

Manipulation and trapping of semiconducting ZnO nanoparticles into nanogap electrodes by dielectrophoresis technique

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The assembly of ZnO nanoparticles into nanogap electrodes using ac dielectrophoresis (DEP) process is reported. DEP parameters such as frequency, voltage, and time were optimized to assemble minimum number of nanoparticles into nanogap electrodes. Frequency variation study revealed that positive DEP is active at frequencies less than 500 kHz; whereas negative DEP starts dominating at 1 MHz. The fabricated device exhibited a nonlinear I - V characteristic and under ultraviolet (UV) illumination a remarkable change in conductivity of one order of magnitude was observed. The results show the potential for realizing future optoelectronic devices such as miniaturized UV sensor. © 2009 American Institute of Physics. [DOI: 10.1063/1.3118588]

Zinc oxide (ZnO) is a II-VI compound semiconductor material with a wide band gap of 3.3 eV. It has drawn broad attention due to its immense potential for applications in electronic, optoelectronics, and optics. In particular, nanostructures of ZnO such as nanowires, nanorods, nanoparticles and other nanostructures have been studied for numerous applications such as ultraviolet (UV) lasers, UV sensor, solar cells, and gas sensors.¹⁻³ Even though recent trends have drawn wide attention in the research and development of nanostructure materials, design and fabrication of devices based on nanostructure materials still remain a major challenge. To investigate the characteristics of the devices based on nanostructure materials, it is important to make electrical contacts to either individual nanosegments or a combination of many. In principle, there are two approaches which can be used to meet these demands and are essential techniques forming the basis of nanotechnology (NT). One is the traditional processing technology where existing tools and structures are downscaled into the nanometer region called as “top-down” approach. The other approach is “bottom-up.” In this approach, self-formation processes and chemical synthesis create refined and perfect nanometer sized particles. It needs new and innovative techniques to efficiently combine and integrate the two fundamental approaches, i.e., top-down and bottom-up to place perfectly formed nanostructures at exactly defined and well controlled positions for future products and devices. One way to integrate these two approaches is to use dielectrophoresis (DEP) in assembling the nano-sized particles on prepatterned nanogap electrodes (top-down). With a history dating back to 1951, DEP is one of the most effective bottom-up approaches for manipulation and alignment of micro- to nanosized particles where the motion of polarizable suspended materials is controlled by the externally applied nonuniform electric field.^{4,5} Over the last decade, many groups have extensively studied the DEP alignment of various material such as gold (Au) nanocolloid,⁵ biomaterials such as DNA,⁶ carbon nanotubes,⁷ and semiconductor nanowires,⁸ and these materials can be exploited

for practical use in the fields of NT as well as biotechnology (BT) such as gas sensor,³ biosensor,⁷ field-effect transistor,⁹ molecular electronics,⁶ and many other potential fields of interest based on fusion technology of information technology, BT, and NT. Instead of these outstanding features of DEP process finding applications in realizing semiconductor based electronic and optoelectronic devices, the fabrication of semiconducting nanodevices based on DEP process is still not well undertaken. Statistically speaking DEP has been extensively used for manipulating metals and carbon nanotubes, however, a little information exists on dielectrophoretic assembly of semiconducting ZnO, which is one of the highly studied materials and has remarkable electrical and optical properties. Sensors configured with semiconducting ZnO nanoparticles into nanogap electrodes can have two major advantages: (1) high sensitivity due to much large surface-to-volume ratio of the nanoparticles than bulk, films, and nanowires; (2) reduced dimensionality between the electrodes shortens the carrier transit time which leads to a fast response time.

In the present letter, we demonstrate the assembly of ZnO nanoparticles (~9 nm) into nanogap electrodes (60 nm) using ac DEP process. DEP parameters are optimized to assemble minimum number of ZnO nanoparticles into nanogap electrodes and results have been discussed.

The Au electrodes with nanogap used in the present work were fabricated on oxide-coated silicon substrate using standard electron-beam lithography and lift-off technique.¹⁰ One chip consisted of 10 pairs of electrodes with a gap size of 60 nm each. ZnO nanoparticles were grown by the simple chemical route of sol-gel process reported by Meulenkamp.¹¹ The average diameter of ZnO nanoparticles estimated by x-ray diffraction analysis was found to be ~9 nm. ZnO nanoparticles were suspended (in the volume ratio of 1:50) in de-ionized (DI) water and sonicated to perform DEP experiment. Figure 1 shows the schematic of the experimental setup used for DEP process of ZnO nanoparticles. Prior to dielectrophoretic assembly, the chip was passed through a cleaning process such as O₂ plasma cleaning and rinsing in ethanol.¹⁰ A drop of ZnO nanoparticles suspended in DI water was placed in the center of the chip using a micropipette

