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Controllable nanogap fabrication on microchip by chronopotentiometry

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Abstract

This work aims to solve one of the key issues for developing molecular and nanoscale devices, i.e., how to controllably fabricate nano/angstrom-size gaps on microchips. It has been shown that with a galvanostat and use of the electrode potential as the feedback, we can be used to electrochemically fabricate metallic electrode pair with controlled gap widths ranging from about ten nanometers down to few angstroms. It is based on probing the potential drop in the electrical double layer across the two electrodes during the narrowing of the gap. The process is simple and controllable, allowing rapid fabrication of nanogaps and adaptation of a commonly used electrochemical instrument.

Keywords: Nanogap fabrication; Electrodeposition; Nanodevices; Chronopotentiometry; Electrical double layer

1. Introduction

Molecular devices and nanodevices have attracted increasing attention because of their important potentials in miniaturization of electronic devices [1–11]. A critical challenge in this field is to connect molecules or nanocrystals to the outside world. A practical way is to fabricate a pair of facing electrodes with a controllable nanogap width on a microchip so that it can meet the specific need to fit with target molecules or nanocrystals whose electron transport properties can be characterized in detail [6–11]. Several methods have been developed along the avenue of pair electrode fabrication [11–24]. One method named as "break junction" is based on a mechanical bending the chip so as to break an ultra-thin metal wire into two electrodes at a certain gap width [11,12]. This gap width can be flexibly and precisely adjusted by mechanical controlling of the camber in order to fit different molecules. However, the involvement of mechanical forces in the fabrication procedure seems unlikely to be promising for use with microchips and nanodevices. Electromigration is another approach, which is realized by passing a large electrical current through an ultrathin metal nanowire. Due to the electromigration of metal atoms, the nanowire is eventually broken to generate a gap [13–15]. The gap width is typically 1 nm depending on the passing current. This method is difficult to flexibly fabricate nanogaps with different width in order to fit target nanocrystals around 1–10 nm scale. Furthermore, both the two methods seem to have limitations to be widely applicable techniques. The precondition for carrying out such an experiment is that the metal nanowire to be broken on the chip should be very thin, typically around 20 nm. Those ultrathin wires can only be obtained by a very expensive e-beam lithography, but not the conventional optical lithography.

Among the techniques developed for this purpose, electrochemical methods involving, e.g., electrodeposition or electrodissolution, is more versatile and can overcome, at least partially, the above-mentioned limitations. By electrodepositing metal atoms into a specific face of electrodes, the gap between two facing electrodes can be sequentially narrowed from the original micrometer scale down to the domain of

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a few angstroms, and eventually the two electrodes connect to form an quantum contact [16–23]. The electrochemical process can be reversed in electrodissolution mode for controlled etching of metal atoms from a wire, thus a gap can be widened from angstrom up to sub-micrometer scales. The most distinctive feature of the electrochemical method is the use of a feedback system to precisely control the resultant gap width [16–23]. Several experimental parameters, such as electrochemical current and electrolyte conductance, have been used as the feedback indicator to critically monitor the gap width, especially when the gap is narrowed down below sub-micrometer scale. For example, Morpurgo and coworkers used the electrolyte conductance between the two working electrodes as the feedback parameter to fabricate pairs of platinum electrodes [19,20]. The electrodeposition process was stopped by switching off the potentiostat when the conductance reached a preset value. It provides an accurate and reproducible way to control the gap width between 3 and 20 nm [19–23].

