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All-inorganic light emitting device based on ZnO nanoparticles

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We report on room-temperature electroluminescence from an all-inorganic light emitting device based on spin-coated ZnO nanoparticles. A tight submicron thick layer was fabricated on a fluorine doped tin oxide glass as a substrate using commercially available ZnO nanoparticles from the gas phase. After the evaporation of the top Al electrode, a diodelike I-V characteristic was obtained. An emission peak at around 390 nm and a broad defect-related electroluminescence in the visible range were observed at voltages below 10 V and ambient air conditions. © 2009 American Institute of *Physics*. [DOI: 10.1063/1.3093675]

Electroluminescent devices with nanoparticles as an active layer are expected to combine reliability, long operating lifetime and high optical quality of semiconductor material systems with low cost, easy handling, and flexible large-area technology of organic light emitting diodes (LEDs).¹⁻⁴ Besides, nanoparticles show high fluorescence efficiency and tunable light emission.⁵ Common nanoparticle hybrid emitting devices consist of a thin nanoparticle layer¹ or monolayer² embedded between two or more organic support layers. An indium tin oxide (ITO) coated glass is usually used as a transparent conductive substrate and Al, Ca, or Mg act as a top electrode.¹⁻⁴ One of the promising materials for the active nanoparticle layer in hybrid emitting devices is ZnO, which consists of nontoxic elements and is not subject to oxidation and therefore suitable for large area applications under ambient air conditions. Another advantage of ZnO is its direct wide band gap and high exciton binding energy at room temperature, which allows efficient emission for LED and laser applications in the ultraviolet (UV) and visible spectral range.^{6,7}

However, the realization of low cost ZnO light emitting devices remains challenging. One of the approaches is to use ZnO nanowires in hybrid systems.⁸⁻¹² The devices showed broad electroluminescence (EL) in the visible range as well as near band gap emission in the UV range.⁸⁻¹² Unfortunately, due to the growth process of the nanowires, in most cases, the low cost production of such devices on flexible large area substrates or completely printable devices is quite challenging and inconvenient. Near band gap and visible EL from ZnO nanoparticles in the dc regime was demonstrated by a hybrid device,^{13,14} where a nanoparticle monolayer was embedded between organic layers in order to support the charge carrier injection into the active nanoparticle layer. On the other hand these organic layers are quite sensitive to oxygen and humidity and therefore expected to limit the lifetime of the device.

Some straightforward concepts used ZnO nanopowder pressed between ITO glass and an Al electrode. EL was observed at voltages of the order of several hundred volts.^{15–17} A significant reduction in the operation voltage could be achieved by reducing the thickness of the nanoparticle layer from 0.3 mm (Ref. 15) down to 500 nm.¹⁸ In both cases,

however, purely defect related emission in the visible range was obtained and a distinctive EL contribution in the near band gap range remained so far out of reach for all-inorganic nanoparticle concepts.

In this letter, we report on a low-voltage, completely inorganic ZnO nanoparticle large-area light emitting device prepared on a fluorine doped tin oxide (FTO) coated glass substrate. A stable I-V characteristic and light emission in the visible range, as well as a pronounced near band gap emission peak, are observed at room temperature under ambient conditions.

We used commercially available gas-phase ZnO nanoparticles, produced by Evonik Degussa GmbH. Figure 1 shows the shape and size distributions of these nanoparticles from the gas phase, analyzed by scanning electron microscopy (SEM). One can mainly distinguish between rods (dark bars), round (light-colored bars), and squared nanoparticles (bars with middle brightness). The statistic shows a wide size distribution from particle sizes below 10 nm in diameter up to rods with a length of 160 nm and even higher. Nevertheless, around 60% of the particles are spherical with a diameter between 10 and 50 nm. The nanoparticles were dispersed in butyl acetate solution and spin coated on top of the FTO coated glass substrate. The thickness of the nanoparticle layer was measured by atomic force microscopy to 350 nm. The SEM image in the inset of Fig. 1 reveals a homogeneous, tight and dense layer. The sample was dried for 30 min at 150 °C on a hotplate under ambient air conditions in



FIG. 1. (Color online) Size and shape distributions of the ZnO nanoparticles. The inset shows an SEM image of the nanoparticle layer on top of the FTO substrate.

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FIG. 2. (Color online) Room temperature *I-V* characteristic of the device. The upper inset shows the schematic of the device while in the bottom inset a simplified energy diagram of the device is depicted.

order to evaporate the residues of the butyl acetate solvent. Afterwards, a 250 nm thick Al contact was evaporated on top of the nanoparticle layer through a shadow mask.

The upper inset on Fig. 2 shows the schematic of the light emitting device, while in the bottom inset of Fig. 2 a simplified energy level diagram of the device structure based on published data for the involved materials^{3,10} is depicted. FTO was chosen as a transparent electrode because of its higher work function compared to ITO and is therefore expected to have higher EL yield. Another reason for choosing FTO was its nanopyramid structure, shown in the inset of Fig. 1, which should improve the adhesion of the nanoparticle layer and also the electrical contact to the ZnO layer for better large-area EL.

EL measurements were performed at room temperature and in ambient air. Figure 2 shows the *I-V* characteristic of the device. A dc voltage between -6 and +10 V was applied to the electrodes according to the scheme in the upper inset of Fig. 2. It shows diodelike behavior in both forward and reverse directions, which is due to quite similar work functions of both Al and FTO contact layers. The currents through the device are in the range of tens of milliamperes, which is typical for nanoparticle light emitting devices, $^{1-3,9-12}$ but significantly lower compared to ZnO nanoparticle light emitting devices with organic support layers of similar lateral size. 13,14 Reverse bias showed overall higher currents than forward bias and leads to a breakdown of the device at about -7 V.

