# Assembly of gold nanoparticles of different diameters between nanogap electrodes

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Gold nanoparticles (NPs) of different diameters i.e., 5, 10, and 20 nm, were assembled between 20 nm gap electrodes using ac dielectrophoresis (DEP) process. DEP parameters, such as frequency, trapping time, and voltage of value 1 MHz, 1 s, and 2–3 V, respectively, led to the pearl-chain assembly corresponding to each type of NPs between 20 nm gap electrodes. Mutual DEP could be attributed to the NPs chaining in low field regions and subsequently the DEP force directs these chains to the trapping region. Such controlled assembly of individual NPs may find application in fabricating devices for molecular electronics. © *2010 American Institute of Physics*. [doi:10.1063/1.3280859]

Exploring the potential of nanoparticles (NPs) in various fields of science and technology has been of decent interest in recent years. Some of the fields where NPs are holding much interest are nano- and molecular electronics. These rapidly growing fields have the potential to combat the miniaturization limits that silicon technology is gradually approaching.[1–4] Due to their inherently small size, nano- and molecular devices are likely to open avenues for ultradense logic and memory.[1,2] One of the ways in realizing devices for nanoelectronics is to assemble molecules or NPs in prepatterned electrodes.[4–6] Such devices promise to provide intriguing information of the NPs assembled in the electrodes gap by studying the electronic transport through them or utilizing such devices to fabricating alternative devices. Out of the various possible means of assembling NPs in electrodes gap, dielectrophoresis (DEP) has emerged as an effective way for manipulation of NPs in electrodes geometry of different types.[2,5,6] Various research groups have attempted the assembly of metallic NPs, such as gold (Au), into planar electrodes of various gap sizes.[5–8] The factors that encourage the research on assembling Au NPs in electrodes gap are as follows: (1) to understand the phenomena of DEP at nanoscale level; (2) trapping minimum NPs in electrodes gap; (3) to assemble NPs into electrodes gap of similar size; and (4) to study electronic transport though the trapped molecules or NPs.

DEP is a process in which the motion of polarizable particles suspended in a medium is controlled by the externally applied nonuniform electric field.[9–11] Many researchers including Pohl, who is credited for introducing the concept of DEP, emphasized that it is theoretically difficult to manipulate particles of smaller size in the nanometer range due to many reasons, one of them being the dependence of DEP force on the volume of the particle.[9] However, recent research results have shown that DEP can be used to manipulate particles of different sizes and has been used successfully to assemble microparticles, NPs such as Au nanocolloids, DNA, micro-organism, nanowires, carbon nanotubes, etc.[2–8,12–15] In addition, DEP has the advantage of selectively placing nano-objects within the electrically defined gaps in quick assembly time and exhibits appreciable reproducibility.[8]

Manipulation of single and few Au NPs in nanogap electrodes has always fascinated the researchers for analyzing the DEP at nanoscale range.[6–8] In particular, it would be of interest to study the DEP of Au NPs having diameter ≤20 nm into 20 nm gap electrodes as a means to realize devices for nanoelectronics. In the present letter, we report the experimental results of trapping Au NPs of different diameters between 20 nm gap electrodes using ac DEP process, and the mechanism of NPs trapping has been discussed.

The Au electrodes used in the present work were fabricated on an oxide-coated silicon substrate using standard electron-beam lithography and lift-off technique.[2,8] The separation between the Au electrodes was 20 nm, and such ten pairs of electrodes were comprised in one chip. The experimental setup used for the DEP process consists of a function generator and a digital storage oscilloscope (Fig. 1, Ref. 2). Au NPs of diameters 5, 10, and 20 nm were purchased from the British Bio Cell International and used at as purchased concentration ($7 \times 10^{11}$ particles/ml). Further details regarding the DEP setup and the experimental procedure can be found elsewhere.[2] Prior to DEP assembling, the chips were passed through a cleaning process such as $O_2$ plasma cleaning (COVANCE-1MP by Femto science, Korea) for 10 min under 30 SCCM (SCCM denotes standard cubic centimeters
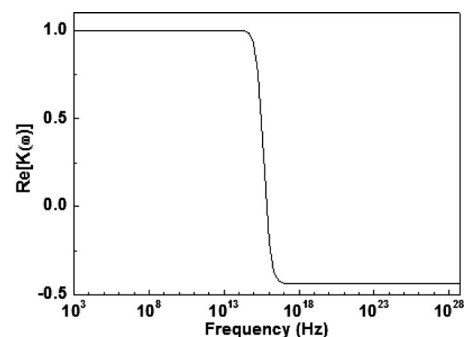


