Growth and Characterization of Wide Band Gap Semiconductors

(Zinc Oxide, Zinc Sulfide)

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Abstract

Zinc Oxide and Zinc Sulfide nanostructures were grown on a variety of substrates using aqueous growth solutions. The chemical composition of the nanostructures was characterized using micro-Raman spectroscopy, energy-dispersive X-Ray spectroscopy, and X-Ray diffraction. A Scanning Electron Microscope reveals a well-aligned, uniform, layer of hexagonally shaped Zinc Oxide nanorods growing up perpendicular to the substrate surface while the Zinc Sulfide formed irregularly shaped spheres on the substrate. Depending on the growth conditions, the diameters of the ZnO nanorods ranged from a few hundred nanometers to about 1 μm. The field emission properties of the ZnO nanorods and the ZnS spheroids were studied, with turn-on voltages found to be around 36 v / μm, as well as the effects on ZnS after exposure to various gases which was found to increase the turn-on voltage in most cases.

Growth of Zinc Oxide Nanorods from Aqueous Solution

Well-aligned Zinc Oxide nanorods were grown with a uniform distribution over a substrate from an aqueous growth solution [1]. The Zinc Oxide nanorods grew perpendicular to the substrate surface as single crystals and with an easily distinguishable hexagonal-rod structure.

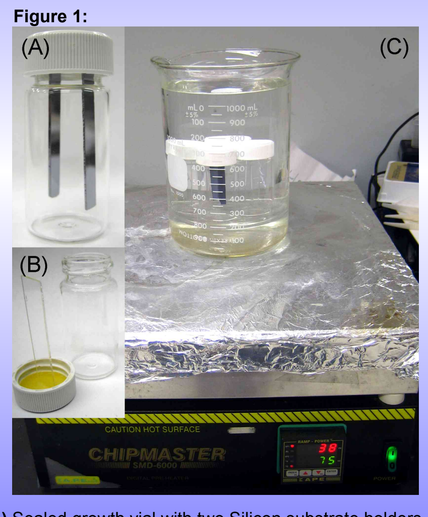
The growth solution was prepared using mixtures of Zinc salt and Hexamine* aqueous solutions and the pH was adjusted using a dilute solution of Ammonium Hydroxide or an acid containing the corresponding anion of the Zinc salt used.

The substrate was mounted vertically inside an autoclavable glass vial containing the prepared growth solution. The sealed vial was submerged in a water bath at the desired temperature maintained by a programmable hot plate.

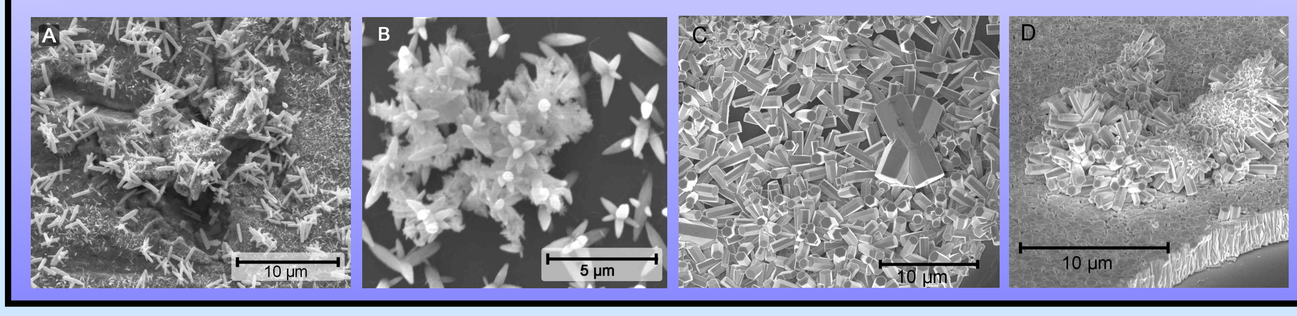
Zinc Nitrate (NO_3^-), Sulfate (SO_4^{2-}), Chloride (Cl^-), and Acetate ($C_2H_3O_2^-$) were used to prepare growth solutions in an equimolar mixture with Hexamine, $C_6H_{12}N_4$. The growth solution concentration ranged from 0.1 M to 5 mM. ZnO nanorods were allowed to grow for 2 to 5 hours at temperatures between 70 and 80 °C. A variety of substrates were used to grow ZnO including Silver, Copper, Nickel, Silicon, and glass.

