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Controllable nanogap fabrication on microchip by chronopotentiometry

Bo Liu [a], Juan Xiang [a], Jing-Hua Tian, Can Zhong [b], Bing-Wei Mao [a],
Fang-Zu Yang [a], Zhao-Bin Chen [a], Sun-Tao Wu [b], Zhong-Qun Tian [a,*]

[a] *State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen 361005, China*
[b] *Pen-Tung Sah Micro-Electro-Mechanical Systems Research Center, Xiamen University, Xiamen 361005, China*

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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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[*] Corresponding author. Tel.: +86 592 2186979; fax: +86 592 2085439.
E-mail address: zqtian@xmu.edu.cn (Z.-Q. Tian).

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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 sub-angstrom 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.

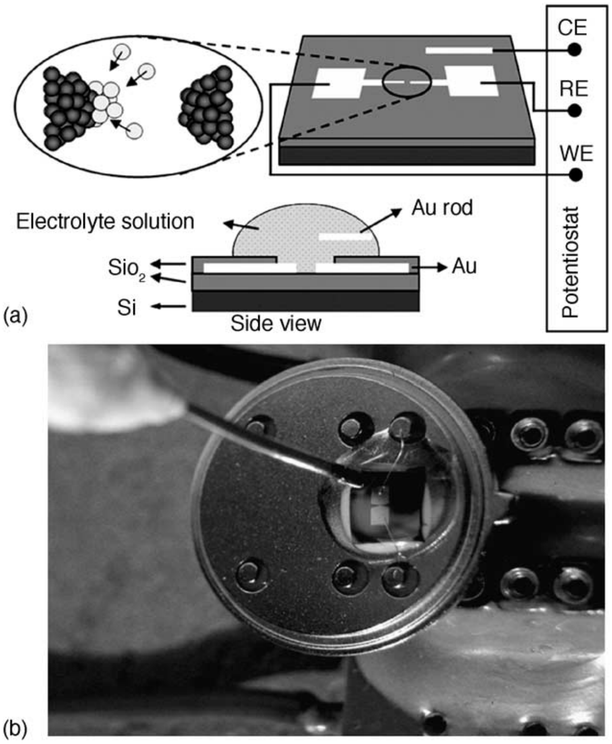

Fig. 1. (a) Schematic drawing of the experimental setup. (b) A photo of top view of the experimental setup.

3. Results and discussion

3.1. Measurement of chronopotentiometric curve

The present approach used a hitherto untried electrode configuration and potential feedback system as seen in Fig. 1). In our design, the pair of facing electrodes serves as the working electrode (WE) and reference electrode (RE), respectively. This configuration differs from the previous approaches using two faced electrodes both as WEs for the conductance feedback mode and tunneling current feedback mode [17–23]. Based on this new electrode arrangement, galvanostatic experiments were carried out by applying a controlled current (see Fig. 1). Metal atoms were deposited layer by layer on the WE face to reduce the gap between WE ad RE (as shown in Fig. 2). The electroplating solution we used in most experiments was 15 mM $KAu(CN)_2$ with 0.3 M $K_3C_6H_5O_7$ and 0.3 M KH_2PO_4 as supporting electrolytes. It should be pointed out that it is essential to choose the suitable constant current (I_{dep}) to ensure the deposited layers to be smooth and compact rather than rough or loose. After a systematic study, it has been found that the depositing current (I_{dep}) of about 0.1 mA cm^{-2} make the coating more uniform (as shown in Fig. 2). Because the original gap fabricated by the optical lithography is quite large, the whole deposition time could take about one hour. To expedite the whole process, one could use a relatively higher current density for 5–10 min in the first stage and then a reduced density of 0.1 mA cm^{-2} in the final important stage. Since the exposed area of the finger electrode of each microchip is not identical, it could be better to calibrate the true electrode area by performing cyclic voltammetry in a solution of 0.5 M H_2SO_4 and measuring the peak area corresponding to the reduction of gold surface oxide layer.

