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Polarization dependence of the optical response in SnO_2 and the effects from heavily F doping

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ABSTRACT

The optical properties of intrinsic SnO_2 (TO) and fluorine doped (FTO) are characterized in terms of the dielectric function $\varepsilon(\hbar\omega)=\varepsilon_1(\hbar\omega)+i\varepsilon_2(\hbar\omega)$ by electronic structure calculations. The intrinsic TO shows intriguing absorption characteristics in the 3.0–8.0 eV region: (i) the low energy region of the fundamental band gap ($3.2<\hbar\omega<3.9$ eV), the optical transitions $\Gamma_3^+ \rightarrow \Gamma_1^+$ (valence-band maximum to conduction-band minimum) is symmetry forbidden, and the band-edge absorption is therefore extremely weak. (ii) In the higher energy region ($3.9<\hbar\omega<5.1$ eV) the $\Gamma_5^- \rightarrow \Gamma_1^+$ transitions (from the second uppermost valence band) is strongly polarized perpendicular to the main *c* axis. (iii) Transitions with polarization axis parallel to *c* axis are generated from $\Gamma_2^- \rightarrow \Gamma_1^+$ transitions (from the third uppermost valence bands), and dominates at high energies ($5.1<\hbar\omega$ eV). Heavily F doped TO (FTO) with doping concentrations $n_F=4\times10^{20}$ cm^{-3} changes the absorption significantly: (iv) Substitutional F_O generates strong inter-conduction band absorption at 0.8, 2.2, and 3.8 eV which affects also the high frequency dielectric constant ε_∞. (v) Interstitial F_i is inactive as a single dopant, but act as a compensating acceptor in highly *n*-type FTO. This explains the measured non-linear dependence of the resistivity with respect to F concentration.

1. Introduction

Cassiterite tin oxide SnO_2 (TO) is an important metal-oxide for efficient dielectrics, electric resistors, catalysis, optical sensor devices, coating oxide technologies [1], and also in gas sensor technologies [2]. Fluorine doped TO (FTO) thin films are inexpensive (compared to indium tin oxide) with conducting-transparent properties of the oxide, which opens for a broad range of low-cost photovoltaics and optoelectronics [3]. FTO can easily be heavily F doped in the order of 10^{20}–10^{21} cm^{-3} showing intriguing resistivity characteristic with respect to the F concentration n_F. Resistivity has been found to decrease for moderate doping concentrations $0<n_F<10^{20}$ cm^{-3}, but increases for doping concentrations $n_F>(1–3)\times10^{21}$ cm^{-3} [4,5]. Optical properties of TO and FTO have been studied in details both experimentally and theoretically [4–12]. However, still the fundamental band-gap energy E_g is not well established ($E_g\approx3.2$–4.7 eV [8,9,11,13–18], and the impact on the resistivity and optical response due to heavily F doping is not fully understood.

In this work, we use density-functional theory to investigate the linear optical response of TO and FTO in terms of the complex dielectric function $\varepsilon(\hbar\omega)=\varepsilon_1(\hbar\omega)+i\varepsilon_2(\hbar\omega)$ with respect to the photon energy $\hbar\omega$. We employ the projector augmented wave (PAW) method [19] within the local density approximation (LDA) and with a modeled on-site self-interaction-like correction (SIC) potential within the LDA$+U^{SIC}$. We analyze the calculated dielectric function $\varepsilon(\hbar\omega)$, refractive index $\tilde{n}(\hbar\omega)=n(\hbar\omega)+i\kappa(\hbar\omega)$ and the absorption coefficient $\alpha(\hbar\omega)$ for TO and FTO, and from this modeling we better understand the resistivity with respect to high F doping of TO. For instance, as a complement to earlier suggestions that the high resistivity at very high F content is due to lattice distortion, we demonstrate that this effect is a consequence of the site preference F dopants. That is, whereas moderate F doping generates *n*-type donors with F mainly on the oxygen site (F_O), the heavily F doped FTO generates also interstitial dopants (F_i) that forms neutralizing F_O–F_i complexes. Thereby, F_i which is a rather inactive atom in the low F concentration, acts as compensating acceptor when FTO is heavily *n*-type doped. Therefore, we suggest that the increased resistivity in the highly doped FTO is explained by the presence of the F_i dopants. This is an intriguing situation where the material generates a self-compensation of an otherwise to strong *n*-type character.

Moreover, the variation in measured E_g of TO is explained by our theoretical analysis of the valence- to conduction-band optical transitions. We find that the low energy band-edge absorption at $3.2<\hbar\omega<3.9$ eV is symmetry forbidden, and is thereby difficult to detect in the absorption measurements, explaining the difficulties to establish the band-gap value. Finally, we report a very strong polarization dependence of the optical response. We suggest that this can be beneficially utilized in future technological applications where polarization is a sensitive detector parameter.

