

Quantification of the strong, phonon-induced Urbach tails in β -Ga₂O₃ and their implications on electrical breakdown

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Abstract

In ultrawide bandgap (UWBG) nitride and oxide semiconductors, increased bandgap (E_g) correlates with greater ionicity and strong electron-phonon coupling. This limits mobility through polar optical phonon scattering, localizes carriers via polarons and self-trapping, broadens optical transitions via dynamic disorder, and modifies the breakdown field. Herein, we use polarized optical transmission spectroscopy from 77-633 K to investigate the Urbach energy (E_u) for many orientations of Fe- and Sn-doped β -Ga₂O₃ bulk crystals. We find E_u values ranging from 60-140 meV at 293 K and static (structural defects plus zero-point phonons) disorder contributes more to E_u than dynamic (finite temperature phonon-induced) disorder. This is evidenced by lack of systematic E_u anisotropy, and E_u correlating more with X-ray diffraction rocking-curve broadening than with Sn-doping. The lowest measured E_u are $\sim 10\times$ larger than for traditional semiconductors, pointing out that band tail effects need to be carefully considered in these materials for high field electronics. We demonstrate that, because optical transmission through thick samples is sensitive to sub-gap absorption, the commonly-used Tauc extraction of bandgap from transmission through Ga₂O₃ > 1-3 μm thick is subject to errors. Combining our $E_u(T)$ from Fe-doped samples with $E_g(T)$ from ellipsometry, we extract a measure of an effective electron-phonon coupling indicating increases in weighted 2nd order deformation potential with temperature and a larger value for $E_{||b}$ than $E_{||c}$. The large electron-phonon coupling in β -Ga₂O₃ suggests that theories of electrical breakdown for traditional semiconductors need expansion to account not just for lower scattering time but also for impact ionization thresholds fluctuating in both time and space.

Keywords: ultrawide bandgap semiconductors, Ga₂O₃, Urbach tails, optical spectroscopy, electrical breakdown

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Introduction

Gallium oxide (Ga_2O_3) is a promising material for next-generation high-power electronics due to its ultrawide wide bandgap (UWBG), expected high breakdown field, and ability to be grown from the melt as well as epitaxially using multiple processes. Ga_2O_3 has many polytypes; among them, $\beta\text{-Ga}_2\text{O}_3$ is thermodynamically stable at ambient conditions and has bandgap (E_g) estimated to be near 4.8-4.9 eV. Its high melting point near 1800 °C, and strong bonding suggests $\beta\text{-Ga}_2\text{O}_3$ for power electronic devices in extreme conditions including e.g. high voltages, high temperatures, or radiation ¹. High breakdown field (E_{cr}) enables higher-efficiency power devices through Baliga's Figure of Merit which scales as E_{cr}^2 or E_{cr}^3 depending on vertical or lateral device geometry. E_{cr} scales empirically as $\sim E_g^2$ for conventional semiconductors, which led to the suggestion that E_{cr} for Ga_2O_3 may be near 8 MV/cm [2,3] or ~ 2 times higher than conventional WBG materials like GaN, SiC, or ZnO with $E_g=3.2\text{-}3.4$ eV ²⁻⁴. Detailed calculations taking into account phonon and electronic band structures of $\beta\text{-Ga}_2\text{O}_3$ predict anisotropic E_{cr} 5.5-7 MV/cm or 5.8 MV/cm ^{5,6}. These papers only considered scattering in momentum space which would tend to suppress carrier acceleration to energies sufficient for impact ionization, but not static and dynamic disorder leading to fluctuating band structure which might be expected to lower the ionization threshold energy. The balance of these effects is difficult to predict a-priori and thus warrants future investigation.

It is well-known that the optical absorption transitions in monoclinic $\beta\text{-Ga}_2\text{O}_3$ are anisotropic; the threshold energies for carrier generation using linearly polarized light depend on crystallographic direction. In a perfect crystal, the onset of a direct optical transition with photon energy would be quite sharp. Disorder, any departure from perfect periodicity, causes a distribution of bandgaps; a missing, extra, or displaced atom at any point changes the local bandgap. Static disorder causes a time-independent, spatially varying bandgap distribution while atoms' random thermal motion due to phonons changes atom positions and thus bandgap dynamically in space and time. The same electron-phonon coupling responsible for the strong polar optical phonon scattering that limits carrier mobility ⁷⁻⁹ mediates this variation in bandgap. Because optical transitions occur much faster than phonon vibrations, each photon absorption is like a snapshot in time of the dynamic disorder.

This phenomenon of phonon-induced exponential bandgap distributions was first observed by Urbach in silver halides and Martienssen in alkalides^{10,11}. The static component of disorder is caused by distributions in bond geometry (non-uniform strain) and any non-periodicity of the crystal from random alloying, point defects, extended structural defects, and in the extreme case, amorphous structure¹². The nature and concentration of imperfections directly influence the slope and magnitude of the Urbach tails^{13,14}. In contrast, dynamic disorder is temperature-dependent and increases with phonon populations as temperature increases. The electron-phonon interaction is the origin of this phenomenon, although the exact details of coupling to each phonon mode are rather complex^{15–18}.

The basic concept of Urbach tails is familiar; that the joint density of states (and thus α) near the bandgap increases exponentially with photon energy $h\nu$ rather than e.g. $\sqrt{h\nu - E_g}$ as expected for isotropic 3D bands. At fixed temperature, Urbach tails follow $\alpha(E) \propto \exp\left(\frac{h\nu - E_g}{E_u}\right)$, but this does not take into account the temperature dependencies of E_g or E_u . Urbach's rule actually goes further; like the Meyer-Neldel rule for Arrhenius processes^{19,20} that relates prefactors to activation energies, Urbach's rule states that linear fits of $\ln(\alpha)$ vs. $h\nu$ for different temperatures all intersect in one focus point (E_o, α_o):²¹

$$\alpha = \alpha_0 \exp \frac{\sigma(T) (h\nu - E_o)}{k_B T} \quad (1)$$

In the above, E_u is the Urbach energy (which is distinct from E_g), $\sigma(T)$ is the dimensionless temperature dependent steepness parameter, and $E_u(T) = \frac{k_B T}{\sigma(T)}$. The underlying physics embedded in Urbach's rule is that $E_g(T)$ and $E_u(T)$ change together; for most semiconductors E_g decreases with temperature while E_u increases in such a way to maintain a single focus point. The covariance of $E_u(T)$ and $E_g(T)$ is rooted in the fact that both are related to phonons through the electron-phonon interaction, but the dependence is not trivial²². One important point to bear in mind is that measured E_u values result from the combination of disorder in the valence and in the conduction band and it is expected that $E_{u,tot}^2 = E_{u,CB}^2 + E_{u,CB}^2$.

