



KPAN005: Application - Photovoltaic Research

“Size and Orientation Dependent Photovoltaic Properties of ZnO Nanorods” -

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Keywords

ZnO, ITO, SPV, Surface Photovoltage, Photovoltaics, WF, Work Function, KP, Kelvin Probe

Abstract

ZnO nanorod arrays on an ITO substrate and nanorod powder have been prepared via a chemical method in aqueous solution at low temperature. Two dimensions of composite nanorods in the arrays were obtained by controlling the reaction time. SEM, XRD, UV-vis transmission, and PL measurements have been utilised to characterise the samples. The surface photovoltage (SPV) spectra of the three samples have been comparatively investigated by a lock-in amplifier with dc bias and Kelvin probe (KP) based measurements. The kinetic features of SPV responses are interpreted in terms of ac SPV phase spectra and SPV transients on a KP. It is demonstrated that the photovoltaic properties of ZnO nanorods not only depend on the rod size, but also rely on the crystallographic orientation. The mechanisms therein have been discussed in detail. The results could lead to better understanding of the photovoltaic properties in ZnO nanostructures.

Research Area

In recent years, considerable attention has been paid to nanostructured ZnO material, which is mostly inspired by its diverse functional properties in mechanics, optics, electronics, magnetism, and catalysis, as well as the accessibility to facile fabrication of nanocrystals with various shapes and controlled dimensions (from quantum dots to three-dimensional networks). Bulk ZnO material has a direct wide band gap (*E.g.* ≈ 3.37 eV, 368 nm) and a large exciton binding energy (~ 60 meV) at room temperature. For ZnO systems with diverse nanostructures, influences of shape and dimension on surface related properties are significant. For example, one-dimensional ZnO nanostructures with controlled tip shapes show modulated visible photoluminescence, as well as tuned current rectification characteristics. ZnO nanorod arrays with similar grain sizes but different morphologies are discrepant on field emission. These modulated properties have been much attributed to the varying oxygen vacancy distribution at the grain surface determined by different shapes. New features coming with a reduced grain size, such as a widened band gap and enhanced exciton-related luminescence, are mainly due to the quantum size effect or confinement effect, and an anomalous blue shift in the emission spectra of ZnO nanorods with reduced sizes that are beyond the quantum confinement regime has been recently observed, which is ascribed to an enhanced surface effect due to a larger surface-to-volume ratio. Potentially improved performance of ZnO in sensors, transducers, catalysts, and solar cells can be expected with properly designed nanostructures. Therefore, it is of practical interest to study the correlation between various nanostructures and the novel properties of ZnO materials for their future applications in functional devices.

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Use of Kelvin Probe

The surface photovoltage (SPV) method is a well-established technique for the characterisation of semiconductors, which provides both optical and transport properties of different regions in the material under study, with high sensitivity to defect states in the sample at its surface, bulk, or any buried interface. The detected SPV response depends on the light absorption, charge separation, and charge transport properties of the system under investigation. A Kelvin probe (KP), as the first elaborate equipment for SPV detection, measures the surface work function and follows the change in the surface potential under steady illumination, which is sensitive to surface charge changing due to either a fast or a slow process.



Figure 1. KP Technology SPS030 System.

KP-based SPV measurements were carried out on the KP Technology Ltd commercial KP system (SPS030.). The width of the gold reference probe is 1.8 mm. The work function of the probe is employed as 5.1 eV after the manufacturer. The SPV was measured by tracking the contact potential difference (CPD) between the sample and the probe. The SPV spectra were obtained by scanning the monochromatic light through the visible and UV range with a rate of ~ 30 nm/min. All the SPV measurements were operated under ambient conditions, and the raw data were not treated further. Constant light intensity at each wavelength was not used, and the monochromatic light intensity depended on the xenon lamp spectral energy distribution. The largest intensity of the incident monochromatic light is less than $80 \mu\text{W}/\text{cm}^2$.

Steady monochromatic light was incident directly onto the top surface of the sample. In Figure 2, the SPV spectra of the three samples are shown. The following points of interest deserve our attention. First, the SPV onset of curve C is dramatically red shifted compared to that of curves A and B in the sub band gap region. The SPV observed likely point to the surface being positively charged upon illumination. The widened spectral region of the more marked SPV response of sample C could be attributed to the dominating orientation adopted by the nanorods in the powder, which makes the surface states on the lateral face of the nanorods much exposed to the probe.

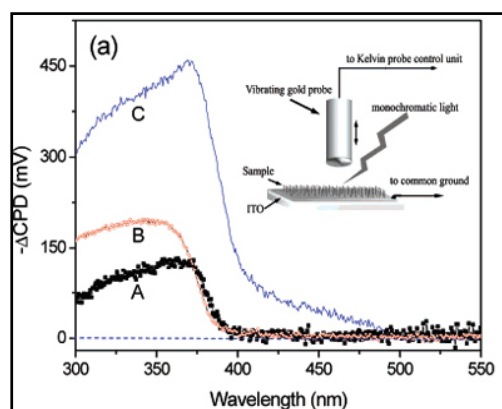


Figure 2. SPV spectra of sample A (curve A), sample B (curve B), and sample C (curve C) with illumination on top taken on the KP. Inset: Schematic set up of the KP-SPV measurement.

