Noble metal nanoslit by dewetting of thermally activated Au film on CNT

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ABSTRACT

Noble metal nanoslit structure has attracted an increasing interest in nanoscale photonic devices, and bio applications. However, methods typically used for fabricating nano-sized slit, such as, e-beam direct etching, template-assisted photolithography, and nano-imprint lithography, have low yield and are limited to sub-nano sized slit. In this work, we observed that slit width of Au metal is gradually changed with various dewetting temperature, and heating time through solid-state dewetting phenomenon of Au film on Carbon nanotube (CNT). Using this phenomenon, 10-30nm sized slits of Au metal were obtained. In addition, slit size and shape was controlled by dewetting temperature and CNT shape, respectively. It is believed that thermally activated Au atoms above the CNT moved to thiol-group region on the substrate to minimize the surface energy of the Au film.

Keywords: noble metal, carbon nanotubes, solid-state dewetting, Au nanoslit

1 INTRODUCTION

Recently, metal nanoslit with sub-wavelength size has attracted great attention, particularly due to its various applications such as surface plasmon resonance [1-4], optical lenses, plasmon lenses [5], planar lenses [6], and wave-guide [7, 8].

It has been studied by many research groups to fabricate nano-sized hole, or slit array of metal film [4, 7-9]. By using various fabrication methods, such as focused-ion beam etching [2], holographic lithography [4], and nano-imprint [9], have been studied. However, there still remain technical difficulties to reduce the slit size below 10nm scale and to simplify the fabrication methods.

Therefore, it is highly desirable to develop a simple and shape controllable fabrication method for metal nanoslit structure. For this purpose, it is critical to have a metal film self-assembled on a substrate without any conventional method.

Here, we present a simple approach to obtain a noble metal nanoslit made by solid-state dewetting phenomenon of CNT/Au film. We fabricated the Au nanoslits ranging from 10nm to 30nm depending on annealing temperature and heating time of the CNT/Au film. Also, Au nano-ring shape could be obtained using CNT ring shape.

To inspect topography and width of Au nanoslit, scanning electron microscopy (SEM) was used.

2 EXPERIMENTAL METHODS

The experimental processes are as followings. A single-crystal p-type silicon wafer was wet oxidized in furnace. Then, SiO_2 wafer was cut into the pieces of 1.5 cm x 2.5 cm before cleaning. SiO_2 substrates were immersed for 10min in Piranha solution (H_2SO_4:H_2O_2 = 6:4). Then the substrates were carefully rinsed with DI water and dried. Piranha cleaned SiO_2 substrate was treated by oxygen plasma to form rich hydroxyl-groups on the surface of the substrate. Previous other articles have described the bonding mechanism for the reaction of oxidized silicon and hydrolyzed silane [10-12]. The hydroxylated-SiO_2 substrates were immersed in 5mM thiol-group terminated 3-mercaptopropyltrimethoxysilane (MPTMS) solution at room temperature for 90min. According to previous report, perfect MPTMS monolayer is obtained on the substrate after 90min reaction [13]. MPTMS were purchased from Sigma Aldrich Korea, Ltd. And then, the substrates were sequentially rinsed with benzene, methanol, DI water, and finally dried in a nitrogen environment to remove the other physisorbed molecules. CNT layer was formed by spin-coating on the substrate prior to deposition of 20nm Au film by thermal evaporation. CNTs were purchased from Iljin Nanotech Co., Ltd. The thermal annealing process of the CNT/Au film is conducted on a hot plate with various heating time and various temperatures

3 RESULT AND DISCUSSION

Figure 1 shows the schematic of solid-state dewetting processes of Au film on CNT. When CNT/Au film as shown in top of fig. 1 is heated, both solid-state dewetting phenomenon, caused by surface energy difference between CNT surface and thiol-terminated surface, and volume fraction change of the film, induced by crystallization, are simultaneously occurred. Black and red dotted segments in the middle of fig. 1 indicate dewetting phenomenon and crystallization, respectively.

