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Dielectrophoretic Arrangement of ZnO Nanorods and Its Influence on the Capacitance

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Two capacitors composed of ZnO nano-rods were fabricated with and without dielectrophoresis on two identical inter-digitated electrode arrays. Scanning electronic microscope images were presented to verify the aligned and not-aligned arrangement of the nano-rods. The capacitances were measured, and some marked improvements on the capacitor fabricated with dielectrophoresis were obtained. The capacitance value of the sample with dielectrophoresis is 2–3 times larger than that of the sample without dielectrophoresis, and it has a better frequency independence, more excellent dc stability and lower dissipation factor between 30 kHz and 5.3 MHz. The influence of the arrangement of the optimal polarization directions on the capacitance is primarily discussed. The comparative results suggested that the ordered arrangement of the optimal polarization directions of the filling materials was expected to be employed potentially to regulate and control the capacitance during the fabrication process.

Keywords Dielectrophoresis; nano-capacitor; arrangement; polarization direction

1. Introduction

Dielectrophoresis (DEP) is a manipulation technique based on Maxwell's classical electromagnetic field theory to make controlled motion of particles in a controlled electric field between the preset electrode structures [1, 2]. It has been demonstrated as an efficient and promising technique to manipulate the small nano-particles. Due to the different shapes and anisotropic properties, the nano-particles have the respective optimal polarization direction that the particle tends to be polarized along with [3, 4]. When they are introduced to two adjacent electrodes applied with an ac electric field, their optimal polarization directions will be aligned along the electric field line. It is a classic and attractive phenomenon, which is expected to have some potential applications in improving the properties of the devices fabricated with nano-particles.

Capacitor is one of the most used elements based on the polarization effect. The static dielectric constant of the filling material will ultimately decide its properties [5]. Therefore, people tend to exploit highly-polarized materials with high dielectric constants as the filling materials all along. Recently, nano-materials with high dielectric constants are considered as potential fillers to improve the properties of capacitors and reduce their volumes. The operation of nano-powder-filled capacitor depends on the collective polarization effect of

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the separated filling particles. In general, the filling particles are arranged arbitrarily with the optimal polarization directions oriented randomly during the common fabrication process of the capacitors. But if their optimal polarization directions can be orientated along the electric line, the dissipation among the separated particles will be limited, the collective polarization and some properties of the capacitor may be greatly changed.

In the present work, DEP was introduced to align the orientations of the fillers along the electric line during the capacitor fabrication process. Two capacitors fabricated with and without DEP were employed to study the influence of the arrangement of the optimal polarization directions of the filling materials on the adjustment and improvement of the capacitance. ZnO, a classic semiconductor function material of wurtzite structure with anisotropic properties, was used to fabricate nano-capacitors [6–8].

2. Theory

Dielectrophoresis is the controlled motion of uncharged polarizable particles in a non-uniform electric field. It originally provides an effective way to manipulate bioparticles automatically and quickly enhances biological sample preparation [9, 10]. Now it is also potential for not only the study of the electric properties in nano-science but also the construction of the nano-sensors or nano-electronic devices using the nano-structured materials as building blocks [11–16].

According to the theory of electromagnetism, nano-particle with a certain shape and/or anisotropic properties exist an induced and/or permanent electric dipole moment and always has an optimal polarization direction when it is introduced to two adjacent electrodes applied with an ac electric field. Here, p is the effective dipole moment of the polarized nano-pariticle.

Under the external electrical field, the electric potential of an isolated electric dipole is defined by:

$$U = -p \cdot E \tag{1}$$

where E is the electric field intensity. The energy of the electric dipole will be the lowest if the orientation of electric dipole moment is along the electric field direction. The force (f) and moment (M) of an isolated electric dipole are given by the following equations:

$$f = p \cdot \nabla E \tag{2}$$

and

$$M = p \times E \tag{3}$$

The force induced by the non uniform electric field expressed in Eq. (2) drive the nano-particle to the region where the magnitude of the electric field is maximum (or minimum) by positive (or negative) dielectrophoresis. The induced moment expressed in Eq. (3) rotates the nano-particle around its centroid. Therefore, in a spatially non-uniform alternating current electric field, the particle with anisotropic properties experience translational and rotational forces as a consequence of the interaction of the polarization of the particle induced. The particle can be deposited between the preset electrodes with the optimal polarization direction orientated along the electric field. The rotational motion is a much faster process

than the translational motion [17]. The complete rotation and a little translation of the nano-particles could be obtained by the control of the DEP manipulation time.

