Reliability Research of ZnO Based Nano Functional Devices
Embedded in the Human Body

Shentong Mo\textsuperscript{1,a}, Boyu Chen\textsuperscript{2,b} and Qiang Zou\textsuperscript{1,c,*}

\textsuperscript{1}School of Electronic Information Engineering, Tianjin University, Nankai District, Tianjin 300072, PR China
\textsuperscript{2}School of Law and Politics, Tianjin University of Technology, Xiqing District, Tianjin 300072, PR China
\textsuperscript{a}moshentong678@126.com, \textsuperscript{b}egg425@qq.com, \textsuperscript{c}zouqiang@tju.edu.cn

Keywords: ZnO, Nano, Embedded Devices, Reliability, Albumin

Abstract. This paper researches the stability problem of structures of embedded ZnO nanodevices and properties under the environment of human serum albumin. The study simulates human environment by putting the ZnO nanodevices into human serum albumin, imitates the human body environment of 37\degree C, and researches the Reaction process and mechanism between the micro-nano structures of embedded ZnO nanodevices and human serum albumin polymer materials. This study will have a great significance in application and reliability performance analysis of embedded nanodevices.

Introduction

In early 2006, Zhong Lin Wang proposed the piezoelectric material synthesized nanowires that transform mechanical energy into electrical energy.\cite{1-3} And he put forward the principles of nano-generators for the first time in the US "Science" magazine paper. Then he applied the electric field produced by the voltage power to controlling the transport process of carriers of semiconductors.\cite{4-5} Therefore, he proposed the new concept of Piezotronics. The nanodevices can be integrated to achieve a real nanosystems by this invention. Nanosystems can collect mechanical energy, vibration energy, and fluid energy.\cite{6} And the nanosystems can translate these energy into electrical energy and provide electrical energy to the nanodevices. This groundbreaking invention causes a tremendous boom it the nano power research of entire academia.

However, if such a device can be made of an embedded nano-generation devices in a living body, we will have to consider the "biological system compatibility" issues and reliability analysis problems of devices.\cite{7-8} When a functional device as "foreign body" is embedded in organism, the immune system of organism will attack them directly. And it will involve the "biological system compatibility" issues, and correspondingly generate series of reliability problems about performance of devices.\cite{9-10}

This paper puts such functional devices as the research object. In order to research the reliability of using ZnO nanodevices, we observe and analyze the performance changes of embedded ZnO nanodevices in albumin solution imitating the human.\cite{11-12}

Experimental

Preparation of ZnO Nanoarray Functional Device. As the Fig.1 shows, we select monocrystalline Si as the substrate material for the first time. Then we use sputtering process of monitoring and controlling. Thirdly, we plate 500 nm of thick layer of Zn film on the Si substrate by 99.9\% of Zn target. In the end, there is a ZnO epitaxial layer on the surface of the Si substrate, after it is heated for two hours under the environment of 500\degree C.

Compared with using the Si substrate directly, ZnO epitaxial layer on the surface is a buffer layer and a transition of the upper ZnO growth. And the epitaxial layer can fully relieve the lattice mismatch caused by Si substrate or growth of ZnO nanoribbons. On the other hand, ZnO buffer layer
is a growth platform of ZnO nanoribbons. Also it can reduce its growth potential barrier to be overcome.

Polyvinyl alcohol (PVA) and deionized beam are mixed in mass ratio of 4: 100, so that it can form clear solution of PVA after standing for forty and eight hours under the environment of 30 °C. Zinc acetate Zn(AC)_2 and PVA are mixed in mass ratio of 2: 1, completed at water bath of 90 °C. And they are mechanically stirred for one hour to two hours in the whole mixing process. The Si substrate with the ZnO epitaxial layer is immersed in the solution, and heated for four hours to five hours under the environment of 120 °C. Then the substrate is transferred to a muffle furnace and heated for three hours to five hours under the environment of 600 °C.

Finally, the samples are removed to be cooled to room temperature. And we get the desired samples as shown in Fig.1.

![Fig.1.Preparation process of ZnO nanoribbons](image)

**Configuration of Albumin Solution.** The 250 mg of Human Serum Albumin(powdered) was purchased from Beijing Hua Lvyuan Technology Corporation. In order to meet the storage temperature (2 °C to 8 °C), it is transported by ice box.

