

Time-resolved absorption and luminescence following electron-hole pair creation in ZnO

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tonic luminescence is less than 5%. This means that there is significant room for improvement in applications aiming to use room-temperature excitonic blue luminescence of ZnO for fast scintillators and light sources. Direct observation that a large majority of excitations are tied up for more than 100 nanoseconds in shallow traps confirms the premise for studies undertaken at Oak Ridge National Laboratory to improve the excitonic luminescence yield and decay rate of ZnO by donor doping. The preliminary results presented here on undoped ZnO suggest that induced absorption measurements should be a useful diagnostic of quantum efficiency while studying such dopant effects.

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We report transient absorption induced by electron-hole excitation in undoped ZnO. A laser pump/continuum probe method covers 2–300 ps, and an electron pulse with lamp transmission covers 8–300 ns. The broad absorption spectrum increases monotonically with wavelength from 900 to 1600 nm. Following a reasonable hypothesis that the free-carrier-like induced infrared absorption is proportional to the total number of free carriers, excitons, and shallow-trapped carriers in the sample, these data allow setting an upper limit on the quantum efficiency of a specified lifetime component of luminescence. For the undoped commercial ZnO studied in this report, the quantum efficiency of room temperature exci-

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1 Introduction Ucer et al. [1] have reported optical absorption on the 2–100 ps time scale induced by band-gap excitation of undoped, single crystal ZnO at $T = 17$ K. A significant part of the absorption signal could be fit with a decay time of 50 ps, which corresponds to the radiative decay time of the neutral donor bound exciton (D^0X) previously measured in the same ZnO sample material in our laboratory [2]. Given the dominance of D^0X luminescence in the low-temperature spectrum of pure ZnO, the 50-ps component of absorption at low temperature was attributed to the population of neutral donor bound excitons.

This report deals primarily with room temperature measurements of transient absorption induced in undoped, single crystal ZnO by two complementary experimental methods: The first is the sub-ps pulsed laser method used in Ref. [1], covering 2–300 picoseconds. The second measures lamp transmission following electron pulse irradiation of the sample, covering the time range 8–300 nano-

seconds. Based on the spectrum observed in both experiments, we suggest that the absorption signal is proportional to the population of shallow trapped carriers produced by band-gap excitation of ZnO. In a highly defect-free material, pulsed band-gap excitation would populate a reservoir of free-carriers and excitons from which radiative recombination luminescence would be observed. In a realistic material, shallow trapped carriers also contribute to the reservoir of excitations, often as the main contributor. From the point of view of scintillator and excitonic light emission applications of ZnO, this “reservoir” of possibly interconverting forms of stored electronic energy represents the maximum amount of energy one could possibly extract in a scintillation pulse or as illumination. In fast scintillator applications of ZnO, one hopes to extract as much excitonic recombination as possible in as short a time as possible. ZnO is attractive for this because its room-temperature excitonic luminescence (actually a pho-

non replica of the free exciton) has a decay time constant on the order of a few hundred picoseconds [3]. Measurements of relative or absolute quantum yield of this particular spectral and lifetime component are of obvious interest in trying to optimize ZnO for fast scintillator applications [4]. The present measurements as discussed below provide a way of measuring quantum yield of a specific lifetime component. In our opinion, the results drive home in a vivid fashion the conclusion that very little of the excitation energy imparted to commercial undoped ZnO comes out in the desired excitonic component. Studies have indicated that it may be possible to increase the yield and decay rate of excitonic fluorescence by doping crystals with donor impurities [4]. A systematic investigation of this strategy has been undertaken by Neal et al. [5] at Oak Ridge National Laboratory, including picosecond time-resolved luminescence measured with the experimental set-up used in this report.

2 Experimental details The 300 fs pulsed-laser method of measuring transient absorption on the 2–300 ps time scale has been described in Ref. [1]. Repeating only a brief summary, optical absorption induced by 2-photon excitation across the band gap of ZnO is probed after a variable time delay by a continuum infrared pulse covering the range 900 nm to 1600 nm. To access the longer time range from 8 to 300 nanoseconds, companion measurements of electron pulse induced transient absorption were conducted at the Institute of Solid State Physics, University of Latvia. Details of the set-up have been described previously by Grigorjeva, Millers et al. [6], and will be summarized only briefly here. A pulse of 270 keV electrons, ~ 8 ns duration, penetrates one flat face of the sample to a small depth. To increase optical path length through the irradiated layer, the probe light is focused into one polished edge of the sample, and is incident on the irradiated flat face at a low angle. The light exits the opposite polished edge of the sample and is imaged onto the entrance slit of the spectrometer. The light source is a xenon flash lamp. Data are acquired with a photomultiplier and digital storage oscilloscope. The undoped ZnO sample used in both experiments was a c-axis oriented epitaxy-substrate wafer from Eagle Picher Co. Its thickness was 0.5 mm.