Recently, Tao and coworkers have developed a new method to fabricate a molecular-size gap by using the tunneling current as feedback to precisely monitor electrochemical deposition/etching [17,18]. When the gap is narrowed down below 1 nm, the tunneling current tends to change in a stepwise fashion, corresponding to a discrete change of gap width. By presetting the tunneling current to one of the stepwise values, they make it possible to fabricate gaps with subangstrom precision. This method affords a great advantage in achieving a suitable gap fitting different molecules. This is an important precondition for fabricating molecular devices and sensors with extremely high molecular selectivity [24]. However, every method has its strength and limitation. This very promising method seems to have two intractable limitations in terms flexibility for application. The first one is the gap width range. As the working principle is based on the detection and feedback of tunneling current, it is more suitable for making a small gap below 1 nm when the tunneling current is sufficiently high. The second limitation is to the use of a relatively sophisticated instrument. Since the two facing electrodes to form gap are both used as the working electrode, the four-electrode bipotentiostat should be used and its necessary function of tunneling current feedback is not commercially available, which may restrict more laboratories to adapt this method. It is therefore necessary to design a new electrode configuration and, in particular, the new operation mode for further developing the electrochemical method.

Recently we reported a short communication on the new electrochemical method by utilizing the potential, instead of current or conductance, as the feedback indicator to control the fabrication process of the nanogap [25]. Here we report the work in more details, especially the concentration influence of the electroplating solution. With the present method, one can controllably fabricate nanogaps on microchips with widths ranging from several angstroms up to several nanometers.

2. Experimental

The pair of facing Au electrodes were fabricated by a conventional optical lithograph technique on an n-type Si wafer of ⟨1 1 1⟩ orientation covered with 2 μm thermally oxidized silicon layer. Au/Ti (300/30 nm thickness) was used for the electrode material. The initial electrode separation was typically 2 μm. Then the electrodes were coated with SiO_2 or Si_3N_4 insulation layer except a small portion of the facing electrodes (see Fig. 1). In our design, two gold electrode fingers serve as the working electrode (WE) and reference electrode (RE), respectively. A gold rod (ca. 1 mm in diameter) was immersed the solution as a counter electrode (CE) (see Fig. 1(b)).

The electrochemical fabrication was realized by using a CHI631A electrochemical workstation (CHI Co., USA). The electroplating solution was $KAu(CN)_2$ with $K_3C_6H_5O_7$ and KH_2PO_4 as supporting electrolytes. All solutions were prepared with analytic reagents and Milli-Q water.

The fabricated nanogap was characterized by using LEO1530 scanning electron microscope (LEO Co., Germany). To measure the gap width smaller than 1 nm, beyond the resolution of SEM, the current–voltage (*I*–*V*) characterization was performed at room temperature by a two-point probe method using a Keithley 4200 semiconductor characterization system.

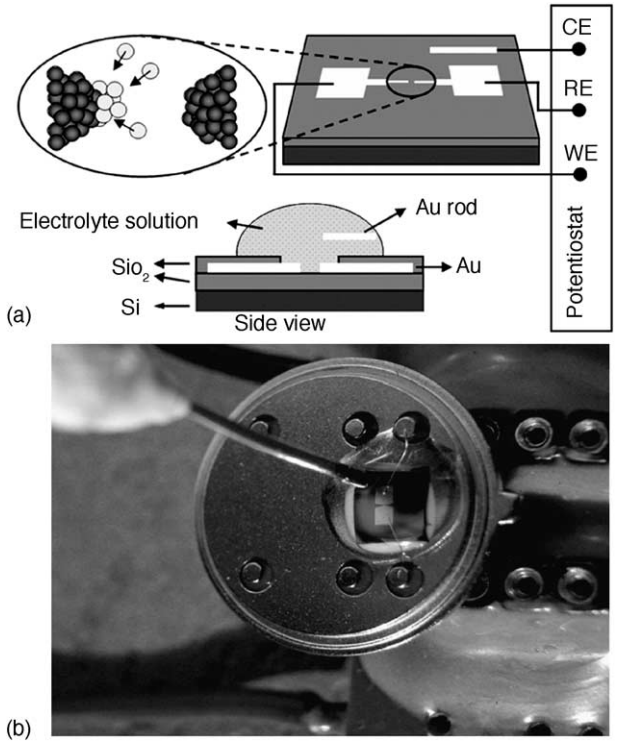

Fig. 1. (a) Schematic drawing of the experimental setup. (b) A photo of top view of the experimental setup.