** Hexamine also known as Hexamethylenetetramine*

Figure 1:



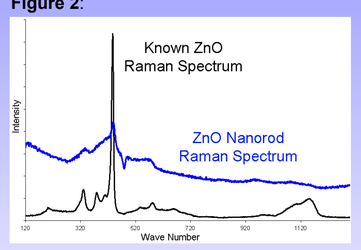
(A) Sealed growth vial with two Silicon substrate holders
(B) Disassembled growth vial with glass substrate holder
(C) Several growth vials in water bath placed on hot plate



Results and Analysis

The chemical identity of the samples was confirmed to be Zinc Oxide using micro-Raman spectroscopy, energy-dispersive X-Ray spectroscopy (EDAX), Photoluminescence, and X-Ray Diffraction (XRD).

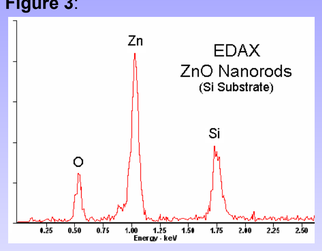
Figure 2:



Left: Raman Spectra of known Zinc Oxide sample and ZnO nanorods

Right: EDAX measurement of ZnO nanorods on a Silicon substrate

Figure 3:



Using a Scanning Electron Microscope (SEM), the ZnO-coated substrates were examined and found to possess a carpet-like layer of hexagonally shaped nanorods growing on their surface. The diameters of the ZnO nanorods ranged (depending on the growth conditions) from only a few hundred nanometers to about 1 micrometer.

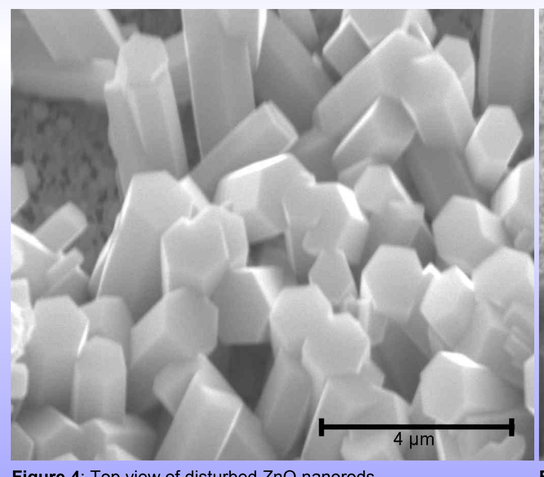


Figure 4: Top view of disturbed ZnO nanorods

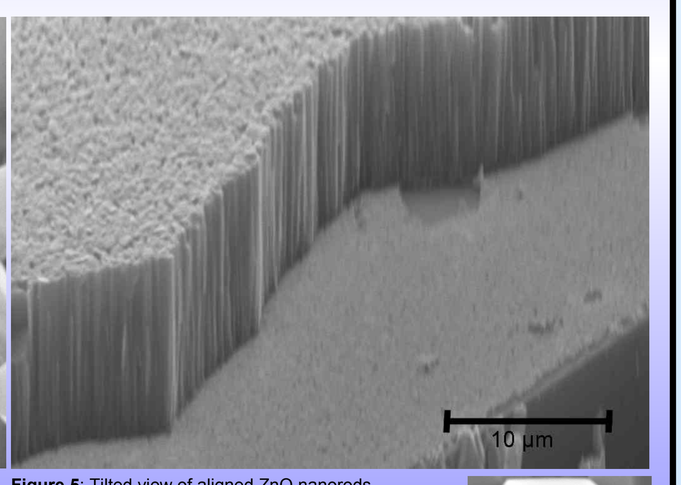
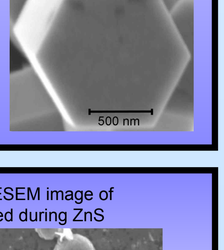