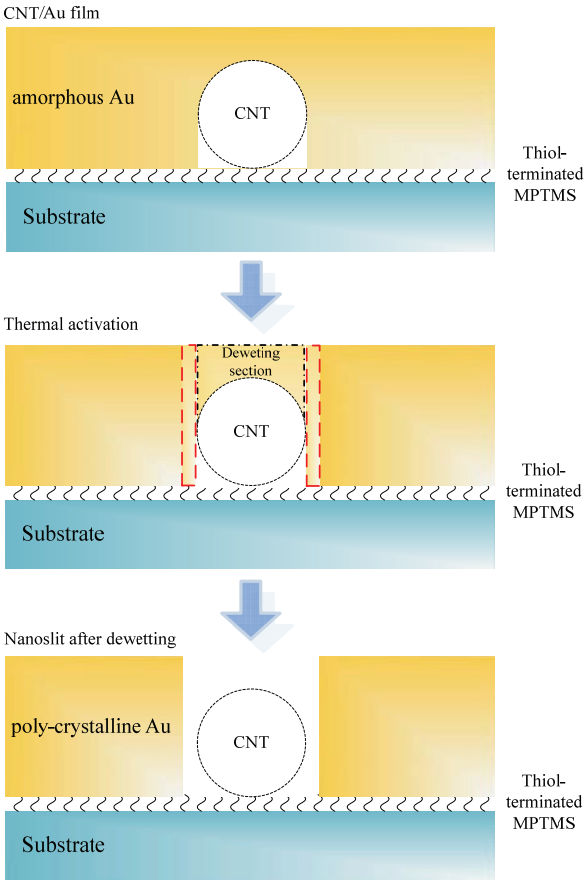

Figure 1: Schematic of the Au nanoslit formation through solid-state dewetting process. In the middle of figure, black and red dotted line segments indicate dewetting section and volume fraction change section, respectively.

There are two reasons why two events coincide. (1) Au atoms or clusters on graphite-like CNT surface easily diffuse due to low diffusion barrier [15, 16]. As a result of heating process, Au atoms on CNT surface are easily detached and moved into the thiol-terminated MPTMS region on substrate to reduce surface energy of Au film. (2) Thermally evaporated Au film is nearly amorphous phase [14]. So, the edge of Au/CNT interface moved due to change of density and volume fraction of the Au film caused by change of amorphous to poly crystalline phase by thermal activation energy.

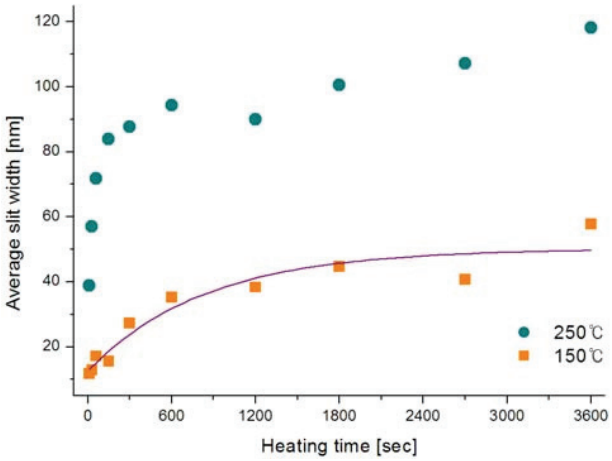

Figure 2: change of average nanoslit width of 10nm thick Au film depending on heating time.

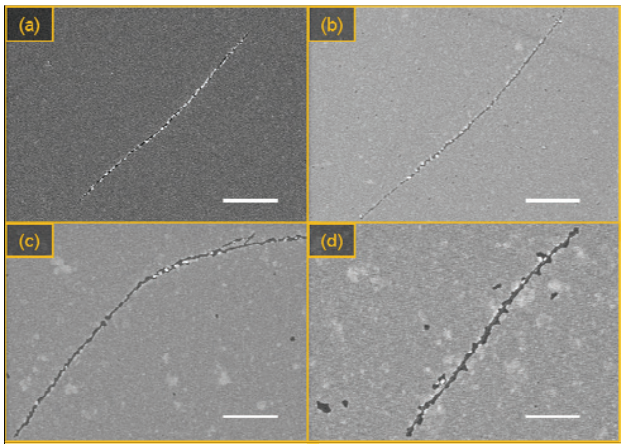

Figure 3: SEM images of dewetted nanoslit of 10nm thick Au film with respect to various heating time at 150℃. a), b), c), and d) are before heating, 60sec, 600sec, and 3600sec, respectively. (Scale bars are 500nm)

In Figure 2 and 3, change of average Au nanoslits width with respect to various heating temperature and SEM images are shown. In early stage, slit width is dramatically increased with increase of heating time. After heating time of 600sec, however, slit width is saturated. Saturated slit

width seems to be determined by dewetting temperature. It is reasonable that slit width is saturated, because volume change rate of the film dependant on change degree of crystallization is determined by thermal activation energy corresponding to the temperature.

