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FELLOWSHIP FINAL REPORT

Investigation of Intrinsic and Extrinsic Defect Centers of ZnO Nanowires for Nano-Generators

Emre Erdem[1,3,§], Camille Justeau[1], Guylaine Poulin-Vittrant[2]

[1]Université François Rabelais de Tours, CNRS, GREMAN UMR 7347, 16 rue Pierre et Marie Curie, 37071 Tours Cedex 2, France
[2] Université François Rabelais de Tours, INSA-CVL, CNRS, GREMAN UMR 7347, 3 rue de la Chocolaterie, CS 23410, 41034 Blois Cedex, France
[3] LE STUDIUM Institute for Advanced Studies, 45000 Orléans, France
[§]present address: Sabanci University, Faculty of Engineering and Science, Tuzla Campus, 34956, Istanbul, Turkey

Emails: emreerdem@sabanciuniv.edu , guylaine.poulin-vittrant@univ.tours.fr

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Fellow: Dr. Emre ERDEM
From University of Freiburg, Institute of Physical Chemistry, Freiburg, Germany
Host laboratory in region Centre-Val de Loire: GREMAN Groupe de Recherche en Matériaux, Microélectronique, Acoustique et Nanotechnologies UMR 7347 CNRS, University of Tours, INSA-CVL, France
Host scientist: Dr. Guylaine POULIN-VITTRANT
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ABSTRACT

For efficient and successful mechanical energy harvesting, a configuration that has garnered much focus in recent research is the piezoelectric nanogenerator. The concept of the nanogenerator has shown potential for harvesting energy from the ambient environment to power systems. Kinetic energy harvesting nanogenrators based on the piezoelectric properties of ZnO nanowires have attracted much interest. The aim of this work is to fabricate hydrothermally synthesized ZnO nanowire-based nanogenerators in order to control the average diameter of wires and also the quality of wire alignment. Intrinsic point defects as well as extrinsic defects introduced via doping of transition metal ions by no doubt play a crucial role not only the amplitude of generated voltage signal from nanogenerators but also the conductivity of ZnO. Despite its advantages, the lack of fundamental knowledge about intrinsic defects and doping ions presents an obstacle to the development of practical devices such as nanogenerators which requires high conductivity for high performance. The difficulty to make reliable ZnO nanowire based nanogenerators is closely related to the intrinsic and extrinsic defects specifically interstitials, vacancies and metal ions (i.e., Mn, Fe). This research provides a fundamental understanding of defects in ZnO that could lead to reliable devices using the peculiarity of nanogenerator. The results of electronic (electron paramagnetic resonance spectroscopy), optical (photoluminescence spectroscopy) and electrical (impedance spectroscopy) characterization investigations could give the basis for the industrial and economic manufacturing of ZnO nanowires. This work provides physical understanding of the defect structures in nanoscale wire form of ZnO.

1- Introduction

In 2007, a new type of piezoelectric micro-generators (PGs) based on piezoelectric semiconducting nanowires (NWs) has shown promising performance for electromechanical conversion. Since then, there is a tremendous interest for using these one-dimensional piezoelectric nanostructures for mechanical energy harvesting. Indeed, in some aspects, they possess superior properties compared to their bulk counterpart: high surface to volume ratio, high piezoelectric coefficients, higher sensitivity to low frequency motion, high mechanical strength, flexibility, mechanical robustness, piezoelectric and semiconducting properties. Among several materials, zinc oxide (ZnO) NWs is one of the most promising candidates. It has high values of piezoelectric coefficients, it can be grown at low temperature on almost any substrates, the carrier density can be tuned by moderate temperature annealing, Schottky and Ohmic contacts are studied for many years, and finally, it is environmentally friendly (lead-free). Today, the output power density generated by the best prototypes in literature reaches about 5 mW/cm^3 or $1\mu W/cm^2$ [1]. The peak values of generated voltage and currents are a few V and a few hundreds of nA, respectively.

