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Fabrication & Test of Semiconductor Nanorods based Field Emitters for Applications in Advanced Sensors

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Abstract: ***In this particular study, the field emitters are fabricated using Zinc oxide (ZnO), a wideband gap semiconductor with a high excitonic binding energy. The nanorods of ZnO are grown through the chemical vapor deposition (CVD) technique, utilizing optimized growth parameters. This growth method ensures the production of uniform nanorods that are approximately vertically aligned on a heavily doped silicon substrate. The resulting nanorod arrays exhibit exceptional structural integrity and morphology, as confirmed by electron microscopy analysis. The nanorods' high crystallinity, essential for optimal performance, is also confirmed through X - ray spectroscopy. The grown nanorods demonstrate excellent field emission properties with a turn - on electric field of approximately 4.5 V/micrometer, indicating their ability to emit electrons at relatively low voltages. Moreover, the observed current density of around 12 microampere/cm^2 underscores the nanorods' efficient electron emission capabilities. The experimental results obtained from the field emission characterization of the grown nanorods hold immense potential for revolutionizing photonics - based sensors and devices.***

Keywords: Nanorods, Field Emitters, Zinc Oxide semiconductor, Chemical Vapor Deposition, Nanotechnology

1. Introduction

The semiconducting metal oxide ZnO possesses a notably wide bandgap of 3.37 eV, a feature that sets it apart. This distinction is further highlighted by its remarkably high exciton binding energy of 60 meV at room temperature, which significantly surpasses its primary competitor, GaN, which stands at 24 meV [1, 2]. ZnO holds a pivotal position within the wurtzite family, with its distinctive characteristics deeply intertwined with the noncentral symmetry structure it exhibits, along with its polar surfaces. This inherent nature renders ZnO a material of exceptional significance, particularly within the realm of functionality. Its manifold applications span various fields, including photonics, piezoelectric - based sensors, nano generators, field emission, and spintronics, among others. This versatile material's capacity to contribute to advancements across these diverse sectors underscores its potential as a cornerstone for future innovations [3, 4].

In the last few decades, various techniques have been invented for the growth of semiconductor nanostructures. The inception of the vapor liquid solid (VLS) also called the chemical vapor deposition (CVD) growth mechanism in 1964 marked a significant milestone in materials science, particularly in the realm of single crystal growth. This concept has since been adapted and extended to encompass the growth of metal oxide nanostructures, including ZnO, utilizing a conventional CVD reactor setup. The evolution of this technique has paved the way for the controlled synthesis of a diverse range of nano materials, holding immense promise for various technological applications [5 - 7].

The CVD - grown nanorods shows excellent crystallinity and high quality with respects of defects because of high temperature growth. The controlled and oriented synthesis of single - crystalline one - dimensional (1D) ZnO nanorods, characterized by a substantial aspect ratio (defined as the ratio of length to diameter), holds tremendous promise for a range of cutting - edge applications. This innovative nanomaterial configuration has garnered considerable attention due to its remarkable potential across diverse technological domains. CVD grown single crystalline nanorods shows excellent field emission properties as reported in various research work. Field emitters play a crucial role in futuristic devices, and nanotechnology offers a promising avenue for producing low - cost and highly efficient field emitters. By leveraging the unique properties of semiconductor nanorods, such as their high aspect ratio and tunable characteristics, it is possible to transform the current technology landscape, which heavily relies on photonics [8 - 11].

The experimental results obtained from the field emission characterization of the grown nanorods hold immense potential for revolutionizing photonics - based sensors and devices. By harnessing the unique field emission properties of these nanorods, it becomes possible to enhance the efficiency, reliability, and performance of a wide range of sensor technologies. Photonics - based sensors and devices, including obstacle detection sensors used in automatic gates, water taps, and escalators can significantly benefit from the integration of these advanced field emitters. These nanorods pave the way for the development of next - generation sensors that offer improved sensitivity, reduced power consumption, and enhanced functionality.