When a single phonon mode of energy $\hbar\omega$ dominates $E_u(T)$, the steepness parameter σ in equation (2) follows the relation

$$\sigma(T) = \sigma_0 \frac{2k_B T}{\hbar\omega} \tanh\left(\frac{\hbar\omega}{2k_B T}\right) \quad (2)$$

In which σ_0 is a constant independent of temperature. The dominant modes may be different in different materials; for example transverse optical (TO) in CdSe and transverse acoustic (TA) in CdS²³. In the current case of the anisotropic, multimodal phonon structure in monoclinic β -Ga₂O₃, presumably multiple modes will contribute for each incident light polarization, but to our knowledge this has not been computed to date. From optical measurements on β -Ga₂O₃, only an effective or averaged mode would be extractable from $E_u(T)$. The model leading to Equation (2) takes into consideration linear interactions between excitons and phonons and assumes a simplified, dispersion less optical phonon mode²². It is noteworthy that σ_0 is inversely related to the electron-phonon coupling strength; since this is strong in β -Ga₂O₃, we expect σ_0 to be rather small. The temperature dependence of E_g is usually explained as arising from anharmonicity of the lattice leading to thermal expansion which in turn reduces wavefunction overlap as the unit cell expands. However in β -Ga₂O₃ it has been shown that the electron phonon coupling is strong enough that displacements within the unit cell caused by temperature-dependent superpositions of phonons also contributes significantly²⁴.

Experimental

We measured optical transmission across a range of Fe-doped and Sn-doped β -Ga₂O₃ samples. Sn-doped samples >500 μ m thick (data was normalized to the actual thickness for each sample) grown using edge-fed growth (EFG) were obtained from Novel Crystal Technologies (NCT) oriented in the (001), (010), and (-201) directions. These were polished by on both sides by NCT except for the (010) for which we polished the back side to optical flatness. A (100)-oriented piece of a Fe-doped crystal grown by Synoptics using Czochralski (CZ) pulling along the (010) direction was meticulously cleaved using razor blades to a final thickness of 109 μ m and 330 μ m. All visible thickness steps were removed from both surfaces over an area larger than the measurement beam size and the 109 μ m sample used for temperature dependent measurements. Additionally, we measured a 36 mm long, 6 mm diameter rod cored from the same crystal and optically-polished on both of its (010) ends. We also obtained a (010) unintentionally-doped (UID) wafer from Synoptics and polished both sides using a 240-grit SiC pad followed by Al₂O₃ grits down to 0.3 μ m then final CMP using 0.050 μ m colloidal silica. We measured the Fe-doped (100)

β -Ga₂O₃ samples from 240 to 500 nm using a Hitachi U-4100 spectrophotometer equipped with an integrating sphere detector and a Rochon prism polarizer. We built a custom, short bore 1” diameter furnace and the actual temperature of the sample using a thermocouple in contact with the sample before commencing measurements. To ensure accuracy, we averaged multiple measurements for high signal-to-noise ratio at low transmitted intensity. Sn-doped and UID β -Ga₂O₃ samples were measured from 240 to 800 nm in a Perkin Elmer Lambda 900 spectrophotometer with broadband polarizer and integrating sphere detector. Extensive details of the data processing used to convert transmission data to absorption coefficient are given in the supplementary material.

Results and Discussion

Figure 1 presents the room temperature absorption coefficient for E||b derived from ellipsometric measurements in ²⁵ presented alongside data obtained in this study from a cleaved sample of 330 μ m thick from a Fe-doped (100) boule grown by Synoptics. While ellipsometry can measure the precise critical point energies, it cannot accurately measure the weak absorption from band tails because of limited dynamic range. Note that the extracted absorption coefficient greatly exceeds the values measurable with optical transmission using samples of a few-hundred μ m thickness. Conversely, Tauc plot analysis typically applied to absorption data²⁶ relies on measuring absorption at energies $>E_g$ corresponding to absorption coefficients $\alpha \gtrsim 10^4 \text{ cm}^{-1}$. This means that Tauc analysis on samples of direct-gap that possibly have band tails and have thickness (t) greater than a few μ m should be suspect because a typical 2-3 orders of magnitude dynamic range in transmission experiments limits optical thickness $\alpha t < 5$. In thicker samples, although band tails have smaller α than above gap, $\alpha t > 5$ can still occur leading to significant underestimation of E_g if this fact is not recognized. In Fig. 1b) we illustrate an extreme case of this effect by applying Tauc analysis to data from the 36 mm (010) Fe-doped rod covering $\alpha = 1 - 10 \text{ cm}^{-1}$. The extrapolation from the highest energy region suggests a “bandgap” 3.1-3.3 eV which is obviously false. Again, this is a result of applying Tauc analysis to absorption data covering a range below the actual bandgap absorption. We speculate that some of the uncertainty and ranges of values of optical absorption thresholds in previously-published β -Ga₂O₃ may arise from these underlying experimental issues.

