Many-electron effects on the dielectric function of cubic In$_2$O$_3$: Effective electron mass, band nonparabolicity, band gap renormalization, and Burstein-Moss shift

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We systematically investigate the influence of free-electron concentrations from $1.5 \times 10^{17}$ cm$^{-3}$ up to $1.6 \times 10^{21}$ cm$^{-3}$ on the optical properties of single-crystalline In$_2$O$_3$ in the cubic bixbyite structure. Dielectric functions of bulk crystals and epitaxial films on various substrates are determined by spectroscopic ellipsometry from the mid-infrared ($37$ meV $\approx 300$ cm$^{-1}$) into the ultraviolet ($6.5$ eV) spectral region. Eight transverse optical phonon modes are resolvable for low carrier-density material. The analysis of the plasma frequencies yields effective electron masses which increase from a zero-density mass of $m_e^* = 0.18 m_0$ to $0.4 m_0$ at $n = 10^{21}$ cm$^{-3}$. This mirrors the nonparabolicity of the conduction band being described by an analytical expression. The onset of absorption due to dipole-allowed interband transitions is found at $3.8$ eV for $n \lesssim 10^{19}$ cm$^{-3}$. It undergoes a blue-shift (effective Burstein-Moss shift) for higher electron densities as a result of the dominating phase-space filling compared to band gap renormalization. A comprehensive model describing the absorption onset is developed, taking nonparabolicity into account, yielding an accurate description and explanation of the observations. The agreement of modeled and measured absorption onset independently supports the effective electron masses derived from infrared data. The high-frequency dielectric constant of undoped In$_2$O$_3$ is found to be $\varepsilon_{\infty} = (4.08 \pm 0.02)$. DOI: 10.1103/PhysRevB.93.045203

I. INTRODUCTION

Indium oxide is a technologically important material known for high conductivity when doped by Sn while maintaining transparency in the visible spectral range [1]. Its typical applications are therefore found in transparent electronics [2], plasmonics [3,4], or as front contacts for optical devices such as solar cells or thin film optical displays [5,6]. Processes to produce such devices are usually large-area coating technologies where the thin In$_2$O$_3$ films are produced by sputtering, i.e., in polycrystalline form. Already decades ago, optical and electrical behavior of polycrystalline In$_2$O$_3$ was described in great detail empirically [7].

Only very recently, bulk bixbyite In$_2$O$_3$ single crystals grown from the melt [8,9] and from the flux [10] became available. Due to their close-to-perfect crystalline structure, they allow unprecedented access to fundamental physical parameters of indium oxide far better than possible by investigating polycrystalline thin films. Plasma-assisted molecular beam epitaxy allows us to realize In$_2$O$_3$ layers with controlled donor concentration up to the high levels reached in polycrystalline material at a similarly high material quality as the single crystals [11].

The effective electron mass is of pivotal importance to understand electrical and optical properties of In$_2$O$_3$. A comprehensive overview of published experimentally obtained values for the zero-density effective electron masses $m_e^*(0)$ is given in Table I. No agreement on its value is found in the literature [12–21], where values scatter between $0.13 m_0$ [16] and $0.55 m_0$ [12]. Recent theoretical calculations predicted a pronounced conduction band nonparabolicity for the doping range under study here [22] and suggested from experimental results decades ago [12]. While different carrier densities are able to explain some of the discrepancies reported, no accepted value for the zero-density effective electron mass is obvious, and therefore analysis values scatter [23–25].

On the other hand, the onset of strong absorption is influenced by many-body effects already outlined in Ref. [26]. The Burstein-Moss effect shifts the absorption edge to higher energies [27,28] while band gap renormalization decreases the band gap simultaneously via exchange interaction. The interplay of both effects is needed to quantitatively explain the experimental findings while taking the nonparabolicity of the conduction band into account. The lowest energy band gap of In$_2$O$_3$ is found to be indirect ($2.75$ eV) [29], allowing us to maintain high transparency for sufficiently thin layers at room temperature. The lowest energy direct transition is dipole forbidden, while the onset of strong absorption due to
TABLE I. Values of experimentally obtained zero-density effective electron masses in In$_2$O$_3$ as reported in the literature in chronological order. The value reported for Ref. [19] (marked by an asterisk) is averaged following Ref. [21].

<table>
<thead>
<tr>
<th>Ref.</th>
<th>$m^*(0)$ ($m_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[12]</td>
<td>0.55</td>
</tr>
<tr>
<td>[13]</td>
<td>0.30</td>
</tr>
<tr>
<td>[14]</td>
<td>0.50 ± 0.05</td>
</tr>
<tr>
<td>[15]</td>
<td>0.35</td>
</tr>
<tr>
<td>[16]</td>
<td>0.14</td>
</tr>
<tr>
<td>[17]</td>
<td>0.35</td>
</tr>
<tr>
<td>[18]</td>
<td>0.297</td>
</tr>
<tr>
<td>[19]</td>
<td>0.21 ± 0.03*</td>
</tr>
<tr>
<td>[20]</td>
<td>0.22</td>
</tr>
<tr>
<td>[21]</td>
<td>0.30 ± 0.03</td>
</tr>
<tr>
<td>This work</td>
<td>0.18 ± 0.02</td>
</tr>
</tbody>
</table>

As demonstrated for other materials, the analysis of the DF in the mid-infrared (IR) yields the frequencies of transverse optical (TO) phonons and the plasmon excitation with highest accuracy [31,32]. From the latter, the electron effective mass and mobility as a function of carrier density are deduced [33,34]. Band gaps and effective Burstein-Moss shift are obtained by a line-shape fitting of the visible to ultraviolet data [18,31,35].

