Parallel fabrication of polymer-protected nanogaps

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Abstract

A method to create an array of sub-5 nm nanogaps with self-aligned holes in a protective polymer overlayer is presented. The parallel formation of the nanogaps, intended for electrical sensing of biomolecules in an aqueous environment, is achieved by electromigration using a simple voltage ramp across parallel-connected electrode patterns with individual constrictions. It was observed that the nanogap always formed on the cathode side of a bowtie electrode, with corresponding hillocks on the anode side, with the distance of the gap/hillock formation from the constriction depending on the ambient temperature. This technique provides a practical means to fabricate a series of polymer-protected nanogaps with considerably higher efficiency than afforded by the normally slow serial process of electromigration.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Electrodes with nanogaps are widely used to contact molecules and other nanosized objects accommodated within the gap to measure their electrical characteristics [1–8]. Although a number of fabrication approaches have been advanced in recent years, each method has certain advantages and disadvantages. Direct patterning of nanogaps using electron-beam lithography is a relatively slow technique due to its serial process and normally has a resolution limit of several nanometers [9, 10]. Electrochemical deposition or etching is a fairly non-uniform process, so gaps must be individually monitored to achieve the desired gap sizes [11]. Mechanically controllable break junctions rely on complicated mechanical feedback set-ups [12] which renders the approach less amenable to monolithic device fabrication, notwithstanding which, break junctions can be created in solution to achieve a fresh surface, which has great advantages in forming self-assembled monolayers [6]. Nanogap formation by shadow evaporation [13] provides a scalable approach to multiple-device fabrication, but a means to protect the lead electrodes leaving the nanogap exposed has yet to be developed. Thermally assisted electromigration of lithographically defined narrow thin wires [14–22] is often used where nanogap spacing in the nanometer range is required due to the relative simplicity of the process. However, nanogap fabrication through electromigration is usually carried out one at a time, and few methods using electromigration [23] have been reported that are able to fabricate sub-2 nm nanogaps in a parallel fashion as required for the production of large-scale integrated molecular circuits. Furthermore, if nanogap devices are used for sensing in an aqueous environment, they are faced with the problem of high extraneous current due to parallel conduction paths through the ionic solution if the latter is in contact with the electrodes leading to the nanogap. To overcome this, a few techniques have been reported to selectively passivate the nanogap device, including local polymer ablation by an electric field [24] or Joule heating [25], as well as traditional lithographic patterning of a protective film [26]. The principle underlying these techniques is to insulate the electrodes from the solution with a polymer layer except for an opening at the nanogap position.

We previously reported the realization of protected sub-2 nm nanogaps through a process of electromigration and
concurrent self-aligned polymer ablation in a polymethylmethacrylate (PMMA)-coated constricted electrode structure, using a simple slow voltage sweep [25]. In the present work, we demonstrate that an array of such protected nanogaps can be fabricated by carrying out the electromigration process using a parallel connection of multiple constricted electrode structures. The formation of many gaps with scalable throughput makes this a viable manufacturing technology. The method for the formation of nanogaps requires neither sophisticated feedback control [16] nor a cryogenic environment [15]. We further examined the topography and the location of the nanogap and observed the formation of gold hillocks and the nanogap placed diametrically opposite around the constriction site. Due to the degree of randomness associated with the location where the nanogap forms, our self-aligned polymer hole-formation approach avoids the issues associated with the alignment needed with traditional lithographic methods.

2. Fabrication of polymer-protected nanogap arrays

PMMA resist was spin-coated onto a silicon die with a 500 nm thick silicon dioxide layer. Electrode patterns with a weak bowtie junction were delineated in PMMA resist patterned by electron-beam lithography (EBL, using a Philips XL30 FEG SEM with Raith ELPHY Plus pattern generator). The electrodes were designed to be 100 µm in length and 5 µm in width with ~200 nm wide constrictions as shown in figure 1(a) (not drawn to scale). Although EBL was used in our experimental work, such bowtie electrodes could also be delineated using deep-ultraviolet (DUV) optical lithography. A metal layer of 18 nm thick gold and 1.5 nm thick Cr (as an adhesion layer) was thermally evaporated (BOC Edwards, Auto 306 Vacuum Evaporator) onto the patterned die and lifted off in acetone, to create the gold electrode. This was followed by optical lithography using AZ5212 photoresist to define large bond pads (400 µm × 400 µm). A second layer of 100 nm thick gold and 10 nm Cr was thermally evaporated and lifted off to form the contact pads. An insulating polymer layer, in this case around 100 nm thick PMMA, was spun on to coat the entire device. The electrodes were connected in a parallel manner. Next, a simple voltage sweep at 1 mV per 7 s was applied to the bowtie structures at room temperature using a Keithley 4200 parameter analyzer to electrically stress the connected electrodes until nanogaps have formed in all the electrodes (figure 1(a)). Sub-2 nm nanogaps and self-aligned PMMA hole structures of 200 nm diameter were simultaneously formed at the constriction sites, similar to what we achieved in [25] for a single constriction. The formation of the sub-2 nm nanogaps was due to thermally assisted electromigration of the gold atoms, while Joule heating caused a rapid temperature rise at the constriction site leading to a local ablation of the PMMA, which resulted in a hole structure right on top of the nanogap (figure 1(b)).

