On the optical band gap of zinc oxide

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Three different values (3.1, 3.2, and 3.3 eV) have been reported for the optical band gap of zinc oxide single crystals at room temperature. By comparing the optical properties of ZnO crystals using a variety of optical techniques it is concluded that the room temperature band gap is 3.3 eV and that the other values are attributable to a valence band-donor transition at ~3.15 eV that can dominate the optical absorption when the bulk of a single crystal is probed. © *1998 American Institute of Physics.* [S0021-8979(98)07510-0]

I. INTRODUCTION

One of the curious features of the literature on zinc oxide is that there remains substantial disagreement as to the value of its band gap with values ranging from 3.1 to 3.3 eV.[1–13] As the majority of optical characterization techniques that can be used to determine band gaps have energy resolutions far superior to the range of these values, 0.2 eV, the differences in the literature cannot be attributed to inferior instrumental resolution. Furthermore, whilst there is substantial variation in the values of the optical band gap quoted for ZnO films,[10–12] there are three distinct values quoted for single crystals, 3.1,[8,9] 3.2,[5] and 3.30 eV.[1–4,6,7] Whilst it can be argued that the higher value must correspond to the true band gap, a detailed knowledge of the optical properties of ZnO near the band edge is of importance particularly as there is a possibility of making blue/uv lasers using ZnO thin films. The variability in the reported values of the band gap in the films can be rationalized on the basis of the existence of growth stresses and thermal expansion mismatch stresses[10] and the presence of dopants,[12,13] but this cannot be a viable cause for the existence of three distinct values for the band gap of single crystals. In seeking to understand the reasons for the different values, we have performed a series of optical measurements, using different techniques, on two different single crystals of ZnO, one clear in color and the other having a yellowish tinge. The techniques have included conventional reflection and transmission absorption measurements (R&T), spectroscopic ellipsometry (SE), Fourier transform infrared spectroscopy (FTIR), and photoluminescence (PL). As will be shown, the data are consistent with the band gap being at 3.30 eV and a valence band-donor transition at 3.15 eV that can, under appropriate measuring conditions, dominate.

II. EXPERIMENTAL SECTION

The colored ZnO crystals were obtained from a commercial vendor, Materials Technology Inc., while the colorless ZnO crystals were obtained from Dr. Abare. The former crystals were received with already polished surfaces whilst the latter were polished by a vendor (Crystal and Coatings, Inc.). Two crystals of each type were investigated and all were *c*-axis oriented as determined by x-ray diffraction. The crystals used in the R&T and FTIR experiments were polished on both sides whereas the crystals used for the spectroscopic ellipsometry were polished on only one side. No differences were noted in any of the experiments described below between the oxygen and zinc terminated surfaces. The SE and the R&T measurements were carried out using a J. A. Woollam Variable Angle Spectroscopic Ellipsometer with illumination provided by a Xenon lamp, attached to a PTI spectrometer, capable of providing monochromatic light from 0.3 to 1.7 μm. Due to the finite size of the source and the detector of the ellipsometer it was not possible to perform normal reflectance measurements. The smallest angle of incidence achievable in this system is 12° and so henceforth whenever we refer to normal reflectance we in fact mean reflectance at a 12° incidence angle. The FTIR measurements were performed using a Nicolet Magna-IR 850 spectrometer, using a deuterium triglycine sulphate (DTGS) KBr detector and a KBr beamsplitter. The room temperature PL spectra was taken using a HeCd laser, with a laser operating at 325 nm.

III. MEASUREMENTS

A. Absorption spectra in the visible range and photoluminescence

These experiments were performed in order to understand the origin of the color in one of the crystals. In Fig. 1 we plot the absorption coefficient of the two crystals in the visible range. Along with the absorption curves the relative sensitivity of the human eye to various colors is also shown. As can be seen the colored sample exhibits a finite absorption at all wavelengths except in the green and the yellow, while the colorless crystal does not exhibit any absorption bands.

