

# Nearfield spectroscopy of a ZnO thin film

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im Forschungsverbund Berlin e.V., Germany (April 2015)

## Introduction

Zinc oxide receives increasing attention as a semiconductor material for UV/blue electro-optic nano-devices. Among the reasons are the high exciton binding energy of 60 meV, the band gap of 3.3 eV, the radiation resistance, low production cost and non-toxicity. Recent advances in ZnO fabrication by radical source epitaxy make high quality films available, that permit the study of excitations in the surface region of the crystal. While the bulk of a semiconductor can be modified and structured by doping and alloying, the semiconductor surface offers the possibility of modification through a much wider range of materials, in particular organic molecules. The interaction may be static or dynamic, including energy and charge transfer or even strong coupling and hybridization. The latter types of interaction sensitively depend on the separation between the excitons in both materials and on their dimensionality (1D or 2D).

There exists a specific excitonic state on high quality ZnO, that is localized just a few nm below the surface, known as the surface exciton (SX). It is often the dominant excitonic feature in ZnO nano-structures at low temperatures. At first glance the SX looks like the perfect candidate for hybridization with organic crystals. But is it really?

To find out, we have looked into the spatially resolved spectral and dynamic properties of the SX at the nano-meter length scale. To this end we utilize a near-field scanning optical microscope (NSOM) that is operated at variable temperatures, down to 5 K. We obtain a spectral map of the SX by photoluminescence (PL) imaging and compare it to another ubiquitous excitonic state, the neutral donor-bound exciton DX.

## The cryogenic NSOM

Perhaps the most common NSOM is based on light confinement by a nanoscopic aperture in the metallic coating of a pointed optical fiber tip. However, to avoid problems with poor transmission and quenching by the metal, we apply all-dielectric tips that achieve a good resolution of  $\lambda/3$  (at 370 nm) paired with near unity transmission. This permits us to work in excitation/collection mode, where the PL is collected through the same tip that is used for excitation, simplifying the optical setup. Using a shear-force feedback, the tip is positioned  $\sim 10$  nm above the sample surface. Thereby, immediate contact with the delicate surface is prevented.

## Application Note

The excitation light is provided by a HeCd laser (32 nm, 3.81 eV). Detection is accomplished with a 50 cm spectrograph (ACTON, SpectraPro 2500i), featuring a grating with 3600 lines/mm, and a cooled CCD camera (Andor Newton). The main requirements of extremely low mechanical vibration, high sensitivity in the near UV, low background current and good uniformity are essential to this experiment. It must be remembered, that the small detection volume delivers a proportionally small signal that cannot be compensated by an increased excitation without driving the excitonic PL into a non-linear regime.

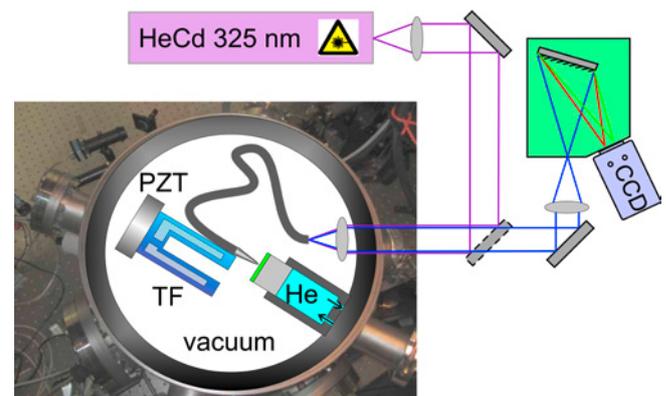


Figure 1: Schematic setup with the optical path and the vacuum chamber housing the NSOM. The near-field tip is glued to a quartz tuning fork and mounted on a 3D piezo translation stage. He: liquid helium flow cryostat, TF: tuning fork, PZT: piezo scanner

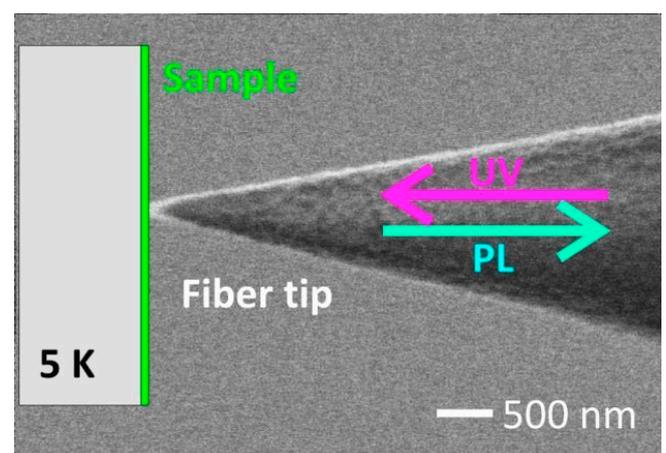


Figure 2: Electron micrograph of a dielectric NSOM tip with the schematic of the measurement geometry.