3 Results and discussion Figure 1 plots the change in transmitted signal following the excitation pulse divided by the transmitted signal immediately preceding the pulse for a succession of probe wavelengths as labeled on each trace. All data in Fig. 1 were measured at 293 K (room temperature). Since the change in transmittance due to creation of absorbing states is negative, the data in Fig. 1 start from $\Delta T/T_0 = 0$ in the upper left just before the laser pulse and decrease toward -1, which would correspond to induced opacity. Because of the desire to show data for a large number of wavelengths by stacking the offset traces, the level of maximum opacity for each trace is not shown. Under the reasonable assumption that the 2-photon excita-

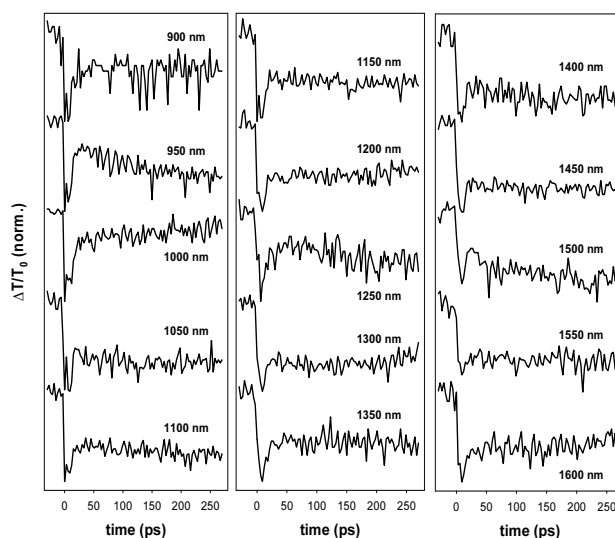


Figure 1 Change in transmittance induced by a 300-fs band-gap excitation pulse in undoped ZnO at room temperature. Each trace shows transmittance at a different wavelength as labelled in the range 900–1600 nm. The traces have been offset vertically for display.

tion density is approximately constant throughout the $d = 0.5$ mm thickness of the sample, the induced absorption coefficient, α , may be expressed in terms of

$$\alpha = -\frac{1}{d} \ln \left(\frac{\Delta T}{T_0} + 1 \right)$$

The common features of the transmission traces are that there is a spike of decreased probe transmission in the first 2 ps, and thereafter the absorption remains approximately unchanged over the 300 ps time range that can be measured with our delay line. The initial spike of probe attenuation has been discussed in Ref. [1], where it was attributed to the phenomenon of 2-photon absorption across the band gap by one pump photon plus one probe photon, which is not of interest. The persistent absorption thereafter is not completely flat, sometimes rising a bit versus time, and sometimes falling a bit. After repetitions of the measurement, we concluded that this variability was due to long-term drifts in the laser energy and/or pulse width over the 30-minute runs required to scan 300 ps. On average, the runs showed that the absorption induced at room temperature changes little between 5 ps and 300 ps at each of the wavelengths sampled in Fig. 1. The sample does not become permanently darkened, so we must presume that the transmission recovers on some time scale. That time scale was found to be in the few hundred nanosecond range using electron pulse experiments described below.

From the data in Fig. 1, absorption spectra corresponding to ~ 10 ps after excitation are plotted in Fig. 2. The dominant trend of the spectra is increasing absorption versus wavelength over the whole measured infrared range.

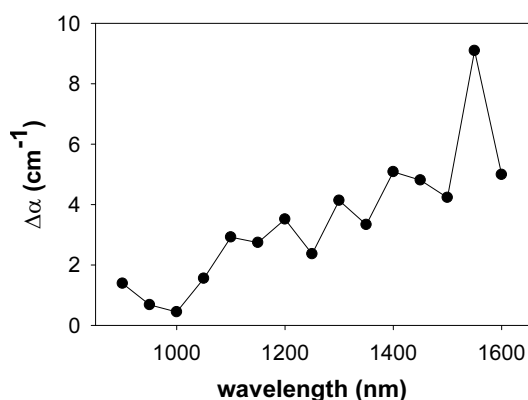


Figure 2 Spectrum of absorption induced 10 ps after band-gap excitation of undoped ZnO by a 300-fs laser pulse at $T = 293$ K.