This manuscript is organized as follows. In Sec. II experimental methods and studied samples are introduced. Sec. III presents experimental results and discusses the data. First, experimental data is shown before a model for the infrared optical response of In$_2$O$_3$ is introduced, which is used to analyze the data (Secs. IIIA and IIIB). This analysis yields effective electron masses as a function of the free electron concentration. In Sec. IIID experimental data and a corresponding model for the ultraviolet spectral region are presented. From this starting point the quantitative description of the energy position of the absorption onset is developed (Sec. IIIE) before the summary in Sec. IV.

II. SAMPLES AND EXPERIMENTAL DETAILS

In this study 17 samples were included. All of the samples are cubic bixbyite In$_2$O$_3$ in its crystalline form, i.e., either bulk samples or epitaxially grown samples on foreign substrates. Three bulk In$_2$O$_3$ single crystals grown from the melt by so-called levitation-assisted self-seeding crystal growth [9] spanned an electron concentration range from 3.7×10$^{17}$ to 4.8×10$^{19}$ cm$^{-3}$. To obtain these electron concentrations, crystals of size of larger than 5×5×0.5 mm$^3$ with (111) surface were prepared and annealed either in an oxidizing atmosphere at temperatures of 1000–1100°C for 20–40 h or in oxidizing and next in reducing atmosphere containing hydrogen at 375°C for 10 h. Details about influence of annealing on melt-grown In$_2$O$_3$ at different atmospheres, temperatures, and times are published elsewhere [36]. The full width at half maximum (FWHM) of the rocking curves of (222) reflexes was 35–50 arc sec. The investigated crystal samples were epi-ready polished.

Epitaxial, continuous In$_2$O$_3$ thin films were grown by plasma-assisted molecular beam epitaxy at substrate temperatures in the range of 600–700°C. Single-crystalline, (001) oriented films were realized on (001) oriented yttria-stabilized zirconia (YSZ) substrates as described in Refs. [37,38]. Textured (111) and (001) oriented films with two and three rotational domains, respectively, were realized on c-plane sapphire substrates, i.e., Al$_2$O$_3$ (0001). The formation of the (111) orientation has been rationalized in Ref. [39] by domain matching, whereas the (001) oriented formation of our highly Sn-doped films (samples 11–17) is likely an effect of the lowered (001) surface tension by the Sn-doping as discussed in Refs. [11] and [40]. The structural quality of all films, gauged by the symmetric out-of-plane x-ray diffraction (004) and (222) ω-rocking curves FWHM of 470–1200 arc sec, was

![FIG. 1. Sketch of the band structure of bixbyite In$_2$O$_3$ in the vicinity of the Γ point of the Brillouin zone. The band structure is discussed to be indirect with the valence band maximum at $k \neq 0$ on the Γ–H line. The onset of strong absorption (represented by the vertical blue arrow for a selected Fermi energy $E_F$) originates from transitions from a lower valence band to the conduction band with its minimum at $k = 0$. These bands are marked in red. Energy values, number, and masses of valence bands are chosen arbitrarily. For a detailed calculated band structure please follow Refs. [22] or [30].](image-url)
higher than that of polycrystalline films and lower than that of bulk single crystals.

The wide range of electron concentrations was covered by unintentionally doped (UID) films [41] for electron concentrations below $10^{18}$ cm$^{-3}$ and Sn-donor-doped films for higher electron concentrations [11]. Annealing treatments in oxygen or vacuum allowed to further decrease or increase the electron concentration, respectively, in the UID and the Sn-doped samples [11,41,42].

The free-electron densities of all samples were determined by Hall-effect measurements in van der Pauw geometry. A comprehensive summary of fundamental data on all samples is presented in Table II. The Hall scattering factor $r_{\text{Hall}}$ was taken into account in these experiments, yielding real carrier concentrations $n_{\text{Hall}}$ and drift mobilities $\mu_D$ [21].