In this current study, the growth of high - quality single - crystalline ZnO nanorods using the chemical vapor deposition (CVD) technique has been presented. This research represents a growth of systematically optimizing a comprehensive set of pivotal CVD parameters for ZnO nanorod growth. A notable outcome of our investigation is the room - temperature photoluminescence (PL) spectra exhibited by the grown samples. Through this photoluminescence analysis, we gain valuable insights into the qualitative assessment of defect concentrations and the crystal quality present within our samples. Furthermore, the grown nanorods have been examined for field emission properties. The results show CVD grown ZnO nanorods base field emission and its applications in advanced sensors is a fascinating area of research and an opportunity for futuristic devices.

2. Experimentation

2.1 Synthesis

For the growth of ZnO nanorods, Si substrates were used. The Si substrates have been cleaned in various processes for the removal of organic impurities and the oxide layer. Cleansed Si substrate was meticulously arranged within a horizontal tube furnace (CVD reactor) on a flat surface alumina boat. To facilitate this growth process, a distinctive combination of source materials has been introduced and the optimized growth temperature was kept at 860°C during the growth process. This amalgamation encompassed an equal measure of high - purity ZnO powder (0.2 g, sourced from Sigma - Aldrich, boasting an impressive 99.99% purity) and graphite (0.2 g, also procured from Sigma - Aldrich, with a purity rating of 99.99%). The strategic utilization of graphite served a dual purpose: it effectively catalyzed the decomposition of ZnO at a notably reduced temperature, thereby contributing to the reduction of the overall growth temperature. After carrying out the CVD reaction for 10 minutes, the furnace's temperature was lowered by 200°C every hour until it reached room temperature. The grown film has been removed from the furnace and used for father processing.

2.2 Characterization:

MIRA3 TESCAN field emission scanning electron microscope has been used to examine the morphology of grown nanorods. On a "Bruker D8" x - ray diffractometer, the structural characteristics of produced ZnO nanorod arrays were examined with Cu K radiation (λ=1.5405 nm). To further understand the structure and native defects of the ZnO nanorod array, micro - Raman spectroscopy was performed using a Renishaw in - Via Raman microscope and the 514.5 nm line of a 50 mW Ar+ ion laser. On a fluorescence spectrophotometer made by HORIBA, the photoluminescence measurements were performed. To evaluate the field emission properties of the grown nanorods, a custom - built field emission setup is employed. This setup incorporates a high vacuum system and a Keithley source meter to accurately measure the field emission characteristics.

3. Results and Discussion

3.1 XRD

The X - ray diffraction pattern of CVD - grown thin film on a Si substrate is depicted in Fig.1. The fact that grown films are highly c - axis oriented with the (002) plane parallel to the substrate is shown by the intense peak in the diffraction plots that corresponds to the (002) plane at 2Θ value of 34.52. Another peak corresponding to (103) plane is also observed in the diffraction pattern. Excellent agreement has been discovered between all of the peak positions and the standard JCPDS data number 36 - 1451 [12].

