Characterization of wurtzite ZnO using valence electron energy loss spectroscopy

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ZnO with superior material properties has attracted considerable interest recently. Of which, physical properties were often analyzed via various optical methods; however, the obtained information was mostly limited within the UV spectral range. Furthermore, the relation between the dielectric function and spectral features has not been established properly [1-2]. In this research, the fundamental electronic structure of bulk wurtzite ZnO is investigated with valence electron energy loss spectroscopy (EELS) in scanning transmission electron microscopy. The spectra were acquired under an aloof beam configuration where a grazing incident electron probe was employed to explore the electronic properties of ZnO and particularly to distinguish between the surface and volume electronic excitations. To qualitatively interpret the characteristic spectral features, the complex dielectric function of ZnO is derived from the corresponding low-loss spectra with careful consideration of the retardation effect.

By scanning the electron probe across the sample from bulk toward vacuum, four surface excitations intrinsic to ZnO can be identified [Fig. 1(a)-(b)]. The surface plasmon (SP) of ZnO is present at around 16 eV, which is different from the previously recognized values [3-4] since, with decreasing sample thickness, the dominant volume plasmon is gradually replaced by this spectral feature. Moreover, the SP excitation criterion of a negative real part ($\varepsilon_1$) of the dielectric constant of ZnO within this energy regime (about 15-17 eV) is met [Fig. 1(c)]. Surface exciton polaritons (SEPs), arising from the strong coupling of the external electromagnetic field with the delocalized excitons at the surface of the medium, are found to appear at 9.5 and 13.5 eV. The relaxed condition for SEP-excitation ($\varepsilon_2 > \varepsilon_1 > 0$) can be fulfilled [Fig. 1(c)], with rather weak excitonic oscillator strength (broad interband transitions). In addition, a surface guided mode that is excited by the retardation of incident electrons can be identified at 3.8 eV just above the ZnO bandgap, which is also predicted from a theoretical calculation employing the Kröger equation (Fig. 2).
References

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Figure 1. (a) A series of STEM-EELS spectra of ZnO acquired from the specimen interior to vacuum, with the circles showing positions in the corresponding HAADF image of ZnO powder (inset). (b) Comparison of EELS spectra acquired in the bulk (black), at the edge (red) and with grazing incidence close to (blue) and far from (green) the specimen/vacuum interface. (c) Derived complex dielectric function of ZnO ($\varepsilon = \varepsilon_1 + i \varepsilon_2$) (inset: variation near the interband transition onset with specimen thickness).

Figure 2. Log-scaled simulated relativistic loss probabilities in the E - $\theta$ maps (E: energy loss and $\theta$: scattering angle of incident electrons) for ZnO slab thicknesses of (a) 240 and (b) 60 nm. Solid and dashed arrows indicate the guided light modes and their extension of dispersive curve to the energy regime of 3.8-5.5 eV, respectively.