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表面修飾半導體基板上之分子自組合結構暨單 分子光學特性及應用(1/3)

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執行單位：國立交通大學應用化學系分子科學研究所

Optical Properties and Applications of Molecular self-assembly and Single Molecule Studies on Surface Modified Semiconductor Substrates

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Introduction

At current stage, we devise techniques for immobilizing and allocating a single nanodiamond on the electron beam (E-beam) patterned smart substrate. The properly designed coordination markers on the semiconductor substrate and the high throughput of the confocal microscope provide us with a convenient tool to single out a nanodiamond with a size less than 100 nm and to study Raman spectroscopy.

On the other end of the spectrum, we have also developed a new technique to pattern molecular self-assembly. A home-made nanoimprinter was built to explore new nanoimprinting techniques for applications such as nano-patterned templates on wafer scale and preparation of anti-reflection nanostructures on solar cells

Summary of major results

A. Spectroscopy of single nanodiamond on patterned silicon templates

In recent years, considerable attention has been focused on the development of techniques for solving applied problems in biology, protein chemistry, molecular biology, etc. In particular, the design of various biomarker systems based on the Raman and fluorescent properties of nanoparticles hold much promise, as opposed to conventional organic fluorophores which suffer from poor photo stability, narrow absorption spectra, and broad emission features. Recent advances in the synthesis of the semiconductor nanocrystals have resulted in biomarkers which are brighter, more sensitive, photo-stable and biocompatible. They have found applications in a variety of biological experiments such as cellular imaging, long-term *in vitro* and *in vivo* labeling, tissue structure mapping, and single particle investigation of dynamical cellular processes.

More recently, sub-100 nm nanodiamonds with nitrogen point defects have been used as single-particle biomarkers in experiments of fixed and live HeLa cells. It has also been recently demonstrated that diamonds with a nominal size of 100 nm or less are capable of producing stable fluorescence from color centers after surface treatment with strong oxidative acids. The fluorescent nanodiamonds could possibly be used as fluorescent biomarkers for *in vitro* as well as

in vivo studies at the single-particle level. Although there are some reports on the optical properties of diamond particles, most of the studies focus on diamond particles in clusters or powder form. By combining a confocal microscope and an e-beam patterned smart substrate, we have been able to study nanodiamond phonon properties on a single nanostructure basis. In contrast to earlier reports on nanodiamond powder or clusters, the factors arising from size distribution can be ruled out and the results can be compared with calculations in parallel. The observed energy red-shift and asymmetrical linewidth broadening of the Raman peak in the experiments as the nanoparticle size decreases are attributed to the phonon- confinement effect.

B. Patterning of molecular magnets on semiconductor substrates

We demonstrate three-dimensionally (3D) self-assemble growth of the metallothionein (Mn,Cd-MT-2) molecules on patterned semiconductor substrates. The MT molecules deposited on the patterned substrates were found to grown into 3D rod or ring type nanostructures, depending on the shape of patterned nanostructures on the substrates. Dense arrays of 3D molecular nanorods or rings with an area density close to 10^{10} cm⁻² were demonstrated with a pore size of 20 nm and a pitch size of 100 nm. Those engineered molecular nanostructures provide an excellent opportunity for biological applications, sensing sources of nano-devices, biochemical reactions on surfaces and even single molecule studies. The MT molecules were shown to self-assemble into 3D nanostructures, depending on the nanostructures patterned on the Si templates. Importantly, this work should not be limited to MT-2 molecules and should be extendable to other type of molecules and proteins.

C. Development of nanoimprinting techniques and a home-made nanoimprinter

With the development of e-beam lithography in our laboratory, we can easily fabricate large area of sub-100 nm nanostructures on Si wafer 、ITO glass (Indium Tin Oxide) 、and quartz (or sapphire) plate. However, the limitation of e-beam lithography technique is the low throughput and high cost of the lithography process. Therefore, we have develop nanoimprinting tools which employ the e-beam writer to manufacture large-area NIL mold and duplicate these nanostructures with fast NIL process rather than using time-consuming e-beam writing.

In our investigation, we build a home-made nano-imprinting tool which has equipped with 150W Xe lamp 、heating system 、and pneumatic system. This home-made equipment can work in H-NIL 、UV-NIL 、and other types of NIL process (ex. Fracture induced structuring 、lithographically induced self-assembly···etc.). Currently we are able to duplicate sub-200 nm nanostructures with this home-made facility. With further improvement, we will be able to fabricate smaller nanostructures with this technique and find their applications in related research fields.

Publications result from this grant

Journal Paper

- (1) K.W. Sun* and C.C. Chang “Patterning of magnetic molecular self-assembly on semiconductor substrates”, Journal of Physics and Chemistry of solids **68**, 1211-1214 (2007)
- (2) Chia-Ching Chang, Kien-Wen Sun*, Shang-Fan Lee and Lou-Sing Kan, “Self-assembled Molecular Magnets on Patterned Silicon Substrates: Bridging Bio-molecules with Nanoelectronics” (**Editorial Invited Leading Opinion Paper**), Biomaterials 28, 1941-1947 (2007).
- (3) K. W. Sun*, J.Y. Wang and T.Y. Ko, “Raman spectroscopy of single nanodiamond: phonon-confinement effects”, accepted for publishing in Applied Physics Letters (2008).
- (4) K. W. Sun*, J.Y. Wang and T.Y. Ko, “Photoluminescence and Raman spectroscopy of Single Diamond Nanoparticle”, accepted for publishing in Journal of Nanoparticle Research (2008).

Conference

- (1) Kien Wen Sun, “Optical Properties of a Single Nanodiamond”, phonon 2007, Paris, France, July 15-20, 2007.
- (2) K.W. Sun, “Photoluminescence and Raman spectroscopy of single diamond nanoparticle”, 2nd IEEE International Nanoelectronics Conference (INEC2008), Pudong, Shanghai China, 24-27 March 2008.