In order to gauge the effect of the absorption bands on the luminescent properties of the crystals, room temperature PL was performed. In Fig. 2 the PL spectra taken from the two crystals is reproduced. All the basic features of the two spectra are the same except that the PL intensity from the colored crystal is nearly an order of magnitude lower than

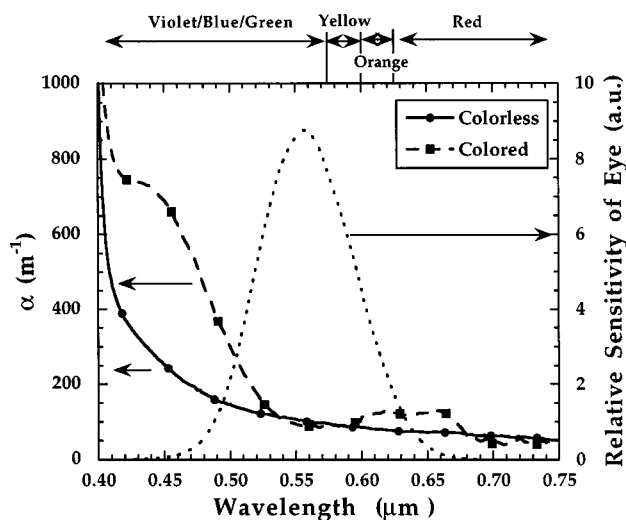[a)]Electronic mail: clarke@engineering.ucsb.edu

FIG. 1. Absorption coefficient as a function of wavelength for the colorless and colored zinc oxide crystals. For comparison, the spectral sensitivity of the eye is superimposed.

that from the colorless one. (The reason for the slight difference in linewidth is not presently known.) Also the relative peak intensities in the two spectra are different and the peak of the broad band from the colored crystal is at a longer wavelength. (The weak peak recorded from the colorless crystal at ~750 nm is a harmonic of the peak at 375 nm.)

B. Band edge determination

The square of the absorption coefficient of the two samples is plotted in Fig. 3. Four different curves are plotted in this figure corresponding to two different absorption curves for each crystal. One set of curves is derived from R&T measurements using

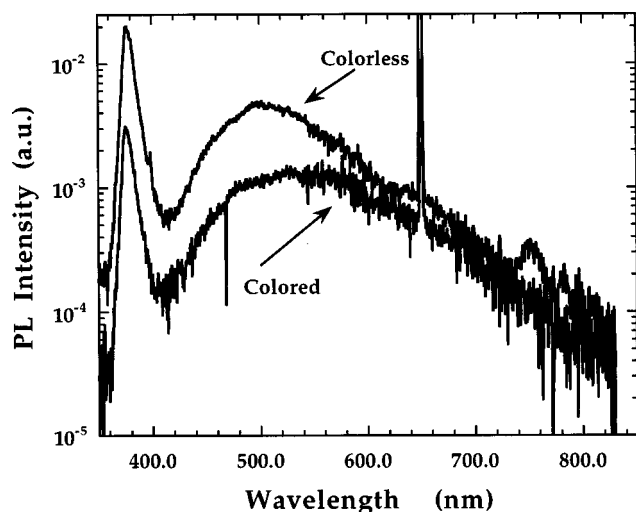$$\alpha t = -\ln\left(\frac{T}{1-R}\right),$$

FIG. 2. Photoluminescence intensity for the colored and colorless crystals.
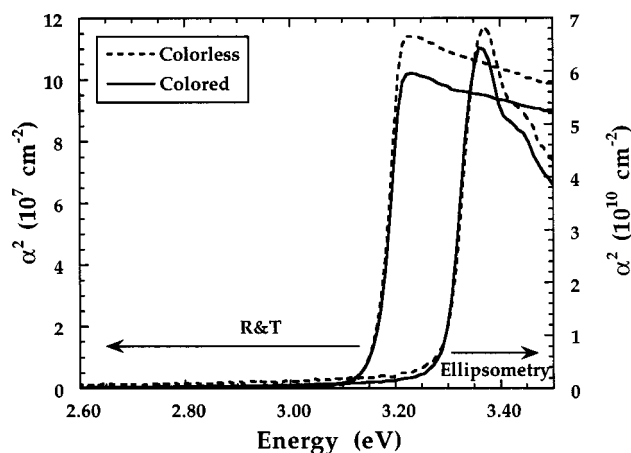

