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A suspended nanogap formed by field-induced atomically sharp tips

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A sub-nanometer scale suspended gap (nanogap) defined by electric field-induced atomically sharp metallic tips is presented. A strong local electric field ($>10^9$ V/m) across micro/nanomachined tips facing each other causes the metal ion migration in the form of dendrite-like growth at the cathode. The nanogap is fully isolated from the substrate eliminating growth mechanisms that involve substrate interactions. The proposed mechanism of ion transportation is verified using real-time imaging of the metal ion transportation using an *in situ* biasing in transmission electron microscope (TEM). The configuration of the micro/nanomachined suspended tips allows nanostructure growth of a wide variety of materials including metals, metal-oxides, and polymers. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4764562>]

Platforms that use nanoscale gaps (nanogaps) defined by metallic tips have been investigated extensively due to their ability to synthesize and/or characterize nanoscale electronic structures.^{1–6} Typically, research on nanogap platforms has focused on only reducing and controlling the size of the nanogap in sub-nanometer length scale without controlling the radii of curvature of the tips. This leads to tethering or growth of nanostructures of interest in uncontrolled orientations and material states. Additionally, in most of these platforms, the nanogaps are in direct physical contact with the substrate, making it difficult to decouple the electrical, magnetic, chemical, or mechanical interactions between the nanostructure and the substrate.^{7,8}

In this letter, the ability to define a precise nanogap size and tip radius of curvature by directly controlling tip-to-tip interaction using an external electric field is presented. A nanogap platform that is truly isolated from substrate with atomically sharp tips of less than 1 nm radius of curvature is presented. Metal ion transport at the cathode tip by an externally applied electric field results in host metal dendrite growth. The grown tips forming the nanogap are self-aligned to each other due to the applied local electric field.

Metal ion migration at nanoscale is an important mechanism in ionic-electronics, e.g., in resistance switching used in memristors.^{9–11} The migrated ions can be used in bottom-up synthesis of nanostructures, defined to the atomic scale. Using controlled atomically sharp tip growth and precise gap size, the nanogap can be an optimal platform for molecular electronics.

The fabrication of the nanogap has been done in two separate steps. The first step is to fabricate a suspended nanogap of length between 5 nm and 80 nm with tip radii of curvatures between 5 nm and 7 nm using bulk-micromachining. In the second step, a voltage applied across the nanogap results in metal cations to extrude out, directed by the induced electric field, forming self-aligned atomically sharp

tips (with radii of curvature <1 nm). The detailed sequence for the first step to form the micromachined nanogap has been described elsewhere.¹² Fig. 1 shows a scanning electron micrograph (SEM) of the micromachined nanogap fabricated on a silicon-on-insulator (SOI) wafer, in which the nanogap is defined by patterning the silicon device layer. Typical radii of curvature of the silicon tips are in the range of 5–7 nm with nanogap lengths of 20–100 nm. The silicon tips and contact pads are then isolated from the substrate by removing the buried oxide layer in 49% aqueous hydrofluoric acid solution. The suspension of nanogap ensures mechanical and electrical isolation from the substrate. The nanogap device is coated with a low-stress silicon nitride (SiN_x) thin film to prevent silicide formation when contact metal (~ 60 nm of nickel) is thermally evaporated on the tips and pads. The SiN_x and metal film coating results in the reduction of the initial gap to 5–80 nm, depending on the micromachined initial gap. The metal film on the pads serves as an electrical conductor for a bias across the gap. The metal film on the tips is a source of metal ions, which become mobile when an electric field is applied across the tips. A nanogap formed by tips coated with 60 nm thick nickel layer by thermal evaporation was used to investigate the metal ion migration under an electric field. A 10 nA DC current bias is applied across the

