Positioning and Alignment of Vanadium Oxide Nanoribbons by AC Dielectrophoresis

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Positioning of semiconductor nanostructures in an organized manner is important for the advancement of their use in future technological devices, specifically in field-effect transistors (FETs). One method that accomplishes this is AC dielectrophoresis which depends on the surface charge of the particles, the dielectric constants of the particles and the medium, and the frequency of the electric field. We have carried out calculations of the dielectrophoretic force dependence on the dielectric constants, surface charge, and electric field frequency. We have also measured the charge of the vanadium oxide nanoribbons by way of zeta potential measurements. To align nanoribbons in FET geometries, we have designed electrode structures using electric field simulations. We have successfully aligned nanoribbons in 2-propanol solution across electrodes with varying gaps and have measured the electrical transport properties. Other variations we have studied in electrode design include fabrication of suspended nanoribbon bridges over deep-etched chromium electrodes and aligning nanoribbons across indium electrodes.

I. INTRODUCTION

Due to the necessity and desire to create smaller and faster computers for the future, research activity in the field of nanomaterials has greatly increased in recent years. Nanomaterials are great candidates for future electronic devices due to their extremely small size, leading to a reduction of functional materials needed and allowing for their massive integration in nanoscale circuits. They have interesting electrical, optical, and mechanical properties and are believed to be the future of electrochemical energy storage as energy becomes a world crisis [1].

Vanadium oxide (VO$_2$) is a semiconductor at room temperature and undergoes a phase transition at 70°C [2]. Nanostructured VO$_2$ has recently been synthesized by a hydrothermal method and holds promise for future electronic devices [3]. These materials must be integrated into circuits, such as field-effect transistors and branching interconnects, with some degree of precision such that the device properties of theses nanostructures can be tested. Dielectrophoretic alignment of these nanostructures is a promising method of building such devices.

The AC dielectrophoretic force arises from a nonuniform electric field acting on the induced dipole moment of an uncharged dielectric and/or conductive object [4]. For an object with dielectric function $\epsilon_1$ in a dielectric medium $\epsilon_2$, the force is proportional to the Clausius-Mossotti (CM) factor, which for a long rod with its major axis parallel to an inhomogeneous alternating electric field is found to be [4, 5]

$$f_{CM} = \frac{\epsilon_p - \epsilon_m}{\epsilon_m + (\epsilon_p - \epsilon_m)L}$$  \hspace{1cm} (1)

$$\bar{\epsilon}_p = \epsilon_p - i\frac{K_p}{\omega}, \quad \bar{\epsilon}_m = \epsilon_m - i\frac{K_m}{\omega}$$  \hspace{1cm} (2)

where $\epsilon$ is the permittivity, $K$ is the conductivity, $\omega$ is the frequency of the electric field, and the subscripts $m$ and $p$ refer to the medium and particle (in this case, 2-propanol
and vanadium oxide nanoribbons), respectively. The value of the depolarization factor $L$ is approximated by $L = \frac{d^2}{l^2} \ln \frac{2l}{d} - 1$, where $l$ and $d$ are the length and diameter of the vanadium oxide particles [6] and here are 5 $\mu$m and 40 nm, respectively.

II. EXPERIMENTAL METHOD

Microelectrodes with varying shapes, geometry, and material makeup are patterned on SiO$_2$ (500 nm)/Si substrates using electron beam lithography. After this patterning step, we used thermal or electron beam evaporation to create Cr, Cr/Au, and Cr/Au/In electrodes. The gap distances between the electrodes range between 1 $\mu$m and 10 $\mu$m with widths ranging from 10 $\mu$m to a sharp point. Another geometry which has been explored is deeply etched electrodes where the silicon and silicon dioxide layers of the wafer are etched away using the inductively coupled plasma (ICP) etching technique resulting in electrodes that are approximately 5 $\mu$m tall.

