig. 1(f)], which indicates the spectral feature at 36 eV reveals a kind of volume excitations. Intriguingly, the q-EELS spectra in Fig 2(b) were obtained along the [001] direction in Fig. 2(a), reveal that the intensity of the spectral peak at ~36 eV increases with increasing the q values. Unlike the exponentially decaying in intensity as a function of q values for both SPs and VPs, the intensity of the spectral peak at ~36 eV increases as a function of q which implies the involving multiple scattering processes as described in ref. [4].

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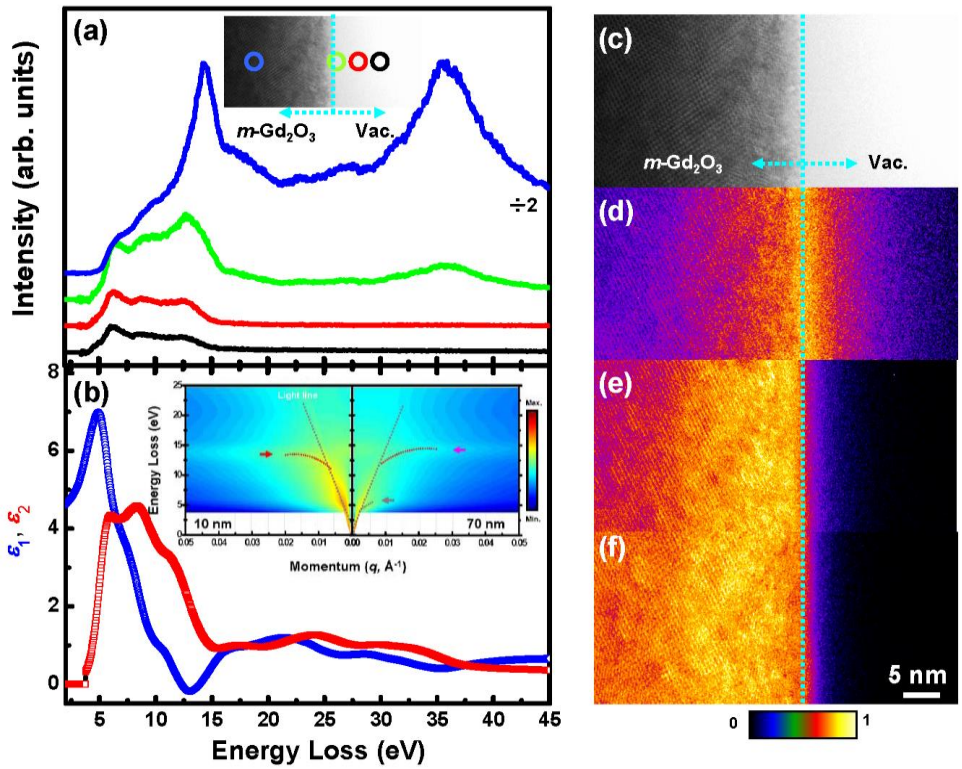

Figure 1. Fig. 1. (a) Position dependent EELS spectra acquired on m- Gd_2O_3 with the electron probe positioned at various locations with color circles in inset HRTEM image. (b) The complex dielectric function of m- Gd_2O_3 derived from the blue spectrum in (a). Inset is the calculated relativistic E-k maps (E is energy loss and k is momentum transfer) for Gd_2O_3 slabs of a thickness of 10 nm (left) and 70 nm (right panel). (c-f) The EFTEM-SI intensity maps acquired from the HRTEM image (c) at different energies of 6~8 eV (d), 14~16 eV (e), and 35~37 eV (f). The dotted blue lines indicate the interface

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between material (left part) and vacuum (right part). The color scale bar represents the linearly normalized image intensity.

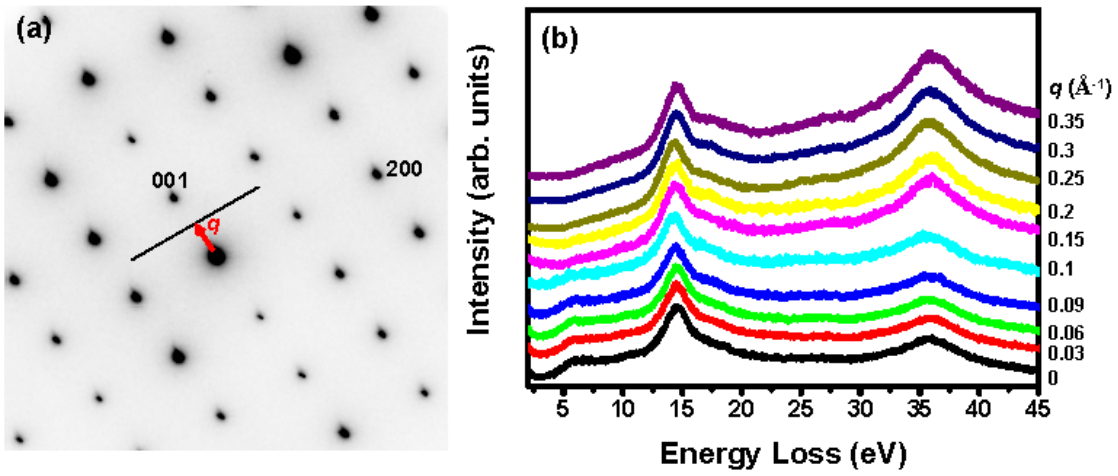

Figure 2. Fig. 2. (a) Electron diffraction pattern acquired along [010] incident electron beam direction. The black-color dash line in (a) indicates the Brillouin zone (B. Z.). The red arrow in (a) shows the momentum transfer range for q-EELS experiments. (b) The q-EELS spectra obtained along the q direction along [001] directions in (a).

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