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Second, the SPV strength of sample B is much stronger than that of sample A in SPV results from both the lock-in amplifier and KP, which also indicates that the surface states play a key role in separating photogenerated electrons and holes to yield SPV response. Third, the SPV onset of sample B has a small blue shift with respect to that of sample A, which can also be discriminated by comparison of sample A with sample B in ac SPV spectra. The SPV onset of sample A is at ~391 nm and that of sample B at ~387 nm. The difference is assigned to the reduced grain size of the nanorods in sample B, which have a smaller average width than those in sample A.

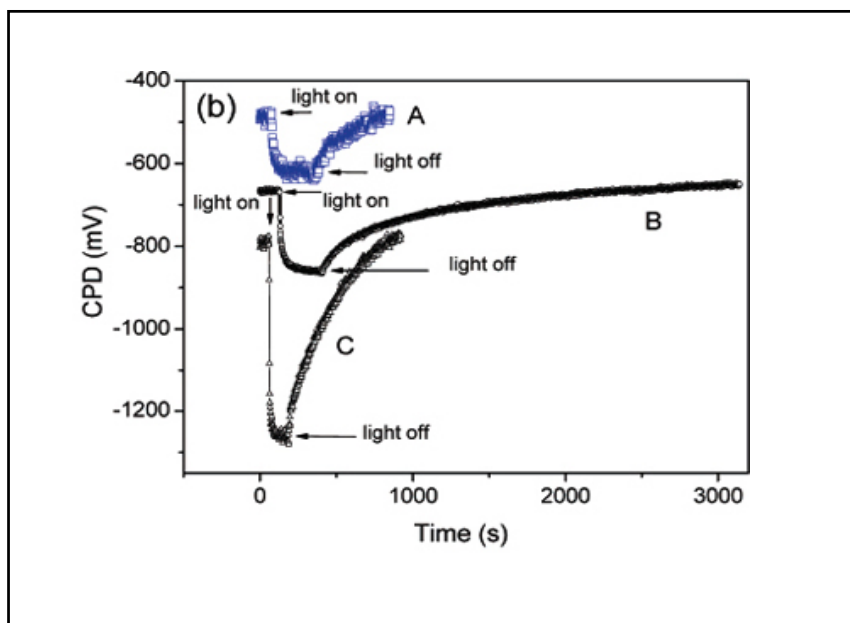


Figure 3. CPD changes with 350 nm light switched on or off: curve A, sample A; curve B, sample B; curve C, sample C. Curve B has been shifted down by 100 mV and curve C by 300 mV for clarity

The KP detection for sample C seems more sensitive than the lock-in method without bias, partially because only one mechanism dominates in the KP configuration, which is without the contact between the top electrode and the sample. The excess charge carriers with two polarities are further separated across grain boundaries between nanorods via diffusion, and the KP detects the accumulated change in the surface potential under steady illumination.

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Conclusion

This investigation has qualitatively investigated the effects of the size and the crystallographic orientation of ZnO nanorods on the spectrum-dependent photovoltaic properties. The detected SPV response depends on the light absorption, charge separation, and transport properties in the sample. The size of the nanorods modulates the absorption and penetration depth of the incident light, determining the position where the electron-hole pairs are generated and the possibility that they are separated into charge carriers. The crystallographic orientation of ZnO nanorods with respect to the probing electrode determines whether the photogenerated electrons related to surface states can be effectively detected because of the localised character of the surface states. The surface states are confirmed to be mostly localised at the lateral non-polar surface of the nanorods rather than at the (001) surface, which is of larger density for reduced nanorod size, and slower SPV relaxation kinetics was observed for the nanorods with a smaller grain size. The growth substrate facilitates the macro built-in field to form along the nanorod axis and effects the photogenerated charge transport. Therefore, for nanostructured ZnO materials, the photovoltaic properties could be modulated on the spectrum by the grain size, surface state distribution with respect to the probing electrode via controlled crystallographic orientation, and the charge transport pathway related to the substrate as well as the specific nanostructure. The results are also helpful in understanding the photovoltaic properties in other types of ZnO nanostructures besides nanorods and benefit the design and fabrication of photoactive components of smart systems based on nanostructured materials.

Reference

1. Original publication: "*Size- and Orientation-Dependent Photovoltaic Properties of ZnO Nanorods*" - Qidong Zhao, Tengfeng Xie, Linlin Peng, Yanhong Lin, Ping Wang, Liang Peng, and Dejun Wang.

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