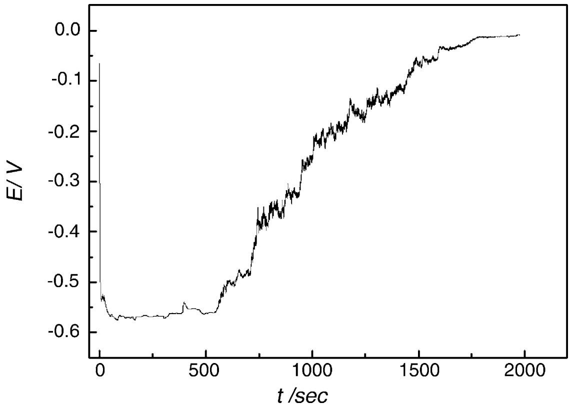

Fig. 3. Chronopotentiometric curve plotted during the electrodeposittion process.

After the surface area calibration, we started the galvanostic depositionat 0.1 mA cm^{-2} and monitor the potential difference between WE and RE (V_{gap}) continuously along the time during the whole electrodeposition process. Fig. 3 shows the chronopotentiometric curve, where the monitored V_{gap} was first at about −0.55 V and kept constant at about 500 s. After that V_{gap} was then gradually reduced irregularly along the time elapses, and finally approached to zero, indicating that WE and RE electrodes were connected. Although the chronopotentiometric curve might be slightly different for different chip, they are quite similar to each other. It infers that when the gap was narrowed below a certain value, the changes of V_{gap} most probably correlated to the change of the gap width. Therefore, it could provide a guide for a presetting V_{gap} value, whereat the termination of the electrodeposition process produces a desired gap width.

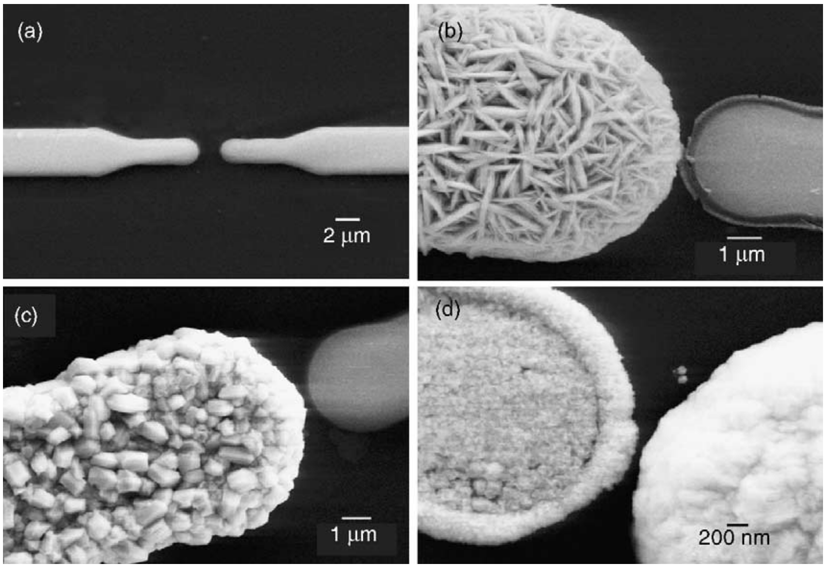

Fig. 2. SEM images of two faced gold finger electrodes. (a) The original electrodes separated in about 2 µm in comparison with the fabricated electrodes using different constant current density: (b) 1.0 mA cm^{-2}, (c) 0.4 mA cm^{-2}, (d) 0.1 mA cm^{-2}.

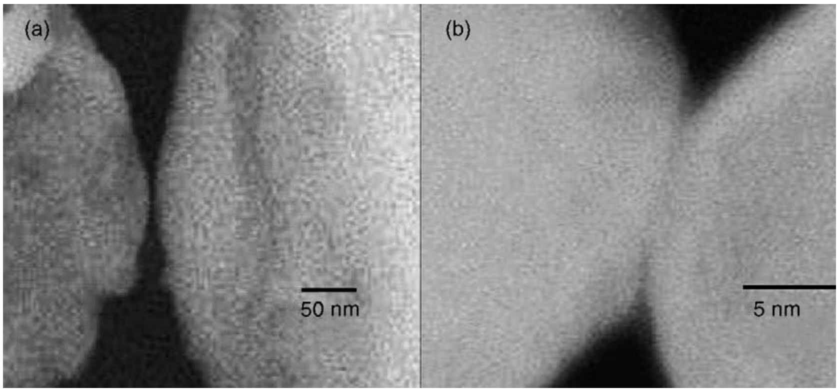

Fig. 4. SEM images of the fabricated gap that was terminated the depositing process when the monitored potential reduced to the preset potential (a) $V_{gap} = -0.55$ V and (b) $V_{gap} = -0.01$ V.

