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The performance of nanogenerators fabricated on rigid and flexible substrates

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ABSTRACT

The manufacturing process of a zinc oxide piezoelectric nanogenerator is discussed in detail. The manufacturing of the nanogenerator on solid and flexible substrate is discussed. It is shown that the choice of substrate greatly affects the output voltage of the nanogenerator. Two main reasons for the difference in output voltage of the different nanogenerators are the method in which the nanowires are bent and the contact resistance between the nanowires and the gold electrode. The influence of these two aspects on the output voltage is discussed and the theory is shown to correctly predict the outcome.

1. Introduction

Wireless and self-powering devices are becoming more desirable as technology expands. One of the major hurdles for wireless devices is the type of power source that is used. Batteries are commonly used to power wireless devices but it is not a sufficient solution. Batteries place extra limitations on the devices as for most devices the battery consumes a lot of space. This will become even more apparent on the nanoscale where conventional batteries are simply too large to use and a different approach is necessary. Batteries have a limited lifetime and must be replaced or recharged in order for the device to function as desired. It is thus highly desirable for the wireless sensors to be self-powered, because it can greatly enhance the adaptability and mobility of the devices [1].

Self-powering devices are not new and various approaches have been successfully demonstrated, including solar powered devices [2,3], electromagnetic harvester [4] and piezoelectric devices [5,6]. Piezoelectric devices has attracted a lot of attention over the last couple of years since Wang has successfully demonstrated self-powering devices using zinc oxide (ZnO) nanowires [7]. Vertical ZnO nanowires are grown on a solid substrate and an electrode is placed on top of the nanowires. Any vibrational force causes the electrode to move which in turn bends the nanowires. As the nanowires bend a piezoelectric potential is generated and an output voltage is observed [8].

In this article ZnO nanowires are used, on various substrates, to manufacture a ZnO nanogenerator. Various piezoelectric materials exist, including quartz, berlinite, PZT, InN and AlN. PZT or lead zirconate titanate, is a commonly used piezoelectric material. It has various applications in its bulk form or as a thin film but the synthesis of PZT nanowires are difficult and thus the applications are limited [9]. The synthesis of PZT nanowires also includes a high temperature phase which limits the choice of substrate [9,10]. Both InN and AlN nanowires exhibits piezoelectric properties that are equal or better than ZnO nanowires but the nanowire growth is at high temperature, which again limits the choice of substrate [11,12,13,14]. In contrast, ZnO nanowires are easily synthesised at low temperature which means the nanogenerator can be manufactured on a variety of substrates.

This article further investigates the effect of contact resistance on the output voltage. Furthermore the manufacturing process of an effective nanogenerator is discussed in detail. The output voltage is shown and the difference in output voltage between a flexible nanogenerator and a non-flexible nanogenerator is also discussed. It is shown that the theory is proven correct through the measurement of the output parameters.

2. Contact resistance

Contact resistance plays an important role in electronics and it is even significant more on the nanoscale. To further complicate matters the contact area is becoming so small that conventional equations for resistance no longer hold true. Fig. 1 shows a graphical representation of the Au electrode that is placed above the nanowires. When a force is applied to the electrode it will move down and bend the nanowires. Only a part of the tip of the nano-

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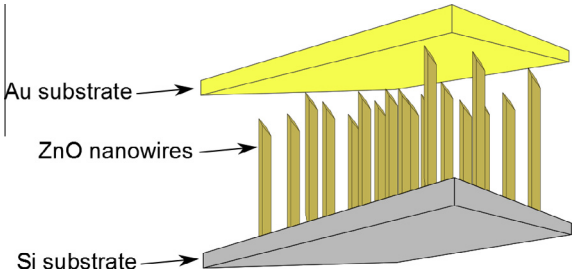

Fig. 1. Graphical representation of a nanogenerator manufactured on Si (100) substrate. At rest, the ZnO nanowires and Au electrode is in contact only with the longest nanowires and only making contact with the top part of these nanowires and not bending them.

wires will be in contact with the electrode. The small contact area causes the contact resistance equations of Holm to break down [15,16]. Ideally, when two different materials are in contact the contact resistance is described by the Holm resistance:

$$R_H = \frac{\rho_1 + \rho_2}{4a} \tag{1}$$

where ρ_1 and ρ_2 is the resistivity of material 1 and 2 respectively, and a is the contact radius. This equation is valid when the contact area is large. When the contact area becomes smaller, the Holm resistance does not give an accurate description of the contact resistance. Instead, the Sharvin resistance is used:

$$R_S = \frac{\rho_F}{N\pi e^2 a^2} \tag{2}$$

where ρ_F is the Fermi momentum of electrons, N is the electron density and e is the electron charge [15,16].

