Low temperature nanocrystalline zinc oxide for photovoltaic applications

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Abstract. Nanocrystalline ZnO was synthesized by a low temperature sol-gel route. The ZnO nano crystals were investigated by X-ray diffraction (XRD), electron paramagnetic resonance (EPR), photoluminescence (PL), and conductivity measurements. The goal was the development of nanocrystalline ZnO as a transparent conductive oxide blocking ultraviolet (uv) light and using a defect photoluminescence band for down-shifting uv light into the visible range, where organic photoactive polymers have their absorption maximum. The resulting defects and physical properties are discussed with respect to the conductivity of ZnO nanocrystals.

1. Introduction
Zinc oxide (ZnO) is a wide bandgap semiconductor with applications in photonics, optoelectronics, and sensor technology [1-5]. Doped with aluminum ZnO (AZO) attracted much attention as a promising substitute material to the currently used indium-tin-oxide (ITO) as a transparent conducting oxide (TCO). While first devices such as flat screens using AZO were recently launched, serious problems limiting the performance of devices due to unwanted defects and unintended doping still exist. Usually omnipresent defects characteristic of specific growth techniques determine optical and electrical properties of ZnO. In particular these defects compensate intended n-doping and cause strong luminescence in the visible spectral range. In most applications these implications have to be avoided. Thus, both properties were subject of detailed studies in the past [6-11]. However, there are also applications like e.g. organic photovoltaic, benefiting from such defect luminescence. Due to its wide bandgap ZnO absorbs ultraviolet (uv) light and, thus, protects photosensitive organic materials as used in organic solar cells from being destroyed by high energy photons. At room temperature in nominally defect-free ZnO is observed strong photoluminescence of free excitons at around 3.1 eV upon uv irradiation. Regarding damageable organic materials used in photovoltaic applications this luminescence is still dangerous and at least unusable for creating a photovoltage. Since ZnO always contains intrinsic defects a second photoluminescence band shows up upon uv irradiation [12,13]. The so-called defect luminescence band is located at around 2.2 eV. This photoluminescence band fits energetically perfect to the absorption spectrum of photoactive polymers used in organic photovoltaics. Downshifting uv light to visible light will enhance photovoltaic output. It turned out that the defect photoluminescence band can be maximized, while at the same time the unwanted free exciton luminescence is quenched. Thus creating certain defects by post-annealing or adapted crystal growth conditions allows tuning ZnO such that it acts as a uv protector and at the same time down-shifting unusable uv light absorbed improving the performance of organic solar cells.
Nano and microcrystalline ZnO have been fabricated by several techniques, such as thermal decomposition (e.g. [14,15]), hydrothermal synthesis (e.g. [16,17], gas-phase reaction [18], and sol–gel method [19-21] with different particle morphologies and sizes. Electrical and optical properties as well as surface-related photocatalytic activity of ZnO nanocrystals strongly depend on dopants and defects [22]. Thus, understanding the role of intrinsic defect centers such as vacancies, interstitials, and antisites is a key toward controlling the electronic and optical properties of nanocrystalline ZnO. Electron paramagnetic resonance (EPR) has successfully been used for the identification of defects and dopants allowing the study of their microscopic and electronic structure. Together with optical properties studies of defect kinetics upon annealing are helpful for solving the described tasks.

In the present study nanocrystalline ZnO particles were prepared at low temperatures by a sol-gel procedure allowing crystal growth. A low temperature process is essential, because ZnO should act as a direct cover layer on top of the photo-active polymer, which otherwise is destroyed at temperatures above around 100°C. We report on characterization by EPR, photoluminescence (PL), conductivity measurements, and X-ray diffraction (XRD).

2. Experimental

2.1 Sample preparation

Several sol-gel routes are known for the growth of nano and micro crystalline zinc oxide [19-21]. In contrast to usual applications, AZO has to be deposited as a nanocrystalline film at rather low temperatures for organic photovoltaics. Therefore we modified a low temperature sol-gel process [44] in order to grow ZnO nanocrystals and nanocrystalline films. The low temperature sol-gel procedure [23] is based on the reaction of Zn$^{2+}$ and OH$^{-}$ in an alcoholic medium (methanol). To prepare undoped ZnO, a solutions of zinc acetate di-hydrate Zn(ac)$_2$$\cdot$2H$_2$O, 45 mmol, purity 99.99%) in 200 ml of methanol was prepared, aided by stirring at 52°C for 2 h. A 140 mmol KOH containing methanol solution (200 ml) was added to the solution containing Zn(ac)$_2$$\cdot$2H$_2$O with constant stirring while heating at 52°C for 2h. The nanocrystals which formed were separated from the solution by centrifugation, washed several times with ethanol, and then dried in air at 25°C to obtain nanocrystalline powder. For the study of defect kinetics some nanocrystals were annealed in different atmospheres at various temperatures up to 600°C. In order to study photoluminescence and the kinetics of defects responsible for photoluminescence bands we performed annealing series including different Al doping levels. The Al doping was done during the sol-gel process by adding Al(NO$_3$)$_3$$\cdot$9 H$_2$O. The samples were characterized with electron paramagnetic resonance, photoluminescence, electron microscopy, X-ray diffraction, and conductivity measurements.