Deposition of vanadium oxide nanoribbons (VONRs) is performed by applying an AC electric field between the electrodes. Typically, 10 $\mu$L of vanadium oxide/2-propanol solution is released in the electrode gap. The dielectrophoretic force acts on the particles depositing the nanoribbons on the electrodes until the 2-propanol has completely evaporated. Following the deposition step, scanning electron microscopy (SEM) images were taken using a Hitachi S4700 instrument operating at 10 kV. Current-voltage measurements of the nanodevices were obtained using a HP4145 semiconductor parameter analyzer.

III. ZETA POTENTIAL MEASUREMENTS

In studying the characteristics of the VONRs that we used in the deposition experiments, it was useful to perform zeta potential measurements using a Malvern Zetasizer Nano Z instrument to determine particle charge and mobility. The magnitude of the zeta potential also indicates how repulsive particles in its medium are from other particles. The zeta potential is the charge on the solvation layer surrounding the particles in solution and reflects the surface charge of the particles. The magnitude of the zeta potential is reflective of the surface conductance of the nanoparticles. This has implications in the dielectrophoretic alignment as discussed since [6]

$$K_p = K_{int} + \frac{2\lambda}{a}$$ (3)

where $K_{int}$ is the particle conductivity, $\lambda$ is the surface conductance, and $a$ is the radius of a spherical particle.

Zeta potential measurements for VONRs in 2-propanol solution show that these particles are negatively charged with a surface charge of $\sim -60$ mV (see FIG. 1).

![FIG. 1: Plot of Intensity versus Zeta Potential for Vanadium Oxide Nanoribbons in 2-propanol solution.](image)

IV. DIELECTROPHORETIC FORCE CALCULATIONS

In order to better understand the effect that the dielectrophoretic (DE) force has on nanoparticles such as VONRs, we performed
A. Dielectrophoretic Force versus $\beta$

The DE force moves particles to regions of high field strength when the CM factor is positive and toward regions of low field strength when the CM factor is negative. Using the expression for the DE force in eqn. 1, we wrote a numerical program showing the relation between the CM factor and the parameter $\beta = K_p/K_m$ for various frequencies.

FIG. 2 shows the variation in the CM factor for parameters $\alpha = \epsilon_p/\epsilon_m$ and $\beta = K_p/K_m$. In these plots we used $\alpha = 1.01$, $2.75$, and $5.49$, $L = 2.89 \times 10^{-4}$ S/m and frequency $\omega = 5$ Hz, $50$ kHz, and $5$ MHz. In FIG. 2 we see that the CM factor for different $\alpha$’s shows nearly the same dependence on frequency. As frequency increases, the variation of the CM factor for different $\alpha$’s appears. At $50$ kHz with $\beta < 0.1$, the CM factor is nearly constant as a function of $\beta$, but negative, nearly zero, and positive for $\alpha = 1.01$, $2.75$, and $5.49$, respectively. As $\beta$ increases, the CM factor decreases and for all $\alpha$’s the CM factor is positive and increasing with $\beta$. The bottom plot in FIG. 2 shows
that at even higher frequencies (5 MHz) the CM factor becomes constant with respect to variations in \( \beta \), changes more with respect to \( \alpha \), and is always positive.

FIG. 3 shows that for various frequencies the CM factor increases with increasing \( \beta \). The increase is larger for smaller field frequencies and nearly constant for frequencies larger than 5 MHz. FIG. 3 also shows that for frequencies larger than 50 kHz the CM factor is always positive, independent of the value of \( \beta \).

**B. Dielectrophoretic Force versus Electric Field Frequency**

An interesting study that was conducted was the dielectrophoretic force dependence on AC field frequency. This was studied both experimentally and numerically (FIG. 4). In our numerical calculations, we found that for high AC frequency fields the CM factor is independent of the conductivities of the particle and medium. However, for low AC frequency fields we found that the CM factor is quite dependent on the different conductivities. At low frequencies, we found that when \( K_p < K_m \) the CMF is negative, when \( K_p = K_m \) the CMF is nearly zero, and that for \( K_p > K_m \) the CMF is always positive (independent of the field frequency). We also found that when \( K_p \approx 5.49 K_m \) then the CM factor is always positive and constant with respect to the AC field frequency.

