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To cite this article: M I Zakirov et al 2016 J. Phys.: Conf. Ser. 741 012028

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## **Optical properties of ZnO fabricated by hydrothermal and** sonochemical synthesis

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Abstract. This paper presents the results of experimental study of photoluminescence (PL) and surface photovoltage of ZnO synthesized in this study. Two types of zinc oxide samples, prepared by hydrothermal and sonochemical methods at two different temperatures, are contrasted. The observed differences in their PL spectra are associated with different mechanisms of formation and resulting concentration of point defects. At a high-temperature synthesis, blue luminescence band prevails. Reducing the temperature causes the increase in intensity of the yellow-red luminescence band.

#### 1. Introduction

Zinc oxide (ZnO) is a kind of nontoxic, low cost and abundant material of fundamental importance and great interest to both academic and industrial communities. As a wide-band-gap semiconductor, zinc oxide attracts much attention in current semiconductor research, due to its superior optical properties. Due to its large energy band gap (3.37 eV at room temperature) ZnO becomes an excellent semiconductor material for application in UV devices [1-3]. The unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photostability make zinc oxide interesting for study and numerous applications in sensors, photocatalysis, field emission, and solar cells [4, 5].

Solid applied aspects of zinc oxide materials have led to the development of a wide range of techniques for producing ZnO. In these applications of ZnO, the control and design of the point defect structure, as well as the surface and interface defect content, are among the major keys to optimize the device performance [5]. In recent years, many efforts have been made for achieving ZnO nanoparticles via different approaches. Besides gaining information about nanoparticle formation mechanisms, many researches have been focused on different possible methods of obtaining desired particle shapes and different point defect contents. Also, different post-processing techniques capable of varying the defect concentration in ZnO have been given particular attention [6–13].

Room-temperature photoluminescence (PL) of ZnO typically exhibits one emission peak in the near-band-edge ultra-violet (UV) region, which is due to the recombination of free excitons, and one or more peaks in the visible spectral range, which are attributed to defect-related emissions [14]. The latter frequently form at least one broad emission band extending from just above 400 nm to 750 nm, which is referenced to as deep level emission (DLE) band. Different reports have discussed the origin of the deep levels involved in the observed radiative transitions [15].

#### Journal of Physics: Conference Series 741 (2016) 012028 2. Experiment and Result

Two fabrication methods, namely hydrothermal and sonochemical synthesis, are employed in this work. The detail synthesis procedure has previously been described elsewhere [16]. In both methods, the synthesis temperature is stabilized in the range from 338 to 351 K. The hydrothermally synthesized samples are named below as "HT1" and "HT2" for the growth temperatures of 338 and 351 K, respectively, whereas the ones obtained sonochemically are named as "US1" and "US2". An N2 laser with the wavelength of  $\lambda$ =337.2 nm (3.67eV) is used as the photogeneration source. Surface photovoltage (SPV) decays were measured in the capacitor arrangement, and details of our setup are given elsewhere [17]. All measurements are performed at room temperature.

The observed changes in the defect-related PL spectra can be associated with the changes in the concentration of point defects. At thermal equilibrium, this concentration is given by

$$c = N_{sites} \exp\left(-\frac{E^f}{kT}\right),\tag{1}$$

where  $E^{f}$  is the formation energy,  $N_{sites}$  is the number of sites the defect can reside, k is the Boltzmann constant and T is the temperature [18]. In this framework, the PL intensity is proportional to the defect concentration, provided the involved recombination channels remain unchanged. We therefore give an account of the bulk versus surface concentration  $N_{sites}$  in the two fabrication routes, comparing the PL and SPV data, commensurable with the bulk and surface defect concentrations. Using the available reported data, the formation energy E of the different defect types can be related as follows [19]

$$E(\mathbf{V}_{Zn}) \leq E(\mathbf{V}_O) \leq E(\mathbf{Zn}_i) \leq E(\mathbf{Zn}_O) \leq E(\mathbf{O}_i) \leq E(\mathbf{O}_{Zn}).$$

PL spectra of our samples are shown in figure 1. Changes in the peak positions and intensities are clearly seen, which are most sufficient in the sonochemically prepared US1 sample.



Figure 1. Comparison of the PL spectra taken in ZnO samples fabricated hydrothermally and sonochemically at temperatures of 338 and 351 K.

Of further notice is the fact that, in hydrothermally synthesized samples, PL spectra consist of a strong peak in the blue region and a weak peak in the orange-red region. In sonochemically fabricated samples, strong orange-red peak dominates the emission in US1 prepared at 338 K, whereas two peaks in the blue and orange-red regions are seen in US2 prepared at 351 K, which are quite similar to that observed in the HT samples.