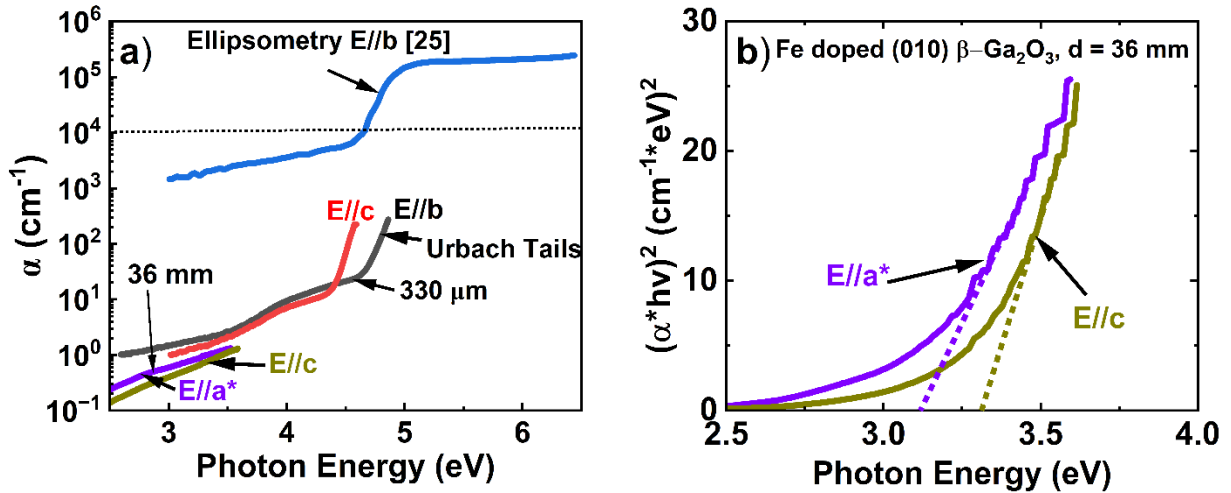


Figure 1 – a) Room temperature β -Ga₂O₃ absorption coefficients determined from spectroscopic ellipsometry²⁵ and from optical transmission measurements herein for a 36 mm rod with (010) polished faces and 330 μ m thick (100) sample cleaved from the same Fe-doped boule. Note the vastly different ranges of α measurable for different techniques and sample thicknesses. b) To illustrate the erroneous bandgap estimates possible from data sets not actually measuring above-gap absorption, Tauc analysis was carried out on the data from the 36 mm rod. Because the data satisfies $\alpha t > 3$ from sub-gap transitions, it suggests a “bandgap” of 3-3.5 eV, while the E//b excitonic gap from ellipsometry is 5.4 eV. Numerical values of the dielectric tensor from Ref.²⁵ courtesy of A. Mock.

As discussed in the Supplementary Materials, we carefully examined the effects of data processing, especially the numerical subtraction of reflectivity given by an index of refraction assumed constant or as a Cauchy function on the extracted values of α . The regions appearing as straight lines in Fig. 1a) for $\alpha > 10$ -20 cm⁻¹ were insignificantly affected by various reflectivity subtraction methods and thus used exclusively for extraction of E_u . The fair agreement with data from the 36 mm rod also gives confidence that the deep sub-gap region has been determined with fair accuracy although the details of reflectivity subtraction do change the detailed shape and magnitude of the extracted α below the Urbach tail region. Also, it could be seen by eye that the Fe distribution was not completely homogeneous through the boule grown by Synoptics in one of their first growth campaigns. Although we refrain from detailed analysis we speculate this deep sub-gap region reflects absorption by impurity (e.g. Fe) and native defect states as internal excitations and or charge transfer excitations measurable by photocapacitance methods such as DLOS²⁷.

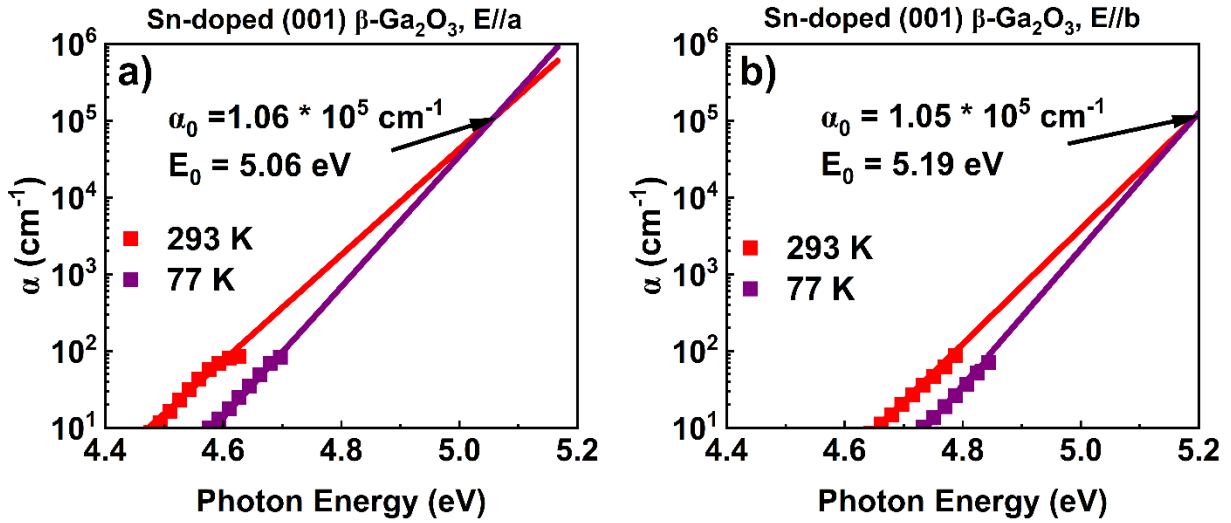


Figure 2 - α for Sn-doped (001) β -Ga₂O₃ for a) E//a and b) E||b at 293K and 77K temperatures. Data is shown as points, while lines result from global fitting using Eq. 1 with α_0 and E_0 constant for both temperatures but different σ_0 values for each temperature.

In this investigation, we endeavored to investigate the contributions to E_u from intrinsic crystalline anisotropy, temperature dependent phonon induced anisotropy, different doping induced disorder, and from structural defects (which might also induce anisotropy). First, we attempted to separate the temperature dependent and static disorder by cooling to cryogenic temperatures. Figure 2 shows the Urbach tail region of α for a Sn (001) β -Ga₂O₃ wafer at room and liquid nitrogen temperature, and the results for the two orthogonal incident polarizations are summarized in Figure 3. This sample exhibited the smallest values of E_u we measured – still ~ 60 meV at room temperature - but cooling to 77 K only reduced E_u by approximately 10 meV. The characteristic phonon energies in β -Ga₂O₃ range from approximately 19-93 meV²⁸, thus the phonon populations (which should be proportional to phonon-induced disorder via the mean-square displacement u^2) for the various modes should be suppressed by factors ranging from ~15 to 25,000 at 77 K. This suggests that the majority of E_u in these bulk crystal samples arises from static disorder rather than dynamic (phonon-induced) disorder – a ratio appearing to be near 5:1.

Similar data was measured at room temperature for a wide variety of Sn-doped samples, Fe doped (100) and a UID (010) sample for different crystal orientations and polarizations. The data are summarized in Fig. 3 along with those shown in Figs. 2. Since two orthogonal in-plane incident light polarizations were investigated for each sample, Figure 3 shows each pair of

measurements from the same sample as two points connected by a line as a guide to the eye. Clearly E_u varies quite radically with orientation within each sample, with doping, and with temperature.

