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Thermal induced single grain boundary break junction for suspended nanogap electrodes

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Construction of molecular devices is one of the most promising approaches for the ultimate miniaturization of electronic devices, the groundwork of which is the fabrication of nanogap electrodes. Here we report a method to fabricate nanogap electrodes through thermal annealing based on single grain boundary junction. By performing low temperature thermal process, single grain boundary junction can be broken and change into a suspended gap with gap width down to sub-5 nanometers, which is beyond the fabrication precision of traditional lithography technologies. With the advantage of shape stability, no debris and high time efficiency, such nanogap electrodes is promising in constructing molecular devices with two or three-terminals.

Nanogap electrodes play an important role in the field of molecular electronics. It can be used not only for the exploration of fundamental electronic, optical, mechanical properties of newly designed and synthesized single molecules but also for constructing single molecular devices, which is among the most promising approaches to continue the trends in the miniaturization of electronic devices. Compared to top-contact junctions using scanning probe microscopy (such as scanning tunneling microscopy (STM) and conducting atomic force microscopy (AFM)) or nanopores [1], nanogap electrodes based molecular devices in planar configuration are more likely to be used in practical applications to construct fully functional circuit [2]. Since molecular devices have shown properties identical or analogous to key components of today's microcircuits such as diodes [3], transistors [4–5], and conductors [6–7], it is of great significance to develop a reliable way to construct single molecule devices which are compatible with the existing integrated circuit (IC) technologies, the precondition of which is the fabrication of nanogap electrodes.

Since the fabrication of nanogap electrodes are beyond the capability of lithography based traditional microfabrication technologies, various approaches are developed to overcome this limit. Until now, several methods for nanogap electrodes are well developed including mechanically break junction [8–10], electromigrated break junctions [11], electrochemical plating [12–15], transmission electron beam (TEM) lithography [15–17], selective etching [18,19] combinations of different methods [20–22] and so on [23–25]. In addition, carbon based materials were also been explored in the application of electrodes and great progress has been made [26–32]. Crucial progress has been made in the field of molecular electronics [4,5,25,33]. Despite unique advantages of each method, the existing drawbacks (such as shape instability, debris, multiple devices cannot be made on one chip, incompatibility with the existing IC technology etc.) [34–39], make barriers for the rapid progress of molecular devices, thus a new method is needed. Recently a new approach is developed to fabricate nanogap electrodes by focused ion beam (FIB) milling based on single grain boundary (GB) junction [39]. The idea of utilizing GB related effect is very creative, yet the usage of FIB to break the single GB junction is of several disadvantages such as the difficulty in precise controlling of the ion dose, high cost of FIB equipment, the low time efficiency of the serial fabrication style, etc. Thus new approach free of these drawbacks to break single GB junction is needed.

Thermal process is always used on polycrystalline thin films for stress relief, structural improving, surface roughness control, and some other purposes [40]. Here we show that the thermal process can be used for the fabrication of nanogap electrodes. The proposed fabrication strategy is illustrated in Fig. 1. Two key steps are involved in the fabrication of the nanogap electrodes: the fabrication of single GB junction and junction break by thermal process.

Similar with the previous study that used electron beam lithography (EBL), reactive ion etching (RIE), and buffer oxide etcher (BOE) to pattern 80 nm Au film on SiO_2

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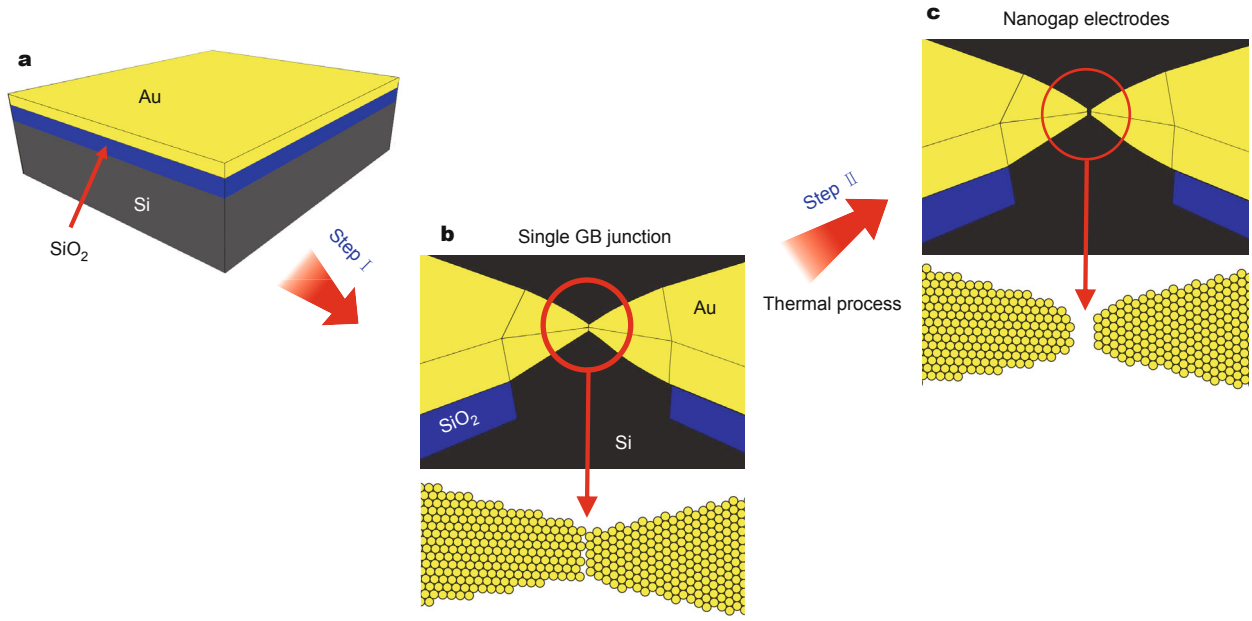