From decay curves at these and other wavelengths, the spectrum of induced absorption has been constructed. The spectrum of absorption measured 10 ns after excitation is plotted in Fig. 4 versus photon energy. Just as in Fig. 2, the absorption rises monotonically with decreasing photon energy (longer wavelength).

Figure 3 shows the production and decay of optical absorption at 1.1 eV (1130 nm) and 1.6 eV (775 nm) follow-

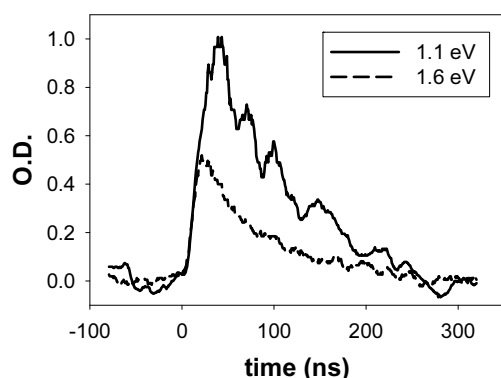


Figure 3 Decay of absorption at 1.1 eV (1130 nm) and 1.6 eV (775 nm) following 8 ns electron pulse excitation at $T = 293$ K.

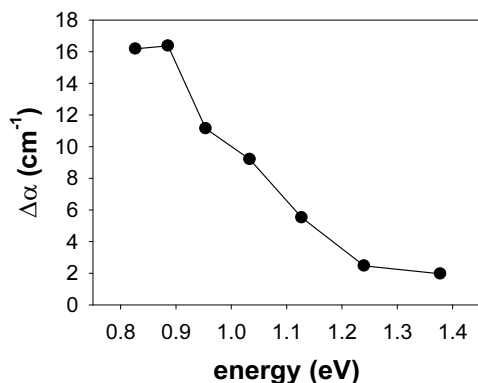


Figure 4 Transient absorption spectrum 10 ns after band-gap excitation by a pulse of high-energy electrons at room temperature.

ing an electron pulse. The time resolution is approximately 8 ns and the time scale extends out to 300 ns. The decay is approximately exponential with the time constant of 120 ns.

In Ref. [1] the excitation-induced IR absorption in the same ZnO at 17 K was seen to have nearly the same broad band shape increasing monotonically with wavelength over the photon energy range 1.3 to 0.8 eV. It was shown on the basis of lifetime analysis that the neutral donor bound exciton (D^0X) accounts for about 38% of the IR absorption at $T = 17$ K. In other words, the IR absorption spectrum shown to be attributable to donor bound excitons looks approximately like the band shape of free carrier absorption. It was argued in Ref. [1] that such a conclusion is reasonable when the optical transition energy so greatly exceeds the binding energy of the exciton. In such a circumstance, the spectral band shape is primarily determined by the density of final free-carrier states that are the photo-ionization break-up products of the highly-excited exciton (or by extension, shallow-trapped carrier). Participation of a phonon greatly expands the number of momentum- and energy-conserving final states and so should control the spectral band shape more or less as in free-carrier absorption.

Thus we hypothesize that the induced IR absorption we observe is due to the collection of all excitons, shallow-trapped carriers, and free carriers induced by the excitation pulse. Within this hypothesis, the transient absorption gives us a measure of the time history of the whole collection of shallow trapped carriers, not just those that result in luminescence. An extension of this interpretation is that the fractional change in IR absorption attributable to a given decay time component gives a measure of the absolute quantum yield for luminescence with the corresponding decay time, assuming the luminescence decay is primarily radiative and that the number of deep traps filled is small. If not, the yield deduced represents an upper limit to the quantum efficiency.