FIG. 1. Graph shows the simulated result of variation in real part of Clausius–Mosotti factor, $\text{Re}[K(\omega)]$ with applied frequency.

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per minute) oxygen atmosphere. After plasma cleaning treatment, chips were rinsed with ethanol for 5 s, and then dried by blowing with $N_2$ gas (pressure ~1 kgf/cm$^2$). A micropipette was used to take approximately ~0.5 $\mu$L drop of aqueous Au NPs solution for the DEP processing. Finally, the trapping of Au NPs into nanogap electrodes was observed by scanning electron microscopy (SEM) (Jeol, Model: JSM-7401F).

We used Au NPs of three different diameters, i.e., 5, 10, and 20 nm, to perform DEP between 20 nm gap electrodes. DEP depends on three parameters, i.e., frequency, peak-to-peak voltage, and the time of trapping. These parameters are optimized to trap NPs of different diameters into 20 nm gap electrodes. To assemble NPs into the electrodes gap where field strength is expected to be maximum, one requires the DEP force to be positive.

The time-average DEP force can be expressed as[2,7]

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

where $\varepsilon_m$ is the permittivity of the medium, $a$ is the radius of the NP, $K(\omega)$ is the Clausius–Mosotti factor, and $E_{\text{rms}}$ is the rms value of the electric field. DEP force is proportional to $K(\omega)$, the volume of the NP, and the gradient of the electric field. The frequency dependent behavior resides in the Clausius–Mosotti factor, $K(\omega)$, which is a complex parameter, and the real part of $K(\omega)$ is given by[2]

$$\text{Re}[K(\omega)] = \frac{(\varepsilon_p - \varepsilon_m)(\varepsilon_p + 2\varepsilon_m) + \frac{1}{\omega^2}(\sigma_p - \sigma_m)(\sigma_p + 2\sigma_m)}{(\varepsilon_p + 2\varepsilon_m)^2 + \frac{1}{\omega^2}(\sigma_p + 2\sigma_m)^2}, \tag{2}$$

where $\varepsilon_p$ is the permittivity of the particle, $\sigma_p$ and $\sigma_m$ are the conductivities of the particle and the medium, $\omega$ is $2\pi f$. Equations (1) and (2) show that the DEP force strongly depends on permittivities and conductivities of the particle and the medium, respectively. DEP force has two types, one is positive DEP and another is negative DEP. The type of DEP force is decided by the value of $\text{Re}[K(\omega)]$. A positive value of $\text{Re}[K(\omega)]$ causes positive DEP and a time-averaged force pulls the NPs toward 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 NPs toward 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.[2] Following Eq. (2) and using the conductivities and permittivities of Au NPs (Ref. 7) ($\varepsilon_p = 6.9\varepsilon_0$, $\sigma_p = 4.5 \times 10^{11}$ $\mu$S/cm) and the medium (de-ionized water) ($\varepsilon_m = 78\varepsilon_0$, $\sigma_m = 1.0$ $\mu$S/cm), we simulated the real part of Clausius–Mosotti factor with applied frequency and found that positive DEP remains active for a wide range of frequency. A crossover to the negative DEP occurs at around $10^{18}$ Hz, which shows that positive DEP could remain active up to few gigahertz frequencies if other parameters, such as electro-osmosis, dielectric dispersion, and related effects, do not show their influence at higher frequencies (Fig. 1).