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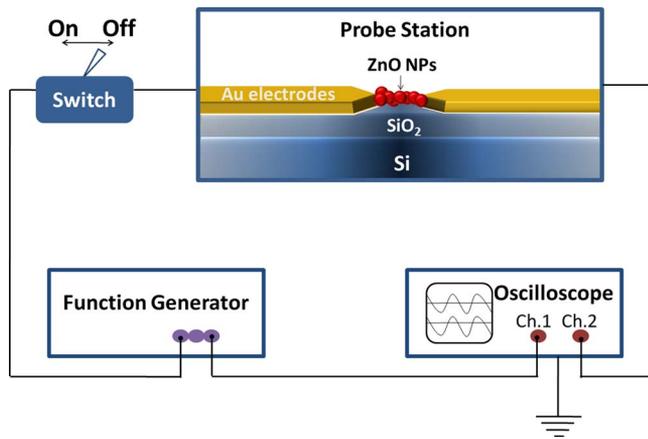


FIG. 1. (Color online) Schematic diagram of the setup used for the DEP assembly of ZnO nanoparticles into nanogap electrodes.

and ac voltage was applied across the electrodes to begin the DEP process. After DEP processing, scanning electron microscopy (SEM) (JEOL, Model: JSM-7401F) was used to examine the dielectrophoretic alignment of nanoparticles into nanogap electrodes. Current-voltage (I - V) characteristics of the assembled ZnO nanoparticles into nanogap electrodes were investigated using I - V measurement system (Keithley, Model: 4200-FCS).

DEP depends on three parameters, i.e., applied frequency (f), applied peak-to-peak voltage (V_{pp}), and time (t) during which DEP is done. It is important to optimize DEP parameters for consistent and reliable assembly of ZnO nanoparticles into nanogap electrodes. Frequency optimization was done by keeping $V_{pp}=2$ V and t was maintained at 30 s. Applied frequency was varied from 50 kHz to 1 MHz, and the assembling of nanoparticles into nanogap electrodes was investigated. It was observed that with an increase in frequency the assembling of ZnO nanoparticles into nanogap electrodes was steadily found to increase up to 150 kHz. Beyond this frequency, the assembly was found to saturate and this behavior continued until a frequency of 500 kHz was reached. Interestingly, after 500 kHz, there was a gradual decrease in assembling of ZnO nanoparticles into nanogap electrodes, and very few nanoparticles were seen in the vicinity of electrodes tip. A further increase in frequency to 1 MHz resulted in an interesting observation where electrodes were completely devoid of nanoparticles and the latter were seen to prefer regions of low electric field strength. Such observations made clear that high frequency of 1 MHz is not suitable for assembling ZnO nanoparticles into nanogap electrodes; however, at a lower frequency of 150 kHz assembling rate was at maximum. Therefore, a frequency of 150 kHz was maintained for further experiments.

During the second DEP parameter optimization, V_{pp} was varied from 1 to 4 V by keeping f and t at 150 kHz and 30 s, respectively. It was observed that $V_{pp}=1$ V did not result in any noticeable assembling of nanoparticles into nanogap electrodes. However, manipulation was significantly influenced for $V_{pp} \sim 2-3$ V. Applied voltage beyond 4 V resulted in the burning of nanogap electrodes. Also, a higher voltage leads to electrolysis, and assembly rate is expected to reduce, therefore, we restricted our experiments for $V_{pp} \leq 4$ V.

In the third DEP parameter optimization, time (t) was found to have a considerable effect on the assembly of con-

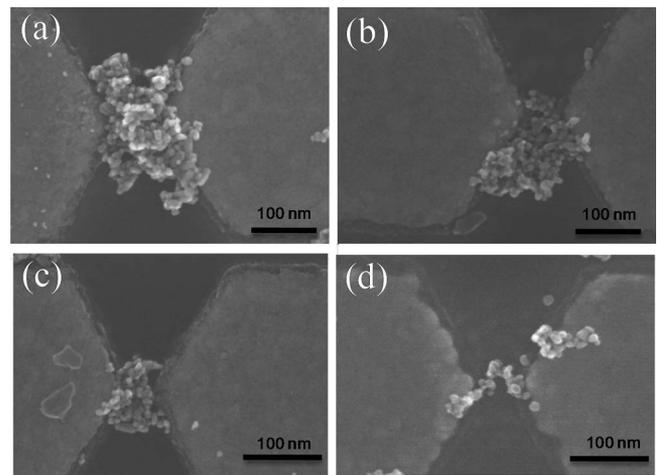


FIG. 2. SEM images of the assembled ZnO nanoparticles into nanogap electrodes when the DEP was carried out at fixed frequency of 150 kHz, applied peak-to-peak voltage of 2 V, and at different times of (a) 90 s, (b) 70 s, (c) 50 s, and (d) 30 s.