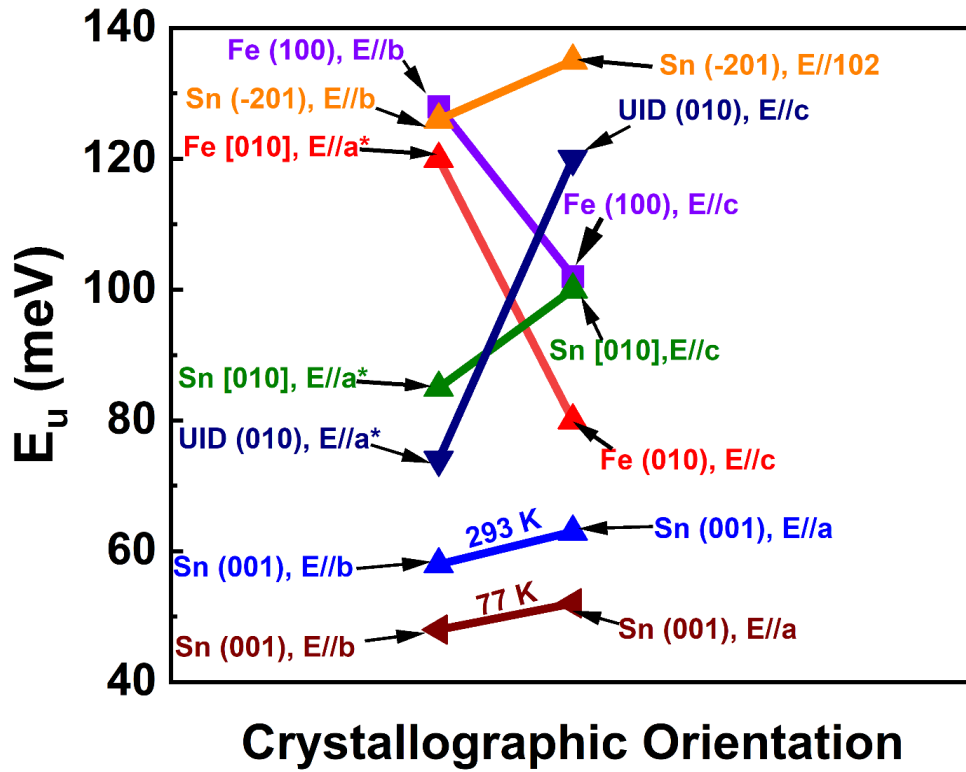


Figure 3 - Summary of measured Urbach energies for Fe-doped, Sn-doped, and UID β -Ga₂O₃ wafers of different crystallographic orientations, labeled by the plane of the wafer. For each different sample and temperature, two values connected by a solid line are shown to help highlight the in-plane anisotropy for orthogonal incident light polarizations. All data are at 293 K except the one labeled as 77 K.

First, we note that across all of the samples we measured, E_u was ~60-140 meV at room temperature which is a very large value compared to those typical for conventional single crystal semiconductors; typically values of a few meV are expected for single crystalline, non-alloyed semiconductors like epitaxial III-V and II-VI semiconductors while values of a few 10's of meV might be observed for high-quality randomly alloyed semiconductors²⁹. Thus, at least in these bulk crystals we have measured, the E_u values are quite significantly higher than those typical for more familiar materials.

Next, we examined the possibility of an underlying crystalline anisotropy in E_u across all the investigated samples; unfortunately we can not deduce any universal trends although we can not rule out the possibility of such effects in more perfect samples. For some samples E_u is larger for $E||a$, others for $E||b$, etc. Thus, from this data set using melt-grown bulk crystals, we deduce that the extrinsic disorder from specific sets of defects present in different samples dominates E_u rather than intrinsic crystalline anisotropy. Samples with much higher crystalline perfection would need to be measured in order to accurately measure the intrinsic crystalline anisotropy in E_u .

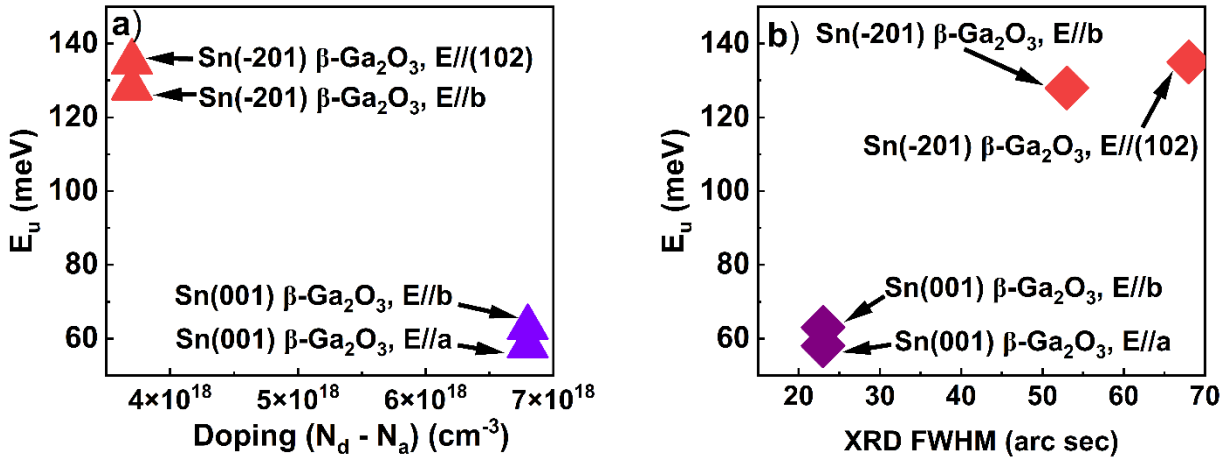


Figure 4 – a) E_u vs. [Sn] and b) E_u vs. on-axis x-ray diffraction FWHM reported by NCT for these wafers. E_u would be expected to increase with Sn doping based on non-uniform strain arguments as well as the expected increasing number of compensating native defects (e.g. V_{Ga} and related complexes). The fact that this is not observed suggests that other sources of structural disorder to which the x-ray diffraction experiments are sensitive dominate E_u .

In order to gain insight into the types of disorder primarily responsible for E_u , we examined the set of Sn-doped wafers of various orientations obtained from NCT since they are all produced from boules grown along the b-axis using EFG but cut on different crystal planes. We hypothesized that the degree of non-uniform strain and numbers of induced compensating native defects would scale with the concentration of Sn doping (which differed within the 10^{18} /cm³ range for the samples we measured), and thus E_u should scale with this variable. However, we found that the E_u actually decreased with the concentration of Sn as shown in Fig. 4a). For each wafer we also had the on-axis Xray rocking curve FWHM specified by NCT. With the exception of one data point not shown, Fig. 4b) indicates better correlation between E_u and the

measured FWHM. On-axis Xray rocking curves measure crystalline disorder in the same plane measured by incident polarized light (the width of q-2q scans measures disorder in the depth direction). The Xray rocking curves will probe both the doping- and point defect induced disorder and that arising from extended defects and near-surface polishing damage. Thus, we conclude that later two effects are dominant contributions to E_u in these samples. From our data we can not discern whether bulk structural defects or near-surface damage from wafer preparation (which can also be anisotropic) is the primary contributor.