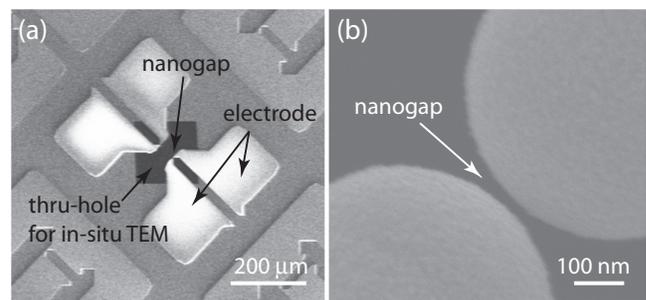


FIG. 1. (a) Overview of nanogap formed by suspended micro/nanomachined tips on an SOI wafer. Electrodes and the tips are electrically isolated from the substrate. (b) A close-up SEM view of the nanogap.

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nanogap, and the maximum voltage drop across the nanogap is limited to 100 V (using bias compliance), that is, the voltage drop is limited by an external circuit. The nanogap forms and open circuit initially, causing the initial current to be zero. High electric field strengths ($\sim 10^9$ V/m) at the tip causes metal ions to migrate from the negatively biased tip (cathode). The migrated ions result in the cathode to extrude out to form a dendrite-like nanostructure. The nanostructure growth by the ion migration is directed towards the anode tip, where the electric field is highest. Fig. 2 shows *in situ* TEM images of the nanostructure growth sequence in time due to the metal ion migration from the cathode tip.

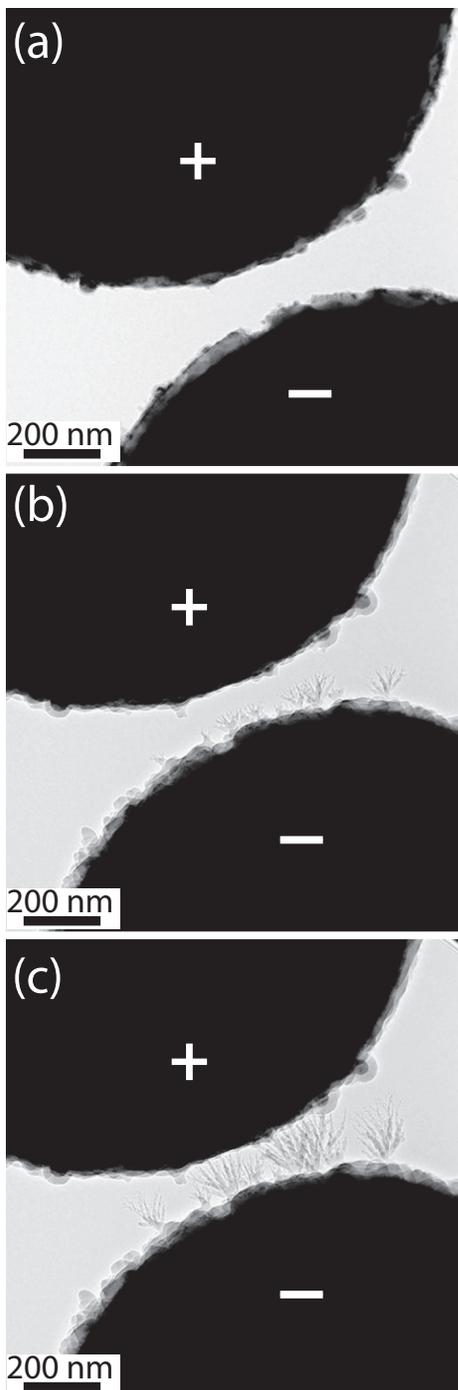


FIG. 2. *In situ* TEM images during a nanostructure growth. Bias polarity is indicated on the tips. (a) Ni covered nanogap at the beginning of bias, (b) dendrite nanostructures start to grow, (c) fully grown nanostructures.