![Figure 1. XRD spectra of sol-gel fabricated nanocrystalline 0.5% Al-doped ZnO. Identified signals are labelled by crystallographic direction according to [24]. The graph labelled ‘as grown’ was without annealing, the graphs labelled ‘450°C’ and ‘600°C’ are from ZnO nanocrystals annealed in argon atmosphere at the temperatures given.](image)

2.2 Characterisation

The structure and surface morphology of sol-gel ZnO nanocrystalline powder was measured by X-ray diffraction (XRD, PANalytical X’Pert PRO with X’Celerator real-time multiple-strip detector (Cu K$_{\alpha}$).
40 kV, 40 mA)), energy dispersive X-ray spectroscopy (EDX, Zeiss Neon 40, not shown here), and scanning electron microscopy (SEM, not shown). EDX definitely shows that the particles obtained by the sol-gel process are ZnO. The crystalline structure of the nano crystals was confirmed to be wurzite by X-ray diffraction analysis. Figure 1 shows examples from different annealing temperatures (annealing in argon atmosphere) of sol-gel ZnO nanocrystals. Already without annealing (figure 1, lower trace) XRD shows the typical reflection peaks of wurzite ZnO. These broad lines become narrower with increasing annealing temperatures (figure 1 upper traces) reflecting the growing size of the crystalline particles. Using Scherrer’s equation [25] we calculated particle diameters of 8 ± 1 nm (0°C), 13 ±1 nm (450°C), and 23 ± 1 nm (600°C).

Photoluminescence of the sol-gel ZnO nanocrystals was measured upon excitation with the light of a He-Cd-LASER (see figure 2). The low energy luminescence band at around 2.2 eV generally is due to defects of various origins, while the band around 3.1 eV is due to free excitons in ZnO. Both bands increase in intensity upon annealing of the ZnO nanocrystals and both are well-known from literature [22]. The exciton band has low intensity if ZnO particles are small and becomes intense upon growing particle size. A slight shift of the photoluminescence band towards higher energy is due to an increasing band gap when the size of the crystals increases. The low energy photoluminescence band (defect photoluminescence band) is also increasing in intensity upon increasing particle size; however, the band shows various small energy shifts and unresolved details within the line shape. The origin of the luminescence is still under discussion and not completely clear. Nevertheless, this band is more intensive than the exciton band in nanocrystals prepared without annealing (figure 2, lowest trace, labelled ‘0°C’). Upon annealing of ZnO nanocrystals in argon atmosphere from 300 to 600°C (see figure 2, further traces) the high energy exciton photoluminescence band becomes stronger, until at 600°C it shows at least the same intensity as the low energy defect luminescence band.

Further defect analysis was performed by EPR. Figure 3 shows an example for a series of nanocrystalline ZnO samples nominally doped by 0.5% Al. Already without annealing an EPR line is observed at the g-factor of shallow donors. The line shape is clearly ‘Dyson’ type [26], thus showing that the EPR is due to conducting electrons. A first annealing step at 100°C almost quenches the signal; while after 300°C annealing numerous new EPR lines appear. They are labelled in figure 3 according to EPR spectra of defects already known from literature (see e.g. [22]). The intense EPR line labelled ‘SD’ is due to shallow donors in ZnO, which are intrinsic and extrinsic having all very similar g-factors and are usually not resolved by EPR.

**Figure 2.** Photoluminescence spectra of ZnO nanocrystals measured at room temperature and prepared by a low-temperature sol-gel procedure (see text). The PL was excited with sub-bandgap light of a HeCd-LASER (see LASER peak at 3.815 eV).
3. Discussion

Our XRD investigations (see figure 1) show that the size of ZnO nanocrystals increases upon annealing. Likewise we observed structural development of lattice defects, such as vacancies (either oxygen or zinc) or surface defects (like $O_2^-$) by EPR. Thus, annealing at around 600°C results in a strong resonance of shallow donors (see figure 3; EPR is proportional to defect concentrations), mainly because of the shallow aluminum donor doping. This unambiguously shows that the crystalline properties of ZnO become dominant at that annealing temperature. This observation is also confirmed by conductivity measurements as shown in figure 4. Annealing at 600°C leads to the highest conductivity in nanocrystalline ZnO, however, in case without annealing the conductivity is almost the same (see figure 4). Since we intend applying low temperature grown nanocrystalline ZnO, having a strong defect photoluminescence band (2.2 eV in figure 2) and weak photoluminescence at 3.1 eV, a preparation of sol-gel ZnO as described above without further annealing seems to be a satisfying choice.

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