Two different spectroscopic ellipsometers were employed for studying the optical properties. In the infrared spectral range (from 300 cm$^{-1}$ to 6000 cm$^{-1}$), a Woollam IR-VASE based on Fourier transform spectrometry was used, while in the visible and ultraviolet spectral range (from 0 to 6.5 eV) a Woollam VASE equipped with autoretarder was employed. Note that the spectral ranges of both instruments overlap. The ellipsometric parameters $\Psi$ and $\Delta$ were recorded at multiple angles of incidence in order to increase the reliability of the obtained DFs. Then multilayer modeling of ellipsometric data yielded dielectric functions [43]. Surface roughness (atomic force microscopy showed root-mean-square values <3 nm for all samples) was modeled using the Bruggeman effective medium approximation. This low refractive index layer accounts also for the surface electron accumulation layer [10,44] as demonstrated previously for cubic and hexagonal InN [31,45]. Therefore, the obtained point-by-point (pbp) DFs represent the optical response of the bulk-like part of the samples. In the primary step, $\varepsilon_1$ and $\varepsilon_2$ were fitted at each wave number (photon energy) [46]. Kramers-Kronig consistency of pbp DFs was checked separately. However, in a second step, these pbp DFs were analyzed by model functions as introduced below in order to determine characteristic frequencies and/or band structure properties.

### III. RESULTS AND DISCUSSION

#### A. Infrared dielectric response

Prior to showing experimental pbp results, the used model is introduced. We analyze the dielectric function of In$_2$O$_3$ in the infrared, consisting of three different contributions: one for infrared active phonons, a second one accounting for free carriers, and finally one describing the dispersion of excitations in the ultraviolet [47,48]. This means we replace the assumption of a constant background high-frequency constant $\varepsilon_{\infty}$ by a quantitatively determined dispersion. For the phonon contributions we use a sum of Lorentzian oscillators,

$$
\varepsilon_{\text{photon}}(\omega) = \sum_i \frac{A_i \omega_{\text{TO},i}^2}{\omega^2 - \omega_{\text{TO},i}^2 - i \omega \gamma_{\text{TO},i}},
$$

where $A_i$ is the amplitude, $\gamma_{\text{TO},i}$ the broadening parameter, and $\omega_{\text{TO},i}$ the resonance wave number of the $i$th phonon. In In$_2$O$_3$ 16 infrared active phonons are predicted from symmetry considerations [49,50]. For the free-carrier contribution to the dielectric function, the Drude model is used, which reads

$$
\varepsilon_{\text{Drude}}(\omega) = -\frac{\omega_p^2}{\omega^2 + i \omega \gamma_p} = -\frac{\omega_p^2}{\omega^2 + \gamma_p^2} + i \frac{\omega_p^2 \gamma_p}{\omega (\omega^2 + \gamma_p^2)},
$$

where $\omega_p$ is the plasma frequency, $\gamma_p$ the corresponding broadening parameter, and $\varepsilon_{\infty}$ the high-frequency constant. The plasma frequency $\omega_p$, and corresponding broadening parameter $\gamma_p$ were determined from model fits to ellipsometric data. Accuracies are ±5% for $n_{\text{Hall}}$ and $\mu_D$, ±5 cm$^{-1}$ for $\omega_p$, and ±2 nm for $\delta$. For the broadening parameter $\gamma_p$ we estimate an accuracy of ±20 cm$^{-1}$.  

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>$d$ (nm)</th>
<th>$n_{\text{Hall}}$ (cm$^{-3}$)</th>
<th>$\mu_D$ (cm$^2$/Vs)</th>
<th>$\omega_p$ (cm$^{-1}$)</th>
<th>$\gamma_p$ (cm$^{-1}$)</th>
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<td>3.7 × 10$^{17}$</td>
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<td></td>
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<td>bulk</td>
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<td>365</td>
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<tr>
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<td></td>
</tr>
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<td>YSZ</td>
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<td>Al$_2$O$_3$</td>
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<td>12</td>
<td>Al$_2$O$_3$</td>
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<td>2.3 × 10$^{20}$</td>
<td>37</td>
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<td>638</td>
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<tr>
<td>13</td>
<td>Al$_2$O$_3$</td>
<td>377</td>
<td>2.3 × 10$^{20}$</td>
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<td>14</td>
<td>Al$_2$O$_3$</td>
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<td>3.1 × 10$^{20}$</td>
<td>46</td>
<td>9752</td>
<td>643</td>
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<tr>
<td>15</td>
<td>Al$_2$O$_3$</td>
<td>403</td>
<td>5.3 × 10$^{20}$</td>
<td>49</td>
<td>11905</td>
<td>524</td>
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<tr>
<td>16</td>
<td>Al$_2$O$_3$</td>
<td>380</td>
<td>5.4 × 10$^{20}$</td>
<td>52</td>
<td>12188</td>
<td>504</td>
</tr>
<tr>
<td>17</td>
<td>Al$_2$O$_3$</td>
<td>298</td>
<td>1.2 × 10$^{21}$</td>
<td>39</td>
<td>15523</td>
<td>497</td>
</tr>
</tbody>
</table>
Here, $\gamma_p$ is the broadening parameter and $\omega_p$ the unscreened plasma frequency:

$$\omega_p = \sqrt{\frac{ne^2}{\varepsilon_0 m^*(n)}}. \quad (4)$$

$\omega_p$ is only dependent on the free carrier density $n$, $e$ is the elementary charge, $\varepsilon_0$ the dielectric constant of vacuum, and $m^*(n)$ the effective electron mass which also depends on $n$. Note, that Eqs. (2) and (3) do not contain the dielectric limit usually labeled $\varepsilon_\infty$. We argue that a constant value for $\varepsilon_\infty$ is not meaningful in infrared analysis, as the dispersion $\varepsilon_1(\omega)$ influences the results in the infrared considerably, especially for very high plasma frequencies related to the high carrier concentrations of some of our samples. A graphical representation of our model is presented in Fig. 2 in comparison to a model with constant $\varepsilon_\infty$.