FIG. 3. Square of the absorption coefficient vs photon energy as determined by conventional reflectance and transmission measurements and that using the spectroscopic ellipsometer. The solid and dashed lines refer to two different crystals.

where t is the sample thickness, T is the transmittance, and R is the reflectance from a double-sided polished sample. The other set of curves were obtained from the ellipsometry data using

$$\alpha = \frac{4\pi k}{\lambda},$$

where k is the imaginary part of the refractive index and λ is the wavelength. It is evident from this figure that there is little difference between the two types of crystal with regard to the absorption coefficient at the band edge. However, the two different techniques lead to quite different values for the band edge, obtained in the standard manner by extrapolating the linear part of the curves to intersect the energy axis. In one case it has a value of 3.15 eV while in the other it has a value of 3.3 eV.

C. FTIR and reflectance spectra

In order to understand the differences in Fig. 3 two other experiments were performed and their results are shown in Figs. 4 and 5. In Fig. 4 the absorption coefficient of the two crystals in the ir regime (0.04–0.4 eV) are shown. The absorption coefficient is calculated based only on the transmission data. Hence, these values of absorption coefficient will be slightly lower than the true values. Nevertheless, the correct trend is anticipated. In Fig. 4 there is a sharp increase in the absorption coefficient around 0.15 eV in both crystals. In Fig. 5(a) the reflectance of the crystals obtained from the SE measurements is presented and in Figs. 5(b) and 5(c) the reflectance determined from the same crystals using the R&T measurements is shown. Notice that whilst the single-side polished crystal shows only a single peak around 3.3 eV [Fig. 5(a)], the double-side polished crystal shows two peaks [Fig. 5(b) and Fig. 5(c)], one around 3.3 and the other around 3.15 eV. The other, regular oscillations in Fig. 5(c) at lower energies are due to the existence of the absorption bands in the crystal at these energies. No depolarization was noted during the course of the SE measurements.
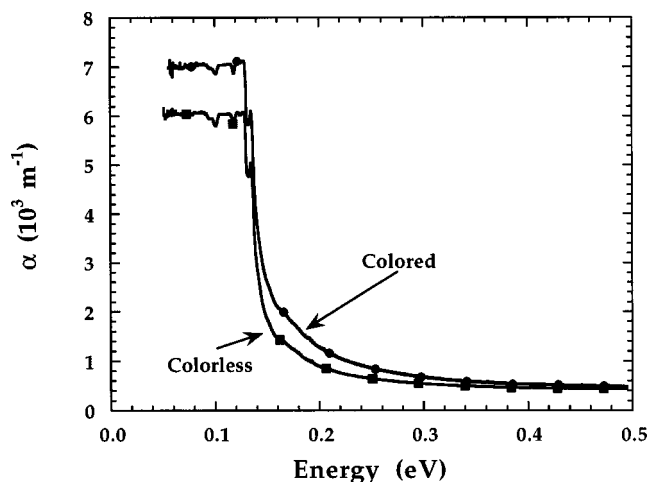
FIG. 4. The absorption coefficient of the two crystals in the infrared regime measured by FTIR.

To summarize, the colored and colorless crystals are in all regards indistinguishable other than in the difference in their absorption bands in the visible range (Fig. 1) and in the intensity of their PL (Fig. 2).

