Storing Deformation Energy of ZnO fine wires in a Mechanical Battery

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Abstract. The characterizations for ZnO arrays on different substrates have been done with the aim of fabricating an experimental battery that uses the strain energy as energy source. The storage principle is based on a common spring which is loaded by the force associated to the energy to be harvested. By following the same principle our approach is based on pressing an array of fine wires (fws) grown vertically on two different substrate surfaces. The ZnO has been chosen as a fabrication material due to its manufacturing which is cheap and simple using the hydrothermal method. A statistical study for quantify the ZnO fws physical dimensions as density, diameters and lengths was firstly done. Secondly a mechanical study showed the mechanical behaviour of the ZnO fine wires as a unit study where boundary conditions of free-fixed and pinned-fixed were used as possible behaviours. Subsequently an electrical IV characterization was done by using an experimental compressor that allows analyse of the current response of the ZnO array to different compression distances in order to seek for a relation between mechanical and electrical properties. The thermionic-emission was considered to relate the contacted area with the current response.

1. Introduction

As part of a continuous interest on powering nanodevices and self-powered systems previous works have been done on storage energy in the mechanical domain. For instance the study of the potential for storing energy by the elastic deformation on carbon nanotubes (CNTs) have been reported [1]. It was reported that the mechanical energy storage is limited due the strength of the material rather than an electrochemical reaction, making easier the energy storage control unlike in an electrochemical battery. Other approaches have been done by molecular dynamics simulation using body-centered cubic tungsten nanowire where it was revealed a theoretical actuation stress > 3GPa, actuation strain > 30% and finally an average efficiency storage > 90% [2, 3]. An important disadvantage that has to be noted is the high cost and complex fabrication of these carbon nanotubes, therefore the fabrication of ZnO nanowires was taken as an alternative material. Its production is easier and low cost through the hydrothermal method that has been successfully used and reported previously [4, 5]. Our mechanical storage approach is based on the same principle of a spring submitted to compression that suffers a deformation and in consequence stores a potential energy than can be released in a single discharge or multiple gradual discharges.

For our particular case the spring is given by a ZnO fine wires array grown on a substrate, our optimization process has been reported previously [6]. For this work we also present a new sample of
ZnO fine wires grown in a different substrate by a ZnO deposition method called Greene method [9] where it was used a Silicon substrate rather than Si/Au. The main focus of this work is the electro-mechanical characterization of the ZnO fine wires array to evaluate its energy storage capability and by comparing both types of samples.

2. Methodology
From our previous experiments reported the best sample of a ZnO array growth on Si/Au and Si substrate were taken.

2.1. Statistical study
Each selected sample was submitted to a SEM image treatment, by taking a 90° and a 45° tilt view of a selected area to quantify diameters and lengths by the construction of a grid. This grid was divided in multiple 100 $\mu$m² cells. Each cell contains the measures of diameters, lengths and densities. Once the hyper matrix was built the standard deviation for each parameter was calculated and average dimensions were approached.

2.2. Theoretical model
Once the average dimensions for the fine wires were calculated a theoretical model can be performed by using the linear elastic theory taking the linear buckling as a first elastic region limit, limiting the stress and strain without reaching the yield stress on the material. To complete the study two boundary conditions are used as possible behaviors which are free-fixed and pinned-fixed. Finally all the theoretical computing is corroborated with a FEM model using the same conditions than in the theoretical one and a relative error is calculated to evaluate accuracy.

2.3. Experimental model
The general set-up for the compression is described in figures 1 and 2. The main aim of the compression test is to measure the IV characteristic of the ZnO arrays when the compression distance is varied. The compression test is done by using an experimental compressor conformed by a metal support that holds an angled compressor arm, which have fixed an electrode made of a 500 $\mu$m Si with a gold coating of 100nm with dimensions of 50 mm². In order to close the circuit the upper electrode has to be approached close enough until it makes contact with the ZnO array located in the samples support. Once the contact is ensured a slope voltage is introduced with the purpose of measuring the output current response. According to previous studies on characterization of ZnO nanowires it has been reported [8, 9] that the thermionic-emission is the main conduction mechanism and can be described by the next expression:

$$I = S A^{**} T^2 \exp \left( -\frac{\varphi_s}{kT} \right) \exp \left( \frac{q^2 N_D (V + V_{bi} - kT/q)}{(8\pi^2 e_s^3)^{1/4}} \right)$$

Where $S$ is the area of the source Schottky barrier, $A^{**}$ is the effective Richardson constant, $q$ is the electron charge, $k$ is the Boltzmann constant, $N_D$ is the donor impurity density, $V_{bi}$ is the build in potential for the barrier and $e_s$ is the permittivity of ZnO. By following the literature the equation (1) can be approached to a linear equation by plotting ln $I$ – $V^{1/4}$ where the behaviour shows a qualitative predominance of the thermionic emission at reversely biased Schottky barrier. In order to analyse the relation of the varying compression with the current response, the varying area can be defined as follow:

$$C = \ln[S A^{**} T^2] - \frac{\varphi_s}{kT}$$

Where $C$ is the independent term of the approached linear equation ln $I$ – $V^{1/4}$ and its change is related with the number of fine wires contacted.
From the hydrothermal growth procedure the best samples were taken for two different substrates. HM_A is made of 500 µm of Si and it was coated with 100 nm Au. The second sample GM_B is made of 500 µm of Si doped type P with a seed deposition of ZnNO₃ by using the Greene Method [7] see figures 3 and 4.

3. Results
From the statistical analysis the general dimensions for the fine wires were obtained and plotted in figures 5 to 8.
The corresponding densities of each sample were a 0.28 SD=0.043 fws/µm² for HM_A and 0.68 SD=0.432 fws/µm² for GM_B. The theoretical and FEM computing are reported in table 1.

| Sample | Boundary Condition | Critical Stress $\sigma_c$(MPa) | Critical Strain $\varepsilon_c$(%) | Strain Energy $U$(pJ) | Strain Energy Density $U/V$(MJ/m³) |
|--------|--------------------|----------------------------------|-------------------------------|----------------------|-----------------------------------|
| HM_A   | Free-fixed         | 88.03                            | 0.54                          | 1.19                 | 0.239                             |
| GM_B   | Free-fixed         | 401.28                           | 2.48                          | 2.93                 | 9.94                              |
| HM_A   | Pinned-fixed       | 718.63                           | 4.43                          | 79.7                 | 15.93                             |
| GM_B   | Pinned-fixed       | 3274.86                          | 20.22                         | 195.14               | 662.02                            |

The FEM computing was compared with the theoretical calculations showing a good agreement with a general relative error < 10%. From the experimental model it was observed only a variation of current against different compression distances for the sample HM_A. For the case of GM_B the currents remained almost constant. Figure 9 shows the IV response for the sample HM_A.
Figure 9. IV Characteristics for different compressions shows as larger is the compression larger is the current. Inset shows a clear increasing trend on the currents.

Figure 10. Independent term behaviour shows an increment with the increase of the compression distance.

4. Conclusions
It has to be noticed that the output currents showed a regular Schottky behaviour and an increasing trend of as larger the compression larger the output current and is consistent with the increase of the independent term observed in figure 10. It can be inferred that the contacted area $S$ has a relation with the independent term as was shown in equation (2), this area increases when the compressor lowers towards the substrate and contacts a larger number of fine wires allowing to conduct more current. A further study has to be done in order to relate accurately the increase of the contacted area with the mechanical properties of the material and extract an experimental strain that allows to compute the strain energy that can be stored.

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