Figure 5: Tilted view of aligned ZnO nanorods

Figure 6 (Left):
(A) Zinc Oxide nanorods on Brass-coated-Copper substrate
(B) Zinc Oxide 'nano-flowers' grown on a Silicon substrate
(C) High resolution SEM showing disturbed, misaligned, nanorods
(D) Tilted, high resolution SEM image showing an edge of ZnO nanorod growth with an extremely uniform height and diameter

Figure 7 (Right): High resolution SEM image of top of ZnO nanorod



Growth of Zinc Sulfide from Aqueous Solution

An attempt was made to grow Zinc Sulfide on a substrate surface using a similar procedure to that used to grow ZnO [2].

A growth solution was prepared using an aqueous mixture of Thiourea (CH_4N_2S), Sodium Citrate ($Na_3C_6H_5O_7$), and a Zinc salt (Zinc Sulfate primarily used). The pH was adjusted using a dilute Ammonium Hydroxide solution until the desired pH level was reached.

Like the Zinc Oxide, growing temperatures for the Zinc Sulfide ranged from about 70 to 80 °C, but the growth time was shorter, usually only lasting 1 or 2 hours. The concentrations of the Zinc salt, Thiourea, and Sodium Citrate present in the growth solution ranged from around 0.05 M to 0.5 mM.

Results and Analysis

Viewed using a Scanning Electron Microscope, irregularly shaped spheres or bumps appear to cover much of the substrate surface. These spheres grew considerably larger than the ZnO nanorods, having a diameter of several micrometers as opposed to the diameters of some of the nanorods which were only a few hundred nanometers.

Using EDAX to analyze the suspected Zinc Sulfide samples, very pronounced peaks were obtained indicating the clear presence of Zinc and Oxygen in roughly a 1 : 1 ratio, as one would expect to see if the sample was of ZnO, with only minute traces of Sulfur by comparison.

Using XRD, no significant amount of Zinc Sulfide was detected and the peaks obtained during the analysis indicate the presence of Zinc Oxide instead.

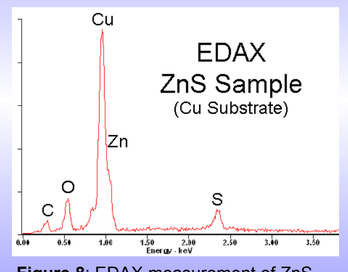
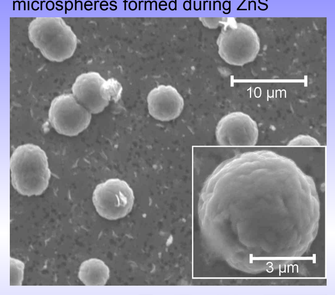


Figure 8: EDAX measurement of ZnS sample on a Copper substrate

Figure 9 (Below): ESEM image of microspheres formed during ZnS



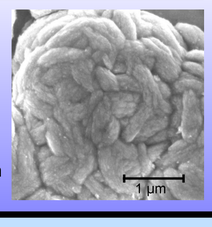


Figure 10 (Right): High resolution SEM image of microsphere

Field Emission

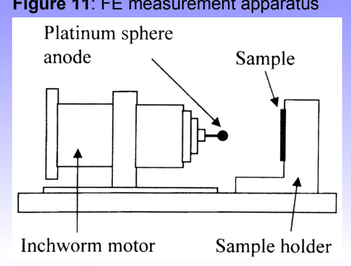
The field emitting properties of both Zinc Oxide and Zinc Sulfide samples were tested. Mounted inside an ultrahigh vacuum (UHV) chamber, a high voltage was applied across the sample and the resulting current was measured.