The change of Au nanoslit width dependant on various dewetting temperature for saturating time of 600sec is shown in figure 4. The nanoslit widths of Au film dewetted at temperature of 150℃, 250℃, 350℃ are about 10nm, 30nm, 120nm, respectively. The slit widths of Au metal are gradually increased with increasing dewetting temperature. As can be seen in inset SEM images, Au nanoslits are well fabricated at 150℃ and 250℃. However, in the case of 350 ℃ temperature, the shape of slit is uneven. It is supposed that void of Au film of amorphous phase grows, as a result of crystallization by high thermal activation energy.

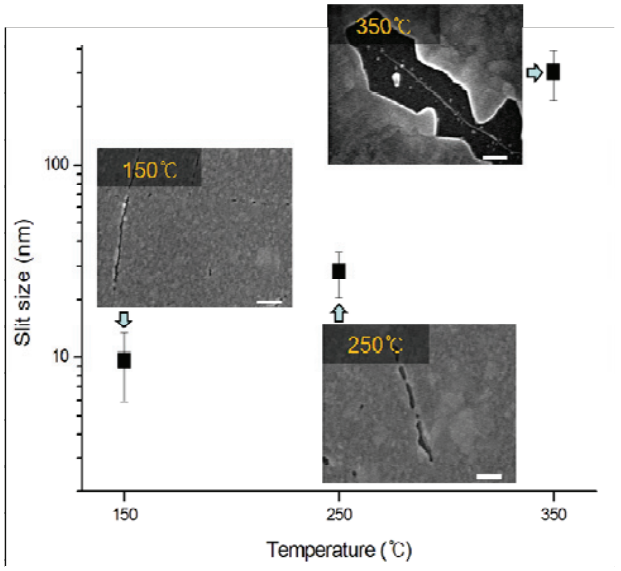

Figure 4: a) Change of Au nanoslit size with respect to the dewetting temperature. The Au film is 20nm thick. And heating time is 600sec (insets: the SEM images of the Au nanoslit at each temperature; Scale bars are 200nm)

Figure 5 shows SEM image of Au nano-ring. It is obvious that dewetted Au nano-structure shape is strongly dependant on CNT shape. According to this result, it is possible to fabricate the Au nano-structure with various shapes, such as hole, honeycomb, or slit array, using various CNT pattern.

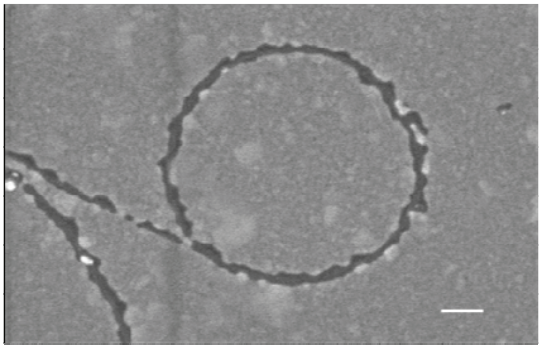

Figure 5: SEM image of Au nano-ring. (Scale bar is 100nm)

4 CONCLUSIONS

An Au metal nanoslit was obtained by solid-state dewetting phenomenon of CNT/Au film. Au atoms or clusters on graphite-like CNT surface easily diffuse due to low diffusion barrier. As a result of heating process, Au atoms on CNT surface are easily detached and moved into the thiol-terminated MPTMS region on substrate to minimize the surface energy of Au film.

Au nanoslit size of 10nm width was obtained. Considering that the CNT bundle, used in this experiment, has diameter of about 10nm, nanoslit width could be reduced by using the single-strand SWNT of 1-2nm diameter.

Au nano-ring shows that Au nano-structure could be controlled with CNT patterns of various shapes using solid-state dewetting phenomenon. Also, if a specimen is prepared with patterned CNT array, an array of Au nanoslits can be fabricated.

Applying this into other metal, it is expected that various metal nanoslit or nano-structure is successfully fabricated.

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