CONTROLLED SHRINKING OF NANOPORES IN SINGLE LAYER GRAPHENE USING ELECTRON BEAM IRRADIATION

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ABSTRACT

This paper reports electron beam induced shrinking of nanopores drilled in free-standing graphene. Nanopores with diameters in the range of 40-60 nm were easily shrunk down to 2 nm and even completely closed by exposure to low beam current densities in a transmission electron microscope (TEM). This method can be used to fine-tune nanopore shape and size, as well as to heal secondary defects and pinholes to produce functional graphene nanopores.

KEYWORDS: Graphene, Nanopore, Pore Shrinking

INTRODUCTION

It has been established that the thickness of the insulating membrane significantly affects the signal to noise ratio [1] and the spatial resolution [2, 3] in nanopore sensors. This has resulted in the development of nanopore devices using single or multilayer graphene for label-free DNA sensing [2, 4, 5]. However, drilling of size controlled nanopores in free-standing graphene still remains a challenge as drilling often results in over-sized, irregularly shaped pores [5], pinholes [4] or complete membrane damage [6]. The shape and diameter of the nanopores can be controlled by shrinking them to the desired size. Shrinking of nanopores drilled in multilayer graphene has been achieved by heating the samples to 400-1200 ^{0}C using thermal specimen holder [7, 8] and by electron beam irradiation [9]. In the current work, we demonstrate controlled shrinking of nanopores in single layer graphene at room temperature using low electron density irradiation in a transmission electron microscope. Our method allows for controlling shrinking of nanopores in single layer graphene with nanometer precision with visual feedback.

EXPERIMENTAL

For sample preparation, chemical vapor deposition grown graphene was transferred onto a nanopore chip (with a 500 nm diameter pore drilled in 50 nm thick free standing Si_xN_y membrane using focused ion beam) as described before [2]. Briefly, graphene deposited on copper film was coated with a thin support layer of 4% PMMA (poly-methyl methacrylate) followed by etching of copper film using ferric chloride, which left PMMA coated graphene floating in the solution. Graphene was then washed in deionized water several times and transferred onto free standing Si_xN_y membrane with a 500 nm pore. The PMMA was then removed by burning in furnace at 400 °C for 4 hours. This resulted in free standing graphene over the 500 nm pore in Si_xN_y layer (Figure 1(a)). Nanopores were drilled in the free standing graphene using converged beam of JEOL 2100F TEM operated at 200 KeV using spot modes 1 (98 pA/cm^2) and 2 (54 pA/cm^2). After drilling the pores, their size and shape was fine-tuned or they were shrunk using converged/ semi-converged beams at spot modes 4 (4.8 pA/cm^2) and 5 (1.4 pA/cm^2).

RESULTS AND DISCUSSION

Our graphene transfer method resulted in clean and defect free graphene over the silicon nitride layer. The free standing region of graphene was focused and selected area diffraction (SAED) pattern was recorded. Figure 1(b) shows typical hexagonal diffraction pattern obtained from the transferred graphene. Figure 1(c) shows intensity profile for diffractions spots enclosed inside the yellow rectangle in Figure 1(b). The intensity ratio for inner and other spots greater than 1 confirmed it to be single layer graphene.

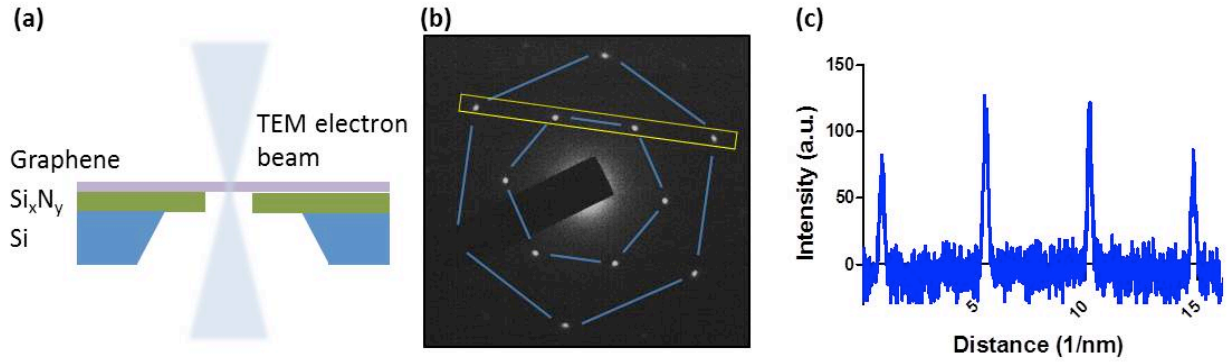

Figure 1. (a) Sample architecture. (b) Diffraction pattern for the transferred graphene. Blues lines are guide for the eye. (c) Intensity profile for diffraction spots enclosed inside yellow rectangle in (b).

