附件一

行政院國家科學委員會補助專題研究計畫

□成果報告☒期中進度報告

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(2/3)

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共同主持人：
計畫參與人員：

成果報告類型(依經費核定清單規定繳交)：☒精簡報告　□完整報告

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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

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

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Introduction

We demonstrate a technique that utilizes functionalized single nanodiamond as a platform for observing molecular-molecular interactions on silicon templates. By combining the e-beam lithography technology and self-assembled 3-Aminopropyltriethoxysiliane (APTES) thin films prepared on the silicon substrate, we were able to pattern the single nanodiamond (ND) into 2D arrays as a bio-labeling probe and to obtain its optical characteristics. The technique that we devised can find possible applications in the fabrication of silicon-based bio-sensing chips or in single molecule detections.

Summary of major results

In this report, we have combined the methods mentioned above to fabricate a 2D array of functionalized nanodiamonds on silicon templates by using the self-assembled monolayer (SAM) and the e-beam lithography techniques. The chip was characterized by using Raman and PL intensity mapping techniques.

The average diameter of nanodiamond (ND) powders used in our experiments is about 100 nm. The nanodiamond powder was treated with 5:1 mixture of concentrated H_2SO_4 and HNO_3 solutions at 75 ^oC for 6 hours and extensively rinsed several times with DI water. The sediment was then collected and dried. The functional COOH group was formed on the ND surface followed by the standard chemical treatment mentioned above.

A Si wafer was first diced into 2 cm x 2 cm chips. A silicon oxide layer was grown on the silicon chips with thickness of about 400 nm by using PECVD. The substrate was cleaned with ultrasonic bath in acetone, isopropyl alcohol, and DI water solution for 5 min. The ZEP520 photoresist was then spin-coated on silicon oxide substrates with a rate of 500 rpm for 10 sec and 5000 rpm for 50 sec and baked at 180 ^oC for 2 min. The thickness of the photoresist was about 300 nm.

Two kinds of patterns were designed to be placed on the Si templates. One is the crossmarks and the other one is nanohole arrays. Figure 1 shows the schematics of patterns. The crossmarks have a length of 600 μm and a width of 20 μm. The hole arrays have an average diameter of 300 nm and a pitch size of 5 micrometer. After being exposed by an electron beam writer, the photoresist was developed by N50. To form an amino-terminated layer on surface, the substrates were immersed in 5vol% solution of 3-aminopropyl triethoxysilane (APTES) in 95% ethanol for 4 hours and later rinsed with ethanol and thermally treated at 120 ^{o}C for 40 min.

The ND solution was prepared by adding 0.1 g of NDs functionalized with the COOH group into 100 ml of DI water followed by an ultrasonic bath for 60 min. The patterned substrate was dipped into 3 ml of the ND solution and 3 ml of 0.1 M MES buffer (2-(N-morpholino) ethane sulfonic acid). Subsequently, 6 ml of 0.025 M EDC solution 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride, 0.025 M NHS solution (N-hydroxysuccinimide) (named below “EDC/NHS solution”) and 8 ml DI water were added and put into reaction for 8 hours. After the reaction was completed, the substrate was washed with acetone. It was then immersed into ZDMAC (dimethylacetamide) solution for 4 hours to remove the photoresist. The substrate was again washed with acetone and dried with N_2. Figures 2(a) and 2(b) show how the functionalized NDs were anchored on the patterned silicon templates and processes for the preparation of substrates.

Figure 3(a) shows the SEM image of one of the corners inside the crossmark. The image of 2D hole arrays with a diameter of 300 nm and the pitch of the hole in 5 μm is shown in Figure 3(b). From the SEM images one can observe that the nanodiamonds bonded with the patterned SAM inside the nano holes. The inset in Figure 3(b) shows a single functionalized ND was isolated inside a nano hole. The cross-section SEM images of the patterned single nanodiamond are shown in Figure 4(a) and 4(b). The images were taken by cutting a trench in front of a patterned single nanodiamond with a focused ion beam (FIB). With the above methods, we were able to arrange NDs with various patterns defined on the silicon substrates.

The optical properties of the patterned NDs are demonstrated as follows. Figures 5(a) and 5(b) show the Raman and PL spectra of NDs with and without the acid treatment at an excitation wavelength of 532 nm. The treatment with acid particularly removed the carbon-like structure from the ND surface. In the Raman spectrum, the peaks at 1350 cm^{-1} and 1580 cm^{-1} (D-band and G-band signals caused by the carbon-like SP^2 structure from the ND surface) were clearly attenuated after the acid treatment. Figure 5(b) shows that the narrower emission band was obtained because the acid treatment reduced the surface disorder and the number of surface defects.