To describe the dispersion of $\varepsilon_1(\omega)$ where $\varepsilon_2$ is zero (below $\hbar\omega \approx 3.75 \text{ eV}$), we make use of an empirical approach published earlier by Shokhovets and co-workers [47]:

$$\varepsilon_{\text{vis}}(\omega) = 1 + \frac{2}{\pi} \left( \frac{A_G}{2} \ln \frac{E_H^2}{E_{G,\text{avg}}^2} - \frac{\hbar \omega}{E_H^2} \right) + \frac{A_H E_H}{E_H^2 - (\hbar \omega)^2}, \quad (5)$$

where $A_G$ and $A_H$ are amplitude parameters, and $E_{G,\text{avg}}$ and $E_H$ energy parameters. Note, that the imaginary part of $\varepsilon_{\text{vis}}$ is zero. This equation does account for the sensitivity of $\varepsilon_1(\omega)$ on the position of the fundamental absorption onset, modeled here by $E_{G,\text{avg}}$. For the three bulk samples included in our study, the parameters converge to $A_G = 2.29$, $A_H = 25.06 \text{ eV}$, $E_{G,\text{avg}} = 3.76 \text{ eV}$, and $E_H = 8.3 \text{ eV}$. From these, we find $\varepsilon_\infty = (4.08 \pm 0.02)$ for intrinsic In$_2$O$_3$.

The full infrared model for the complex dielectric function then reads

$$\varepsilon_{\text{IR}}(\omega) = \varepsilon_{\text{phonon}}(\omega) + \varepsilon_{\text{Drude}}(\omega) + \varepsilon_{\text{vis}}(\omega). \quad (6)$$

Because the highest energy transverse optical phonon in In$_2$O$_3$ is at around 600 cm$^{-1}$ (Table III), the free-carrier contribution to the dielectric function $\omega_{\text{Drude}}(\omega)$ is not accurately detectable for low carrier densities ($n \approx 10^{19} \text{ cm}^{-3}$), i.e., low plasma frequencies $\omega_p$. We therefore limit the results for $\omega_p$ and $\gamma_p$ given in Table II to values where $\omega_p > 600 \text{ cm}^{-1}$.

Examples for the fits performed to analyze the ellipsometric parameters in the infrared spectral range are shown for three selected samples. Figure 3 presents data for the bulk (sample 1), for an epitaxial layer on yttria stabilized zirconia (sample 4), and for a layer on Al$_2$O$_3$ (sample 9). All three have low free electron concentrations and therefore are representative of the intrinsic material properties.

The corresponding extracted point-by-point fitted dielectric functions of these In$_2$O$_3$ samples are shown in Fig. 4. From the 16 predicted phonons only 8 are detectable in the frequency range investigated (Table III). The further modes that are not observable are expected for lower frequencies [49,51]. Irrespective of substrate material, for low or undoped samples the results are dominated by the contributions of transverse optical phonon modes $l = 2,3,5$. However, the much weaker phonon modes $l = 1,4,6,7,8$ are clearly visible in all point-by-point DFs.

The use of Eq. (6) to describe successfully the DF is justified exemplarily by Fig. 5 for sample 2. The sum of Lorentz oscillators and the Drude contribution describes the point-by-point fitted results almost perfectly.

For increased free-electron concentration, the phonon contributions of both the In$_2$O$_3$ thin film and the corresponding substrate (here, YSZ and sapphire) decrease in prominence. This is mainly related to the increasing free-electron absorption contribution mirrored mathematically by an increase of $\varepsilon_2$ in the Drude term for increasing $n$ (Eq. (3)). Additionally, scattering rates of phonons may increase for higher electron densities or doping concentrations, which leads to shorter phonon lifetimes and thus broadened and weakened phonon resonances. In point-by-point fitted dielectric functions, the phonon peaks are therefore not resolvable for very high $n$ (Fig. 6).

**TABLE III.** Transverse optical phonon frequencies and oscillator strengths found by model fitting to point-by-point dielectric functions by using Eq. (2). The results are given explicitly for the bulk sample 1. Given error values stem from comparison between undoped samples 1-4, and represent the maximum deviation from sample 1.