3.2. *Characterization of nano/angstrom-size gap*

In order to get a deep insight of the evolution of the gap when V_{gap} started to decrease corresponding to the chronopotential response in Fig. 3, we carried out a set of experiments by stopping the deposition process when V_{gap} reached a certain value. Then the chip was taken out, washed throughout by distilled water, dried and then examined by SEM. Fig. 4(a) shows the SEM image of the gap fabricated at the initial changing stage, with a chronopotential value $V_{gap} = -0.55$ V. It can be seen quite clearly that the gap width is estimated to be approximately 4.5 nm. If we preset the chronopotential value $V_{gap} = -0.01$ V as the terminating value of the deposition, which is very close to the condition where two electrode directly contact to each other, Fig. 4(b) shows that the gap to be too small and beyond the resolution of SEM. We therefore had to find an alternative method to characterize the gap width. Because the gap width is smaller than 1 nm, it could be reasonable to estimate the gap based on the tunneling current method. The current–voltage (*I*–*V*) characterization of nanogap electrodes was performed at room temperature by a two-point probe method using a Keithley 4200 semiconductor characterization system. For the case in Fig. 3(b), we measured the *I*–*V* characteristic curve for the gap in air, which shows good linearity [25]. We thus can estimate the gap width using the formula $I \propto V\exp(-ks)$ where I is the tunneling current, V the bias potential, s the gap width, and k is a constant. Since we are not able to find the k value in air, we have to substitute k with an average of that in vacuum [26] and in solution [27] so as to calculate the gap width to be approximately 1.5 Å.

It has been shown that the gap width larger than 2 nm can be measured by SEM while that smaller than 1 nm can be estimated by the tunneling current versus applied voltage curves. Accordingly, we performed a set of experiments by presetting a set of potentials from −0.55 to −0.01 V as the feedback to control the nanogap fabrication, then measuring their gap widths by SEM or *I*–*V* values. The V_{gap} versus the gap width is plotted in Fig. 5, and shows that the gap can be controllably fabricated and ranged from about 4.5 nm to 2 Å. This set of experiments persuasively demonstrates that electrode separation gap ranging from several angstroms to several nanometers could be constructed by simply choosing a preset potential in our method.

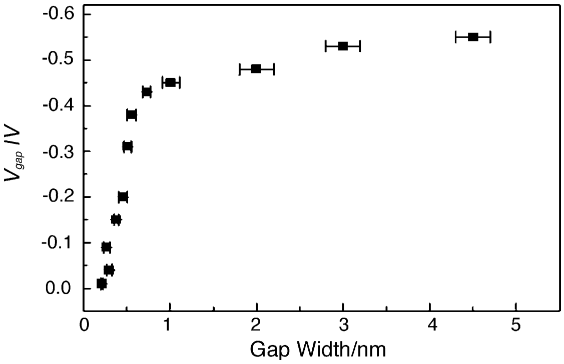

Fig. 5. The correlation of the monitored gap width vs. V_{gap}.

3.3. *The correlation of the double layer*

After knowing that the change of V_{gap} is mainly caused by the gap width narrowed down bellow 5 nm under the present electrode configuration, one could easily infer that this behavior could be most probably originated from the pattern of potential drops in the electrical double layer. It is well known that a simple double layer model of solid/liquid interface consists of a compact layer (CL) with a sharp potential drop, and a diffuse layer (DL) with a slow potential drop [28–30], and no potential drop occurs beyond the double layer region as shown in Fig. 6(a). Regarding the present electrodeposition process, the gap is narrowed down to several nanometers or even less, RE as the potential probe can be considered to penetrate into the double-layer region of WE as shown in Fig. 6(b). V_{gap} will be decreased dramatically if the gap width is about the CL thickness (see Fig. 6(c)).