The micro-Raman spectra were also excited inside the reference crossmarks, nano holes, and outside the nano holes with a laser beam of about 1 μm in diameter. The Raman signals, as shown in Figure 6(a), were only found inside the crossmarks and nano holes where the NDs were anchored. However, with the laser beam placed outside the nano holes (pattern-out area), no diamond-related signals were collected. This indicates that NDs were only allocated on the SAM inside the crossmarks and the nano holes. The locations of the anchored NDs were further examined with the photoluminescence spectra excited at a wavelength of 532 nm. The PL spectra are shown in Figure 6(b). The PL spectrum of the ND clusters is also shown in Figure 6(b) for comparison. Again, no PL signals can be found outside the pattern area.

A 1D Raman intensity image mapping was carried out along a selected nano hole array, as shown in Figure 7(a). The laser beam with a diameter of 1 μm was scanned along a distance of 20 μm with a 500 nm step. The intensity of the 1332 cm^{-1} Raman peak as a function of the scanning distance was plotted in Figure 7(b). We also performed a two-dimensional Raman spectra mapping in a selected square area (the area is shown by the red square in Figure 8(a)). The 2D image of integrated Raman intensity mapping of the 1332cm^{-1} Raman peak is shown in Figure 8(b). Keep in mind that the hole array was designed with a pitch of 5 μm. When compared with the results from the 2D Raman intensity mapping, we found that the intensity distribution was perfectly correlated with the spatial distribution of the nano hole arrays. The results indicate that the NDs were only anchored inside the nano holes and were perfectly distributed on the template according to the pattern defined by the e-beam lithography technique.

In summary, we have demonstrated new methods and techniques to anchor functionalized NDs on a patterned silicon template using e-beam lithography and SAM techniques. The patterned NDs were characterized and verified by the Raman, PL microscopy, as well as 1D and 2D Raman intensity image mappings. With properly designed nano hole arrays, it is possible to isolate a single ND in each nano hole. The device demonstrated here is suitable for applications on bio-sensing chips and single molecule detection

Figure 1 Schematics of the pattern design.

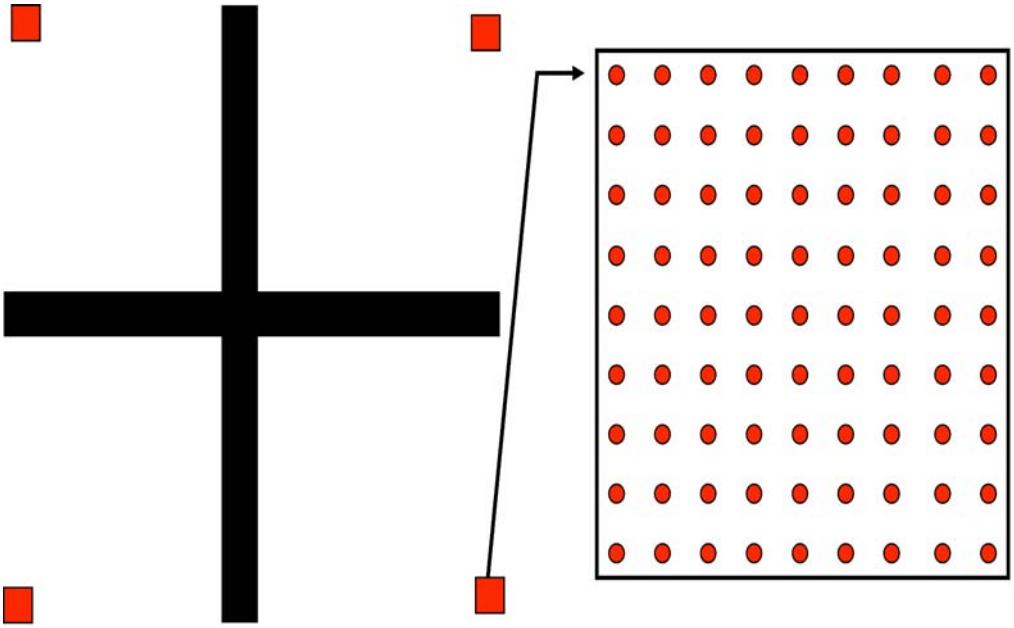
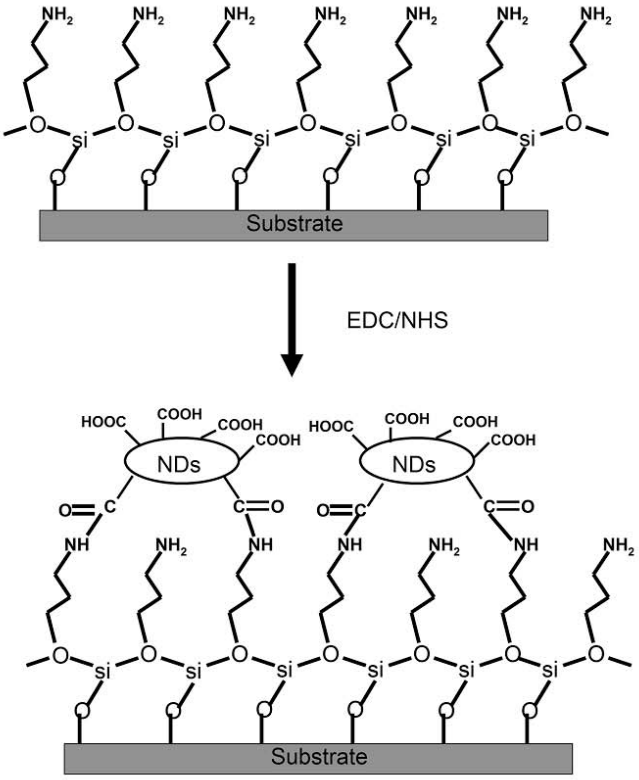