<table>
<thead>
<tr>
<th>$l$</th>
<th>$A_l$</th>
<th>$\gamma_{\text{TO},l}$ (cm$^{-1}$)</th>
<th>$\omega_{\text{TO},l}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.28 ± 0.11</td>
<td>6.8 ± 3.1</td>
<td>307.3 ± 1.6</td>
</tr>
<tr>
<td>2</td>
<td>1.58 ± 0.15</td>
<td>6.4 ± 0.4</td>
<td>327.3 ± 0.2</td>
</tr>
<tr>
<td>3</td>
<td>2.41 ± 0.23</td>
<td>6.0 ± 3.3</td>
<td>361.7 ± 0.6</td>
</tr>
<tr>
<td>4</td>
<td>0.08 ± 0.03</td>
<td>6.2 ± 2.2</td>
<td>386.2 ± 0.9</td>
</tr>
<tr>
<td>5</td>
<td>1.01 ± 0.15</td>
<td>6.3 ± 1.8</td>
<td>408.0 ± 1.0</td>
</tr>
<tr>
<td>6</td>
<td>0.06 ± 0.01</td>
<td>10.9 ± 1.4</td>
<td>534.1 ± 0.4</td>
</tr>
<tr>
<td>7</td>
<td>0.06 ± 0.01</td>
<td>8.8 ± 2.0</td>
<td>560.5 ± 0.8</td>
</tr>
<tr>
<td>8</td>
<td>0.06 ± 0.01</td>
<td>10.8 ± 2.5</td>
<td>595.5 ± 0.6</td>
</tr>
</tbody>
</table>

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**B. Effective electron mass**

Equation (6) is now applied to reproduce the parameter-free point-by-point dielectric functions presented in Fig. 6.
The most important parameters are therefore the free carrier density \( n \), which was taken from Hall effect experiments, and the effective electron mass \( m^*(n) \), which is the result of the analysis. Obtained values of \( m^*(n) \) are displayed in Fig. 7 as a function of \( n_{\text{Hall}} \). A systematic increase of effective electron masses with increasing carrier concentration is obvious. To understand this behavior, the relationship between effective mass and band dispersion must be accounted for. Generally, the reciprocal curvature of the band dispersion is expressed as effective mass:

\[
m^* = \frac{\hbar^2}{\delta^2 E(k)} \left( \frac{\delta^2 E(k)}{\delta k^2} \right)^{-1}.
\]  

Only for the special case of parabolic bands, i.e., \( E(k) \propto k^2 \), is the curvature constant, and thus the effective mass has a constant value as well. This assumption is generally valid only for a region close to the conduction band minimum. The doping levels investigated here shift the Fermi energy to values high above the conduction band minimum, where the conduction band cannot be described as parabolic anymore. This is known as conduction band nonparabolicity. To mathematically describe a nonparabolic band dispersion, several attempts can be found in the literature [52,53].

A suitable model to approximate the nonparabolic conduction band shape suggests expressing the relationship between energy and momentum as [53]

\[
E(k) + C E(k)^2 = \frac{\hbar^2 k^2}{2m_0^*}.
\]  

where \( C \) is an empirical material system dependent parameter and \( m_0^* \) is the effective electron mass at the conduction band minimum. The effective mass is derived by dividing
momentum by group velocity,

\[ m^*(k) = \frac{\hbar^2 k}{\delta E(k)/\delta k}. \quad (9) \]

which yields

\[ m^*(k) = m^*_0(1 + 2CE(k)). \quad (10) \]

In the framework of our study it is important to write Eq. (10) as a function of the electron density and not as function of wave vector. Therefore, a relationship between \(E(k)\) and \(n\) has to be found. This is obtained by integrating over the density of states approximating the Fermi-Dirac distribution by a step function. One obtains

\[ m^*(n) = \sqrt{m^*0^2 + 2C\hbar^2 m^*_0(3\pi^2n)^{2/3}}. \quad (11) \]

Equation (11) is fitted to the experimental effective electron mass values (Fig. 7), yielding the parameters \(m^*_0 = 0.18m_0\) and \(C = 0.5\text{ eV}^{-1}\). Possible sources of error include the accuracy of Hall effect carrier densities (±5%) and the determined value of \(\omega_p\) (estimated to be ±5 cm\(^{-1}\)). Together with the multisample fitting procedure, this yields overall errors of ±0.02\(m_0\) for \(m^*_0\) and ±0.02 eV\(^{-1}\) for \(C\).

\[ \gamma = -\frac{\omega\varepsilon_2\text{Drude}}{\varepsilon_1\text{Drude}}. \quad (12) \]