An inchworm, with a spherical Platinum electrode tip, was used to slowly approach the sample until it made contact. Afterward, the tip was retracted at a known rate until the desired distance between the electrode and sample was achieved. The current emitted by the sample was measured as a function of the voltage applied across it at a given tip separation distance.

$$I = A \cdot V^2 \, e^{\frac{b\phi^{3/2}}{\beta V}} \qquad (1)$$

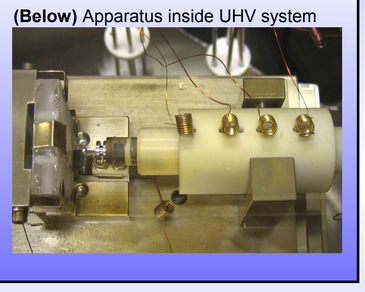
The Fowler-Nordheim (F-N) equation (1) was used to determine the "turn-on" voltage of the sample, the smallest voltage at which the emitted current increases above the 'leakage current' by graphing on an axis of $\ln\left(\frac{I}{V^2}\right)$ versus $\frac{1}{V}$.

Figure 11: FE measurement apparatus



(Above) Diagram

(Below) Apparatus inside UHV system



Field Emission and Gas Exposure Data

A turn-on voltage of 540 volts was measured when the ZnO nanorod sample-to-tip separation was about 15 micrometers (36 volts per μm).

The effects on the field emitting properties of Zinc Sulfide when exposed to various gasses was measured and compared to that of an unexposed Zinc Sulfide sample. The ZnS sample was exposed to Argon (Ar), Nitrogen gas (N_2), Hydrogen gas (H_2), Oxygen gas (O_2), Carbon Dioxide (CO_2), and water vapor (H_2O) for 65, 650, and 6500 Langmuirs
(1 L = 1 x 10^{-6} Torr seconds).

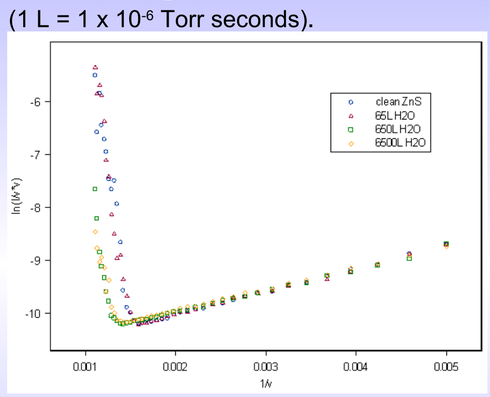


Figure 13 (A) (Above): F-N plot of FE of ZnS at 15 μm, H_2O exposure

It was found that Ar, CO_2, O_2, and water vapor degraded the field emitting ability of the ZnS sample while N_2 showed a slight improvement. H_2 initially improved the field emitting ability of the sample but then caused degradation upon longer exposure.

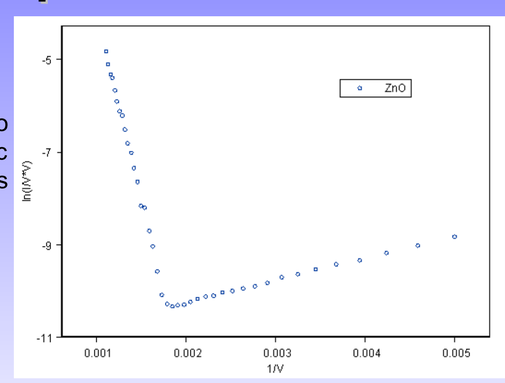
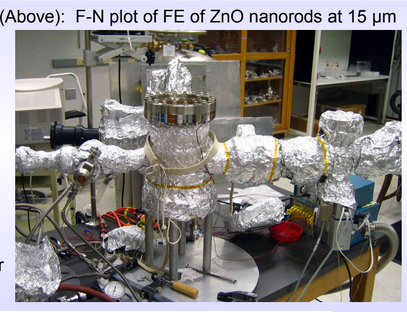