We saw similar behavior experimentally. When a high frequency field was applied, alignment of the vanadium oxide was quite strong and followed the electric field lines. For low frequency fields we saw no pattern of nanoribbon alignment with the field, but a disorganized deposition on the electrodes. We also applied AC fields of intermediate frequency and saw some alignment with the field but the alignment was not as noticeable as that of the high frequency fields and we saw extra debris from the solution drawn into the gap.
V. ELECTRIC FIELD SIMULATIONS

The dielectrophoretic force on a particle in a medium is proportional to the square of the gradient of the electric field. Therefore, the regions where the electric field changes most will be where the VONRs are pulled into since it experiences an attractive force due to the difference between the dielectric constants of the VONRs and the 2-propanol medium. With this in mind, we conducted electric field simulations for different electrode design. From the simulations, we were able to create electrodes that showed strong electric fields in regions where we wanted to deposit the nanoribbons. See FIG. 5.

VI. NANORIBBON ALIGNMENT ACROSS ELECTRODE GAP

Nanoribbon alignment depends on many parameters including AC voltage and frequency, electrode geometry, materials used in device fabrication, and concentration of nanoribbons in solution. The optimization of these parameters is important for dielectrophoresis being a viable method of constructing functional device architectures.

A. AC Electric Field Frequency Dependence

According to the Claussius-Mossoti factor, the particles in a medium will experience a DE force which is dependent on the frequency of the AC electric field that it is in. Following the numerical calculations of the CM factor dependence on frequency, we conducted experiments during which we placed 10 µL of solution of VONRs in 2-propanol between Cr/Au electrodes that were 3 µm apart. The frequency of the AC field was varied between 5 Hz and 5 MHz by a factor of 10, resulting in the deposition of VONRs on electrodes for
7 different frequencies.

We saw that when the field frequency was high (5 MHz and 500 kHz) the alignment of VONRs across the electrode gap was quite uniform and efficient in positioning them in the high field region. For intermediate field frequencies (50 kHz, 5 kHz, and 500 Hz), we saw some alignment between the gap and relatively more debris enter the gap from the solution. For low frequency fields (50 Hz and 5 Hz), there was still deposition between the electrodes; however, no obvious alignment was observed.

**FIG. 6:** SEM images of VONRs dielectrophoretically deposited on gold electrodes with 3 \( \mu \)m gap using an AC electric field with frequency: a) 5 Hz and b) 5 MHz.

**B. Electric Field Magnitude**

The magnitude of the electric field between the electrodes increases for shorter gap distances, resulting in more deposition since VONRs are pulled toward regions of high electric field. The gap distances between the electrodes were varied throughout our experiments as we sought a distance that would optimize control of VONR deposition on the microelectrodes. Distances used were 1 \( \mu \)m, 3 \( \mu \)m, and 10 \( \mu \)m.

**FIG. 7:** SEM images of VONRs dielectrophoretically deposited onto gold electrodes with gap distances: a) 1 \( \mu \)m, b) 3 \( \mu \)m, and c) 10 \( \mu \)m.

When we used 10 \( \mu \)m gaps between electrodes we saw fewer nanoribbons across the gap. When there was deposition across the gap, the VONRs would either align with the
field reaching only partially across the gap or the VONRs would touch other VONRs and they would together complete a circuit across the gap. For electrodes of smaller gap distances, we saw more deposition of VONRs across the gap because the VONRs used were on average shorter than the 10 µm gap and could not reach across the gap but were long enough to span across the 3 µm gap. We found that 3 µm is short enough to allow deposition across the gap while also being wide enough to control deposition so that not too many VONRs deposited across the gap that it was hard to distinguish between VONRs (FIG. 7).