It should be noted that Fig. 6 is the simplest representation of the potential distribution in the nanogap. The real situation must be much more complicated because we have omitted

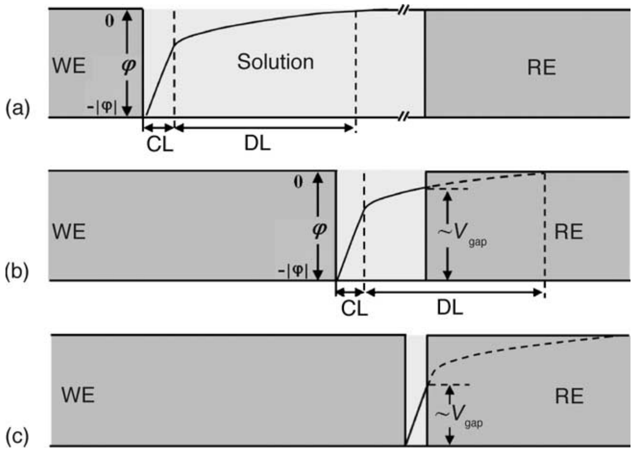

Fig. 6. A brief representation of the working principle of electrochemically fabricating nano/angstrom-gap electrodes.

many influencing factors to the chronopotential characteristic in the present model. For instance, the double layer of RE has not been taken into account in our preliminary model. The influence of the potential drop on the side of RE (the gold electrode at the open circuit potential) could be small than that of WE at the polarized condition. However, the double layer overlapping for WE and RE certainly plays a role [31,32]. How to make the quantitative calculation of the potential distribution in this special case is a very difficult task. However, in return, it will help us to get the clear and detailed picture of the double layer structure.

3.4. *Influence of the electrolyte concentration*

In order to verify the above assumption that V_{gap} is closely determined by the property of the double layer, we designed the experiment to examine if the relationship of V_{gap} and gap width depends on the electrolyte concentration because the double layer thickness is considerably dependent on the concentration. A set of experiments, same as that in Fig. 5, were performed in the solution with increase concentration of 1000 times. The chronopotential curve in Fig. 7(a) shows that the evolution time of the deposition process is considerably short because the concentration of gold ion is much higher. The most important feature is the detailed correlation of the preset potential value and the gap width, as shown in Fig. 7(b). Comparing the results shown in Fig. 5, it can be confirmed that the gap width fabricated in the concentrated solution should be smaller. The data reveal that V_{gap} starts to decrease when the gap width is only about 0.7 nm, considerably smaller than the previous one. It illustrates that the potential distribution in the WE/solution interface relies significantly on the electrolyte concentration. This character could be explained by the decrease of the double layer thickness. For the high concentration electrolyte solution, the double layer become very thin and in an extremity, there is no diffuse layer existed. In another word, the potential distribution in the electrode/solution interface is limited in the compact layer region. The thickness of 0.7 nm seems to be relatively large for the impact layer, which could be due to the double layer overlapping of WE and RE and the specific adsorption of CN^- ion at the electrode surface.

It should be pointed out that for fabrication of nanogaps smaller than 1 nm, our method does not have advantages in comparison with the method using tunneling current as the feedback [17,18], except that our instrument is simpler and conventionally available. The method developed by Tao's group and other groups has an important advantage in terms of precisely controlling the gap width AT sub-angstrom scale [17,18], which is essential to selectively locate different molecules with tiny difference in size for molecular devices.

The advantage of our method using the potential feedback could be its capability of fabricating electrode gaps with the wider range, from several angstroms up to several nanometers. The larger gap width can meet the specific need to fit with target nanocrystals such as quantum dots whose electron transport properties can be characterized. It is well known that the lower the electrolyte concentration is, the thicker the double layer. The variation of the double layer thickness on the electrolyte concentration would enable a higher sensitivity in monitoring the potential change in diluted solutions and thus termination of fabrication at large gap widths. For example, the diffuse layer thickness could be, in general, extended to about 100 nm in a 100 μM electrolyte solution. It is

