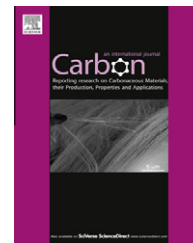


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In situ studies on the shrinkage and expansion of graphene nanopores under electron beam irradiation at temperatures in the range of 400–1200 °C

Ning Lu ^a, Jinguo Wang ^a, Herman C. Floresca ^a, Moon J. Kim ^{a,b,*}

^a Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, TX 75080, USA

^b Department of Nanobio Materials and Electronics, World Class University, Gwangju Institute of Science and Technology, Gwangju 500-712, Republic of Korea

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ABSTRACT

We report in situ studies on the shrinkage and expansion of graphene nanopores under electron beam irradiation at temperatures of 400–1200 °C using a thermal specimen holder in a transmission electron microscope. The shrinkage of nanopores of various sizes is observed. At all temperatures studied in the present work, nanopores with relatively small diameters could be fully closed. And at the low end of our temperature range, 400 °C, larger nanopores (those with a diameter of 10 nm) could also be closed completely. The nanopore shrinking process can be stopped by blocking the electron beam. We demonstrate an approach for tailoring the size of the graphene nanopore through a combination of electron beam irradiation and controlled heat.

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1. Introduction

Nanopores have recently attracted great interest as a powerful new technique for detecting single molecules [1–3]. When molecules are driven through a nanopore in an electrolyte, a characteristic pore conductance signal is generated. Nanopores are usually created in thin Si₃N₄ [4,5], SiO₂ [6], or Al₂O₃ [7] membranes by ion or electron beam sculpting. However, these membranes are too thick to explore the fine structure of a molecule [8]. Therefore, for sequencing single DNA molecules, a sub-nanometer membrane is needed.

Graphene, which has a single atomic layer of carbon atoms bonded in a hexagonal lattice, is among the few materials that are stable in two dimensions and free-standing when suspended [9]. It also exhibits extraordinary mechanical [10,11] and electronic properties [12]. Over the past 2 years, researchers have attempted to use nanopores in graphene for ultrarapid sequencing of single DNA molecules [13–15].

Nanopores were drilled through suspended graphene sheets by a focused electron beam (e-beam) in a transmission electron microscope (TEM) [16]. A 200 or 300 keV electron beam was employed for sculpting at room temperature, however, and that was higher than the 140 keV knock-on voltage for carbon atoms in graphene [17], damage was easily induced into the graphene around the nanopores. The damage yielded undesirable amorphization of the crystalline lattice as well as carbon deposition on the surface, which might alter the electronic properties of the graphene device. Recently, high temperature annealing above 600 °C has been reported to keep graphene in a crystalline state even under electron beam sculpting at 300 kV [18]. Moreover, there is a great demand for the ability to control the size of nanopores, so that investigators can explore a variety of complex biologic systems [19]. Normally the minimum pore diameter drilled by a focused electron beam tends to be 2–5 nm [13–16]. It is well known that nanopores can be enlarged by continuous beam

* Corresponding author at: Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, TX 75080, USA. Fax: +1 972 8835725.

E-mail address: moonkim@utdallas.edu (M.J. Kim).
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exposure. However, there have been no reports of shrinking the graphene nanopore. Here, we report *in situ* TEM studies on both the shrinkage and expansion of graphene nanopores under electron beam irradiation at temperatures in the range of 400–1200 °C.

2. Experimental

A JEOL 2100F transmission electron microscope operated at 200 kV with a current density of 0.3 and 5.1 pA/nm² is used for imaging and sculpting in the present work. To *in situ* heat the graphene, we use a MEMS-based localized heating specimen holder (by Protochips). The holder allows the specimen to be heated up to 1200 °C within milliseconds. The graphene samples are prepared by manually grinding small highly ordered pyrolytic graphite blocks into fine powder and dispersing the powder onto the membrane. The range of the sample thickness is roughly 3–10 graphene layers.

3. Results and discussion

Fig. 1 shows the shrinkage of two nanopores with different sizes in a graphene sheet at 400 °C. In Fig. 1a, a nanopore of about 2.3 nm in diameter is drilled by condensed electron beam for about 5 s. The graphene remains relatively intact although amorphization occurs near the edges of the nanopore. Interestingly, under continuous irradiation by a 0.3 pA/nm² beam at 400 °C, the nanopore shrinks. After about 3 min, the diameter of the nanopore decreases to ~1.2 nm (Fig. 1b). After another 3 min, the nanopore closes completely (Fig. 1c). It can clearly be seen that the refilled area has very poor crystallinity. Fig. 1d shows a larger size nanopore, about 9 nm in diameter. Because of the longer e-beam irradiation required to drill the larger hole, more amorphization is

observed compared with Fig. 1a. Under the same *in situ* heating experimental conditions as the smaller nanopore in Fig. 1a and c the larger size nanopore also tends to be shrunk with new graphene layers. Fig. 1e is acquired after 9 min. The pore is finally filled up through entire 22.5 min, as shown in Fig. 1f. More interestingly, the shrinkage of the graphene nanopore at 400 °C can be terminated at any time by blocking the electron beam, and therefore the size of a shrinking nanopore with diameter ≤ 10 nm is controllable at 400 °C. It has to be noticed that the structure of the edge of the partly closed nanopore is different from that of a hole directly drilled in a single crystalline graphene sheet.