3. Experimental Details

3.1. Solution-Based Growth of ZnO

Equimolar zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and methenamine ($C_6H_{12}N_4$) was dissolved in de-ionized water as the precursor with the Zn^{2+} concentration of 0.01 M. Then they were mixed under vigorous stirring for 30 min in the glass beakers. Before growth, the glass substrate was cleaned carefully and put into the glass beaker. The sealed glass beaker was then placed into an oven. The growth time and temperature were 24 h and 95°C, respectively. After growth, the substrate was taken out of the solution, thoroughly washed with de-ionized water, treated in an ultrasonic water bath and dried at room temperature. Then, the sample was annealed at 500°C for 10–30 min and was preserved for DEP manipulation.

3.2. Fabrication of Microelectrodes

The micro-electrodes were fabricated using standard micro-fabrication techniques [11]. 2-inch silicon wafers were cleaned by hot piranha solution (H_2SO_4:H_2O_2 = 3:1 in volume) for 10 minutes, followed by rinsing with de-ionized water. The wafers were oxidized in 1050°C for 2 h. A SiO_2 layer of 200 nm was thermally grown on the wafers in order to insulate between the metal electrode and the wafer. A resist layer was spun onto the substrate and patterned photo-lithographically using the mask for the electrode system. A Ti/Au layer of 200 nm was deposited onto the patterned resist to serve as the conductor by means of DC magnetron sputtering. A Ti layer of 50 nm was used to improve the adhesion of the gold layer to the SiO_2 layer. Finally, the electrode arrays were patterned on the surface of the stack using the lift-off technique.

3.3. Dielectrophoresis Operation

The particles to be manipulated were suspended in de-ionized water and ultra-sonicated for 20 min. The suspension was dropped onto the electrode gap using a micro-pipette. A function generator (EM33031) was used to generate the AC signal applied to the electrodes. The movement of the particles were observed using a Leica precision-optical microscope (INM100) fitted with a color CCD video camera connected with a personal computer via an image acquisition card (Lifeview Flyvideo 4200). A diagram of the experimental apparatus is given in Fig. 1. All the experiments were carried out at room temperature in a super-clean room.

3.3. Characterization Tool

Scanning Electronic Microscope (Phillips XL-30) has been used to show the appearance of the ZnO nano-rods and to indicate the arranged particles between the electrodes. Electrical properties tests were performed using an Alpha-A High Performance Frequency Analyzer (Novocontrol BDS40).

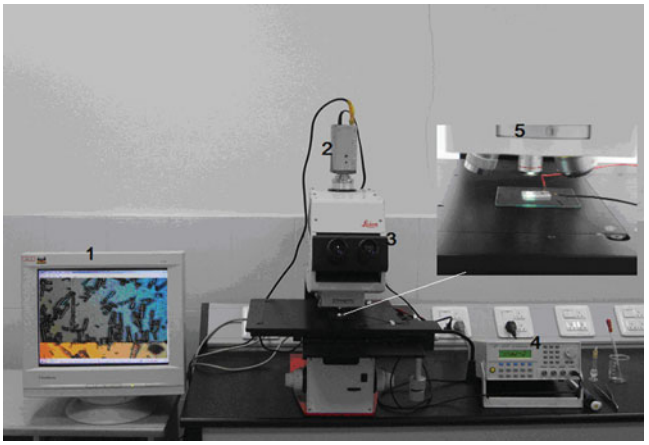

Figure 1. Diagram of the experiment set-up: (1) PC with video/image acquisition card, (2) CCD camera, (3) microscope, (4) function, (5) dielectrophoresis micro-device.

4. Results

Figure 2 is scanning electron microscopy (SEM) images of the ZnO grown by the chemical solution method. Figure 2(b) is the zoom of single nano-rod. It is found that the rod-like ZnO had been prepared with the length of $\sim$10 μm and the radius of $\sim$200 nm. They were used as targets for DEP manipulation due to their tendency to polarize along the axis direction. When they are in the electric field, their optimal polarization directions will be along their axis directions.

4.1. Dielectrophoretic Manipulation of ZnO Nano-Rods

Two inter-digitated electrode arrays with an identical electrode distance of $\sim$200 μm were fabricated. The ZnO suspension was dropped onto the two electrode platforms. Sample 1 was fabricated with DEP performed with the sinusoidal wave form of 1 MHz and 8 $V_{p\text{-}p}$, and sample 2 was fabricated without DEP. After the solvent was completely evaporated, SEM images were presented to indicate the arrangement of the located particles between the electrodes. Figure 3 is SEM image of aligned ZnO rods and Fig. 4 is SEM image of not-aligned ZnO rods, which are presented to draw a comparison between the two samples.