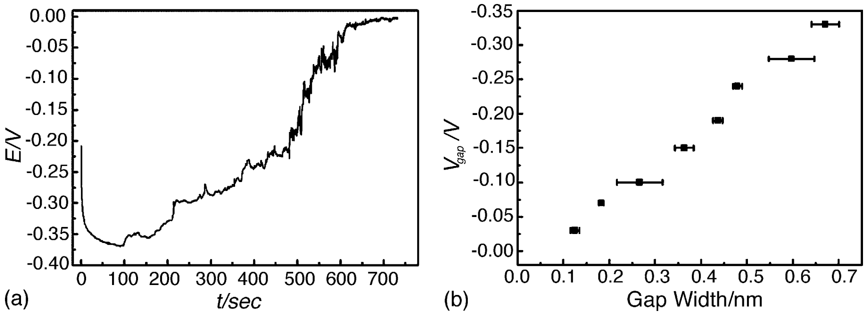

Fig. 7. (a) A chronopotential response curve during the whole electrodeposition process as Au is deposited on the WE. The solution was 15 mM $KAu(CN)_2$ with 0.3 M $K_3C_6H_5O_7$ and 0.3 M KH_2PO_4 as supporting electrolytes. (b) The relationship of the preset chronopotential value and the gap width corresponding to (a).

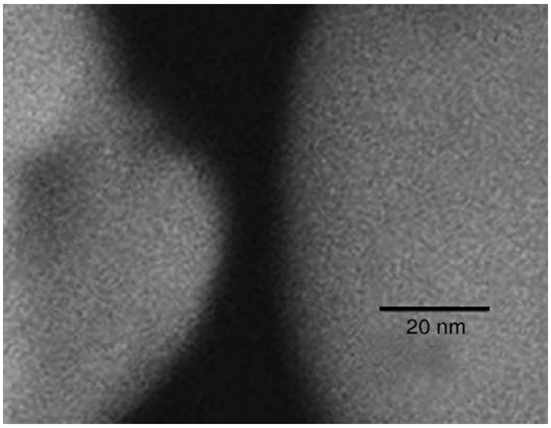

Fig. 8. The largest fabricated gap width can reach about 10 nm when the electroplating solution was diluted substantially.

surprised to notice, however, that the up limit of the controllable gap width is much lower than expected. For example, with an extremely diluted solution of 0.15 μM $KAu(CN)_2$ with 3 μM $K_3C_6H_5O_7$ and 3 μM KH_2PO_4, the gap width of only 10 nm is accessible for fabrication (see in Fig. 8). It should be noted that the plating solution used in the present study is rather complex. It has also been found that CN^- species from the plating solution can strongly adsorb at the electrode, which caused problems for further study, such as on the double layer structure of the nanogap system, using other electrolyte solution. Therefore, it is highly desirable to use other electroplating solution free of strongly adsorbing species. This systematic investigation has been underway in our laboratory.

4. Conclusion and remarks

In summary, we have demonstrated a simple electrochemical method to controllably fabricate Au metallic electrode gap from several nanometers down to several angstroms. The largest gap width that was controllably fabricated in the present study is about ten nanometers. It is correlated, to some extent, to the thickness of electrical double layer that is basically determined by electrolyte concentration. The overall process using chronopotentiometry is simple and controllable, allowing rapid fabrication of electrode pairs on microchip with high efficiency. The experiment is conducted by using the commonly used electrochemical instrument having galvanostatic function. This method has potential of leading to a mean to further electrochemically grows a nanocrystal or quantum dot of semiconductor by simply changing the electroplating solution, as has been demonstrated by He et al. for growing and studying electric conductive polymers [33,34]. Since the desired material is grown directly from the electrode, robust connection of this nanodot or nanorod with the integrated circuit can be assured, which is an important precondition for nanodevice applications.

Development of this method can be made if further experimental as well as theoretical investigation performed to a clear insight of the role played by the double layer structure and especially the double layer overlapping within the nanogap is essential. The Gouy–Chapman–Stern model, based on which the estimation on the concentration dependence of the double layer thickness was made in the present study, is in fact a highly simplified model of the electrochemical interface. The electronic structure of the nanoelectrode could be distinctively different from that of an ordinary plane electrode. Furthermore, while the synthesis and characterization of solid nanoparticles has become a very hot field, much less attention has been paid so far to nanoscale liquid phases. It is obvious that the structure and property of the nanoscale liquid phase, especially the nanoelectrolyte solution, is very important not only for electrochemistry but also for biologic systems. Unfortunately, such nanoscale liquid phases are much more complicated than any solid state nanoparticles, and the characterizing techniques for the former are also much less powerful than the later, for instance, that can be analyzed in detail by high resolution TEM, etc. However, works along the direction of nanoscale electrochemistry could be very helpful in providing a platform to study the nanoscale liquid phase, in particular, the distribution of potential and of species at the interface [35,36], which is one of the fundamental issues in electrochemistry.

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