Using point-by-point fitted dielectric functions in Eq. (12), a possible frequency dependency of \(\gamma\) should be observable. We limited the analysis to the spectral range 700 < \(\omega\) < 6000 cm\(^{-1}\). At lower frequency the influence of phonons dominates, while at higher frequencies the influence of the dispersion of \(\varepsilon_1(\omega)\) increases. This dispersion stems from interband contributions to the dielectric function and has been already discussed in the context of Fig. 2. To separate \(\varepsilon_1(\omega)\text{Drude}\) from measured \(\varepsilon_1(\omega)\) we therefore used

\[ \varepsilon_1\text{Drude}(\omega) = \varepsilon_1(\omega) - \varepsilon_\text{vis}(\omega), \quad (13) \]

with \(\varepsilon_\text{vis}(\omega)\) as given by Eq. (5) for each sample. Results for samples 14 and 17 are shown exemplarily in Fig. 8. The plasma broadening parameter \(\gamma_p\) is for a wide frequency range independent on the frequency; or in other words, the simple Drude model is valid for our samples. Deviations at higher frequencies in Fig. 8 result from higher influence of \(\varepsilon_\text{vis}(\omega)\) and lower absolute values of \(\varepsilon_1\text{Drude}(\omega)\) and \(\varepsilon_2\text{Drude}(\omega)\) at the same time. The comparison of –1600\(\varepsilon_1\text{Drude}\) and \(\omega\varepsilon_2\text{Drude}\) derived from point-by-point data and directly calculated after the Drude model is shown in Fig. 8. The factor –1600 is only used to scale \(\varepsilon_1\text{Drude}\) into the same region as \(\omega\varepsilon_2\text{Drude}\) for plotting. The validity of the Drude model is obvious as well from the agreements of point-by-point and model data.

The broadening parameter of the free carrier contribution \(\gamma_p\) in Eq. (3) is related to the mobility of the charge carriers by [54]

\[ \gamma_p = \frac{e}{\mu \hbar}, \quad (14) \]
where the mobility is assumed to follow a constant free-charge scattering and therefore is identical to the inverse momentum scattering time of the carriers [54]. Analyzing this relationship for our set of samples requires knowledge of the effective electron mass for each individual sample. The good agreement for our set of samples requires knowledge of the effective parameter \( \gamma \) which are unintentionally doped or low doped. Deviating data points basically stem from samples 2 and 10 (see Table II) which are unintentionally doped or low doped. Thus for these samples the experimental error in determining a reliable broadening parameter is large.

D. Visible and ultraviolet spectral region

In the visible and ultraviolet part of the spectrum (between 0.5 and 6.5 eV) ellipsometric parameters \( \Psi \) and \( \Delta \) are modeled similarly to the analysis of the infrared spectral region by point-by-point fits. Therefore, the dielectric functions of the substrate materials (no substrate for bulk samples, Al\(_2\)O\(_3\) [55], or YSZ [56]), layer thicknesses, and surface roughness had to be taken into account. Finally we are able to reproduce the experimental data very well, yielding dielectric functions of In\(_2\)O\(_3\). Example fits to ellipsometric data for two different samples are shown in Fig. 10.

All dielectric functions are summarized in Fig. 11 in the spectral range between 0.5 and 6.5 eV for different samples as a function of free-electron concentration. For very low photon energies, the influence of free carrier absorption is obvious, as discussed above in great detail. The other prominent feature is the shift of the absorption onset to higher photon energies with increasing \( n \).

To quantitatively analyze the obtained dielectric functions, Elliott’s theory [57] was modified to match the current case. Therefore, \( \varepsilon_2(\hbar\omega) \) of each sample was fitted by a sum of two or three different contributions. For samples below \( \approx 10^{19} \text{ cm}^{-3} \) electron density, an exciton contribution was taken into account by the equation

\[
\varepsilon_2^X(\hbar\omega) = \frac{C_X}{\gamma_X \hbar\omega} \exp \left( -\frac{(\hbar\omega - E_g + E_{b,X})^2}{\gamma_X^2} \right),
\]

and the corresponding exciton continuum was modeled by

\[
\varepsilon_2^{\text{cont.}}(\hbar\omega) = \frac{C_X}{\hbar\omega} \frac{1 + \text{erf} \left( \frac{\hbar\omega - E_g}{\gamma_X} \right)}{1 - \exp \left( -2\pi r \frac{E_{b,X}}{|\hbar\omega - E_g|} \right)}. \tag{16}
\]

FIG. 10. Measured (black continuous curves) and modeled (red/blue dashed curves) ellipsometric angles \( \Psi \) and \( \Delta \) for different angles of incidence (46°/53° up to 74° in steps of 7°) of sample 11 (bottom) with \( n = 2.2 \times 10^{20} \text{ cm}^{-3} \) and sample 15 (top) with \( n = 5.3 \times 10^{20} \text{ cm}^{-3} \) on sapphire. Near perfect agreement is obtained.

FIG. 8. Frequency dependence of the plasma broadening parameter \( \gamma \) determined by point-by-point fitted dielectric functions (black). Shown are results for samples 14 and 17. Within accuracy, no frequency dependence of \( \gamma \) is found. The real (red, continuous curve) and imaginary (blue, continuous curve) parts of the point-by-point dielectric functions multiplied by \( -1600 \) and \( \omega \), respectively, are shown as dotted curves.