For clarifying the origin of PL spectral bands we can decompose the spectra into individual Gaussian shapes. It is found that each spectrum consists of three elementary bands, which can be associated with three DLE recombination transitions. The data on the featured elementary bands and their relative intensities are given in Table 1. Here we give the peak position, relative intensity of the band (in brackets) with the dominating spectral band marked by asterix, and the likely PL formation mechanism, which is developed using the data of Refs. [20,21].

**Table 1**. Decomposed elementary spectral bands forming the PL spectra given in figure 1. formation mechanism.

Samples	HT1	HT2	US1	US2
Band 1 (Blue): peak position in nm (relative intensity) likely DLE origin	420 nm $(0.63)^*$ CB-V <sub>Zn</sub> , Zn <sub>i</sub> -V <sub>Zn</sub>	426 nm (0.73)* CB-V <sub>Zn</sub>	421 nm (0.17) CB-V <sub>Zn</sub> , Zn <sub>i</sub> -V <sub>Zn</sub>	418 nm $(0.63)^*$ CB-V <sub>Zn</sub> , Zn <sub>i</sub> -V <sub>Zn</sub>
Band 2(Blue-green): peak position in nm (relative intensity) likely DLE origin	456 nm (0.53) Z $n_i$ -V $_{Zn}$	489 nm (0.34) CB-V <sub>0</sub>	571 nm (0.54) Zn <sub>i</sub> -V <sub>0</sub> , CB-V <sub>0</sub>	460 nm (0.49) Zn <sub>i</sub> -V <sub>Zn</sub>
Band 3(Orange-red): peak position in nm (relative intensity) likely DLE origin	673 nm (0.65)* V <sub>0</sub> -VB	681 nm (0.67)* CB-V <sub>0</sub>	713 nm (0.8)* V <sub>O</sub> -VB	646 nm (0.50) CB-O <sub>i</sub>

According to the data of Table 1, the HT samples have two elementary bands of nearly equal intensities (two different PL formation mechanisms have the same intensity), while in the US samples one dominant band is observed. Speaking most generally, the observed differences in the PL spectra can be related to different chemistry of defects and their concentrations imposed by different fabrication mechanisms.

At the greater synthesis temperature for hydrothermal method, the long-wavelength shift of the individual band is observed. In clear contrast, sonochemical synthesis produces the short-wavelength shift of the individual band. Significantly, the  $O_i$  defect, having rather large formation energy, is realized in the sonochemical route, which can arise in the cavitation process.

The normalized SPV decays for hydrothermally and sonochemically synthesized samples are contrasted in figure 2. It is seen that increasing the synthesis temperature speeds up the SPV decays. Our analysis shows that the decay curves given in figure 1 demonstrate three-component exponential decays. Moore and Thompson [22] observed a two-component exponential decay for ZnO thin films. The fast component in the photocurrent relaxation can be associated with the recombination of free electron-hole pairs [23]. The slow component can be attributed to the lattice relaxation process of a surface state [24]. The SPV decays can also be explained by taking into account the recombination of conduction-band electrons with photogenerated holes captured at the surface [25].

Considering our decays shown in figure 2, we find that the first SPV component, associated with the electron-hole recombination, is present in the inserting. This component is very similar both in the HT and US samples produced at 351 K, whereas it is faster in the sonochemical sample than that in the hydrothermal sample grown at 338 K.

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Figure 2. SPV decays in hydrothermally and sonochemically synthesized samples.

The second SPV component, associated with a lattice relaxation process of surface states, exhibit slightly different slopes on a semilog scale (see figure 2) which can be associated with a different concentration of surface states. The data evidence that the greater fabrication temperature causes greater concentration of surface defects.

The third component of the SPV decay is associated with the charge transfer through surfaces defects. There are two causes for observed different density of surface states, including different growing mechanism for both synthesis procedures and temperature.

#### 3. Conclusion

Zinc oxide has been synthesized via hydrothermal and sonochemical procedure at equal temperatures. Both the PL spectra and SPV decays are found to change with the fabrication route. The observed differences are shown to originate from the interplay between bulk and near-surface concentration of point defects. Increasing the synthesis temperature causes the long-wavelength shift of the PL spectrum in hydrothermal samples. On the other hand, for sonochemical synthesis, increasing the temperature causes the short-wavelength shift of the PL band. The increase in the synthesis temperature has no strong effect on the SPV decays in hydrothermal samples. In contrast, SPV decays are sensitive to the growth temperature in sonochemical samples, indicative of varying transited charge transfer processes and surface state densities. The sonochemical route is therefore capable of improving the distribution of defect concentrations, which is important for improving light emission of photonic devices.

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