trolled number of nanoparticles into nanogap electrodes. Figure 2 shows the SEM images of the assembly of ZnO nanoparticles into nanogap electrodes when DEP was carried out for different time by maintaining f and V_{pp} at 150 kHz and 2 V, respectively. When the DEP was carried out for 90 s, a large number of ZnO nanoparticles were found to assemble in between the nanogap electrodes [Fig. 2(a)]. Interestingly, in reducing time to 70 s, a comparatively less number of nanoparticles were seen in the nanogap and the quantity was further reduced in decreasing the assembling time from 70 to 30 s (Fig. 2). This shows the large assembly is observed with increasing DEP time. A similar observation of large assembly with elapsed time was reported for dielectrophoretic assembly of ZnO nanowires.¹² It is important to note that the number of nanoparticles assembled in the nanogap electrodes at assembling time of 30 s was reduced to less than 9% ($\sim 7-8$ nanoparticles) of the number of nanoparticles ($\sim 90-100$) that was assembled at 90 s (Fig. 2). It may further be noted that the yield of assembly was almost 70%.^{4,13}

The time-average DEP force can be expressed as^{4,13}

$$F_{\text{DEP}} = 2\pi\epsilon_o\epsilon_m a^3 \text{Re}[K(\omega)] \nabla E_{\text{rms}}^2, \quad (1)$$

where ϵ_m is the permittivity of the medium, a is the radius of the nanoparticle, $K(\omega)$ is the Clausius–Mosotti factor, and E_{rms} is the rms value of the electric field. The DEP force is proportional to $K(\omega)$, the volume of the nanoparticle, and the gradient of the electric field. The frequency-dependent behavior resides in the Clausius–Mosotti factor, $K(\omega)$, and is given by

$$K(\omega) = \frac{\epsilon_p - \epsilon_m - \frac{j}{\omega(\sigma_p - \sigma_m)}}{\epsilon_p + 2\epsilon_m - \frac{j}{\omega(\sigma_p + 2\sigma_m)}}, \quad (2)$$

where ϵ_p and ϵ_m are the permittivities of the particle and medium, σ_p and σ_m are the conductivities of the particle and medium, j is $\sqrt{-1}$, and ω is $2\pi f$. Solving Eq. (2) for the real part of $K(\omega)$, we have

$$\text{Re}[K(\omega)] = \frac{(\epsilon_p - \epsilon_m)(\epsilon_p + 2\epsilon_m) + \frac{1}{\omega^2}(\sigma_p - \sigma_m)(\sigma_p + 2\sigma_m)}{(\epsilon_p + 2\epsilon_m)^2 + \frac{1}{\omega^2}(\sigma_p + 2\sigma_m)^2} \quad (3)$$

DEP force has two types, one is positive DEP and another is negative DEP. Positive DEP occurs when the $\text{Re}[K(\omega)]$ has positive value, and at that time a time-averaged force pulls the nanoparticles toward the area of strong electric field strength. The negative value of $\text{Re}[K(\omega)]$ causes negative DEP and corresponds to time-averaged force, directing the nanoparticles toward the area of weak electric field strength. In the Clausius–Mosotti factor, the conductivity terms are dominant at low frequencies while the permittivity terms are dominant at high frequencies.^{4,5,13} In the present work, positive DEP was dominant for frequency values up to 500 kHz, where the maximum assembly of ZnO nanoparticles was observed near the area of high field strength. Subsequently, positive DEP became weak beyond this frequency, and negative DEP prevailed at frequencies close to 1 MHz. This was evident by the fact that nanoparticles could not be trapped near the field of high strength, and their assembly was observed in low field areas. Following Eq. (3) and using the conductivities and permittivities of ZnO nanoparticles ($\epsilon_p = 10\epsilon_0$, $\sigma_p = 25 \mu\text{S}/\text{cm}$) and the medium (DI water) ($\epsilon_m = 80\epsilon_0$, $\sigma_m = 7 \mu\text{S}/\text{cm}$), we simulated the real part of $K(\omega)$ with f , and the result is shown as a graph in Fig. 3(a). The simulated result is quite in agreement with the observed behavior of positive and negative DEP forces at lower and higher frequencies, respectively. A little variation in results obtained experimentally and by theoretical simulation could be attributed to many factors which influence the DEP force, such as size-dependent permittivity and conductivity, electrode polarization, thermal effects, and ac electro-osmosis, etc.⁴

Figure 3(b) shows the I - V characteristic of ZnO nanoparticles based device fabricated by DEP process with and without UV illumination. Inset of Fig. 3(b) shows the schematics to study the photoconductivity in assembled ZnO nanoparticles into nanogap electrodes. I - V curve shows a typical nonlinear semiconducting behavior when performed without UV illumination. However, a remarkable change in conductivity of almost one order of magnitude was observed under UV illumination intensity of $1.0 \text{ mW}/\text{cm}^2$ ($\lambda = 365 \text{ nm}$). Under UV illumination photogenerated charge carriers are produced and lead to increase in photocurrent. A detailed study on the photoconductivity characteristics of dielectrophoretic assembled ZnO nanoparticles in nanogap electrodes is beyond the scope of this communication and would be published elsewhere.