We can see from Fig. 3 that ZnO nano-rods, which were deposited and oriented randomly in Fig. 4, were rotated and aligned with their optimal polarization directions along the electric field direction in an uniform way between the electrodes. A thin and uniform dielectric layer between the electrodes was fabricated by ZnO nano-particles. The aligned orientation is somewhat random and crossed in some regions. It is the influence of fluid surface tension produced in the process of the solvent evaporation.

4.2. Capacitance Test

Frequency evolution of the capacitance and dissipation factor between 1 KHz and 1 MHz was measured by an Alpha-A High Performance Frequency Analyzer in the electric field of 1 Vrms and 237 frequency sampling points. The results are shown in Fig. 5.

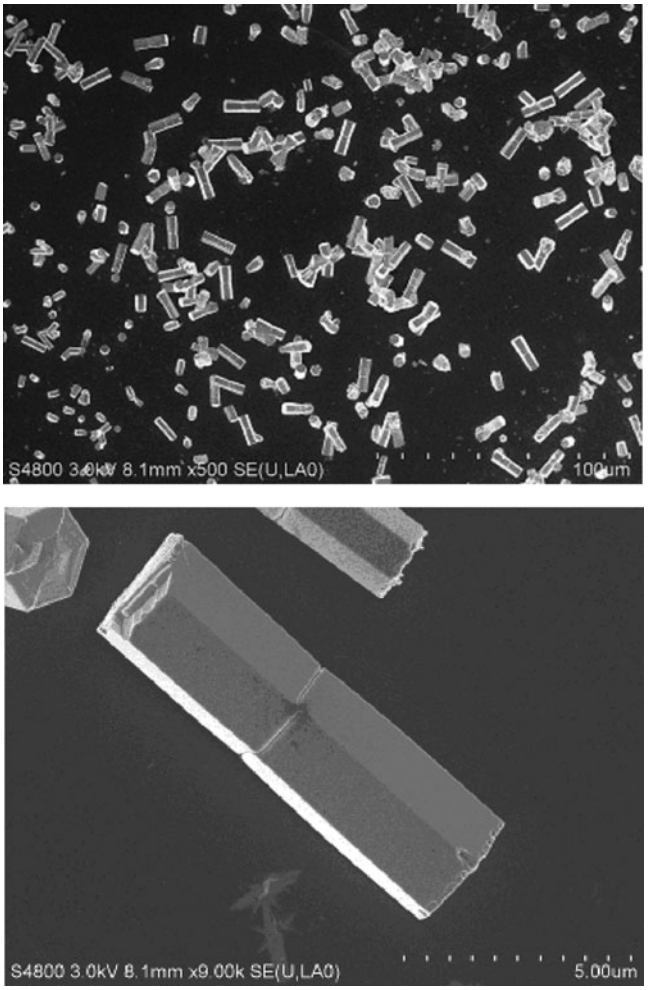

Figure 2. SEM images of the ZnO rods (a) photo in whole; (b) zoom of single rod.

In general, the dielectric constant of ZnO nano-rods decreases with the increase of the detection frequency. Therefore, with the increasing of the test frequency, the capacitances decrease. The decline of the capacitance fabricated with DEP is much smaller than that of sample 2. The two curves changed with the frequency were compared in Fig. 5(a). For sample 1, the capacitance fluctuation is within about 1.1% (from 200 pF to 197.8 pF) as the frequency increases from 3 kHz to 1 MHz. For sample 2, the capacitance is observed rapidly decreasing with an increasing test frequency under the same frequency domain, and the decline of the capacitance is 23.7% (from 93 pF to 71 pF). The capacitance value of the sample 1 is obviously about 2–3 times larger than that of sample 2. At the same time, the sample1 has an outstanding frequency independence with the testing frequency from 3 kHz to 1 MHz.

The dissipation factors of the two samples were presented in Fig. 5(b). Tan (delta) of both samples are very small. Between 30 kHz and 5.3 MHz, the dissipation factor of sample 1 is slightly lower than that of sample 2, and also it appears better frequency independence.