IV. DISCUSSION

Comparison of the absorption spectra presented in Fig. 1 indicates that the colored crystal appears greenish yellow because it exhibits absorption bands at all visible wavelengths except those in the yellow and parts of the green. Since the two sets of crystal are identical except for the absorption band in the visible and their PL intensities, it is likely that the lower PL intensity from the colored crystal is related to the defects responsible for the absorption in the visible. Although it is not known, it is possible that these defects act as nonradiative recombination sites and hence lower the luminescence efficiency. Thomas[14] has argued that there is a possibility that the color of single crystal ZnO might have its origins in band tailing. The results in Fig. 1 clearly indicate that definite absorption bands exist in the visible range and that the color is not a direct consequence of band tailing. It has also been proposed previously that heating a ZnO single crystal in air at high temperatures results in defects that enhance the color of the sample. This indicates that the color is related to oxygen vacancies. Incidentally, we did notice that on roughening the back side of the double-side polished colorless crystal, it took on a slightly yellowish color suggesting that the damage caused by roughening also leads to absorption bands in the visible region. Unfortunately, the density of these defects was too small to be measured accurately.

The reason for the difference in absorption in the vicinity of the band edge (Fig. 3) between the results obtained by R&T and SE is less obvious. One important difference though lies in the two measurement techniques; the spectroscopic ellipsometry probes only the surface whereas the R&T measurements probe the bulk of the crystal. Hence, one possible explanation for the lower band edge determined from the R&T measurements is that there is a deep level donor (with direct transitions taking place between the va-
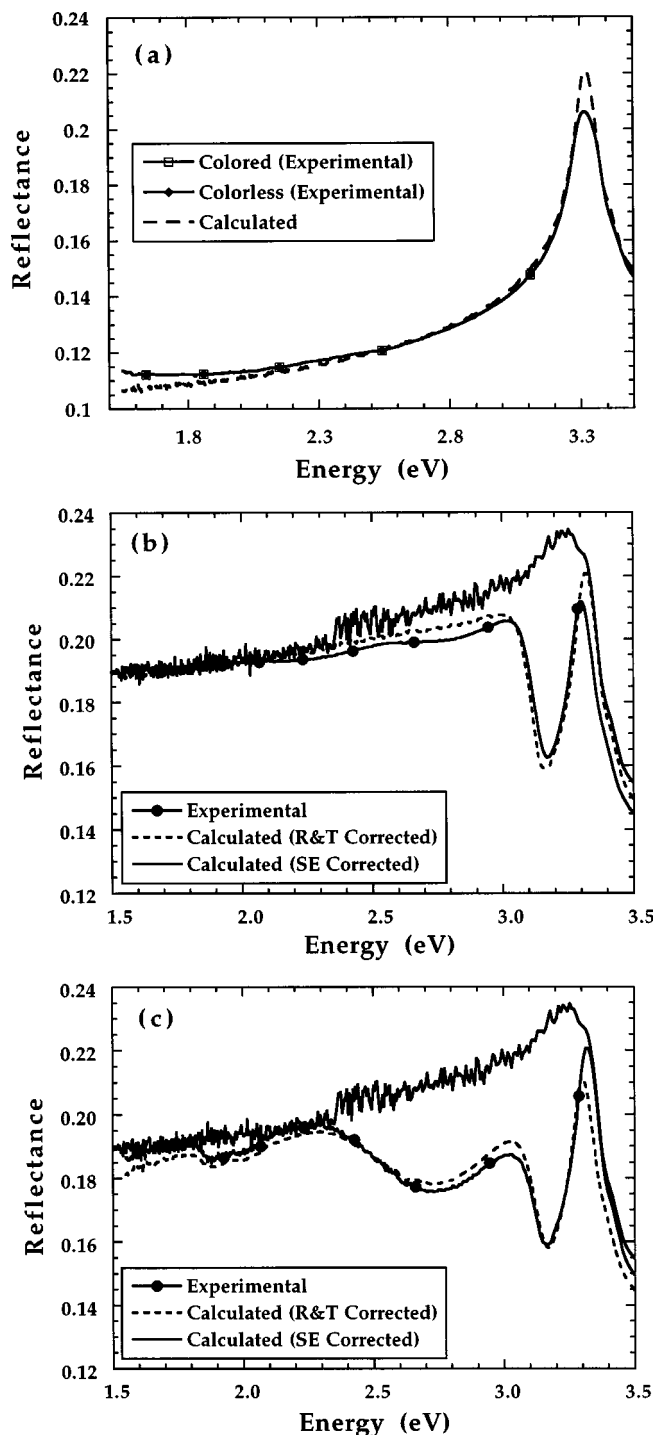