DEP experiments were performed at an applied frequency of 1 MHz, peak-to-peak voltage of 2–3 V, and the trapping time was maintained at 1 s. In the first set of experiments, 20-nm-diameter Au NPs were used to perform DEP. The experimental parameters were as follows: frequency, 1 MHz; peak-to-peak voltage, 2 V; and trapping time, 1 s.
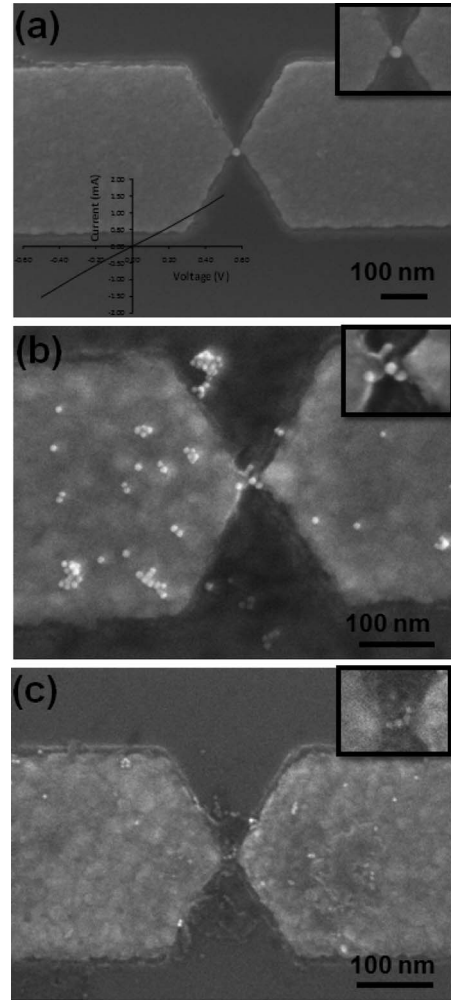


FIG. 2. SEM images of the trapped Au NPs of different diameters i.e., 20, 10, and 5 nm, into 20 nm gap electrodes. DEP was carried out by maintaining the frequency and trapping time to 1 MHz and 1 s, respectively, and the applied peak-to-peak voltage was maintained to: (a) 2 V for 20-nm-diameter Au NPs; (b) 2.5 V for 10-nm-diameter Au NPs; and (c) 3 V for 5-nm-diameter Au NPs. Insets on the top right side of all images show a magnified view of the assembly of NPs in the electrodes gap. Inset on the bottom left in (a) shows an *I-V* curve observed on a device consisting of a 20-nm-diameter Au NP assembled into 20 nm gap electrodes.

Under these conditions, it was found that a single Au NP was trapped into 20 nm gap electrodes [Fig. 2(a)], and the yield of such assembly was more than 50%. For 10-nm-diameter Au NPs, the experimental conditions were same as in the case of 20-nm-diameter NPs, except the applied peak-to-peak voltage was increased to 2.5 V. It was observed that within 1 s, no single 10-nm-diameter Au NP was trapped in the region (20 nm) between the electrodes, instead, in majority of the cases, two NPs were seen to remain trapped in the electrodes gap, and the yield of such success was ~30% [Fig. 2(b)]. In the case of 5-nm-diameter Au NPs, without changing the frequency and trapping time, the applied voltage was increased to 3 V. Within a trapping time of 1 s and under an applied voltage of 3 V, an interesting assembly of four 5-nm-diameter Au NPs was observed into 20 nm gap electrodes [Fig. 2(c)].

Equation (1) reveals that DEP force depends on the volume of NP under consideration. In the case of 20-nm-diameter Au NPs, within 1 s, the DEP force is ~8 and 64 times stronger than that for 10- and 5-nm-diameter Au NPs,
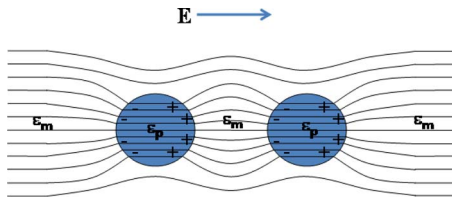
FIG. 3. (Color online) Diagram shows the mechanism of mutual DEP taking place between the neighboring NPs having permittivity $\varepsilon_p$ dispersed in a medium of permittivity $\varepsilon_m$ under the application of a nonuniform electric field.

respectively [Eq. (1)]. Therefore, the trapping of 20-nm-diameter NPs into 20 nm gap electrodes is more favorable, which in turn leads to single particle assembly. Also, the DEP force depends on the applied electrical field, therefore, to allow the trapping of smaller particles (5 and 10 nm), within a trapping time of 1 s, the applied voltage was increased from 2 to 2.5–3 V to correspondingly increase the DEP force.