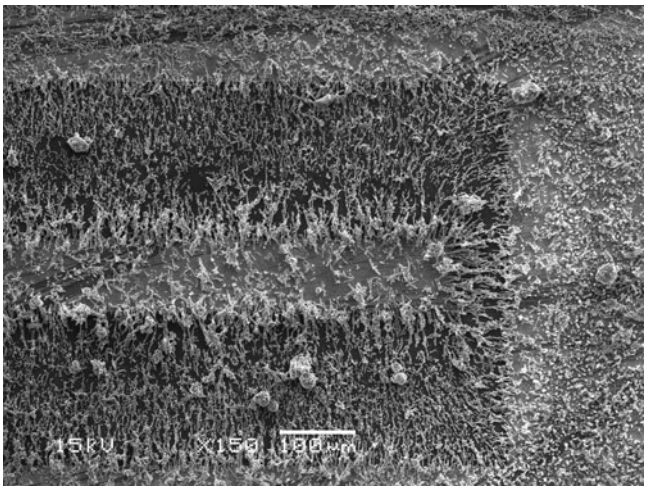

Figure 3. SEM image of aligned ZnO rods.

The dissipation factor of sample 2 is slowly increasing when the frequency of the testing signal rises due to the increasing of the polarization relaxation rate.

For a capacitor in the applications, good dc stability, the ability to maintain capacitance under dc bias, is required. Figure 6 gives the voltage evolution of the capacitances (1 kHz, 100 kHz, and 1000 kHz). It reveals the relationship between the capacitances of the two samples and the applied voltage, which demonstrates that the both capacitors have excellent dc stability in the measured ranges. And also, we can find that the capacitance of the sample 1 have a better stability than that of the sample 2 at 100 and 1000 kHz.

From the above results, we can consider that the ordered arrangement of the filling materials via DEP have a great influence on the capacitance. Some differences can be obviously found between the two samples fabricated with and without DEP. The capacitance

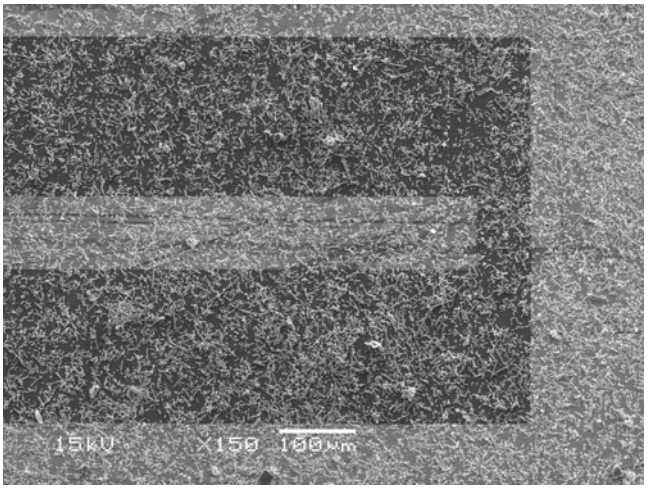

Figure 4. SEM image of not-aligned ZnO rods.

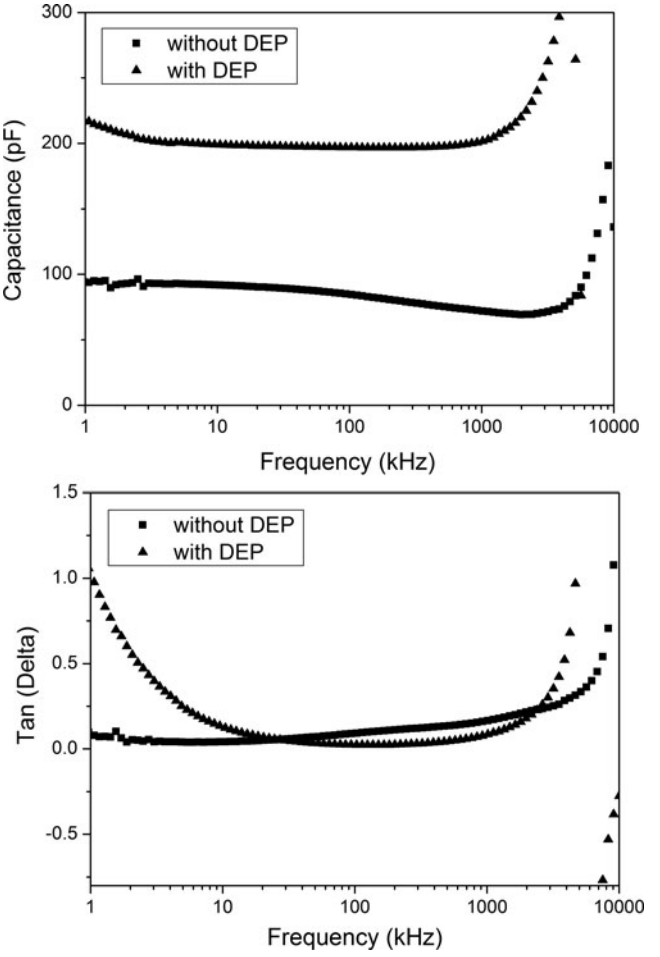

Figure 5. Frequency evolution of (a) the capacitance and (b) the dissipation factor of two samples.

value of the sample with DEP is improved by 2–3 times, and it has a better frequency independence, more excellent dc stability and lower dissipation factor between 30 kHz and 5.3 MHz.