A combination of above two equations give:

$$R = \frac{4(\rho_1 + \rho_2)\lambda}{9\pi a^2} + \frac{\rho_1 + \rho_2}{2a\pi^2} \arctan\left(\frac{\pi a}{\lambda}\right) \tag{3}$$

where ρ_i is the resistivity of material i, a is the contact area and λ is the mean free path. The equation can be used to calculate the contact resistance independent of the contact size [16]. The contact resistance decreases as the contact size is increased, as expected. A contact size of 25 nm^2 the contact resistance will be more than 1 MΩ.

Fig. 2 shows a graphical representation of an improved contact between the nanowires and Au electrode. In this case the nanowire tips are covered by the Au electrode to a depth of a few nanometers. This means that the contact area is a lot larger compared to the first case, which in turn means that the contact resistance will be a lot less. Using Eq. (3), and assuming a contact area of 100 nm^2, the contact resistance will be less than 100 kΩ. The resistance is thus more than 10× smaller, which will lead to considerably less losses internally, over the contact resistance.

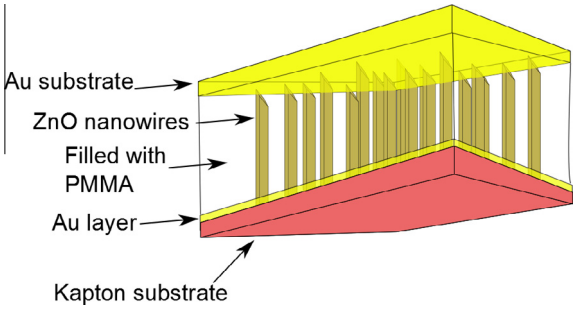

Fig. 2. Graphical representation of a nanogenerator manufactured on Kapton film substrate. The ZnO nanowires are always in contact with the Au electrode, as the Au electrode covers the nanowire tips to a depth of a few nanometers.

3. Experimental

The nanogenerator is manufactured on either silicon (Si) (100) substrates or Kapton HN polyimide film. Si (100) is a hard, non-flexible material, where the Kapton film is a soft flexible material. The manufacture of the nanogenerator on these two different substrates shows that it can easily be adapted to work on many materials.

In both cases the ZnO nanowires are grown from a solution on top of the coated film. The solution consists of an equimolar aqueous solution (30 mM) of $Zn(NO_3)_2 6H_2O$ and hexamethylenetetramine (HMTA) [17,18]. The film is placed upside down on top of the solution. Due to the surface tension the film floats on top of the solution. The solution is sealed and placed inside an oven at 85 °C for 8 h. The exact growth mechanism can be found at [17,18]. After the growth the film is rinsed in deionised water and dried with nitrogen gas.

The Si substrate used is 10 mm by 10 mm in size. A thin layer of ZnO is sputtered on the substrate by ICM sputtering. The sputtering is done in an oxygen atmosphere at 125 W for 3 min, resulting in a 20 nm layer of ZnO deposited on the Si substrate. A small section of the substrate is covered with photoresist after deposition and no growth will take place on this region. The substrate is next placed on top of the solution and growth takes place as described above. After the nanowire growth one coating of Poly (methyl methacrylate) (PMMA) is applied to the substrate. The coating is done via a spin coater at 6000 rpm for 10 s and then placed on a hotplate at 115 °C for 1 min. The photoresist is carefully removed to leave an exposed ZnO area. A separate Si substrate is used for the manufacturing of the Au electrode. A 10 mm by 10 mm substrate is again used and Au is deposited on the substrate with DC sputtering. The sputtering is performed in an argon atmosphere at 1.5 kV and 25 mA for 5 min resulting in a 50–60 nm Au layer. Silver paste is then used to add a conducting wire to the nanowire substrate, at the exposed ZnO area and a separate wire to the Au electrode. The electrode is then placed on top of the ZnO nanowires, completing the manufacturing of the solid substrate nanogenerator.

The Kapton film substrate is 20 mm by 15 mm in size. The first step in the manufacturing is the deposition of a thin Au layer on the film. The sputtering is done with DC sputtering with the same parameters as above, but only for 2 min, resulting in a 20 nm layer. Next, the ZnO layer is sputtered using the same method as for the solid nanogenerator. The substrate is then placed in the solution for nanowire growth. Again a small area in covered with photoresist, and this is done before the deposition of the ZnO layer. After growth PMMA is spin onto the substrate. Five to six spin coatings are done, in contrast to the one run for the solid substrate case. The PMMA now fills the substrate exposing only the nanowire tips. The tips are then covered by sputtering an Au layer on top of the PMMA. The photoresist is again carefully removed leaving the bottom Au layer exposed. Conducting wires are added to the bottom and top Au electrode using silver paste.

A Phenom Fei table top SEM is used to examine the growth after each step of the manufacturing process. The output voltage of the nanogenerator is then measured and displayed on a computer using an A/D converter. The measurement setup can be found at [19]. Current is measured with an HP4140B pico-ampere meter with a 10 kΩ load connected.

4. Results and discussion

Fig. 3 shows SEM images of the nanowires grown on the flexible film. The image in Fig. 3(a) was taken at 6900× magnification and from this image the growth density can be seen. Fig. 3(b), shows a