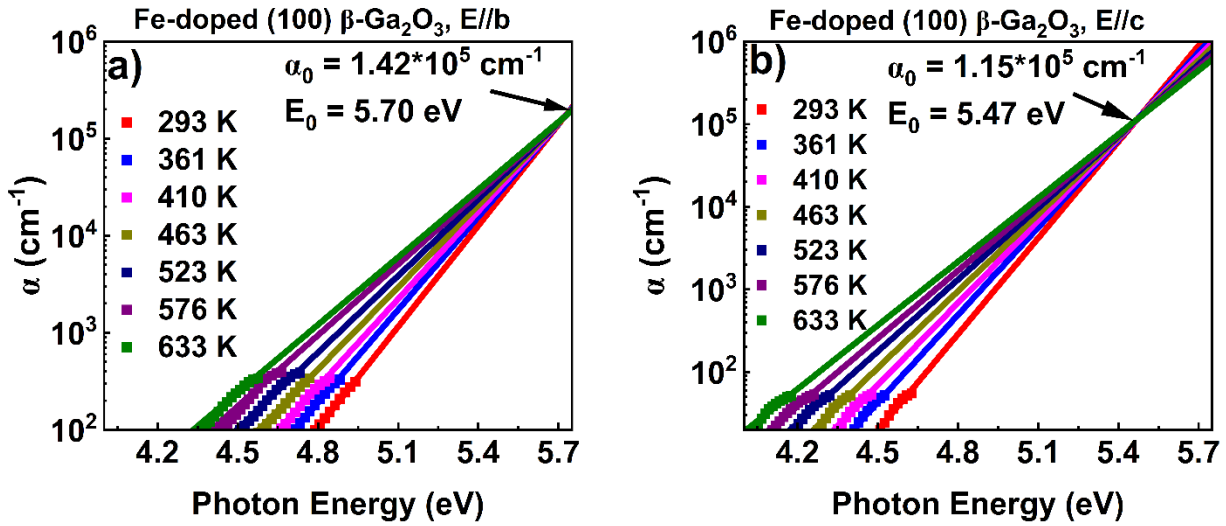


Figure 5 - Extracted $\alpha(E, T)$ for Fe-doped (100) β -Ga₂O₃ as a function of photon energy for a) E||b and b) E||c at varying temperatures up to 633 K. Measured data is shown as points, while the lines show the results of global fitting to Eq. 1 with α_0 and E_0 constant but σ_0 different for each temperature. From these data taken from the same sample we can extract information about the magnitude and anisotropy of the phonon-induced contributions to E_u .

We next examine the temperature-dependent contributions to E_u through measurements at elevated temperatures. Figure 5 shows the extracted absorption coefficients for temperature dependent data on a Fe-doped (100) sample for a) E||b and b) E||c incidences and global fitting (data from all temperatures fit together) to Eq. 1. Separately for the two incident linear polarizations, the Urbach focus (α_0 , E_0) is determined from all temperature data, while E_u (and thus σ_0) change with temperature. We estimate uncertainties of ± 2 meV for all Urbach energies, arising from both noise in the data and the variation induced in numerical data processing. The values of E_0 and α_0 are indicated in the figure for each incident polarization, and the extracted $E_u(T)$ values

up to 633 K are plotted as Fig. 6. Data obtained at higher temperatures was less reliable and repeatable because of the onset of blackbody emission from the furnace and the more significant convection-driven turbulence in the open-air optical path and thus is not included in further analysis. The onset of significant changes in native defect concentrations in n-type Ga_2O_3 is known to be above $\sim 900^\circ\text{C}$ in air, although it is possible that redistributions of impurities may occur. The fact that these wafers were grown from the melt and cooled through temperature ranges much greater than those used for measurements argues against this being significant.

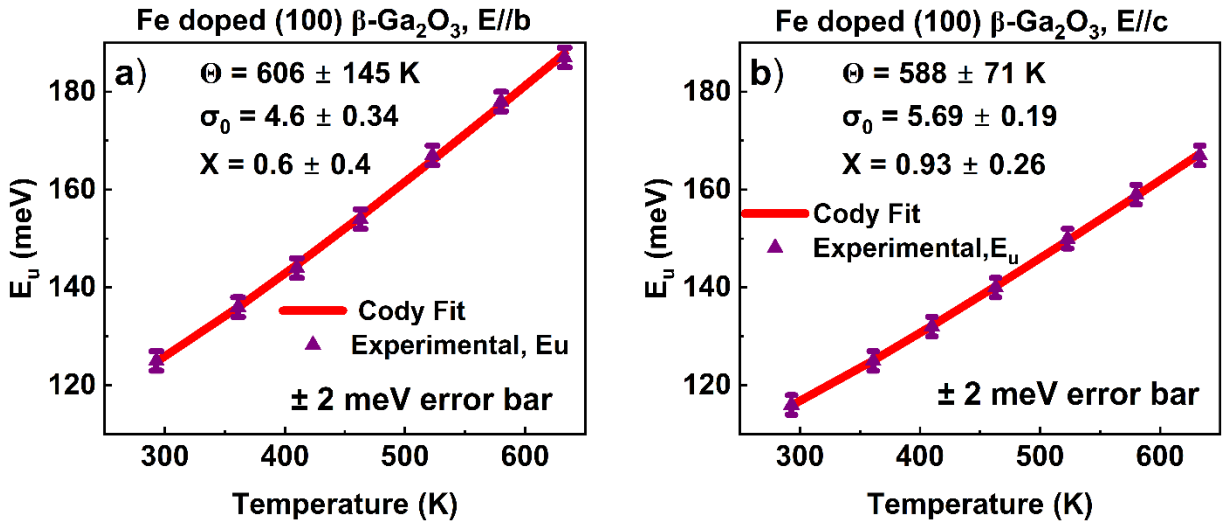


Figure 6: $E_u(T)$ for a) $E||b$ and b) $E||c$ incident polarization directions for Fe-doped (100) $\beta\text{-Ga}_2\text{O}_3$ extracted from the data in Figure 2. The red lines are the best-fits to Eq. 3 and the fitting parameters are noted in the figure.