At temperatures above 600 °C, graphene is observed to be in a crystalline state under 200 kV electron beam irradiation, which is consistent with the results of Song et al. [18]. It has been reported that even nanopores with atomic size tend to expand under 80 kV e-beam irradiation [20]. We did observe the expansion of nanopores under e-beam irradiation at 800 °C, but only among those nanopores with diameters larger than 3 nm. On the other hand, we observed the shrinkage of the nanopores with diameters smaller than 2.5 nm under e-beam irradiation at 800 °C.

Fig. 2a and c shows the shrinkage of a ~1.6-nm-diameter nanopore in a graphene sheet under e-beam irradiation at 800 °C. It takes ~3 min before the nanopore is filled with crystalline graphene layers. Fig. 2d–f presents a ~5-nm-diameter nanopore being enlarged at 800 °C under continuous e-beam exposure. The expansion of any size nanopore is a common phenomenon of suspended graphene sheets in TEM observation, even at room temperature [16]. Fig. 2e and f are taken after 4 and 10 min, respectively.

At 1200 °C, nanopores exhibit similar shrinkage (of smaller size pore) and expansion (of larger size pore) behaviors as the ones at 800 °C, but at a faster rate. As shown in Fig. 3a

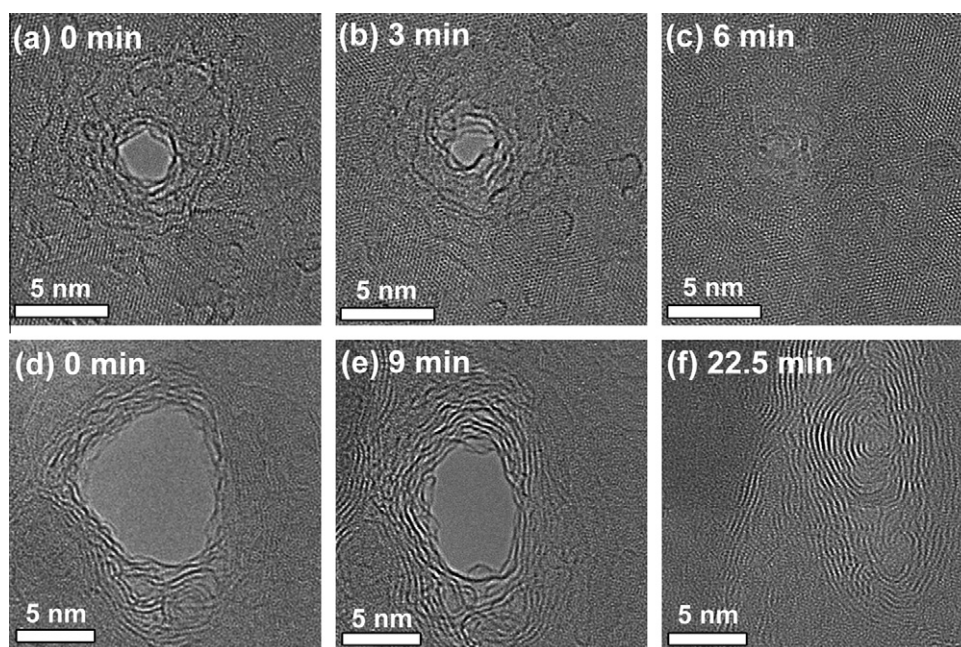


Fig. 1 – Shrinkage of nanopores in a graphene sheet at 400 °C. Sequential TEM images of nanopores with initial diameter of ~2.3 nm (a–c) and ~9 nm (d–f).