Figure 12 (Above): F-N plot of FE of ZnO nanorods at 15 μm

Figure 14 (Right): UHV Field Emission Chamber



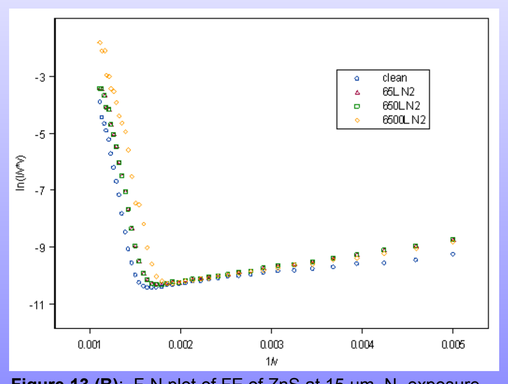


Figure 13 (B): F-N plot of FE of ZnS at 15 μm, N_2 exposure

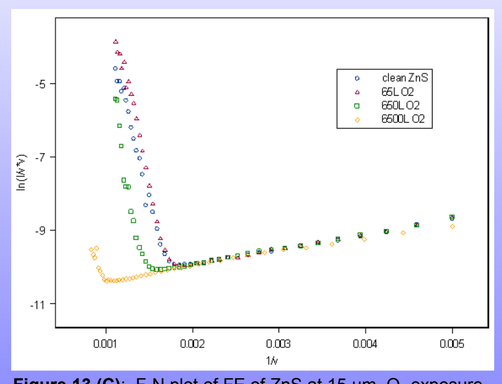


Figure 13 (C): F-N plot of FE of ZnS at 15 μm, O_2 exposure

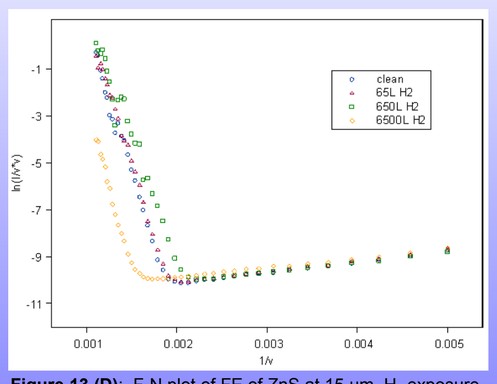


Figure 13 (D): F-N plot of FE of ZnS at 15 μm, H_2 exposure

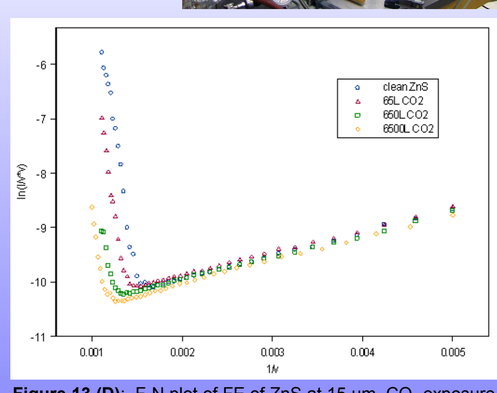


Figure 13 (D): F-N plot of FE of ZnS at 15 μm, CO_2 exposure

Conclusion

Using an aqueous chemical growth procedure, well-aligned, uniform, layers of Zinc Oxide nanorods were successfully grown on various substrate surfaces. These Zinc Oxide nanorods were found to field emit with a measured turn-on voltage corresponding to about 36 volts per micrometer.

Attempts at growing Zinc Sulfide from aqueous solution produced irregular spherical-shaped structures which were found to be made up of mostly Zinc Oxide with only small, barely detectable, amounts of Zinc Sulfide. The effects of exposure to various gases (Ar, N_2, H_2, O_2, CO_2, H_2O) on the field emitting properties of the ZnO-ZnS spheroids was measured showing an increase in the turn-on voltages in all cases except Nitrogen gas which showed a slight decrease in the turn-on voltage.

References

[1] L. Vayssieres, *Adv. Mater.* **2003**, *15*, 464.

[2] D. A. Johnston, M. H. Carletto, K. T. R. Reddy, I. Forbes, R. W. Miles, *Thin Solid Films* **2002**, *403 – 404*, 102.

Acknowledgements

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