FIG. 5. The experimentally measured and calculated reflectance is plotted as a function of wavelength for (a) a single-side polished colored and colorless sample, (b) a double-side polished colored sample, and (c) a double-side polished colorless sample. As described in the text, the curves calculated from the SE data appear noisy since they are calculated from the derived refractive index, k.

lence band and the donor level) or acceptor (with direct transitions taking place between the acceptor and the conduction band). This would suggest that the spectroscopic ellipsometry measurements give the true band edge of ZnO while the R&T measurements do not. A closer examination at energies slightly higher than the band edge shows that while the spectroscopic ellipsometry spectra shows a sharp decline in the
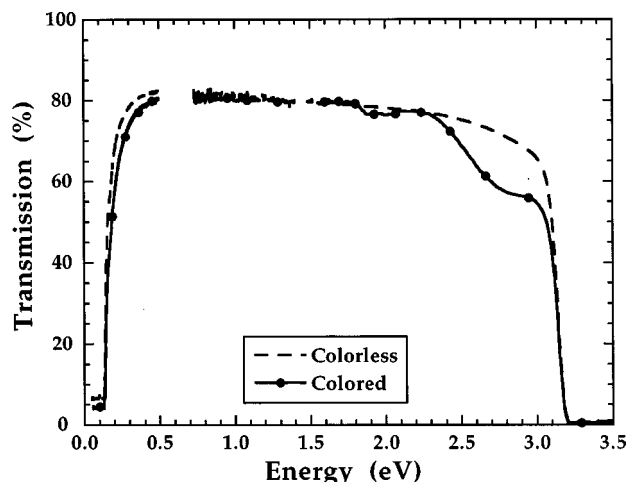
FIG. 6. Transmission as a function of photon energy in the uv-VIS and ir for the colorless and colored crystals.

FIG. 7. Dispersion curve for single crystal ZnO in the wavelength range of interest deduced from the spectroscopic ellipsometry results.

absorption coefficient the R&T spectra shows a rather slow decay. A sharp drop in the absorption coefficient is more reminiscent of sharp exitonic transitions just below the band edge whereas a slow drop off in the absorption value is indicative of a whole band being involved. This also seems to indicate that the R&T measurements probe a non-band-to-band transition. In support of this conclusion, deep-level transient spectroscopy measurements on bulk ZnO varistors (polycrystalline materials with a host of dopants) have shown the existence of an intrinsic donor level, ~0.15–0.17 eV below the conduction band.[15] This would, in turn, indicate that the the transition measured in the R&T measurements is a valence band-donor transition. Furthermore, the only reference[3] reporting a value of 3.3 eV for the band gap using transmission experiments on single crystals of ZnO, is the one in which rather thin (~0.1 μm) crystals were investigated. Their results match with those obtained on epitaxial ZnO films on sapphire[10] as expected, presumably because of the small volume of material probed in both cases.

The existence of a donor transition is also supported by the FTIR transmission experiments (Fig. 4) which show a sharp rise in the absorption coefficient at around 0.15 eV, consistent with a donor level 0.15 eV below the conduction band. It can be shown, by employing semiconductor statistics,[16] that for a donor level 0.15 eV below the band edge and a density of 5×10^{16}/cm^3, about half the donor states are occupied at room temperature, assuming that no other defect states exist. This implies that both the donor-conduction band transition and the valence band-donor transitions will be equally strong provided the matrix elements involved in the calculation of the transition probabilities have the same value. Indeed, when the transmission results in the uv-VIS range and the ir range are plotted in the same graph (Fig. 6), we see that the drop in intensity of the transmitted light is of the same magnitude.