Figure 1 Illustration diagram of the proposed strategy of nanogap electrodes fabrication. Two key steps are involved: (I) the fabrication of single GB junction and (II) the break of single GB junction via thermal process induced intergranular fracture.

(300 nm)/Si substrate into bridge-shaped structures, the suspended bridge part of the structure was milled by Gallium (Ga) FIB into single GB junction. Thermal process was then used to break the single GB junction, which was carried out on a hot plate in air (temperature of the hot plate was fixed, then the sample was put on it for a period of time and removed, cooling naturally in air). The feature size of the obtained nanogap electrode was characterized by scanning electron microscopy (SEM) after the sample was cooled to room temperature.

The configuration of the fabricated suspended single GB junction of Au on SiO_2/Si substrate is illustrated in Fig. 1b. Nanogap electrodes (Fig. 1c) fabricated from this configuration could be used directly to construct molecular devices with two or three terminals such as single molecule transistors with substrate as gate electrodes. For single GB junctions in this configuration as shown in Figs 2a-1 and b-1, after a thermal process of 90°C for 30 s, nanogaps appeared along the original GB with gap width down to 3.6 and 3.8 nm as shown in Figs 2a-2 and b-2, which proves that thermal process indeed can be used to break GB junction to fabricate nanogap electrodes. In order to check the influence of thermal process parameters on the gap width, a subsequent thermal process of 100°C for 30 s was carried out on the same sample, and the result is shown in Figs 2a-3 and b-3. The gap widths are changed from 3.6 and 3.8 nm into 4.0 and 3.8 nm for the two samples respectively. It should be noted that the parameters of the thermal process (namely temperature and time) used to break the GB can be greatly influenced by the cleanliness of the sample.

Thermal grooving phenomenon is one of those thermal induced effects on polycrystalline film. Grooves along grain boundaries where it intersects with the surface will appear under high temperature, which rely on preferential transfer of matter away from grain boundaries during heating [41–43]. Studies on the profile of the grooves have shown that thermal groove possesses a cross section shape similar to triangle or trapezoid [44,45]. However, the cross section of the fabricated nanogap electrodes does not show a triangular or trapezoidal shape; instead relatively parallel end surfaces of the two electrodes are resulted. Therefore thermal grooving is not the predominant mechanism of thermal induced break of single GB junction.

GB is the interface between two grains, regions of atomic mismatch and less dense atomic packing. With atomic vacancies along the GB, atomic diffusion can happen more easily along GBs, which can be proved by the phenomenon of the preferential removal of the materials near the grain boundaries during thermal and chemical etching processes [46]. During the fabrication process of single GB junction, the diffusion of Ga can happen along the GB under Ga^+ FIB irradiation. Similar phenomenon was reported that liquid Ga penetration can happen along GBs on metal polycrystals [47,48]. Such Ga distribution along the GBs could re-