Electronic, magnetic, optical and structural properties of ZnO based materials are very sensitive to defects and impurities which have localized electronic states with energy levels in the band gap [2,3]. Resonance spectroscopy techniques, particularly electron paramagnetic resonance (EPR) spectroscopy, are not only able to detect, distinguish and characterize stable or meta-stable band gap energy states but also give detailed information about their microscopic origin [5, 6]. Even relatively small concentrations of defects and impurities can significantly affect the electronic, magnetic and optical properties of both *bulk* and nano-size semiconductors. Therefore, understanding the role of defect centers (i.e. vacancies, interstitials and antisites) and the incorporation of stable or meta-stable defects is a key tool toward controlling the electronic properties of ZnO. EPR is well suited for this task, since it provides a direct method to monitor different paramagnetic states of vacancies and, thus, complements other experimental techniques such as photoluminescence (PL) spectroscopy [4]. The detection limit of the EPR spectrometer is 10^{10} spins. In this sense, EPR does not only work very well on the identification of defects but also one may obtain reliable correlation to the luminescence properties of bound excitons. Nonetheless, just from the basic principles of defect formation, it is hard to understand or predict what kind of defects will be present in the sample. From the EPR point of view, so far different EPR spectra have been assigned to the same defect site, or the same spectrum has been assigned to the different paramagnetic centers in ZnO. Thus, the nature of the defects and the interpretation of the defects are still controversial issues. Up to now, different types of defect centers were reported in undoped ZnO in experimental (EPR and PL) and theoretical studies, namely: Neutral singly charged and doubly charged zinc vacancies, neutral zinc interstitials, singly charged zinc interstitial, neutral oxygen vacancies, singly charged oxygen vacancy, oxygen interstitial and complex of an oxygen vacancy and zinc interstitial. On the other hand, doping ZnO with transition metal ions, like Fe, Co, Mn or Cr, leads to materials with entirely different behavior towards magnetic and optical excitation [5]. This new research direction is named as diluted magnetic semiconductors (DMS) [6,7]. DMS materials which are based on ZnO could show not only ferromagnetism at room temperature upon doping with transition metal ions, e.g., Fe^{3+}, Cr^{3+}, Co^{2+}, and Mn^{2+}, but simultaneously also exhibit ferromagnetic and semiconducting properties. Recently, Mn-doped ZnO revealed ferromagnetism above room temperature, which is important for new spintronic devices (spin LED's, spin valve transistors) and magneto-optic components. By this work we are aiming at gaining more information on the piezoelectric and conductive behavior of ZnO NWs mainly by EPR. Therefore the main focus was given to identifying and controlling the defect centers. In the framework of this research, changes in the physical (structural, electronic, optic and magnetic) properties of ZnO NWs, due to size effects, has been investigated in a detailed way by EPR spectroscopy. The EPR results were compared by the complementary methods such as photoluminescence (PL) spectroscopy, scanning electron microscopy (SEM) and x-ray diffraction (XRD).

2- Experimental details

Among all synthesis routes of ZnO, hydrothermal is one of the powerful one to produce nicely aligned, high aspect ratio NWs. Hydrothermal synthesis is a cost-effective synthesis, fully compatible with industrial manufacturing processes. Therefore, controlling the natural doping of ZnO NWs is a challenge that may promote them for the next generation of piezo generators, based on a lead-free and biocompatible material. Details of hydrothermal route can be found elsewhere [8]. X-band (9.86 GHz) EPR measurements were performed with Bruker EMX spectrometer using a rectangular TE102 (X-band) resonator. The magnetic field was determined using an NMR gaussmeter (ER 035M, Bruker); for magnetic-field calibration, polycrystalline DPPH with $g = 2.0036$ was used.

3- Results and discussion

X band EPR spectroscopy were employed to the hydrothermally synthesized ZnO NWs. Basically we have synthesized four different samples namely pristine, 2 h, 4 h and 6 h samples. 2, 4 and 6 h samples were grown depending on their growth time in hydrothermal autoclave at 80 °C. EPR results revealed that by controlling the growth time it is also possible to control and monitor the defect concentrations not only on the core but also on the surface. While by state-of-art EPR technique we succeeded to distinguish the surface and core defects by the analysis of g-factors. The defects on the core are more localized in crystal therefore the spin-orbit coupling is large which cause deviations from the free electron g-values. Such bounded electrons may deviate largely from the free electron g-factor which is 2.0023. In this case ZnO has plenty of defects mostly singly and doubly ionized oxygen vacancies. They give EPR signal around 1.962 [9]. When we increase the growth time surface defects starts to effects the whole EPR spectra and we observe that surface defects become highly visible. This depends on the concentration of surface defects with respect to NW crystal quality and aspect ratio. The surface defects revealed g-factor around g=2.004 which is close to free electron g-value indicating unbounded defect states. These results indeed can be correlated with the photolouminescence (PL) emission. Both surface and core defects collectively gives PL emission in visible light region of PL spectra [10]. In this work we observed similar dependency of defects obtained from EPR and PL. More details on these results will be published elsewhere.

4- Conclusion

We successfully synthesized high-quality piezolectric ZnO NWs on the substrate and by the aid of EPR spectroscopy we have identified two distinct paramagnetically active EPR signals. These signals has been attributed to the defect centers which are located at the core and surface of the ZnO NWs. Such semi-empiric interpretation has been done by the analysis of g-factors which enables us at least safely to distinguish between surface and bulk defects. Such preliminary results are quite promising to correlate the effect of defects by the piezoelectric thus electrical performance of the produced ZnO nanogenerator devices.

5- Perspectives of future collaborations with the host laboratory

There is quite promising potential between the host and guest institutions in terms of exchange knowledge and mobility of young researchers. The knowledge and the results collected from present research will be published by collaborative publications between two institutions.

6- Publications and Scientific activities in the framework of the fellowship

We have presented 2 posters in Le Studium conference "*Frontiers in Nanomaterials for Energy Harvesting and Storage*" which has been organized in Tours, 27-29 August 2018. The presented posters entitled 1) Influence of the synthesis parameters on hydrothermally grown ZnO nanowires dedicated to mechanical energy harvesting and 2) Zinc oxide nanowire-parylene composite nanogenerators for low frequency mechanical energy harvesting. On 5th of April 2018 E.E. presented an oral contribution entitled "*Role of functional nanomaterials for energy harvesting. Future energy systems, challenges and opportunities*" in the vicinity of Le Studium Program. Finally, E.E. presented a seminar on "Advanced EPR studies in functional nanomaterials: "*From ferroelectrics to semiconductors*" in "Oxides for Energy" group in University of Tours on 19 April 2018. A manuscript is in preparation and will be submitted to a high-rank international journal soon.

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