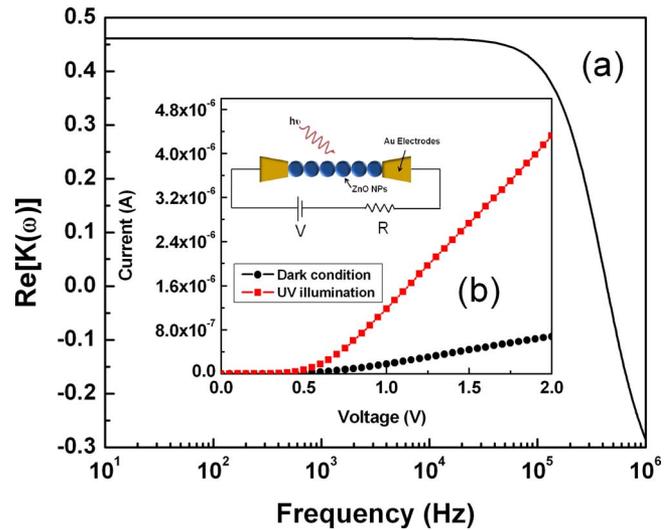


FIG. 3. (Color online) (a) Graph shows the simulated result of variation in real parameter of Clausius–Mosotti factor, $\text{Re}[K(\omega)]$ with applied frequency (f); (b) I - V characteristics of the dielectrophoretically fabricated device consisted of assembled ZnO nanoparticles into nanogap electrodes with and without UV radiation illumination. Inset shows the schematic diagram of photoconductivity measurement in assembled ZnO nanoparticles into nanogap electrodes.

In conclusion, we have demonstrated the assembly of ZnO nanoparticles ($\sim 9 \text{ nm}$) into nanogap electrodes (60 nm) using ac DEP process. The fabricated ZnO nanoparticles based device was found to respond to low intensity UV illumination, and shows tremendous potential for realizing miniaturized UV sensors for myriad applications.

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- ¹S. Kumar, G.-H. Kim, K. Sreenivas, and R. P. Tandon, *J. Phys.: Condens. Matter* **19**, 472202 (2007).
- ²L. Liao, H. B. Lu, J. C. Li, C. Liu, D. J. Fu, and Y. L. Liu, *Appl. Phys. Lett.* **91**, 173110 (2007).
- ³J. F. Conley, L. Stecker, and Y. Ono, *Appl. Phys. Lett.* **87**, 223114 (2005).
- ⁴B. C. Gierhart, D. G. Howitt, S. J. Chen, R. L. Smith, and S. D. Collins, *Langmuir* **23**, 12450 (2007).
- ⁵R. J. Barsotti, Jr., M. D. Vahey, R. Wartena, Y. M. Chiang, J. Voldman, and F. Stellacci, *Small* **3**, 488 (2007).
- ⁶C. L. Asbury, A. H. Diercks, and G. van den Engh, *Electrophoresis* **23**, 2658 (2002).
- ⁷F. Dewarraf, M. Calame, and C. Schenberger, *Single Mol.* **3**, 189 (2002).
- ⁸L. Zheng, S. Li, J. P. Brody, and P. J. Burke, *Langmuir* **20**, 8612 (2004).
- ⁹S. K. Lee, S. Y. Lee, J. H. Hyung, C. O. Jang, D. J. Kim, and D. I. Suh, *J. Nanosci. Nanotechnol.* **8**, 3473 (2008).
- ¹⁰S.-H. Yoon, S. Kumar, G.-H. Kim, Y.-S. Choi, T. W. Kim, and S. I. Khondaker, *J. Nanosci. Nanotechnol.* **8**, 3427 (2008).
- ¹¹E. A. Meulenkaamp, *J. Phys. Chem. B* **102**, 5566 (1998).
- ¹²J. Suehiro, N. Nakagawa, S. Hidaka, M. Ueda, K. Imasaka, M. Higashihata, T. Okada, and M. Hara, *Nanotechnology* **17**, 2567 (2006).
- ¹³P. R. C. Gascoyne and J. Vykoukal, *Electrophoresis* **23**, 1973 (2002).