EL signal from the device was collected through the FTO glass substrate in a standard luminescence setup simultaneously with the *I-V* characterization. The intensity of the EL in reverse (squared data points, dashed line as a guide to the eye) and in forward (triangular data points, continuous line as a guide to the eye) direction versus current is shown in Fig. 3. The fact that EL is observed in both directions is comparable to other nanoparticle emitting devices, ¹⁹ where it was related to the small difference in the working functions of Al and FTO (see Fig. 2). Note that FTO can also be used as electron injection layer in case of a Au top contact.¹⁰ The EL intensity in forward direction is at least two times higher than the EL intensity at the same current in reverse direction. This indicates that the leakage currents through the active nanoparticle layer, e.g., through defect states, under reverse



FIG. 3. (Color online) EL intensity of the device as a function of the current in forward (continuous line) and reverse (dashed line) directions. The inset shows a photograph of the emitting device at +8 V forward bias.

bias are higher and therefore the EL yield is lower than in forward direction. The inset of Fig. 3 shows a photograph of the light emitting device at +8 V. Although the whole contacted area of the nanoparticle layer shows EL, the intensity over the emitting region remains inhomogeneous. Some of the possible reasons might be inhomogeneities of the active layer due to the wide size and shape distribution of the nanoparticles (as shown in Fig. 1) as well as lateral inhomogeneities within the contact layers.

Room temperature photoluminescence (PL) measurements of the ZnO nanoparticles were performed as a reference for understanding the EL spectra. For this, the same ZnO nanoparticles were deposited on a Si substrate and studied in a standard PL setup under excitation by the 334.5 nm Ar⁺ laser line. As shown in Fig. 4(a), the PL signal of the nanoparticles is mainly dominated by the high energy part of the visible spectral range and the UV range with some contribution of the longer wavelength regime, which is typical for ZnO nanostructures.²⁰ The PL spectrum is strongly dominated by the near band gap recombination at about 385 nm and a strong emission peak at about 435 nm, often observed in literature.^{7,11,20} The green emissions forming a wide spectral shoulder at the low energy tail. The origins of the visible emission in ZnO nanostructures are often natural defects like oxygen vacancies or Zn defects,²¹ which result in additional



FIG. 4. (Color online) (a) Room temperature PL spectrum of the involved nanoparticles, (b) EL spectra of the device at different voltages in the forward direction, and (c) comparison of those EL spectra at 10 and 4 V.

energy levels within the band gap of ZnO.^{20,21}

The EL spectrum of the device in forward direction is shown in Figs. 4(b) and 4(c). A measurable EL was already observed at 4 V. The spectrum shows a peak at about 780 nm indicating that at 4 V low energy defects within the band gap are accessed. An increase in the applied voltage leads to a broadening of the EL spectrum toward the high energy side. Most of the visible spectrum is covered at 6–8 V and causes a white color of the EL well visible to the naked eye. Similar EL spectra were already observed in ZnO nanowire and thin film light emitting devices^{8,22} and also related to defect and impurity centers. A significant contribution of the characteristic ZnO near band gap emission becomes visible at a forward bias of 9 V and higher. The near band gap EL peak at 10 V is already quite pronounced. This is shown together with EL at 4 V magnified by a factor of 40 in Fig. 4(c). The increase in the bias voltage also leads to a continuous enhancement in the EL intensity and, at 10 V, the EL intensity is almost 200 times higher than at 4 V.

Comparing EL and PL measurements, the dominant role of the ZnO nanoparticles as an origin of the EL signal becomes very obvious. Both PL and EL show a pronounced peak in the near band gap region. The position of the near band gap emission in EL of the device is about 6 nm redshifted with respect to the PL spectrum of the same nanoparticles. One reason is the fact that the EL spectrum is collected through the FTO coated glass, which absorbs UV light while the PL spectrum is obtained in reflection geometry from the top of the nanoparticle layer, i.e., without transmittance through the glass. In addition, such a redshift of the EL spectrum as compared to the PL spectrum is quite common for a nanoparticle^{1,23,25} and nanorod devices¹⁰ and attributed to reabsorption of the EL signal within the nanoparticle layer,¹ energy transfer from small to big nanoparticles,^{1,23} Stark effect from high local fields,²⁴ or local heating due to poor thermal conductivity of the emitting layer.²⁵ The contribution of the defect states to the overall EL emission is different as compared to the PL signal indicating that deep defect states are apparently more easily populated during electrical carrier injection, while the high excess energy in case of optical excitation favors short wavelength emission.⁸

In conclusion, we fabricated a ZnO nanoparticle based large-area light emitting device without the use of any organic support layers. The active layer with a typical thickness of 350 nm was formed by spin coating of a butyl acetate dispersion of nanoparticles from the gas phase. The device operates at low voltages between 4 and 10 V and shows spectrally broad EL, visible to the naked eye, as well as a pronounced near band gap emission in the UV range. The device showed stable operation at room temperature under ambient air conditions. The complete fabrication is easy and compatible with large-area manufacturing on flexible substrates. This might be a first step toward low cost inorganic nanoparticle luminescent devices.

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