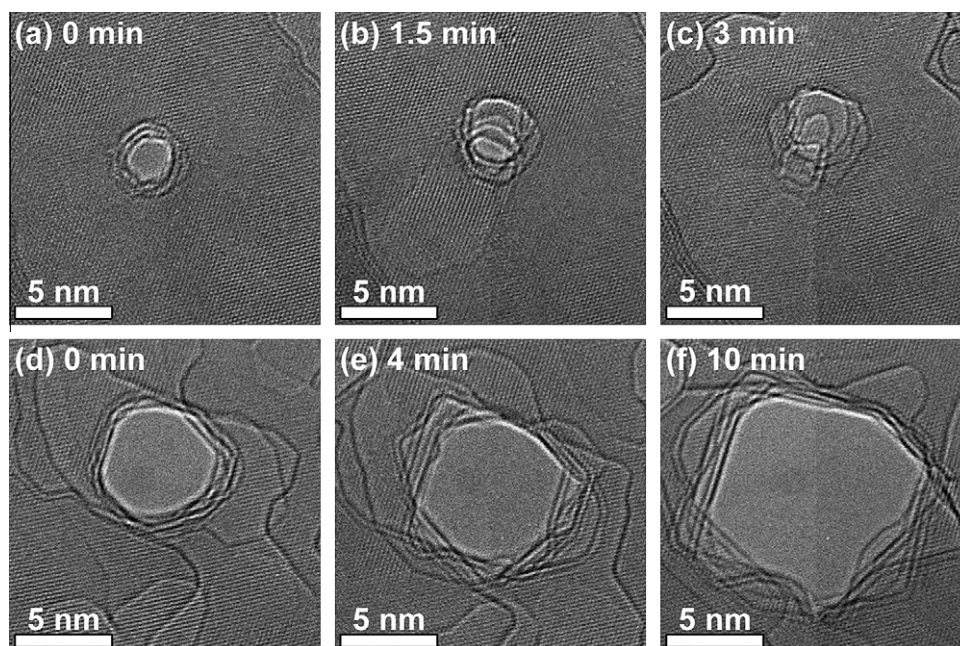


Fig. 2 – (a–c) Shrinkage of a ~ 1.6 -nm-diameter nanopore, and (d–f) enlargement of a ~ 5 -nm-diameter nanopore in a graphene sheet at $800\text{ }^{\circ}\text{C}$.

nanopore with ~ 3.3 -nm-diameter is drilled by e-beam at $1200\text{ }^{\circ}\text{C}$, indicated by a circle. The nanopore is on a monolayer graphene within a larger terrace-like hole created by removing several other layers. At $1200\text{ }^{\circ}\text{C}$, we find that a monolayer graphene sheet can be produced by removing excess graphite layer by layer under e-beam irradiation. This procedure is much easier to perform at $1200\text{ }^{\circ}\text{C}$ than at lower temperatures. In addition, some of the monolayer graphene edges reconstruct into wrapped species at high temperature, which

agrees with the report of Huang et al. [21]. After 1 min, the diameter of the nanopore decreases to ~ 2 nm (Fig. 3b). Over a span of ~ 1.5 min, the monolayer graphene is completely self-repaired with the filling of the crystalline graphene layer (Fig. 3c). It is valuable to notice that the larger terrace-like hole is expanding during the shrinkage of the nanopore on the monolayer graphene. In this case, it is reasonable to conclude that the carbon atoms knocked out from other multilayers are displaced to the monolayer as ad-atoms for the healing of the

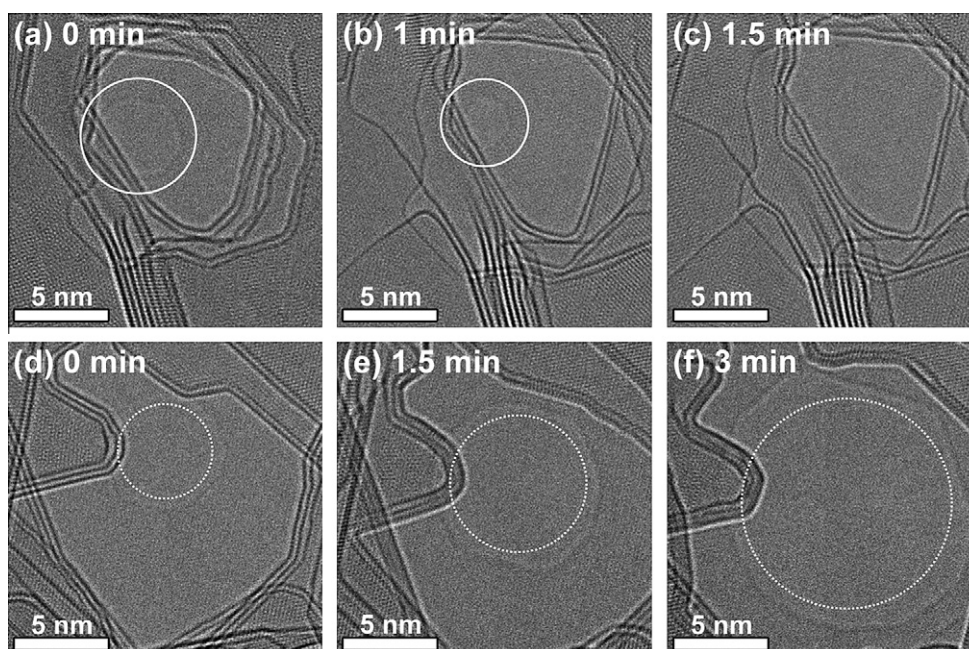


Fig. 3 – (a–c) Shrinkage of a ~ 3.3 -nm-diameter nanopore, indicated by circles, and (d–f) enlargement of a ~ 6 -nm-diameter nanopore in a graphene sheet at $1200\text{ }^{\circ}\text{C}$.