We analyze the data in Fig. 6 within the framework first introduced by Cody et al., for analysis of a-Si. The premise underlying Cody's decomposition of the measured Urbach energies into static and dynamic contributions is that the degree of atomic displacement from their periodic lattice sites caused by either structural disorder or atomic vibrations is linked to the measured E_u . It is only non-uniform strain that causes broadening of the absorption edge, and likewise the first moment of atomic displacements averaged in time caused by phonons is zero. Thus the $E_u = \frac{k_B T}{\sigma}$ should be proportional to the mean squared displacement $\langle u^2 \rangle$ which is the quadrature sum of the static and thermal components^{30–32}.

$$E_u(T, X) = K \left[\langle u^2 \rangle_x + \langle u \rangle_T \right] = \frac{\theta}{\sigma_0} \left[\frac{1+X}{2} + \frac{1}{\exp\left(\frac{\theta}{T}\right) - 1} \right] \quad (3)$$

In the first expression, K is the proportionality constant, $\langle u^2 \rangle_T$ represents the thermal (phonon) component, and $\langle u^2 \rangle_x$ is the contribution of structural disorder. In the second expression, K is defined as $\frac{\theta}{\sigma_0}$, the $\frac{1}{2}$ in the first term includes the contributions of zero-point phonon displacements, while X parameterizes displacements from static disorder relative to the zero-point displacements. The zero-point excitation of the lattice produces a finite Urbach energy $E_u(0,0) = \frac{\theta}{2\sigma_0}$. The mean square thermal displacements are proportional to the population of phonons, given by the Einstein model in which θ can be recognized as $\frac{\hbar\omega}{k_b}$. Cody points out that the Debye temperature modeled for acoustic modes $\theta_D = \frac{4}{3}\theta$. Because of the large number of phonon modes within a small energy range for β -Ga₂O₃, it will not be possible to separate their contributions from temperature-dependent E_u measurements alone. Thus, we take θ to represent a properly-averaged representative phonon mode in the following analysis.

Figure 6 shows the results of fitting of our measured E_u data for Fe-doped (100) β -Ga₂O₃ with equation (3). The uncertainty estimates were derived from sensitivity analysis of the fitting (thus the different uncertainties for the two data sets). The best fit parameters are $\theta=606 \pm 145$ K for E||b and 588 ± 71 K for E||c corresponding to Debye temperatures of 808 ± 193 K and 784 ± 93 K for E||b and for E||c respectively. These values are in reasonable agreement with the experimental value of 738 K³³ and the predicted value from first principles calculations of 872 K³⁴. We find the steepness parameter $\sigma_0=4.60\pm0.34$ (5.69 ± 0.19) and structural disorder $X=0.60\pm0.40$ (0.93 ± 0.26) for E||b (E||c). Examining the static structural disorder, we note that for E||b its mean square displacement is about half that of the zero point phonons, while for E||c the two effects are nearly equal. Thus the zero point phonon contributions are larger for both directions than either the structural defect or finite-temperature phonon contributions, Despite X being larger for E||c, it is offset by σ_0 also being higher which ultimately results in measured E_u values for E||b being larger overall. Using the fitting values and Eq. 3, we determine that the E_u at 0 K are predicted to be 106 meV for E||b and 100 meV for E||c for this Fe-doped sample. For E||b, 69 meV would be from zero-point phonons and 37 meV from structural disorder, while for E||c 52 meV would be from zero-point phonons and 48 meV from structural disorder. Thus, we find evidence for intrinsic anisotropy in static E_u of order 17 meV and minimum possible values at room temperature of 88 meV for E||b and 68 meV for E||c. These values are summarized in Table 1.

Table 1 – Analysis of contributions to E_u based on fitting our elevated temperature data from Fig. 6 with Eq. 3. In the rightmost column, we compute the ratio of apparent anisotropy to its uncertainty. If this is >1 the anisotropy is statistically significant, while there is no clear evidence for anisotropy otherwise.

	E_u E b (meV)	E_u E c (meV)	Anisotropy $E_{u,b}-E_{u,c}$ (meV)	Anisotropy / Uncertainty Ratio
E_u (X, 293 K) Total (measured)	125 ± 2	116 ± 2	9 ± 3	3.0 (significant)
$E_u(0, 293 \text{ K})$ phonons (Indicated minimum intrinsic value at room temperature)	85 ± 11	68 ± 4	17 ± 12	1.4 (somewhat significant)
$E_u(X, 293 \text{ K}) - E_u(0, 293 \text{ K})$ structural disorder	40 ± 11	48 ± 4	8 ± 12	0.66 (ambiguous)
$E_u(X, 0 \text{ K})$ Total (modeled)	106 ± 38	100 ± 18	6 ± 42	0.14 (ambiguous)
$E_u(0, 0 \text{ K})$ zero-point phonons	66 ± 17	52 ± 7	14 ± 18	0.78 (ambiguous)
$E_u(X, 0 \text{ K}) - E_u(0, 0 \text{ K})$ structural disorder	40 ± 29	48 ± 15	-8 ± 33	0.24 (ambiguous)

From Fig. 6 and Table 1, we have measured anisotropy in E_u between b and c directions at elevated temperatures. Using the fitting values from Eq. 3, we can deduce the various causes of E_u and its anisotropy. The fitting from the sample used for elevated temperature measurements, with $X=0$ gives an estimate for the phonon-only minimum possible values of E_u at 293 K (85 and 68 meV) and at 0 K (66 and 52 meV) for b and c directions respectively. As discussed before, these values are 2-10 times larger than values for more traditional semiconductors. We do note that the (001) Fe-doped sample we measured which showed $E_u(293 \text{ K})$ slightly larger than 60 meV demonstrates that slightly smaller values are possible; we suspect but can not prove from the present data sets that very thin but highly damaged surface layers related to polishing may contribute on the order of ~ 10 meV, which would bring the uncertainties between samples close

to alignment. Looking at the breakdown of contributions to E_u at 0 K, first we define the bottom 3 rows of Table 1. $E_u(X,0)$ denotes the modeled E_u using $T=0$ and the fit parameters from Fig. 6, while $E_u(0,0)$ is only the zero-point phonon component and the final row is computed as $\frac{\theta X}{2 \sigma_0}$. We see that anisotropy in the modeled zero-point phonon component $E_u(0,0)$ is just below the threshold for being significant, while both the total E_u and the isolated component for structural defects are isotropic within our uncertainties. Thus, since anisotropy in X (from structural defects) would be the same at 0 K and elevated temperatures, we conclude that the anisotropy in E_u observed at 293 K is caused by phonon anisotropy. At the highest temperature of 633 K, we measure 187 meV and 167 meV for $E_{||b}$ and $E_{||c}$ respectively yielding a 20 meV anisotropy with uncertainty estimated as 2-3 meV. Eq. 3 gives the same values but with much higher uncertainty. Thus we conclude experimentally that there is some minor anisotropy on the order of 5% of the total E_u at room temperature induced by the anisotropic phonons in β -Ga₂O₃.

