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論 文 の 要 約

報告番号	甲 乙 第 259 号	氏 名	徐微微
学位論文題目	Fabrication of silver nanostructures with laser-induced chemical reaction (レーザー誘起化学反応による銀ナノ構造の作製)		

Introduction to silver nanostructures

Nanostructures have attracted lots of attention for its size effect, surface effect, quantum confined effect, quantum tunnel effect, and dielectric confined effect. Metal Nanostructures have been widely used as plasmonic antenna, sensing, molecular detection and photoelectrochemical applications. These works are very important and instructive in fabrication of silver micro/nanostructures.
Still problems need to be solved.

(1). In-situ fabrication metal structures: Specifically, for example, in the current high precision complex micro-nano metal microdevices process, the traditional preparation technology is facing a severe challenge, especially for complicated microelectromechanical system (MEMS), mechanical and electrical systems (MES) and other applications of the in situ three-dimensional metal wiring or other complex conductive structure, these systems are not flat and often require a metal micro-nano structure should be compatible with other functional units or components, which is difficult for the traditional processing technology.

(2). Positioning size controllable nanocrystals arrays. For example, Raman spectroscopy provides unique molecular fingerprint information by many narrow peaks, which represent the functional groups of the molecular vibration mode and make the detection of molecular species possible. However, the intensity of SERS is determined via molecular dipolar polarizability, which is usually very low in normal Raman scattering. To achieve strong signals, nanostructured metals are required to create a strong localized electric field. The most common used SERS substrate mainly has three categories: rough surface of metals, nanoparticles sol, periodic structure which can achieve large area, stability, uniform and high intensity. And it seems periodic nanocrystals were the best options but difficult to fabricate quickly and controllably.

Laser fabrication technology is an emerging area with a wide variety of applications, ranging from bulk machining in metal forming to micromachining and microstructuring in electronics and biomedical applications. Laser micro-processing methods include the laser direct writing and laser interference. For the laser direct writing, especially the ultrafast pulsed laser, it exhibits great advantages in the following. (1). High power intensity for extensive material processing. (2). Cold process for femtosecond laser fabrication. (3). High precision and 3D processing ability for femtosecond laser fabrication. Laser interference is a convenient, inexpensive technique to fabricate large-area, periodic and biofunctional templates such as gratings, 2D and 3D nanobarriers.

Aims and contents with laser fabrication technology

Femtosecond laser direct writing of silver nanostructures.

Assisted with two-photon or multi-photon absorption, reactions only take place in the focus described by waist and effective length of focus. Thus by moving the light focus and the sample, 2D and 3D structures can be fabricated. Although varies patterns and nanoelectrodes have been fabricated with this method, the threshold for fabrication is not stable in the first scanning and last. The differences of power make it not uniform for nanoelectrodes and difficult for line scanning in large area. In the laser induced reduction, the initial high fabrication threshold was attributed to the reason that there were no seeds or nucleation first in the solution. After several seconds irradiation to generate silver seeds, They began to attract cluster due to the laser induced plasmon effect and the threshold would decrease. To testify the handling ability and processing capacity based on the precursor with Ag seeds, different kinds of micropatterns were fabricated. These fast-developed and high-quality micropatterns indicate that the femtosecond laser direct writing processing precursor with Ag seeds is an effective way to produce laser-induced microstructures.

In-situ fabrication of silver vanadium oxide flowers

We carefully analyze the mechanism of laser induced silver reduction process and find the seed effect which can be used to combine with atoms or compounds. Herein, based on this idea, we successful fabricate silver vanadium oxide flowers on the fixed position. SVO flowers could be formed around the laser beam and pushed on the surface by light trapping. Petals became intensive with the exposure time and grew in cross direction.

Preparing silver nanocrystal arrays for SERS

Surface Enhanced Raman scattering (SERS) is a surface-sensitive technique that enhances Raman scattering by molecules adsorbed on rough metal surfaces. So if we want to get stable intensity of SERS, uniform nanocrystal arrays was required, size and interval shape controllable. Therefore, we propose a novel method for fabricating large-area periodic silver nanocrystal patterns on silicon using the template galvanic battery reaction method.

(1). Fabrication of nanocells in large area: The particle size and spacing can be controlled by limiting the chemical reaction into tens or hundreds of nanometer cells. Specifically, the cells can be easily obtained with a soft template via laser interference.

(2). Based on the limitation effects, controllable reduction of silver nanocrystals inside the nanocells: Silver nanocrystals are gradually grown in the cell through a galvanic battery reaction. Given the limited contact area, the growing speed in a large area becomes controllable and uniform.

(3). SERS detection: The substrate that was used for SERS showed the excellent ability of the spectroscopy even at 10^{-11} M Rhodamine 6G (Rh6G).

Fabrication process, First cleaned by acetone, alcohol and deionized water, silicon was coated by diluted SU8 of thickness about 80 nm Prebaked for 10 min at 95 °C. the substrate was irradiated by laser interference for 80~120 ms. Then templates were obtained by exposure and acetone for developing 1min. Thus grating template would be formed on silicon. After HF and AgNO3 etching, Silver nanocrystal would be growing inside the the nanogratings by galvanic battery reactions. Removing the SU8 gratings, one-dimensional periodic and size controlled silver nanocrystals arrays can be obtained on silicon substrate. Then twice and three times exposure of two-beam interference were conducted to get two dimensional silver nanostructures. Nanocrystal width was controlled by the grating period and etching time, which can be attributed to the limitation effect of the SU8 gratings. The silver nanocrystals show an excellent detecting accuracy and uniform value after soaking in Rh6G solution for 1 h. It shows the average SERS data from 10 random dots on the 5 mm × 5 mm substrate for different concentration. The intensity linearly increased along with the logarithm of concentration.

Summary and Conclusions

Silver (Ag) seeds for assisting femtosecond laser direct writing (FsLDW) were employed in the fabrication of microelectrodes (MEs). Pattern-controllable and size-tunable MEs can be easily constructed by introducing Ag seeds to the ion precursor solution in the process of laser-induced photo-reduction of the Ag ions. The fabrication process is stable under sufficient material supply, these high-quality silver microstructures were fabricated, and the applied laser power is reduced to one-tenth of that without Ag seeds. An organic field effect transistor (OFET) was fabricated, based on fabricated Ag ME, the OFET exhibited good photoelectric properties, and achieved an on–off ratio of 200.

Based on the seed effect of laser induced reduction, we successful fabricate SVO flowers. Adding by the special ability of in-situ reduction, diverse patterns of SVO have been obtained just as the designed. SVO exhibited great potential for electrochromic devices, cathodic electrodes for lithium batteries, catalysts, gas sensors, and electrical and optical devices.

We have proposed a novel method for revealing large-area silver nanocrystal patterns for high sensitive and uniform SERS. By combining the nano-tailoring method with the soft template method, rapid galvanic battery reaction was controlled to obtain nanocrystal gratings and two-dimensional arrays. Those nanocrystals with sizes between 30 and 200 nm and with gaps between 10 and 20 nm can both be determined by period and etching time. Rh6G was used as a detection molecule, and the intensity linearly increased with the logarithm of concentration from 10^{-8} mol/L to 10^{-11} mol/L. Therefore, the optimized silver arrays have great potential for ultrasensitive molecular sensing in terms of its high SERS enhancement ability, favorable stability, and excellent reproducibility.