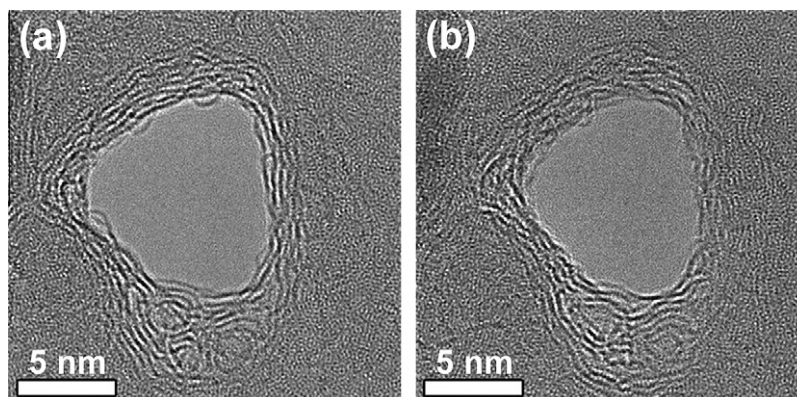


Fig. 4 – TEM images of a nanopore (a) before and (b) after annealing 6 min at 400 °C without irradiation.

nanopore [22]. Fig. 3d shows a ~ 6 -nm-diameter nanopore (indicated by a dotted circle) that was drilled under e-beam irradiation at 1200 °C. Under e-beam exposure and *in situ* heating at 1200 °C, images were acquired at 1.5 and 3 min, shown in Fig. 3e and f, respectively. After 3 min, the nanopore has rapidly expanded to ~ 13.5 nm.

An electron beam usually has two effects on a graphene nanopore: the sputtering of carbon atoms along the edge and the generation of carbon ad-atoms around the nanopore. Fig. 4a shows a shrinking nanopore at 400 °C. After blocking the e-beam, the nanopore is annealed for 6 min at 400 °C. Though the edges are reconstructed by annealing, the shrinkage of the nanopore is stopped, as shown in Fig. 4b. When e-beam irradiation is renewed, the shrinkage of the nanopore continues. This phenomenon is also observed at 800 °C and 1200 °C. Clearly carbon ad-atoms are needed to fill the nanopore. Without e-beam irradiation, the shrinkage of the nanopore is stopped. We conclude that the carbon ad-atoms originate mainly from the knock-out atoms in the area exposed to the e-beam. On the other hand, it is well known that the beam sputtering of the edge atoms along a nanopore results in the expansion of the nanopore. These two processes (sputtering of carbon atoms along the edge and generation of carbon ad-atoms around the nanopore), both caused by e-beam irradiation, are competing with each other. High temperature accelerates the diffusion of the ad-atoms over the surface of graphene [23]. However, with the increase of temperature, the ad-atoms tend to be desorbed from graphene [24]. At high temperature, the carbon environment around the nanopore plays another important role. Less carbon supply and longer migration distance, such as the situation in Fig. 3d, the desorption of the ad-atoms prevails, and hence, the nanopore expands under irradiation. The rearrangement of carbon atoms at the edge of nanopores also occurs under e-beam irradiation [25]. At 400 °C, because the process of generating carbon ad-atoms is more pronounced, larger nanopore (about 10 nm) are shrinkable, at 1200 °C, since the desorbing of the carbon ad-atoms is more effective, smaller nanopores (about 3 nm) are expandable. Therefore, the size of a nanopore can be controlled by the input and output processes of carbon atoms to the edge of holes through a combination of e-beam irradiation and controlled heat.

4. Conclusion

In summary, we report *in situ* TEM studies on the shrinkage and expansion of graphene nanopores under electron beam irradiation at temperatures in the range of 400–1200 °C. The shrinkage of nanopores of various sizes is observed at temperatures of 400–1200 °C. Nanopores with smaller diameters can be fully closed at all temperatures studied in the present work. Especially at the lowest temperature studied (400 °C), nanopores with a relatively large diameter (~ 10 nm) also tended to close completely. The nanopore shrinking process can be stopped by blocking the electron beam. Our results thus provide an approach for tailoring the size of graphene nanopores through a combination of electron beam irradiation and controlled heat.

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