FIG. 9. Broadening parameter of the free carrier contribution \( \gamma_0 \) taken from the model as a function of the inverse of Hall mobility multiplied by the effective electron mass. The dashed line corresponds to the expectation from Eq. (14).
Here, $C_X$ and $C_g$ are amplitude factors of exciton and continuum, respectively. $\gamma_X$ and $\gamma_g$ are broadening factors. $E_g$ is the characteristic energy of the direct and dipole-allowed transition mainly contributing to the absorption onset around 3.8 eV. $E_{b,X}$ is the exciton binding energy of In$_2$O$_3$ where the excitons consist of electrons from the conduction band minimum and holes from the valence band which contribute to this absorption onset. No unambiguous value for $E_{b,X}$ can be found in the literature. Most studies tackling this subject are based on photoluminescence data of nanostructured In$_2$O$_3$ material which shows luminescence peaks suggesting that these samples are contaminated by unintentional presence of ZnO. We estimate an exciton binding energy by effective mass theory of $E_{b,X} \approx 31$ meV when approximating the reduced effective mass by the zero-density electron effective mass, an approach which will be justified later (Sec. III E). Line-shape fitting to dielectric functions yielded slightly higher values for $E_{b,X}$. However, the onset of continuum absorption $E_g$ is insensitive to the choice of $E_{b,X}$, which was tested systematically by variations in the fitting procedure.

For samples with electron density above $10^{19}$ cm$^{-3}$, the exciton contribution was omitted ($C_X = 0$) as high carrier densities are expected to screen the Coulomb interaction mediating exciton formation. Therefore, we modified Eq. (16) for this case to

$$\varepsilon_2^{\text{cont}}(\hbar\omega) = \frac{C_g}{\hbar\omega} \left[ 1 + \frac{1}{\gamma_g}(\hbar\omega - E_g)\right].$$

Finally, to model the weak absorption contributions we use

$$\varepsilon_2^{\text{ind}}(\hbar\omega) = \frac{C_{\text{ind}}}{\hbar\omega} \left( \hbar\omega - E_g^{\text{ind}} \right)^2 \Theta(\hbar\omega - E_g^{\text{ind}}).$$

Here, $\Theta$ is a Heaviside (step) function, $C_{\text{ind}}$ is an amplitude factor, and $E_g^{\text{ind}}$ is the fundamental band gap energy. Equation (18) is utilized to represent all further contributions stemming from transitions below the strong absorption onset around 3.8 eV. This might include the indirect fundamental band gap, further valence bands, and absorption at higher momentum. The weak increase of experimentally observed absorption below $\approx 3.8$ eV does not allow us to unambiguously deconvolve its origins. The prefactor in Eqs. (15) to (18) is $1/(\hbar\omega)^2$, in contrast to classical Elliott’s theory where it is $1/(\hbar\omega)^4$. This modification was developed earlier to account for nonparabolic band structures [58].

The imaginary part of the dielectric function therefore is written as

$$\varepsilon_2(\hbar\omega) = \varepsilon_2^{\text{ind}}(\hbar\omega) + \varepsilon_2^{\text{X}}(\hbar\omega) + \varepsilon_2^{\text{cont}}(\hbar\omega).$$

Example fits to two imaginary parts of dielectric functions of differently high doped samples are presented in Fig. 12. The obtained values for $E_g(n)$ are then used for further analysis as explained in the next section.

### E. Shift of the absorption onset

The analytical expression [53] for the effective electron mass [Eq. (11)] is now used to calculate the expected Burstein-Moss shift in the conduction band, i.e., the position of the Fermi energy above the conduction band minimum, which is

$$\Delta E_{\text{BMS}}(n) = \frac{1}{2C} \left( \sqrt{1 + 2C \frac{\hbar^2}{m^*_e} (3\pi^2 n)^{2/3}} - 1 \right).$$

To estimate the band gap renormalization, i.e., the reduction of the band gap due to exchange interaction, the input parameters effective Bohr radius, Fermi vector, and Thomas-Fermi screening length have to include the carrier dependent

![FIG. 11. Point-by-point fitted dielectric functions in the visible and ultraviolet spectral range. The free-carrier concentration is mirrored by the color of the curves. At low photon energies the influence of free carriers is clearly visible. Furthermore, the absorption onset blue-shifts systematically with increasing free-electron concentration.](image)