The 250 ml of protein is dissolved in 6 ml of distilled water. The aim is to get 42 mg/ml of human serum albumin solution(The albumin concentration of human body is 40 mg/ml to 55 mg/ml). The 1ml of protein solution is diverted into 1.5 ml of EP tube specifications by the use of pipette. And the protein solution is loaded in all six EP tube.

Firstly, ZnO nanoribbons arrays are placed in albumin solution. The EP tube is placed in the incubator of 37 °C. Then the ZnO nanoribbons arrays are in contact with human albumin solution of the same concentration for different periods. The periods are 0.5 h, 1h (as shown in Fig. 2(a)), 1.5 h, 2 h(as shown in Fig. 2(b)), 2.5 h, 3 h(as shown in Fig. 2(c)). Finally we analyze and discuss by the use of Raman spectroscopy(as shown in Fig. 2).

**Solution Biofilm After the Reaction.** To make the solution hang on SiO₂ substrate better, the slide is used as a substrate. And it is polished with sandpaper. The protein solution is dropped on the polished sandpaper.

**Discussion and Results**

It is inevitable that the ZnO nano-generator implanted in the body will be attacked by the immune system. The membrane surface protein of immune cells(antibody receptor protein, prevalent on immune cells) will attack the human foreign body.

In the state of oxygen vacancies, Zn²⁺ in the free state is easily out and react with surrounding materials. Protein interactions are generally van der Waals forces, hydrogen bonding, ionic bonding. Thus, the Zn²⁺ is likely to be in the protein. The Zn²⁺ may cause the sites of protein disease, lesions protein and inactivation phenomena.

There are large amounts of amino in Albumin (585 per molecule). Compared to hydroxyl, carboxyl, their electronegativity will be stronger. And they are easier to coordinately complexed with the metal ions. Under the body fluid environment of pH7.2-pH7.4, the albumin is anion. Every molecule may have two hundred or more negative charges. So it is very easy for the albumin to be complexed with the metal ions.
When the ZnO material is downsizing from planes in two dimensions to particles in zero dimension, even to the lines in one dimension, the surface area is dramatically increasing. And the tip exposed ZnO molecules are in contact with protein. They are increasing in geometric order of magnitude. The $\text{Zn}^{2+}$ on tip of ZnO nanowires are mutually attractive with amino, but the $\text{O}^{2-}$ and amino are mutually exclusive. When the scale of ZnO arrays reduces to the nanometer level, the attraction between $\text{Zn}^{2+}$ and amino gradually balances the attraction between $\text{Zn}^{2+}$ and $\text{O}^{2-}$. When the mutual attraction between $\text{Zn}^{2+}$ and amino is greater than the attraction between $\text{Zn}^{2+}$ and $\text{O}^{2-}$, the $\text{Zn}^{2+}$ will be separated from the ZnO and be into the protein solution.

As the Fig.2 shows, the $\text{Zn}^{2+}$ is complexed with amino, which results in some albumin inactivation and the decrease of active protein content in solution. So the peak intensity of Raman spectra albumin is decreasing. The $\text{Zn}^{2+}$ is complexed with albumin, which results in the decrease of ZnO content in solution. Thus, the peak intensity of Raman spectra ZnO is decreasing.

**Conclusions**

It will be certainly faced in the field of nanotechnology that ZnO nanodevices are implanted in the body in the near future. And in the process of implantation in the human body, we may ignore the effects of ZnO device itself. Because the device has been implanted in the body while we consider the performance of the device itself.
When ZnO nanodevices are implanted in the body, the immune system will inevitably attack them. The membrane surface protein of immune cells (antibody receptor protein, prevalent on immune cells) will attack the human foreign body. When ZnO substrate nanoarrays are in contact with the human body protein and other substances, it is necessary to ensure no interferences in vivo protein and no material exchanges. Otherwise, the degree of danger is as much as the introduction of large doses of Zn and other metal particles to the human body.

From the perspective of ZnO and serum albumin, the ZnO device may bring effects on the human body. And the effects are preliminarily explored in this paper. So in the field of ergonomic micro-nano fabrication, we make a reasonable request, namely biological compatibility.

Acknowledgments

This work was supported by Science and Technology Support Project of Science and Technology Office in Xin Jiang(2015), Marine Demonstration Project of the State Oceanic Administration (2014), and Special Project of Tianjin University in Wuqing District (2013).

References