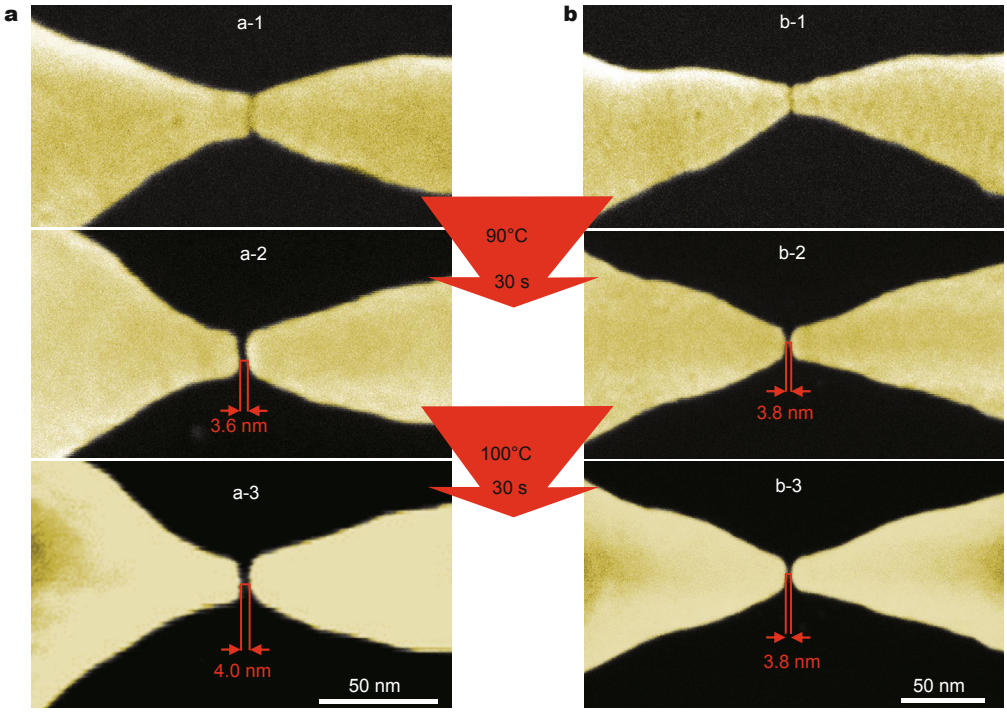

Figure 2 Nanogap electrodes fabrication with single GB junction by thermal process. SEM images of two single GB junctions (a-1 and b-1), the same sample after a thermal process of 90°C for 30 s (a-2 and b-2), and a subsequent thermal process of 100°C for 30 s (a-3 and b-3).

sult in decohesion between grains, which will cause intergranular fracture at high temperature. Considering that the GBs in nano-grained metals are relatively unstable due to the excess free energy [46], the break of the junction is attributed to thermal induced stress relief process [40].

For small-volume metals with large surface such as nanogap electrodes, surface energy induced atomic migration is expected to cause shape change, which is one of the drawbacks of several nanogap fabrication methods [34–38,49]. Hence it is essential to do the stability test before its application. Au films with GBs almost perpendicular to the substrate plane are always formed to minimize the total energy of the system [50], and the interface between GBs always possesses relatively flat interfaces which are perpendicular to the substrate. For single GB junctions with a relatively large cross section area, the resulted nanogap electrodes will be of relatively large flat surface. Since the shape change is caused by the big surface energy of the tip with big curvature, the fabricated nanogap electrodes with a relatively large flat surface is expected to be stable. Still such assumption needs to be proved by stability test, and one of the single GB junctions is selected as shown in Fig. 3a-1. The selection criterion is that if a single GB junction with small junction area is stable, then the stability of a bigger one is unquestionable. Fig. 3a-1 displays the SEM image of a single GB junction with a relatively small junction area, the dimension of which is a few nanometers. After thermal process the junction is broken and nanogap electrodes are fabricated as shown in Fig. 3a-2. In comparison with the SEM images of the single GB junction, the nanogap electrodes show a much smoother surface with round tips, which means atomic migration takes place during the thermal process. Such surface reorganization of metal atoms always happens during low temperature thermal process under the driving force of minimizing the Gibbs free energy [40], which is beneficial for the stability of the structures. SEM image of the nanogap electrodes after being kept in ambient condition for 6 days is shown in Fig. 3a-3. And no obvious change in the gap width can be observed, showing that the nanogap electrodes fabricated through the break of the single GB junction by thermal process are of great stability.