On comparing the three assemblies we find that in the case of 20-nm-diameter Au NPs, DEP led to the trapping of only one NP in the electrodes gap during a trapping time of 1 s. However, for the other two cases, NPs chaining was observed in the electrodes gap. This means that there could be two possibilities for the chaining formation, either (1) NPs come to the trapping region due to DEP force and form pearl-chain or (2) first the NPs chain together away from the trapping region and subsequently move to the trapping region due to DEP force.

It appears that NPs, due to polarization and mutual DEP, form pearl-chain in the region near the electrodes. Since in the present work, the volume of colloidal NPs was ~0.5 $\mu$L and the electrodes gap was 20 nm, therefore, it is expected that due to the presence of applied ac field, the field lines do extend away from the electrodes tip, and in this way help mutual DEP between the NPs; however, mutual DEP force is comparatively weaker than the actual DEP force.[9] The mutual DEP is related to a threshold field defined by[7,9]

$$E_{\text{th}} = 1.7 \frac{1}{|K(\omega)|} \sqrt{\frac{k_B T}{\epsilon_p a^3}}, \qquad (3)$$

where $k_B$ is the Boltzmann constant and $T$ is the operating temperature. It has been mentioned that mutual DEP force could lead to chaining of particles at some distance away from the electrodes where the field strength exceeds $E_{\text{th}}$, which for 15 nm Au NPs, as taken from literature, is 5.6 $\times 10^7$ V/cm.[7] This threshold field value is much lower than the electric field strength present between 20 nm gap electrodes used in the present work. As mentioned earlier different applied voltages were used for the DEP of different Au NPs (2 V for 20 nm, 2.5 V for 10 nm, and 3 V for 5 nm) and the corresponding field strengths are much higher than the threshold value, which suggest the formation of pearl-chain away from the electrodes. Figure 3 explains the mechanism of mutual DEP observed in the present work. In the presence of nonuniform electric field, each NP, being spherical, exhibits a uniform electric field within its interior. Furthermore, if the NP and the medium both are isotropic, homogeneous,

and linear dielectrics, then each NP starts experiencing a nonuniform field near each other. In this situation, the field lines within the NP and outside are different.[9] This imhomogeneity of the field about the NP causes two or more NPs to be mutually attracted to each other and gives rise to the pearl chaining of the particle. Due to the strong positive DEP force present in the 20 nm gap electrodes, the polarized NPs forming pearl-chain near the electrodes, move to the area of strongest electric field and get assembled in the trapping region (Fig. 2).

All the three devices were performed for current-voltage (I-V) measurement at the room temperature and the device corresponding to 20-nm-diameter Au NP trapped into 20 nm gap electrodes showed linear I-V characteristic, as shown in the inset of Fig. 2(a). It may be noted that a slight change in the slope of the I-V curve could be due to the Joule heating effect which occurs due to the flow of current through the Au NP. The other two devices didn't show any appreciable I-V behavior as the NPs could not completely bridge the electrodes. The resistance measured for the device consisting of a 20-nm-diameter Au NP between 20 nm gap electrodes was ~330 $\Omega$ and showed a good Ohmic contact between Au NP and the electrodes.

In conclusion, DEP of Au NPs of different diameters was performed between electrodes with a gap of 20 nm. Mutual DEP could be attributed to the chaining of 5- and 10-nm-diameter Au NPs and subsequently positive DEP force traps the clubbed two 10-nm-diameter and four 5-nm-diameter Au NPs into 20 nm gap electrodes. Such devices might have potential for use in molecular electronics.

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