We next interpret the temperature dependence measured and estimate the electron-phonon coupling implied, which should also affect carrier mobility and E_{cr} . Cody et al.³² also posit that temperature dependence of the energy gap, which arises solely from phonon-induced distortions of the lattice, can be written as

$$E_g(T) = E_g(0) - D (\langle u^2 \rangle_T - \langle u^2 \rangle_0) \quad (4)$$

in which $E_g(0)$ is the optical bandgap gap at 0 K and $D = \frac{\partial^2 E}{\partial r^2}$ is a second-order deformation potential (eV/Å²), which characterizes the electron-phonon coupling. This formulation implies that any bandgap changes caused by static disorder (from both zero-point phonons and structural imperfection) contribute to $E_g(0)$. Herein we take D as a scalar although generalization to tensor form would of course be possible in more advanced treatments. Since the mean-squared displacement increases as phonon mode occupation, we see that this quantity is also related to the derivative of eigenvalue energies with respect to phonon occupation¹⁸. Since the temperature dependencies of both E_u and E_g share the same root cause of phonons, the mean square lattice displacement in equation (4) can be written as in terms of E_u leading to:

$$E_g(T, X) = E_g(0,0) - \langle u^2 \rangle_0 D \left(\frac{E_u(T, X)}{E_u(0,0)} - 1 \right) \quad (5)$$

Rearranging equation (5) to take the ratio of the two temperature dependencies yields an expression for the quantity $\langle u^2 \rangle_0 D$ (in eV) which would be the magnitude of the electron-phonon coupling at 0 K.

$$\langle u^2 \rangle_0 D = - \frac{E_g(T,X) - E_g(0,0)}{\left(\frac{E_u(T,X)}{E_u(0,0)} - 1 \right)} \quad (6)$$

Thus, we can extract this measure of the electron-phonon coupling by combining temperature dependent measurements of both E_g and E_u . As per the discussion of Fig. 1, ellipsometric measurements of E_g are more reliable unless few-mm thick samples are available for transmission, while transmission measurements of E_u are more reliable. First, we observe that small amounts of structural disorder should have negligible effect on E_g ; thus we assume that $E_g(0, X) \approx E_g(0,0)$ – this is also justified by the dominance of zero-point phonons in the static disorder. Making this assumption, the numerator of Eq. 6 is calculated at each of our measured temperatures from the Bose-Einstein parameterization of the $E_g(T, X) - E_g(0, X)$ given in Ref. ²⁵. $E_u(T, X)$ is our measured temperature-dependent Urbach energy data and $E_u(0,0)$ is given in Table 1. The extracted values of $\langle u^2 \rangle_0 D$ are given in Fig. 7 below; we note that in Ga_2O_3 which has many modes, this represents some weighted average across all of the modes including any subtle differences between phonons' effects on E_u and E_g . The values we extract consistently increase with temperature, which we interpret as arising from this population-weighting of phonon modes which would favor lower-energy modes at lower temperatures but include all of the modes at very high temperatures.

The product $\langle u^2 \rangle_0 D$ gives a measure of the electron-phonon coupling as an energy, which we find to have some temperature dependence. Because the zero-point displacements are by definition temperature independent, this must arise from the population weighting of phonon modes which have different effective D values. Phonons in $\beta\text{-Ga}_2\text{O}_3$ are plentiful, complex, and anisotropic, with energies spanning approximately 10-100 meV ²⁸. An interesting open question is how exactly to quantify the coupling between the phonons' displacements and or induced dipoles and the distribution of bandgaps at each temperature that generate the Urbach edges. The simplest but most computationally expensive method would appear to be direct calculation of bandgaps in a large number of supercells with different superpositions of the phonon displacements applied and fitting the Urbach formula to the resulting distribution of bandgaps.

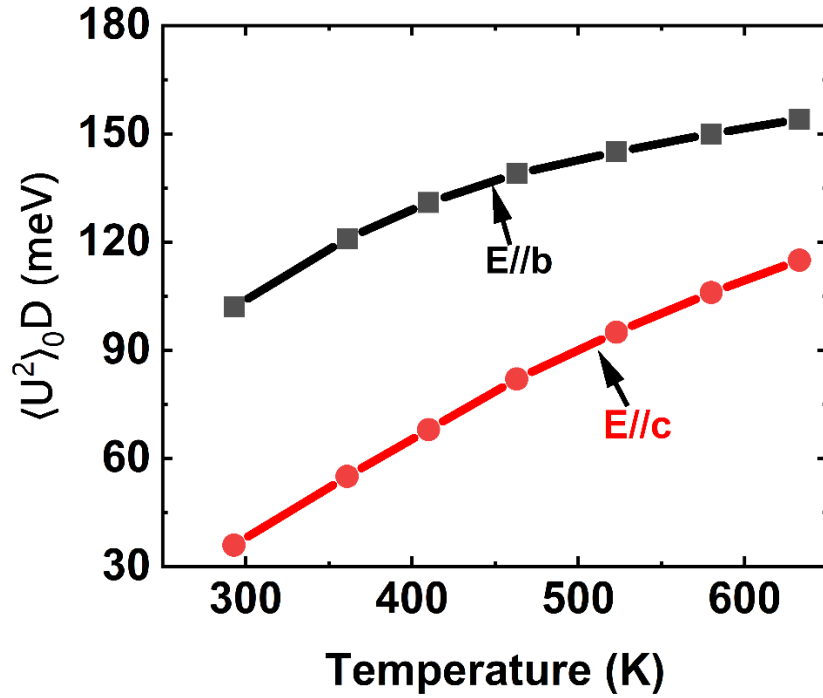


Figure 7: $\langle u^2 \rangle_0 D$ extracted for Fe-doped (100) β -Ga₂O₃ in E||b and E||c at temperatures from 293 K to 633 K. These represent averages of the electron-phonon coupling across subsets of the full phonon spectrum, properly summed in k-space, and accounting for phonon occupations at each temperature.

It has been established that the dominant intrinsic carrier scattering mechanism (i.e. excluding ionized-impurity scattering) in β -Ga₂O₃ at room temperature is polar-optical phonon (POP) scattering. In compound semiconductors with polar bonds, Frölich coupling is typically assumed in which carriers scatter from the fluctuating dipole field induced by transverse-optical phonons. The 2nd order deformation potential extracted here is not identical to the Frölich coupling energy scale responsible for POP phonon scattering⁶. For example, internally we have assessed whether the POP-limited scattering lifetime for electrons in the 10⁻¹³ sec range could be interpreted as lifetime broadening of the band edge states. This simple estimate results in micro-eV broadening thus demonstrating that, while μ , mobility, and breakdown all depend on electron phonon coupling, they each have different dependencies and must be carefully interpreted.