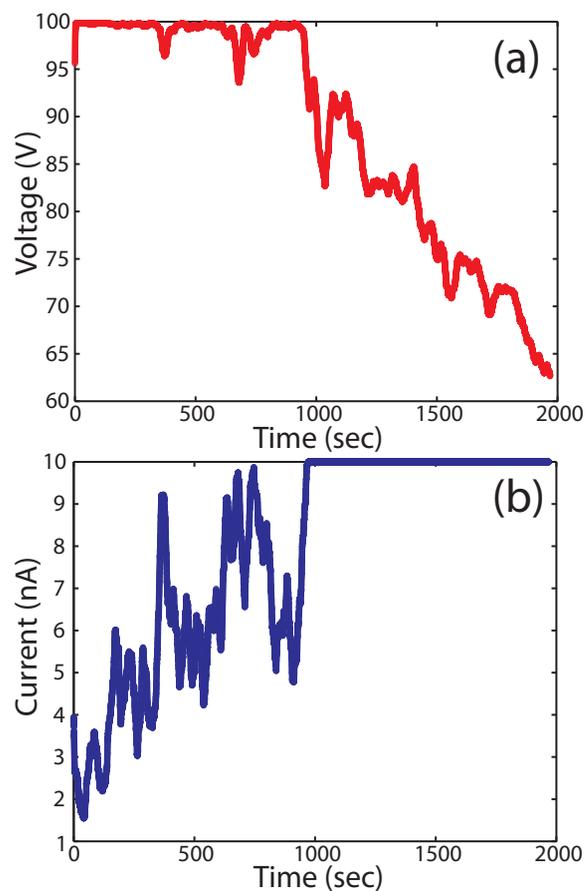


FIG. 3. Measured DC bias during the growth. (a) Voltage drop across the nanogap. (b) Current profile across the nanogap.

When the ion migration occurs at the cathode tip, the electrical current across the nanogap increases as shown in Fig. 3. Although the current fluctuates throughout the growth phase of the tip, it shows an increasing trend till it equals the set bias current of 10 nA, which indicates that the tip from the cathode has bridged the nanogap. We suggest that the fluctuation of the current is due to the multiple nanostructure growth on the cathode tip, which distorts the local electric fields. The length and growth rate of the nanostructure is shown in Fig. 4, showing a growth rate of ~ 0.04 nm/s during the most of growth duration. The growth rate of the nanostructure increases as the tip approaches the anode, which is explained by the increase in electric field across the nanogap as the distance between the tips gets progressively shorter. Results from energy-filtered TEM (EFTEM) supports this growth mechanism by showing that nickel is one of the two predominant materials grown (Fig. 5). The presence of carbon is likely an artifact due to electron-beam induced deposition during *in situ* TEM experiment.¹³

In general, nanostructure growth by metal ion migration under an electric field can be due to one or more of the following four different mechanisms: electromigration,¹⁴ field ion emission,¹⁵ cation migration,⁸ and anion migration.¹⁰ The mechanisms of both the field ion emission and cation migration on a substrate are caused by the electrochemical growth and dissolution of metallic filaments at the anode.^{8,10,15} Cation migration is also closely related to the ion mobility in the substrate materials (specifically, in dielectrics).⁸ On the other hand, anion migration has been