After the graphene was characterized, converged beam of TEM at spot mode 1 & 2 was used to drill 40-50 nm diameter pores in the free standing graphene. The drilled pores could then be adjusted/ shrunk using semi-converged beam at spot modes 4 & 5. Figure 2 shows drilling and shrinking kinetics using different spot modes and current densities. While drilling, spot mode 2 showed some lag as compared to spot mode 1 because of low electron beam density; however, both spot modes resulted in pore of comparable size after 90 seconds of beam exposure (N=4). The shrinking process was slow relative to drilling and for all pores there was 1-2 minutes of lag time before they started to shrink. The use of semi-converged beam during shrinking allowed for visual feedback and nanometer scale control on the size of the final pore. We propose that exposing the nanopore edges to low electron beam densities at spot modes 4 & 5 results in beam induced local heating of the membrane. This temperature gradient attracts ad-atoms/contaminants to the pore vicinity and these ad-atoms saturate the binding sites on the pore periphery and lead to inward growth of the nanopores. Shrinking of pores larger than 50 nm is challenging but can be achieved by focusing the beam on one edge of the pore instead of the pore center. Sequential images of a 25 nm pore being shrunk to a 6 nm pore are shown in Figure 3. The pore was shrunk at spot mode 4 and was imaged at 30-50 seconds intervals.

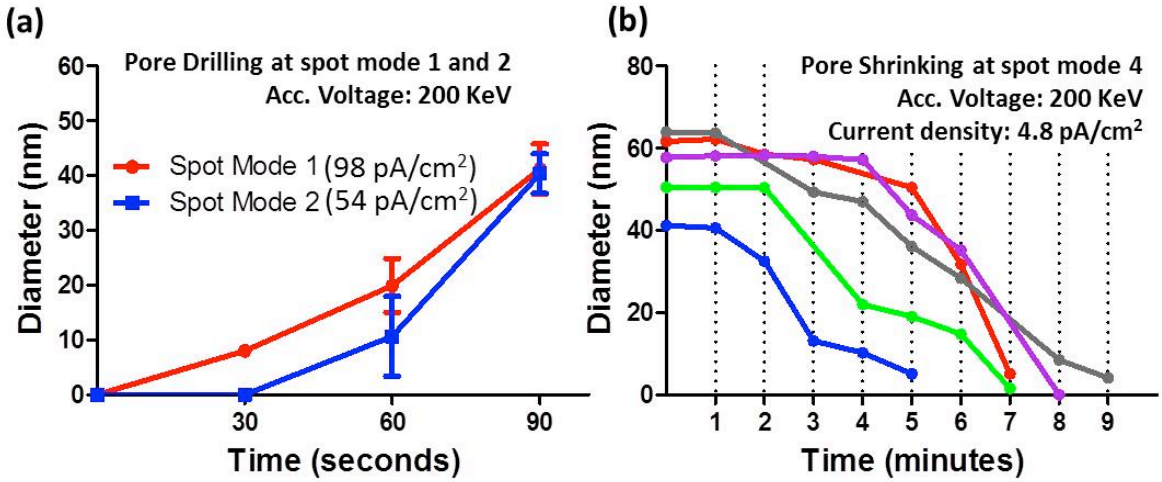

Figure 2. Nanopore drilling (a) and shrinking (b) kinetics. Pores were drilled using converged beam at spot modes 1 and 2 and shrinking was achieved using spot mode 4. For pore shrinking, each line graph represents one pore. An initial lag of 1-2 minutes was typically observed before 40-60 nm pores started shrinking. Current densities reported were recorded at the phosphor screen of the TEM.

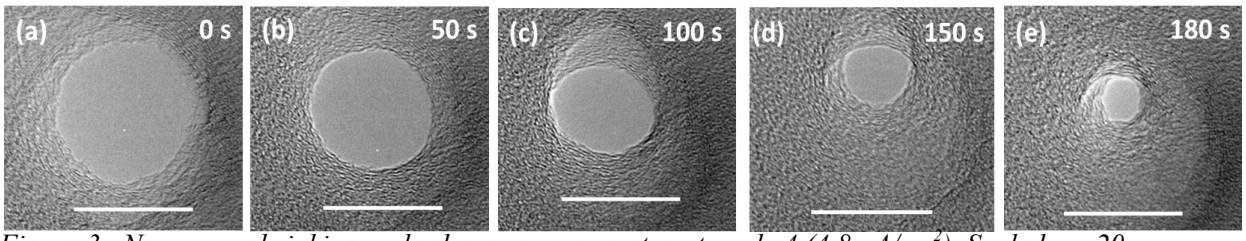

Figure 3. Nanopore shrinking under beam exposure at spot mode 4 (4.8 pA/cm^2). Scale bar: 20 nm.

CONCLUSION

Using our method, 40-60 nm pores can be shrunk to 2 nm within 5-8 minutes as compared to much longer in-situ annealing time reported for multilayer graphene. Our method also allows for visual feedback, resulting in precise control over nanopore diameter. Moreover, very small (20 nm) beam spread at spot mode 5 allows for surgical shrinking/ healing without affecting other areas of the membrane. Control over graphene nanopore size would lead to more effective nanopore sensors and advance the efforts towards nanopore based DNA sequencing.

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