![FIG. 12. Imaginary parts of dielectric functions for samples 1 and 11 with free electron densities of $n = 3.7 \times 10^{17}$ cm$^{-3}$ and $2.2 \times 10^{20}$ cm$^{-3}$, respectively. The decomposition into the different contributions constituting the direct absorption edge is shown for both cases: pbp represents the point-by-point fitted result from experimental data analysis, indirect $\varepsilon_2^{\text{ind}}$, exc. $\varepsilon_2^{\text{exc}}$, direct $\varepsilon_2^{\text{cont}}$, and “sum” denotes the added-up contributions. The vertical arrow marks the energy of the direct absorption onset, i.e., the characteristic energy of $\varepsilon_2^{\text{cont}}$.](image)
effective mass as well. Thus the effective Bohr radius is in our case
\[ a^*(n) = \frac{4\pi \varepsilon_0 \varepsilon_S \hbar^2}{e^2 m_0 \sqrt{m_0} + 2C \hbar^2 m_0^2 (3\pi^2 n)^{2/3}}. \] (21)
the Fermi vector
\[ k_F(n) = \sqrt{2m_0 m^*(n) \Delta E_{BMS}(n) / \hbar^2} \] (22)
\[ = \left[ \frac{m_0}{\hbar^2 C} \sqrt{m_0^2 + 2C \hbar^2 m_0^2 (3\pi^2 n)^{2/3}} \right]^{-1/2}, \] (23)
\[ \times \left( 1 + 2C \frac{\hbar^2}{m_0^2 (3\pi^2 n)^{2/3}} - 1 \right)^{1/2}, \] (24)
and for the Thomas-Fermi screening length the approximate dependence on the Fermi vector is used:
\[ k_{TF}(n) = \frac{4k_F(n)}{\pi a^*(n)}. \] (25)
Here, \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon_S \) the static dielectric constant of In\(_2\)O\(_3\) which equals 8.9 [7], and \( e \) is the elementary charge.

The band gap renormalization mainly consists of the sum of electron-electron interaction (\( \Delta E_{ee} \)) and electron-ion interaction (\( \Delta E_{ai} \)). Both contributions are estimated in their usual form [59,60] but accounting for carrier density dependent parameters:
\[ \Delta E_{ee}(n) = -\frac{e^2 k_F(n)}{2\pi^2 \varepsilon_0 \varepsilon_S} \arctan \left( \frac{k_F(n)}{k_{TF}(n)} \right), \] (26)
\[ \Delta E_{ai}(n) = -\frac{e^2 n}{\varepsilon_0 \varepsilon_S a^*(n) k_{TF}(n)^3}, \] (27)
\[ \Delta E_{BGR}(n) = \Delta E_{ee}(n) + \Delta E_{ai}(n). \] (28)

In Fig. 13, energy differences of the different contributions to \( \Delta E_{BGR} \) are shown as a function of free electron concentration in comparison to experimentally derived absorption onsets. It can be clearly seen that \( \Delta E_{BMS}(n) \) overestimates the observed shift, and only its summation with the band gap renormalization is able to explain the experimental findings. The overall dependence of absorption onset on free electron density is thus
\[ E(n) = 3.8\text{eV} + \Delta E_{BMS}(n) + \Delta E_{BGR}(n). \] (29)
where the constant value of 3.8 eV accounts for the zero density absorption onset of In\(_2\)O\(_3\). For the description of the absorption onset in Fig. 13, it is very important to take the the nonparabolicity of the conduction band into account. To show this clearly, we present in Fig. 13 additionally Burstein-Moss shift and band gap renormalization for the case when the conduction band is assumed to be parabolic with constant \( m^* = 0.18m_0 \). This means that \( C = 0 \) and Eqs. (8)–(28) can be written in a simpler form explicitly given already in Ref. [35]. However, a parabolic conduction band cannot describe the experimental results for \( n > 5 \times 10^{19} \text{cm}^{-3} \). In the parabolic case, the conduction band curvature clearly leads to too high transition energies from the Burstein-Moss shift, which cannot be balanced by the band gap renormalization in this case. This is true even when considering the fact that the band gap renormalization effect is stronger in the parabolic case. Note that for the description of the Burstein-Moss shift in both cases, parabolic and nonparabolic, we did not take the contribution from the valence band into account. This approximation is justified, considering the curvatures of valence bands in comparison to the conduction band in calculated band structures [22]. Neglecting the valence band contribution is synonymous to assuming an infinite hole mass, which is sensible for the very weak effective hole dispersions predicted [22,61] and found experimentally [62].

IV. SUMMARY

We have investigated the optical properties of cubic In\(_2\)O\(_3\) in its crystalline form by means of spectroscopic ellipsometry. Dielectric functions for the spectral range from the phonon range up to the ultraviolet were obtained. By analyzing the free-carrier contribution with a Drude model and comparison to Hall-effect measurements, we determined the effective electron mass as a function of electron concentration. A zero-density effective electron mass of \( m^* = 0.18m_0 \) was found, while for \( n > 5 \times 10^{19} \text{cm}^{-3} \) the nonparabolic curvature of the conduction band is very pronounced, resulting in an effective mass of \( m^* = 0.40m_0 \) at \( n = 10^{22} \text{cm}^{-3} \), e.g., valid for ITO.

In the same set of samples, we recorded the absorption onset of In\(_2\)O\(_3\) being strongly dependent on free-electron density. The shape of the imaginary part of the dielectric function was described by Elliott’s model taking Coulomb interaction into account. A shift to higher absorption onset energies with increasing electron densities was explained by the interplay
of Burstein-Moss shift and band gap renormalization when taking the band nonparabolicity into account. The very good agreement of our model and the experimental data independently corroborates the effective electron mass data obtained by infrared data.

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[56] The dielectric function of yttria stabilized zirconia relies on our own experimental analysis of reference substrate material up to 10 eV (unpublished).