Combining the results of both the laser and electron-pulse experiments, we have a vision of the room-temperature decay of excitation-induced absorption extending more than 5 decades from 2 ps to 300 ns, except for a gap from 0.3 to 8 ns that falls between presently accessible methods for the two experimental methods. Assuming that there is no big decay component in the missing decade, we conclude that at room temperature in undoped ZnO, the free and shallow-trapped carrier population undergoes negligible depletion until approximately 120 ns after excitation. We know that there must be a depletion of some of the carriers associated in excitons because the phonon-replica of free exciton luminescence at 3.26 eV decays at room temperature with the shortest two time constants being of order 0.44 ns and 5 ns. Because the intensity of a luminescence transition is proportional to the rate of radiative decay of the upper level population, the shortest time constant is typically dominant in terms of instantaneous intensity. Many of the fast scintillator and light emitting applications considered for ZnO are attractive because of the sub-nanosecond or few-nanosecond time con-

stant of its blue excitonic transitions. They are indeed attractively fast. But because the population contributing radiatively to the transition is proportional to the time integral of the luminescence, a longer-lifetime, weaker component can often represent the larger excited-state population as seen in absorption measurements. The comparison of luminescence and induced absorption in the present study indicates that the excited-state depletion associated with the observed room-temperature blue luminescence occurring on a sub-nanosecond time scale is only a small fraction of the total available excited-state population. Most of the excited-state population monitored by the “free-carrier-like” IR absorption, likely due to shallow trapped carriers resembling free carrier spectra in the sampled range, decays in 120 ns. This is too slow for the corresponding luminescence to be interesting for many fast emitter applications. This luminescence of the long-trapped carriers could be in the visible defect bands, or recombination could be non-radiative.

The conclusion we draw from our hypothesis that the broad infrared absorption in ZnO represents a monitor of the population of all free and shallow-trapped carriers [1] is that the absolute quantum efficiency of the subnanosecond blue excitonic luminescence at room temperature is very low in undoped single-crystal ZnO typified by the Eagle-Picher material. An estimate of the maximum quantum efficiency in this hypothesis would correspond to the maximum fraction of induced absorption that can be assigned a decay time corresponding to the 440 ps short time constant of phonon-assisted free exciton decay measured in the same crystal at room temperature. Fitting our data to a sum of exponentials with decay times of 8 ps, 440 ps and 120 ns, we find that the 440 ps component is 5% of the overall signal. According to our model this would represent the upper limit on the quantum efficiency of the blue transition in this Eagle-Picher material. The first implication is that there is a lot of room for improvement of material response. One may try to remedy this by going to noticeably more perfect ZnO or conversely by optimally doping, e.g. with donor defects [see below]. The conclusion based on our hypothesis about the origin of the IR absorption should ideally be checked by directly measuring the absolute quantum efficiency of the fast blue luminescence. This is in fact a difficult task to do accurately. In the meantime the transient absorption may give a more trustworthy measure of an upper limit on the quantum efficiency of fast excitonic transitions with an identifiable lifetime. As an example, Ref. [1] succeeded by this method in assigning a quantum efficiency of 38% to the neutral donor bound exciton luminescence transition at $T = 17$ K. Such a value is plausible because the D^0X luminescence is typically very strong and fast in undoped ZnO at low temperature.

The low quantum efficiency of the blue excitonic room-temperature luminescence in undoped ZnO implied by the results of this work relates directly to the ongoing efforts of some of the present authors and others [5] to optimize simultaneously the quantum efficiency and short

time response of room-temperature excitonic luminescence in ZnO by introducing dopants. Due to space limitations we must refer the reader to Ref. [5] for discussion of the application and detailed influence of doping on the yield and lifetime. However in the context of the present discussion, it is worth pointing out that the conclusion of this paper implying poor quantum yield of excitonic luminescence in ordinary undoped ZnO supports a viewpoint on scintillator design described to us by Derenzo [7]. The general concept is to focus on one carrier, e.g. holes, produced in the initial excitation of e–h pairs. By doping, one hopes to make sure that an electron can find each hole in a short time to undergo recombination, rather than allow the holes (and scant supply of electrons) time to encounter traps and non-radiative recombination sites. Even if electrons and holes finally recombine radiatively after residence on traps, it is likely to be beyond the time window of useful response, particularly for applications like modern fast scintillators where the time window could be sub-nanosecond. Getting rid of the traps is one fruitful way to get more prompt excitonic response. Another productive approach investigated by Derenzo et al. [4] and now Neal et al. [5] is to dope the material rather heavily with donors to sustain a constant supply of conduction electrons. In principle, one of the numerous conduction electrons should dive in almost immediately on each hole produced in the excitation event. Ref. [5] has investigated the effect on relative yield and on luminescence lifetime, as well as finding a limitation to the trend at high doping levels, which we attribute to onset of Auger decay. We are keen on including excited-state absorption measurements on the same doped sample series, to see how the excess free carriers (and the donors as traps, by the way) influence the evolution of free and shallow-trapped excitons and carriers, controlling the yield and lifetime of fast luminescence response.

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