3. Results and discussion

3.1. Parallel polymer-protected nanogap formation

As proof-of-concept experiments, we have successfully fabricated arrays of eight nanogaps in parallel with individual conformal holes in the PMMA layer—the number of parallel-connected electrodes can be further increased but would be limited by the amount of current that the instrumentation can supply. An SEM image of an array of electrodes with pre-patterned constrictions before electrical stressing is shown in figure 2(a). Figure 2(b) is the plot of conductance versus voltage as the voltage was ramped during electrical stressing. Each step of conductance drop corresponds to the formation of one nanogap while the last step indicated the near-simultaneous formation of two nanogaps as estimated by the conductance drop. An SEM image and an I–V tunneling characteristic of a typical nanogap are inset in figure 2(b). Due to the random nature of electromigration by atom movement, the geometry of the crack in the vicinity of the nanogap is not perfectly uniform [20, 27, 28]. Tunneling occurs through the closest points between two electrodes which constitute the actual nanogap. The topographic atomic force microscopy (AFM) image of the PMMA-protected nanogaps in figure 2(c) indicates that a 200 nm diameter PMMA hole was formed at each constriction site.

Due to inherent variability in the lithographically defined constrictions, the thinnest constriction experiences the highest
current density and will begin to electromigrate at a smaller applied voltage than the others. As the thinnest constriction electromigrates, its resistance increases and the current lowers, and the rate of electromigration naturally rebalances among the parallel-connected constrictions so that they can evolve together. At some point in time, one junction undergoes final evolution to result in a nanogap, and the next thinnest junction becomes pinned. The process repeats until all the constrictions have turned into nanogaps and the program stops. Nanogaps with tunneling currents ranging from $10^{-12}$ to $10^{-7}$ A at 0.5 V (figure 3(a)) were obtained and estimated to be sub-2 nm in size, which is similar to what we have observed for single nanogap formation [25] by electromigration. Every ångström increase in the size of the nanogap would lead to almost one order-of-magnitude decrease in the tunneling current [18]. The tunneling current range corresponds to a variation in nanogap size of less than 0.6 nm out of 36 nanogaps from nine batches of parallel-connected electrodes. The average size of the PMMA hole obtained is 216.5 nm ± 50.5 nm (36 samples). Figure 3(b) shows typical topographical images of PMMA holes formed from one batch of four parallel-connected electrodes. The diameter spread is attributed to variations in the constriction dimensions and local temperatures in the final breakdown phase of nanogap formation.

3.2. Nanogap topography

As noted in figures 2(b), (c) and 3(b), neither the nanogaps nor the PMMA holes were formed right at the center of the constriction site but were biased towards one side. In
all cases, the gaps occurred on the cathode side of the constriction (i.e. the side of the wires where electrons flow into the constriction) rather than at the narrowest point of the constriction (figure 4(a)). In addition, it was observed that there were always bright spots placed approximately symmetrically opposite to the gap location on a sample not coated with PMMA. These bright spots observed in SEM images suggest surface protrusions that give rise to higher secondary electron yield [29]. Imaging using AFM (figure 4(b)) further confirms that there is hillock formation on the anode side of the constriction. The formation of hillocks is the result of gold atom migration from the cathode side.

It is noted that the gaps and hillocks form at a short distance from the constriction. If these were due to local structure or defects that affect the electromigration flux, it would be expected that the gap and hillock locations would vary significantly from experiment to experiment, which was not observed in our experiments. To understand what controls the location of the gaps and hillocks it should first be noted that the electromigration-induced atomic flux $J$ scales with temperature $T$ and current density $j$ according to the formula