Figure 2 (a) Schematics of the functionalized NDs bonded to the SAM substrates and (b) flow chart of the template fabrication processes.

(a)



(b)

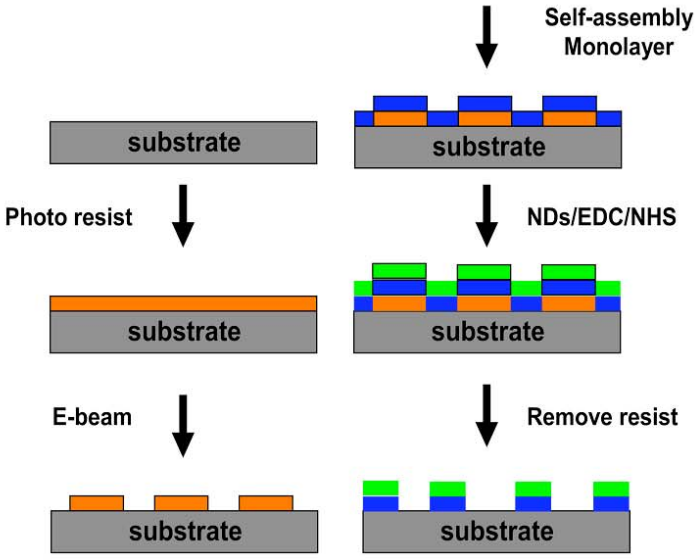
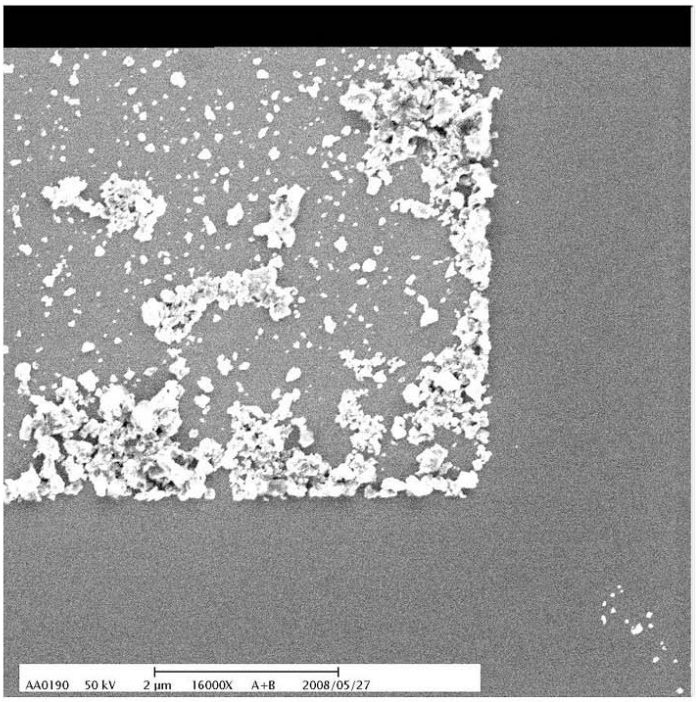


Figure 3 SEM images of (a) one of the corners of the cross marks (b) the nano holes array

(a)



(b)