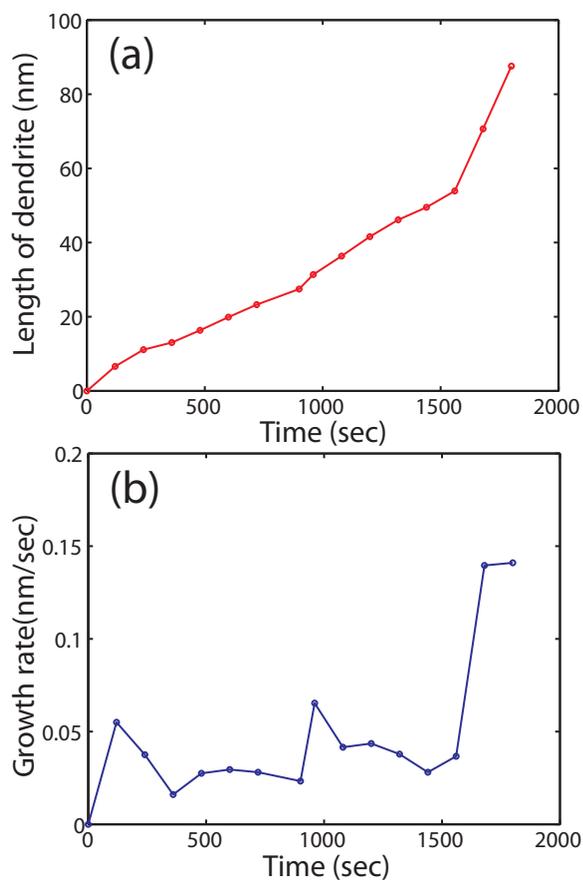


FIG. 4. (a) Length of the nanostructure growth as a function of time. (b) Growth rate.

described by the migration of oxygen vacancies toward the cathode,¹⁰ which also depends on the interaction with the host material. In the current work, since the nanogaps are fully suspended, any direct interactions between metal ions and the substrate can be excluded. Thus the ion-migration is solely due to the interaction with the electric field and/or electron tunneling current. Eliminating the mechanisms that are explained based on substrate interaction, it is postulated that the ion migration occurs only at the cathode tips. This is also supported well by *in situ* TEMs during growth showing dendrite nanostructure growth occurring at the cathode tip with no discernible change at the anode tip. This result is in

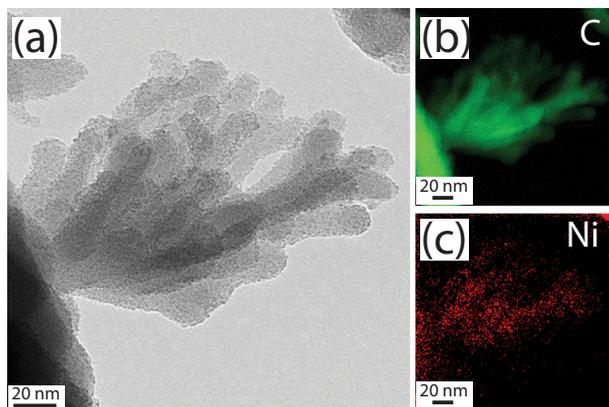


FIG. 5. Elemental mapping by EFTEM analysis for the grown nanostructure in Fig. 2. (a) the grown nanostructure, (b) carbon, and (c) Ni.

contrast to metal filament growth at the anode reported in Refs. 8 and 15. Based on the *in situ* real-time TEM images of the growth and the ex situ study reported before,¹² it is likely that the nanostructure growth is due to the ionization of Ni and/or NiO by electron tunneling (Fig. 3) and transport of the ions under the high electric field at the cathode.¹⁶ The dendrite form of the nanostructure growth is suggested to be due to the local electric field distortion by the nanostructure.⁸ The tip radius of curvature of the dendrite is typically less than 1 nm as grown.

A method to fabricate a precise nanogap with atomically sharp metallic tips formed by field-induced ion transport has been presented. The growth of metallic nanostructure was imaged in real-time using *in situ* TEM and was used to identify the ion migration mechanism under the applied electric field. The composition of the grown nanostructure was demonstrated to be the same as the host material using EFTEM analysis. By coating the suspended tips with different materials such as metals, polymers, and oxide-based materials, a wide range of materials can be grown, making this a versatile platform for nanoscale synthesis and characterization. The growth by ion migration occurs at atomic scales, resulting in a dendrite nanostructure due to a localized high electric field. The distance between the tip of dendrite and the other electrode can be controlled by terminating bias at the desired nanogap size. The atomically sharp tip formed by ion-migration could be optimal electrodes as a nanogap platform for single-molecule electronics.

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