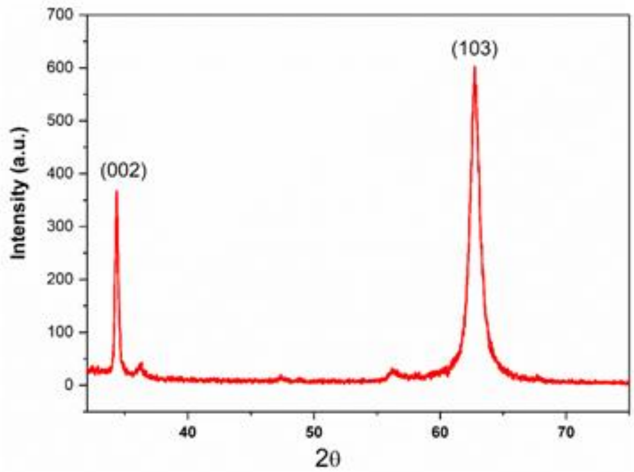
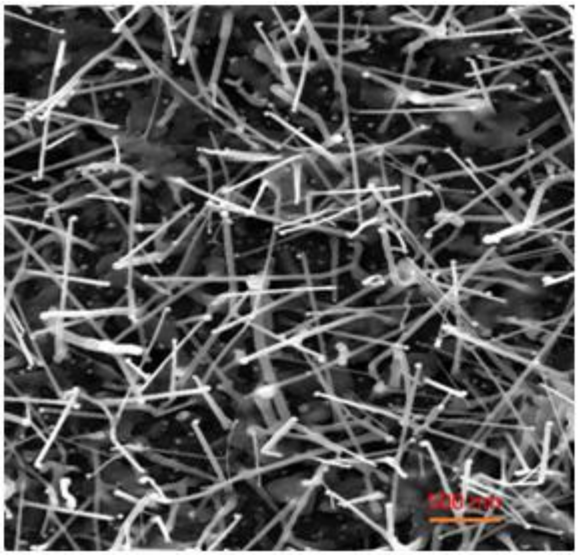


Figure 1: XRD diffractogram of as grown ZnO nanorods array

3.2 FESEM

Figure 2 shows typical FESEM images of CVD - grown thin films at 860°C on a Si substrate. High - quality nanorods with exceptionally high aspect ratios can be seen in the image. Nanorod structures with an average diameter of 20 nm and length of approximately 1000nm are observed on the substrate. The nanorods are not aligned vertically on the substrate because guided growth is not possible in this situation because there is no catalyst layer, which prevents adequate diffusion sites for ZnO precursors from being present and the growth was carried out at very high temperatures.



3.3 Photoluminescence

A potent technique for illuminating the band structure and energy levels of materials is photoluminescence (PL) spectroscopy. The room temperature PL emission spectra of ZnO nanorods grown by CVD on Si substrate are shown in Figure 3 with an excitation wavelength of 266 nm. The PL spectra of ZnO nanorods consists primarily of a strong emission band at 382nm corresponding to bend edge emissions. Another small, sharp peak, located at 400 nm in the visible spectrum's blue area, was shown to be caused by zinc interstitial flaws. Due to a low oxygen supply during the growth process in the CVD reactor, these defects form. Typically, oxygen vacancy defects get spontaneously gets created during ZnO nanorods growth, and the reported PL emission peak is located at 500 nm in the green portion of the spectrum. This film has no green emission peak, which suggests that it is free of flaws such oxygen vacancies [13, 14].

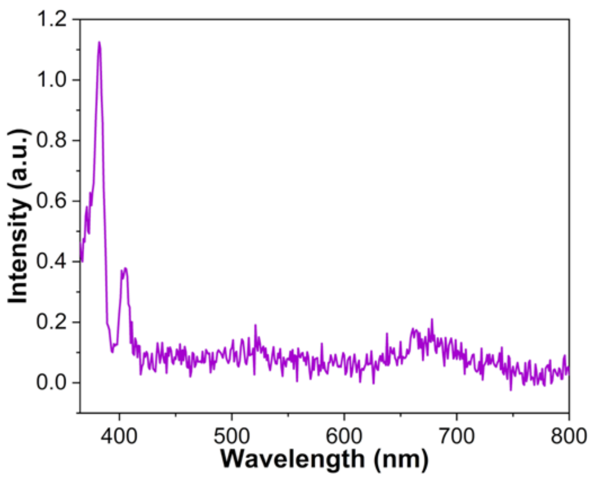


Figure 3: Photoluminescence Spectrum of CVD grown ZnO nanostructures

3.4 Raman Spectroscopy

The typical Raman spectra for grown ZnO nanorods are shown in Figure 4. The spectra show three significant Raman modes at 99, 436, and 575 cm^{-1}, which correspond to the hexagonal wurtzite crystal structure of ZnO's nonpolar optical E2 (high) and longitudinal optical A1 (LO) modes, respectively. The distinct ZnO characteristic Raman bands and lack of any additional impurity bands indicate that the produced nanostructures are pure and of excellent quality [15].