In order to show the capability of the method in the fabrication of nanogap with gap width down to nanometer scale, transmission electron microscopy (TEM) was used to characterize the feature of the nanogap electrodes which are beyond the resolution of SEM. Similar procedure with our previous report was adopted on the preparation of the single GB junction suitable for TEM characterization. A simplified preparation process is illustrated in Fig. 3b, in

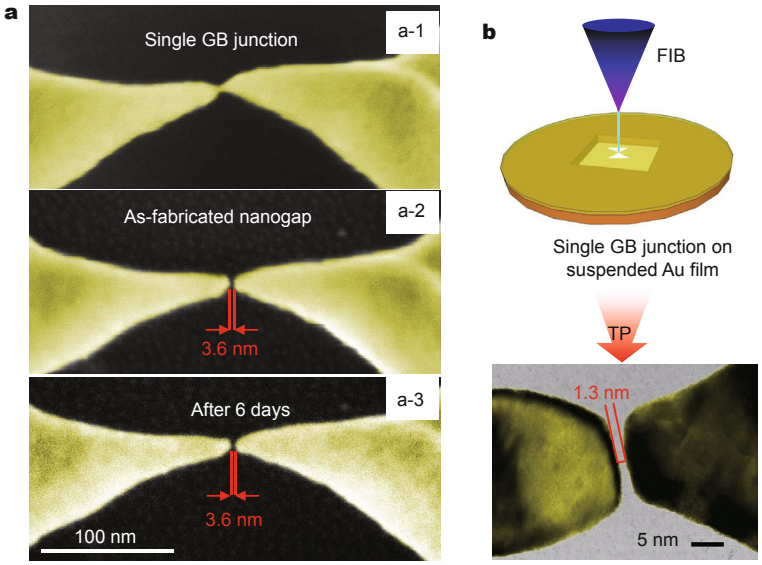

Figure 3 (a) Stability test results: a-1, SEM image of the as fabricated single GB junction; a-2, SEM image of the same sample after a thermal process, indicating the formation of nanogap electrodes after thermal process; a-3, SEM image of the same sample after being kept in ambient condition for 6 days, which does not show any observable change in size. The SEM images were taken with 45° sample tilt. (b) TEM characterization of the nanogap fabricated through thermal induced intergranular fracture: simplified fabrication process and the TEM image of the obtained nanogap with a gap width of 1.3 nm. TP stands for thermol process.

which FIB is used for the fabrication of single GB junctions on suspended Au film on a TEM mesh. As shown in Fig. 3b, nanogap electrode with gap width down to 1.3 nm is obtained by breaking the single GB junction through thermal process, demonstrating the capability of such method in the fabrication of nanogap electrode. A relatively flat surface of the electrodes is also demonstrated.

Under the inspiration of various GB related effects, we have demonstrated the application of thermal induced intergranular fracture for the fabrication of nanogap electrodes. Besides the advantages of no debris in the gap, great stability, and the ability to construct devices with two and three terminals, thermal induced intergranular fracture for nanogap fabrication shows superiorities over the previous methods of using FIB for the break of single GB junction in several aspects. First, the time and cost is greatly reduced since a lot of single GB junctions can be break at the same time through a simple thermal process. Second, thermal induced atomic migration is beneficial for the morphologies and stability of such structures, which is of great significance in the application of such nanogap electrodes. Third, the ion beam induced defect on the surface of the electrodes namely compositional and microstructural changes is greatly reduced not only because the non-ions pollution nature of the thermal process, but also the structure improvement during the thermal process.

In conclusion, combining the technology of single GB junction fabrication and thermal induced intergranular fracture phenomenon, a nanogap fabrication strategy is proposed and demonstrated. The mechanism behind the thermal induced intergranular fracture can be contributed to Ga penetration along the GB induced decohesion and thermal induced stress relief. Thermal induced atomic migration plays an important role in defects repairmen, morphology improvement and the stability of the fabricated nanogap electrodes. Free of debris in the gap, and with nanometers gap width, great stability, and relatively low cost of time and money, such nanogap electrodes show a great potential in molecular electronic field and could be used to explore not only the properties of molecules but also new materials in nano scale such as organic-inorganic halide perovskite [51].

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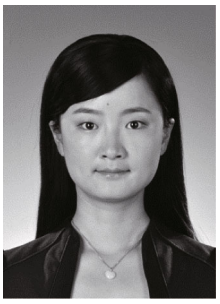
Author contributions Hu W and Cui A designed the project and the experiments; Cui A, Liu Z, and Wang Y performed the experiments; Cui A wrote the paper with the support from Hu W. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.



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中文摘要 纳米尺度分子器件是最有可能实现超高密度集成电路的途径之一, 而纳米间隙电极对的制备是分子器件的构筑基础. 本文利用热处理诱导晶间断裂现象来进行纳米间隙电极对的构筑. 通过低温热处理过程实现单个金晶界结的断裂, 使其从晶界结转化为悬空纳米间隙电极对. 所制备的纳米间隙电极对的间隙尺寸可达到亚5纳米, 采用传统的微纳米加工方法很难实现该尺寸间隙电极对. 利用热处理诱导晶间断裂所制备的纳米间隙电极对具有诸多优点, 如形状稳定性好、间隙中无杂质颗粒残留等, 有望用来构筑两端或三端分子器件.