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2. Computational details

TO crystallizes in space group D_{4h}^{14}. F substituting an O site (i.e., F_O) lowers the crystallographic symmetry C_{2v}, and F on an interstitial site [i.e., F_i at (1/2, 0, 1/2) or (0, 1/2, 1/2)] to C_{2h}. The theoretical analysis is performed with the PAW/LDA+U^{SIC} method [19] using U_d(cation) = 10 eV and U_s(anion) = −6 eV which corrects the LDA band gap and improve the localization of cation *d*-states [20,21]. Doping is modeled by 3×3×4 supercells of originally 216 atoms, considering the experimental lattice parameters of TO: $a = 4.737$ Å, $c = 3.185$ Å, and $u = 0.307$ [13]. Three different types of heavily F doped systems are investigated: TO with a F substituting oxygen (FTO:F_O; $n_F = 3.9 \times 10^{20}$ cm^{-3}), TO with a F interstitial (FTO:F_i; $n_F = 3.9 \times 10^{20}$ cm^{-3}), and TO with F_O plus F_i (hFTO: $F_O + F_i$; $n_F = 7.8 \times 10^{20}$ cm^{-3}). The ions of FTO are relaxed by means of

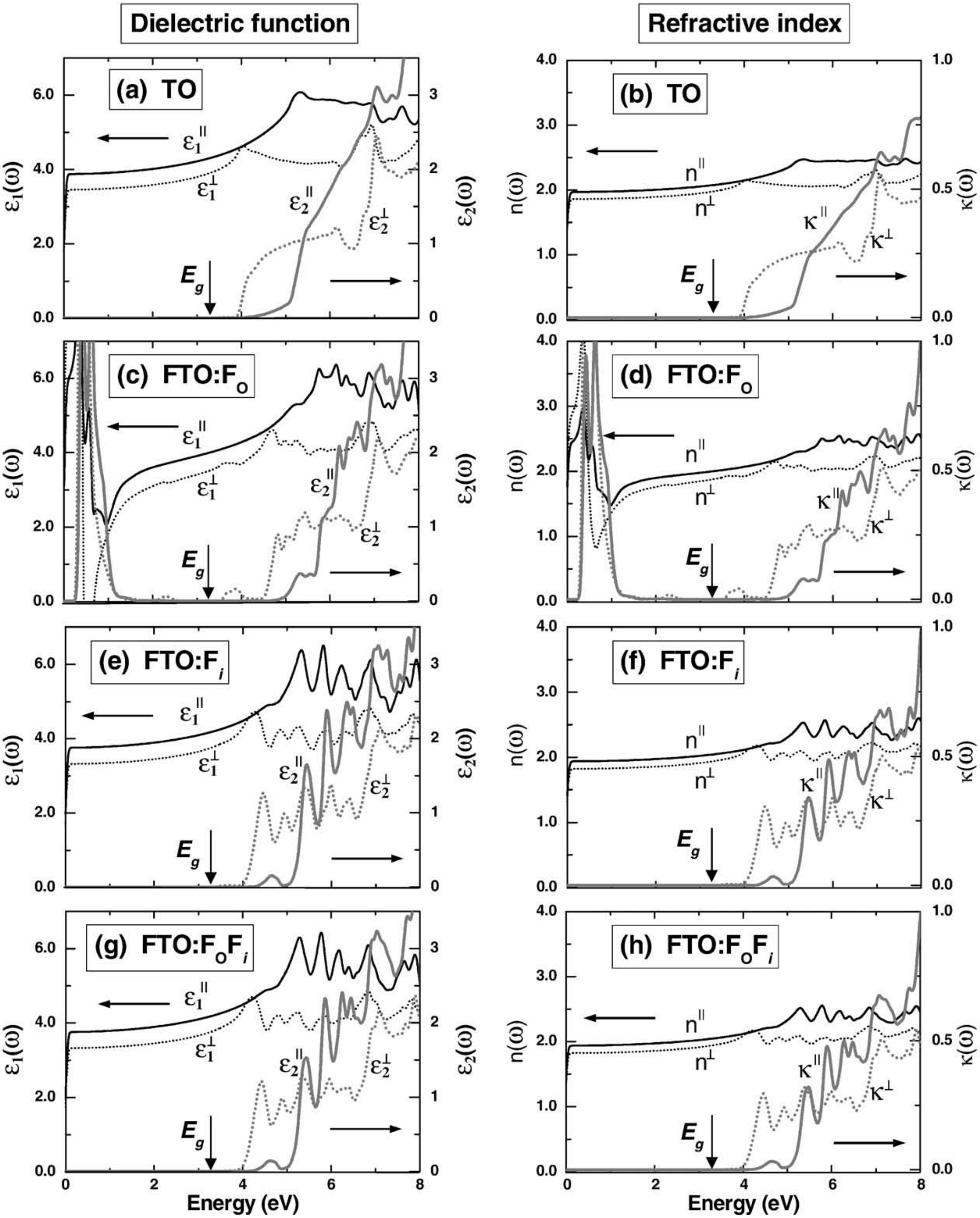

Fig. 1. The dielectric function $\varepsilon(\hbar\omega) = \varepsilon_1(\hbar\omega) + i\varepsilon_2(\hbar\omega)$ (left column) and refractive index $\tilde{n}(\hbar\omega) = n(\hbar\omega) + i\kappa(\hbar\omega)$ (right column) for TO and FTO show strong polarization dependence. The fundamental band gap is $E_g \approx 3.2$ eV for all both TO and FTO but onset to optical absorption across the gap occurs at around 4 eV with predominantly perpendicular polarization. F_O is a donor (c–d) changing the optical response. Single F_i is inactive dopant (e–f) but acts as a compensating acceptor in highly n-type FTO (g–h). A Lorentzian broadening of 40 meV was used for $\varepsilon(\hbar\omega)$ and $\tilde{n}(\hbar\omega)$.