Despite its seeming straightforwardness, electrical breakdown in inorganic crystalline materials like β -Ga₂O₃ is a complex topic. The fact that Ga₂O₃ exhibits strong Urbach tails predicts qualitatively that the mobility and thus mean free path for carrier acceleration in a high field are curtailed, making it less likely for carriers to reach kinetic energies sufficient to impact

ionize. However, an unexamined topic (to our knowledge) is how the energy required for impact ionization varies in the presence of significant time-and-space bandgap disorder associated with Urbach tails. For example, if we use the empirical scaling that breakdown field is proportional to E_g^2 we would expect perhaps 10% variation in E_{cr} with position in Ga_2O_3 . These two physical effects associated with phonon-induced bandgap disorder push the critical breakdown field in different directions thus the net effect is difficult to predict. Breakdown in a-Se and a-Si:H – extreme examples of static structural disorder having Urbach tails on-par with what is observed for Ga_2O_3 - has been studied and in general it is found that avalanche multiplication in these materials occurs at higher fields than for ordered semiconductors with similar bandgap materials³⁵. This argues that in the case of static disorder, the lower mobility prevents carriers from easily accelerating to high energies in a field. The effects of *phonon-related* disorder – bandgap fluctuations and carrier scattering from phonons especially in the case of large electron-phonon coupling as in β - Ga_2O_3 – have not been elucidated. If the effects are similar to structural disorder, which may be likely since the root cause of both is mean squared displacement from ideal sites, we may expect that materials with higher electron-phonon coupling might have even higher breakdown fields than their counterparts of the same bandgap. It has been established that POP phonon scattering should reduce the empirically predicted breakdown field in perfectly-crystalline Ga_2O_3 of ~ 8 MV/cm to ~ 5 -6 MV/cm⁵, but the effects of the combination of thermal and structural disorder have not been accounted to date. This issue will have a profound effect across all materials because it has not been incorporated into theoretical frameworks and thus has priority for future investigations.

Conclusions

We investigated the sub-gap absorption of a number of bulk β - Ga_2O_3 wafers using linearly-polarized transmission. Overall, we find significant Urbach tails that range from 60 to nearly 140 meV at room temperature depending on doping, crystallographic direction, and individual sample. Static disorder in the form of structural defects and zero-point phonons accounts for the majority of the effect, but a non-negligible component arises from finite temperature phonons. There is some evidence for the phonons inducing some anisotropy into the Urbach energies, although this is at the 10% level so not dominant compared to the mean isotropic values. We predict based on comparison to results from amorphous materials, that UWBG materials with high electron-phonon

coupling may have even larger breakdown fields than predicted using scaling from conventional semiconductors where this is weaker. Detailed theory will be needed to resolve whether or not the impact ionization threshold also varies as a result of static disorder and whether this changes E_{cr} .

Supplementary Material

Extraction of Absorption Coefficient from Transmission Data and Error Estimates

The absorption coefficient α can be approximately extracted from transmission through a material slab (neglecting internal coherent reflections) as

$$\alpha = -\frac{1}{d} \ln\left(\frac{T}{1-R}\right) \quad (1)$$

Where d is the thickness of the sample which should be much greater than the wavelength and or have incoherent internal reflections, T is the measured transmittance, and R is the total reflectance, given for slab with index of refraction $\tilde{n} = n + ik$ in air as:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (2)$$

We were unable to record accurate reflectance versus wavelength from these samples, thus we tested the use of both constant and wavelength-dependent index of refraction to model and subtract out the reflectance. At long wavelengths in the visible to near-infrared (energies far below the bandgap, but well above phonon energies), insulating Ga₂O₃ crystals should exhibit near-constant, purely real index of refraction ($k=0$). In this region, R can be estimated as $1-T=R$ leading with equation 2 to:

$$n = \frac{1 + \sqrt{1-T^2}}{T} \quad (3)$$

As the bandgap is approached and the imaginary part of k increases, Kramers-Kronig relations dictate that the real part must also increase and thus so must R . This makes it difficult to accurately extract α in the range where absorption does not yet dominate reflection (small absorption coefficients). The resonant bandgap absorption is commonly modeled as a Lorentzian oscillator or some other peaked function), thus the increase in real part can be understood as the tail of the oscillator response, which would be further broadened by Urbach tails. Cauchy's model (truncated at 2nd order) is a simple empirical parameterization capable of capturing this behavior:

$$n = A + \frac{B}{\lambda^2} = A + CE^2 \quad (4)$$

in which A, B, and C are fitting constants. We investigated processing the data with both constant reflectivity and that derived from the Cauchy index of refraction (Eq. 4); the extracted absorption coefficient changed for small values but was unaffected at larger values where we determined the Urbach energies. In Figure 1 for example, this significantly affected only the regions below 20-30 cm^{-1} and made only ~ 1 meV changes in the fit Urbach energies when the fitting was restricted to the linear portion at larger values. One might be tempted to interpret the sub-gap absorption below 20-30 cm^{-1} as defect-related; however the fact that the reflectivity subtraction so greatly affects the shape and magnitude in this region cautions against overinterpreting this region of the data.

For Sn doped samples, free carrier absorption affects the transmission data across the entire visible to near-infrared spectrum; thus a minimum constant reflectivity was used and again data was ignored for low absorption coefficient in the Urbach fitting and details of the chosen constant value minimally-impacted the extracted Urbach energies.

Finally, at large values of the absorption coefficient such that $\alpha d \gg 1$ or so, the transmitted light becomes indistinguishable from the spectrometer's background. Thus the data was truncated at a different wavelength / absorption coefficient value for each sample and orientation when it clearly became dominated by noise and tended to become constant with increasing energy. We again evaluated the effects of including and excluding different individual data points in the Urbach fitting and our overall error estimate is given as ± 2 meV.

Acknowledgements:

The authors would like to acknowledge the funding provided by the Air Force Office of Scientific Research under Award FA9550-21-0078 (Program Manager: Dr. Ali Sayir). We thank Alyssa Mock for sharing the ellipsometry data used for Figure 1.

Authors Declaration

Conflict Of Interest

The authors have no conflict of interest.

Data Availability

The data that support the findings of this study are available within the article. Additional data are available from the corresponding author upon reasonable request.

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