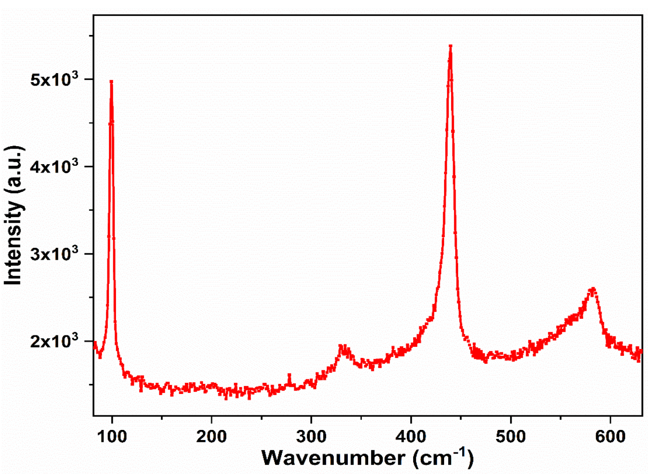


Figure 4: Raman spectroscopy of grown nanorods

3.5 Field Emission Properties

The field emission measurements were done on CVD grown nanorods in the range of 0.2 V/µm to 10 V/µm on high vacuum electrode setup. The distance between anode and cathode was fixed at 280 µm and the pressure in chamber were maintained at $1x10^{-7}$ mbar at room temperature. Figure 5 (a) and (b) represents the field emission current density Vs applied electric field and Fowler - Nordheim (F - N) plot respectively. Based on the results presented in figure threshold field, turn - on field and the local field emission factor have been calculated. The general expression for the field emission current derived from Fowler - Nordheim equation is given by equation 1.

$$J = \frac{A\beta\beta^2E^2}{\phi} e^{(-\frac{B\phi^{\frac{3}{2}}}{\beta E})} \quad (1)$$

Here, ϕ represents the work function of the emitting material, β stands for the local field enhancement factor (β - factor) at the emitting tip, E denotes the applied electric field, and A (with a value of 1.544×10^{-6} AeVV - 2) along with B (which has a value of 6.83×109 $eV^{-3/2}Vm^{-1}$) are the constants. The film achieves a maximum current density of 12 µA/cm2 under the highest applied electric field of 8.5 V/µm. The turn - on field is estimated to be 4.5 V/µm. The field enhancement factor is determined for the films using the F - N plot method, involving the calculation of its slope in the high electric field region [16, 17].

$$\beta = \frac{B\phi^{\frac{3}{2}}}{S_{FN}} B \quad (2)$$

In this context, S_{FN} represents the slope of the F - N plot, while ϕ pertains to the work function of the ZnO nanorod tip. The reported work function for most CVD grown ZnO nanorods is approximately 5eV, and for the purposes of this discussion, a value of 5.04 eV is adopted as the work function of the grown ZnO nanorods. The β - factor is computed and determined to be 1.6×10^4.

The presence of various native defects within the nanorods could impede the electron transport across them, leading to a reduction in field emission current. Furthermore, the quality of the crystal, the alignment of the nanorods and spatial distribution play pivotal roles in determining emission current density and the threshold electric field. CVD - grown nanorods exhibit single crystallinity, and their high crystalline nature contributes to strong band edge photoluminescence (PL) emission, thereby indicating their potential for use in field emission devices. Although the current density may be relatively low in the case of metal oxide nanostructures, the stability of emission current and the unbeatable performance in terms of duty cycles for metal oxide semiconductors are notable attribute [18 - 20].