C. Concentration of VO$_2$ Solution

Another variable that can be controlled is the concentration of vanadium oxide nanoribbons in 2-propanol solution. When the solution of concentration 0.42 mg/L was placed between the gap during the deposition step, many VONRs enter the gap and were deposited between the electrodes. Much better control and alignment is achieved when the solution is diluted to obtain 0.21 mg/L solution in 2-propanol, as seen in FIG. 8.

D. Electrode Geometry

Electrode geometry is an important factor in controlling the alignment and positioning of VONRs using AC dielectrophoresis. The DE force is proportional to the square of the gradient of the electric field. Therefore, to optimize alignment of nanoparticles using this method it is best to use an electrode geometry that creates a large value of the gradient of the electric field. Some possible geometries include square electrodes, electrodes that are narrowed from 10 µm at the base of the electrode to 1 µm at the end, pointed electrodes, and pointed electrodes with floating posts that act as hotspots of the electric field, guiding nanoparticles to align across the gap. With square electrodes we are able to apply a strong uniform field between the gap, while with pointed electrodes we are able to control better the deposition of only a few nanoparticles across the gap, as in FIG. 9.
E. Indium Electrodes

To create better conducting devices by decreasing contact resistance, we built Cr/Au/In electrodes. Our standard electrodes were fabricated with gold, but we felt that using indium (a very soft metal with a low melting point) would allow us to heat up VONR devices made from indium in a thermogravimetric analyzer (TGA) and melt the metal around the nanoribbon creating a better surface contact. We performed current-voltage measurements on such devices both before and after melting the indium. However, we did not see a large increase in current through the device (FIG. 10).

![FIG. 10: SEM image of VONR bridging the gap between a) pointed Cr/Au/In electrodes with 10 µm gap and b) pointed Cr/Au electrodes with 5 µm gap.](image)

F. Deeply Etched Electrodes

Another electrode design that we experimented with was that of deeply etched chromium electrodes. The majority of these electrodes were approximately 5 µm tall and were made of chromium because metals such as gold and indium could not survive the fabrication process and would have been etched away simultaneously with the silicon and silicon dioxide. We were able to suspend VONRs across such electrodes only when the gap between the electrodes was small. For geometries with large gaps (~10 µm) there was no deposition across the electrodes. An example of a deeply etched electrode device is seen in FIG. 11. These devices are not only beautiful looking, but also show the power of AC dielectrophoresis as a method of fabricating complex nanocircuits.

![FIG. 11: SEM image of VONR bridging the gap between deeply etched chromium electrodes 3 µm apart and 5 µm tall.](image)

VII. DEVICE PROPERTIES

The device properties of these dielectrophoretically constructed VONR devices were studied after assembly. These devices act as p-type semiconductors and their current-voltage curves show significant gate dependence. From the curves, we also see that the devices shows a sharp increase in current around -40 V (See FIG. 12).
VIII. CONCLUSIONS

We have gained control and understanding of alignment of vanadium oxide nanoribbons onto electron beam patterned microelectrodes by AC dielectrophoresis. These devices have the prospect of future use in electronic devices such as field-effect transistors. Theoretical plots have been made to better understand dielectrophoresis and its dependence on the dielectric constants and surface charges of the particles and medium and its dependence on the frequency of the applied AC electric field. Theoretical simulations have been made showing the electric field for various electrode geometries. Nanoribbon devices have been fabricated successfully with various electrode gap distances, AC field frequencies, vanadium oxide solution concentrations, and electrode geometries. Future work will include continuing to optimize the fabrication parameters, understanding the metal-insulator transition of VO$_2$ devices at strong electric fields, and constructing more complex nanoribbon devices.

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[2] Yong-Sik Lim, et al. Los Alamos National Laboratory, Preprint Archive, Con-