Further evidence for the valence band-donor transition can be found in analyzing the reflectance data. In Figs. 5(a), 5(b), and 5(c) the calculated reflectance of single-sided and double-sided polished ZnO are compared with the experi-
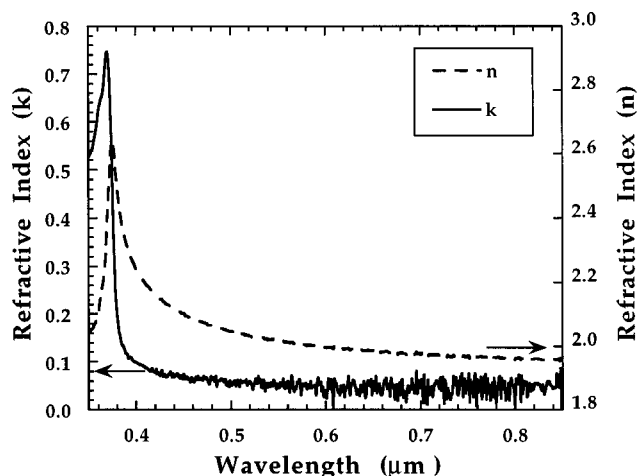
mental measurements. In calculating the reflectance as a function of wavelength for a single-side polished crystal we have used the dispersion curve of ZnO determined from the SE (see Fig. 7). The calculated curve in Fig. 5(a) is based on

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

where n and k are the real and imaginary parts of the refractive index and assuming that the reflectance is measured under normal incidence. As can be seen, the match between the calculated and the experimental curve in Fig. 5(a) is excellent implying that the dispersion curve (Fig. 7) we calculated from the spectroscopic ellipsometry measurements is correct. However, when these same values are used in conjunction with the absorption curve predicted from the ellipsometric measurements[17] [curve labeled ''Ellip-corrected'' in Figs. 5(b) and 5(c)] we are unable to reproduce all the features of the reflectance measured from the double-side polished crystal.[18] The scatter in the visible range of the reflectance calculated using the ellipsometric measurements arises due to scatter in the dispersion curve of the imaginary part of the refractive index of single crystal ZnO (see Fig. 7). A second calculated curve (labeled ''R&T corrected'') is also shown in Figs. 5(b) and 5(c), and was calculated using the absorption coefficient determined from the R&T measurements. This second curve clearly fits all of the features of the reflectance curve from the double-sided polished crystal.

From the theory of optical transitions in semiconductors[19] it is known that in the vicinity of a band edge there is a peak in the reflectance. In fact, in the single-side polished crystal only one peak, around 3.3 eV, is observed. In marked contrast, the reflectance of a double-side polished crystal exhibits two peaks, one at 3.3 eV and the other at around 3.15 eV. This demonstrates that the second peak is due to some other transition which only becomes important when the bulk is sampled as is the case with a double-side polished sample. As we know that a peak in the reflectance must occur near a band edge (whether for a single-side or double-side polished sample) we conclude again that the true band edge of bulk ZnO is at 3.3 eV and that there exists a

valence band-donor transition at 3.15 eV (as determined above) which dominates whenever the bulk of the single crystal is probed.

V. CONCLUSION

By comparing measurements of the same crystals made by a variety of different techniques, it is concluded that the optical band gap of ZnO at room temperature is 3.3 eV. The reports of an apparent band gap at 3.1 and 3.2 eV are concluded to be due to the existence of a valence band-donor transition at 3.15 eV which can dominate the absorption spectrum when the bulk, as distinct from the surface, of a crystal is probed.

ACKNOWLEDGMENTS

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[17] The absorption coefficient calculated from the ellipsometric measurements is usually an overprediction and so a correction is needed. We have scaled the absorption coefficient such that the part of the reflection curve where the reflection coefficient decreases with decreasing wavelength match up. This is reasonable because the reflection coefficient of a double-side polished sample should be the same as a single-side polished sample above the band gap.

[18] The reflection coefficient for a double-side polished sample, R', can be calculated knowing the reflection coefficient of a one-side polished sample, R, the absorption coefficient, α, and the sample thickness, t, using the following relation: $R' = R + R(1-R)^2 \exp-2\alpha t$.

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