5. Discussion

The improvement of the capacitor fabricated with DEP is analyzed as below. In sample 2, the electric moments of the nano-rods seriously canceled out due to their unorganized optimal polarization directions. In sample 1, the optimal polarization directions of the filling nano-rods arranged orderly along the electric field, the electric moments canceled out slightly, and the collective polarization was enlarged. The strong depolarization field was generated by the surface bound charges of the dielectric medium, It canceled out a part of the electric field induced by the free charges and decreased the electric field and electric potential difference between the two electrodes. Thus, the number of the charges loaded between the electrodes in sample 1 was larger than that in sample 2. The capacitance was increased by the dielectrophoretic arrangement of the optimal polarization directions of the filling materials.

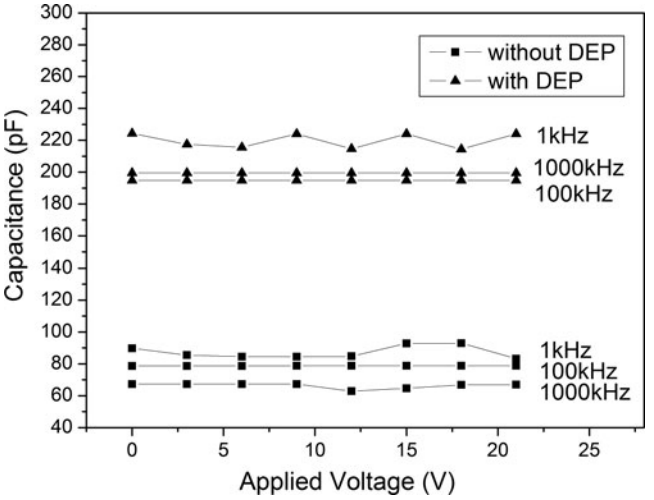

Figure 6. Voltage evolution of the capacitances (1 kHz, 100 kHz, 1000 kHz).

And also, with the optimal polarization directions orientated along the electric line, the dissipation among the separated particles can be limited. So, the capacitor fabricated with DEP has a better frequency independent property, more excellent dc stability and lower dissipation factor in the specific frequency domain, which is decided by dielectric property of the filling materials. For ZnO, such specific frequency domain is about between 30 kHz and 5.3 MHz.

With the positive DEP, ZnO nano-rods were forced to the region between the electrodes, especially to the vicinity of the electrode edges where the electric field was expected to be the strongest. The number of the nano-rods between the electrodes on sample1 tends to be little larger than that on sample 2, which could lead to the increase of the capacitance. In the present work, in order to demonstrate the further improvement of the capacitance via the orientation of their optimal polarization directions, the materials on two samples were controlled to be almost equal, and the complete rotation and a little translation of the nano-particles were obtained by the control of the manipulation time with the observation through the precision-optical microscope. The influence of the number and the translational motion of the particles between the electrodes on the capacitance of the two samples are limited. Therefore, the difference between the two capacitors is mainly originated from the different arrangement of the optimal polarization directions of the nano-particles.

6. Conclusions

The influence of the dielectrophoretic arrangement of the optimal polarization directions of filling particles on the capacitance has been preliminarily investigated. Two capacitors composed of ZnO nano-rods were fabricated with and without DEP on two identical inter-digitated electrode arrays. SEM images were presented to verify the aligned and not-aligned arrangement of the nano-rods on the two samples. The optimal polarization directions of the nano-particles, which were oriented randomly without DEP, were aligned in a highly uniform way and orientated along the electric field direction by DEP force. Some differences can be obviously found between the two samples. The capacitance of the sample fabricated with DEP is improved by 2–3 times, and it has a better frequency independence, more

excellent dc stability and lower dissipation factor between 30 kHz and 5.3 MHz. It is just a novel application of the ordered dielectrophoretic arrangement of the optimal polarization directions of the particles along the electric field in the capacitor fabrication process. And it is also a helpful theoretical experiment, which indicates the capacitor can be improved by the arrangement and rotation of the optimal polarization directions of the filling materials in some potential applications when the needed loose environment for the rotation of the filling particles is presented.

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