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## Spatial distribution of SX and DX

To observe the spatial properties of excitons near the ZnO surface, a special sample has been grown consisting of a 20 nm ZnO thin film and a 350 nm Zn<sub>0.88</sub>Mg<sub>0.12</sub>O blocking layer on a ZnO substrate. The blocking layer absorbs all photons that transmitted by the thin film and prevents them from reaching the substrate. Thus, all photons in the ZnO PL band must originate from the thin film. Consequently, a high surface-to-volume ratio of a nanostructure is achieved, but in a clear two-dimensional geometry. The thin film is furthermore decorated with a monolayer of stearic acid. This molecule is known to enhance the SX on the ZnO surface through its COOH anchor group. The chemisorbed molecule thus acts as a surface impurity capable of binding an exciton to the surface with a localization energy around 10 meV which corresponds to a resonance energy of 3.3665 eV. In Figure 3a the spectral signature of the SX can clearly be recognized. The width is around 6 meV. In addition, there is the ubiquitous DX resonance at 3.3615 eV corresponding to an exciton bound to a neutral donor common to most ZnO crystals. Sharp lines limited by the instrument resolution of 0.5 meV can be observed here. As shown in the spatially resolved spectrum in figure 3b, the DX lines are spatially localized and fluctuate in energy. At the same time, the SX remains broad and featureless, just as the spatially averaged spectrum. We can thus conclude that the character of the SX differs from the common DX in terms of the localization behavior.

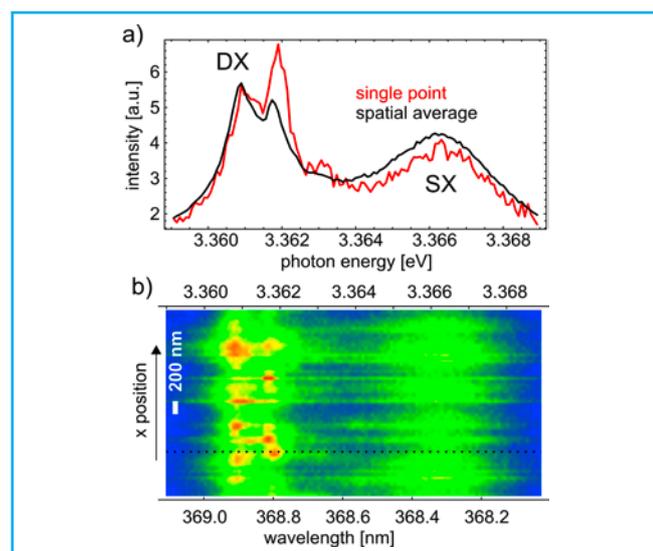


Figure 3: a) Spatially averaged (black) and single point (red) spectra of the ZnO thin film showing the DX and SX resonances. b) Spatially resolved spectra over 2.8  $\mu\text{m}$  showing the DX fine structure. The dotted line highlights to the spectrum shown in (a). Fluctuations of the intensity at some scan positions are caused by mechanical vibrations of the flow cryostat.

## Application Note

It may be argued, that the resolution of 100 nm ( $\sim\lambda/3$ , Sparrow criterion) is insufficient to resolve individual SX resonances. However, the temperature dependence of the SX lifetime  $\tau(T)$  and a time-resolved transport measurement  $I_{\text{pl}}(t)$  provide evidence that the SX is delocalized and two-dimensionally extended. The transport was observed from the shortening of the SX lifetime under the local excitation and local detection scheme provided by the NSOM. Diffusion of excitons out of the detection area acts like an additional decay channel for the exciton population that was initially created during the excitation. The two-dimensional character of the SX is beneficial for the coupling to organic crystals deposited on top of the ZnO since the distance dependence of the coupling strength is more relaxed than in the case of two point-like dipoles. Thus the SX is a hot candidate for future hybrid opto-electronic nano-devices.

## Conclusions

The Andor Newton DU920P-OE could be easily integrated in an NSOM setup operating in the near UV for the investigation of novel wide band gap semiconductor structures. High efficiency paired with a low background current, low mechanical noise, easy integration into a control program based on LabView, and a high degree of flexibility are distinguishing qualities of this camera.

## References

S. Friede, S. Kühn, S. Sadofev, S. Blumstengel, F. Henneberger, T. Elsaesser, Phys. Rev. B 91, 121415 (R) (2015)

## Contact

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