$$J \propto j \exp\left(-\frac{Q}{kT}\right)$$

where $Q$ is the activation energy for atom migration and $k$ is Boltzmann’s constant. The current crowding that occurs at the constriction leads to a maximum in $j$ at the constriction. Joule heating also leads to a maximum temperature at the constriction. There will therefore be an especially sharp maximum in the atomic flux at the constriction. Voids (gaps) and hillocks develop when there is a divergence in the atomic flux, i.e. where the gradient of $J$ is high so that more material enters (leaves) a volume than leaves (enters) the volume. On the cathode side, the flux diverges from slow to fast as the electrode cross-sectional area decreases, so material is depleted and tensile stress develops. This stress eventually leads to void formation and growth of voids to form a nanogap. On the anode side, the flux diverges from fast to slow, leading to compressive stress and consequently to gradual formation of hillocks. Failure occurs at the peak flux divergence so that the locations of the voids and hillocks can be found where $|dJ/dx|$ is maximum or when $d^2J/dx^2$ is zero. Since the structure is symmetric, the locations of the voids and hillocks are symmetric about the constriction. The schematic in figure 5(b) illustrates the mechanism of formation of the nanogap and hillocks.

3.3. Temperature dependence

The influence of ambient temperature on nanogap formation was also studied. As discussed above, if Joule heating were affecting the locations of the flux divergences, the local temperature should have a significant effect on the location of the voids and hillocks. The location of the hillocks/voids is dependent on the shape of the temperature ($T$) versus position ($x$) curve. According to our interpretation, changing the ambient temperature would change the shape of the $T(x)$ curve and consequently the $J(x)$ curve, thereby affecting the location of the voids and hillocks. Specifically, for a given current, an increase in the ambient temperature would broaden the peak in the atomic flux around the constriction. To test this, a set of experiments was carried out in vacuum (to eliminate heat loss due to convection) at different temperatures ($T_1 = 298$ K, $T_2 = 323$ K and $T_3 = 363$ K) within a tube furnace. To avoid any
Figure 6. (a) Schematic plot of the current density $J$, $dJ/dx$ and $d^2J/dx^2$ for various temperatures, $T_1 < T_2 < T_3$; (b) SEM images of nanogap structures at 298, 323 and 363 K (from top to bottom). The dashed lines show the mean positions of gold hillocks and gaps. Scale bar are 200 nm.

possible surface interference and suppression, all the nanogaps were formed without the polymer layer. From figure 6(a), it can be seen that the location of gaps/hillocks is further away from the constriction when the ambient temperature is higher. The higher the ambient temperature, the less steep the $T(x)$ curve, and likewise the $J(x)$ curve. The flux density would change more gradually along the length of the electrode. Hence, the location of maximum $|dJ/dx|$ would be further away from the constriction. A sketch of $J$, $dJ/dx$ and $d^2J/dx^2$ curves at three different temperatures (figure 6(a)) is shown alongside the SEM pictures in figure 6(b).

The formation of the nanogap away from the constriction poses a problem in locating a hole in a passivation layer if the intention is to create the hole by a conventional lithographic process that requires alignment. Alignment to a nanogap that has already been formed is subject to uncertainty as the actual nanogap may be among one of several locations along the crack resulting from the electromigration process (see figure 4(a)). Likewise, if the center of the constriction is taken as the alignment reference point, then the hole needs to be sufficiently large to cover the width of the tapered electrode portion where the electromigration crack forms, the nanogap proper being located at an unpredictable position along this crack. For room-temperature formation of the nanogap, the gap forms within 250 nm of the constriction, which imposes a $\sim 500$ nm lower bound on the hole diameter for our 45° tapered (half-angle) electrode structure. In contrast, our hole structure formed by polymer ablation is inherently self-aligned to the nanogap. The temperature increases rapidly by Joule heating during electrical stressing at the constriction site, and therefore the polymer layer experiences a local expansion and gradually reflows. A dome-shaped structure is then formed due to buckling and eventually the polymer is locally ablated, resulting in the formation of a hole located precisely at the final breakdown point of the electrode where the temperature is highest [25].

4. Conclusion

In conclusion, we fabricated polymer-protected nanogap devices in a parallel manner with considerably higher efficiency than afforded by the normally slow serial process of electromigration using a simple voltage sweep. The topography of the obtained nanogap was investigated and the mechanisms that influence the nanogap location were discussed. The observation of the nanogap not forming right at the center of the constriction site supports the advantage of our self-aligned polymer ablation technique to protect the nanogap. The fabricated nanogap array should be useful for constructing complex circuits for molecular electronics. The nanogaps could be used in parallel connection, for example, to conduct surface-enhanced Raman spectroscopy of molecules [30], or individually to study the electrical properties of nano-objects, depending on the specific goals. The possibility of integrating the nanogap array with nanofluidic channels may also open up doors to a whole range of exciting discoveries, such as DNA detection [3] and sequencing [31].

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