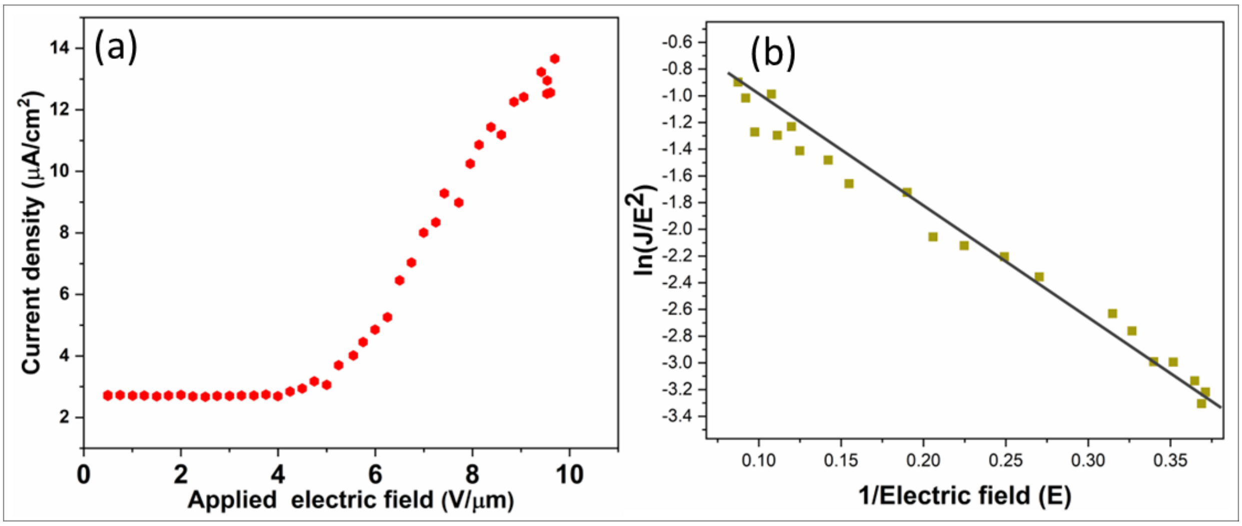


Figure 5: (a) Field emission current density Vs applied electric field of CVD grown nanorods (b) The F - N plot with liner fit curve indicating field emission behavior.

4. Conclusion

4.1 Final Conclusion:

Single crystalline ZnO nanorods with high aspect ratio on Si substrate had been growth by CVD technique. The spatial distribution of nanorods on substrate was found to be excellent for field emission applications. The grown nanorods demonstrate a turn - on electric field of approximately 4.5 V/micrometer, indicating their ability to emit electrons at relatively low voltages. The observed current density of around 12 microampere/cm^2 demonstrates the nanorods efficient electron emission capabilities. The experimental results obtained from the field emission characterization of the grown nanorods hold immense potential for revolutionizing photonics - based sensors and devices. By harnessing the unique field emission properties of these nanorods, it becomes possible to enhance the efficiency, reliability, and performance of a wide range of sensor technologies. Photonics - based sensors and devices, including obstacle detection sensors used in automatic gates, water taps, and escalators can significantly benefit from the integration of these advanced field emitters. These nanorods pave the way for the development of next - generation sensors that offer improved sensitivity, reduced power consumption, and enhanced functionality.

4.2 Future Plan

In future work, further exploration and optimization of the field emission properties of these nanorods can be pursued. This may involve studying the effects of different growth parameters, such as temperature and precursor concentrations, on the nanorod properties and field emission characteristics. Additionally, efforts can be directed towards integrating these nanorods into specific sensor configurations to evaluate their performance in real - world applications. The ultimate goal is to leverage the capabilities of semiconductor nanorods to develop advanced sensor technologies that offer unprecedented sensitivity, reliability, and cost - effectiveness, thereby driving the advancement of various industries and sectors.

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