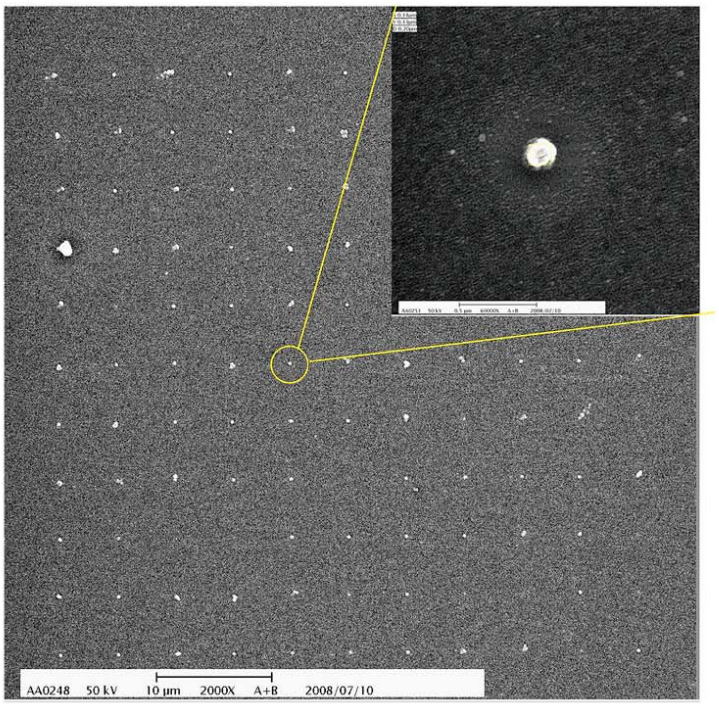
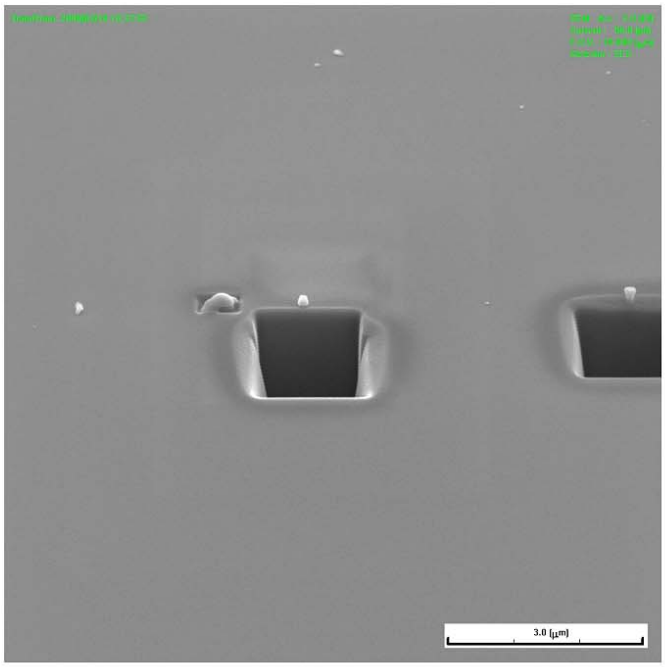


Figure 4 (a) and (b) SEM images of the cross-section of a patterned single nanodiamond.

(a)



(b)

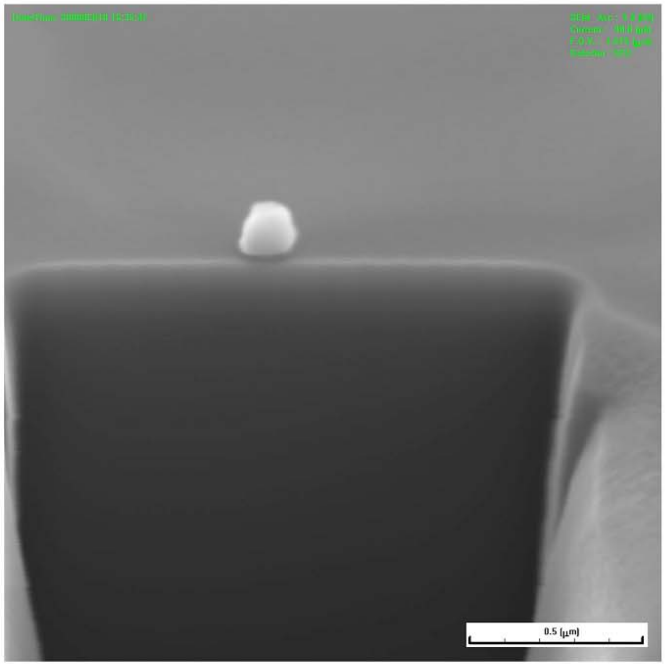
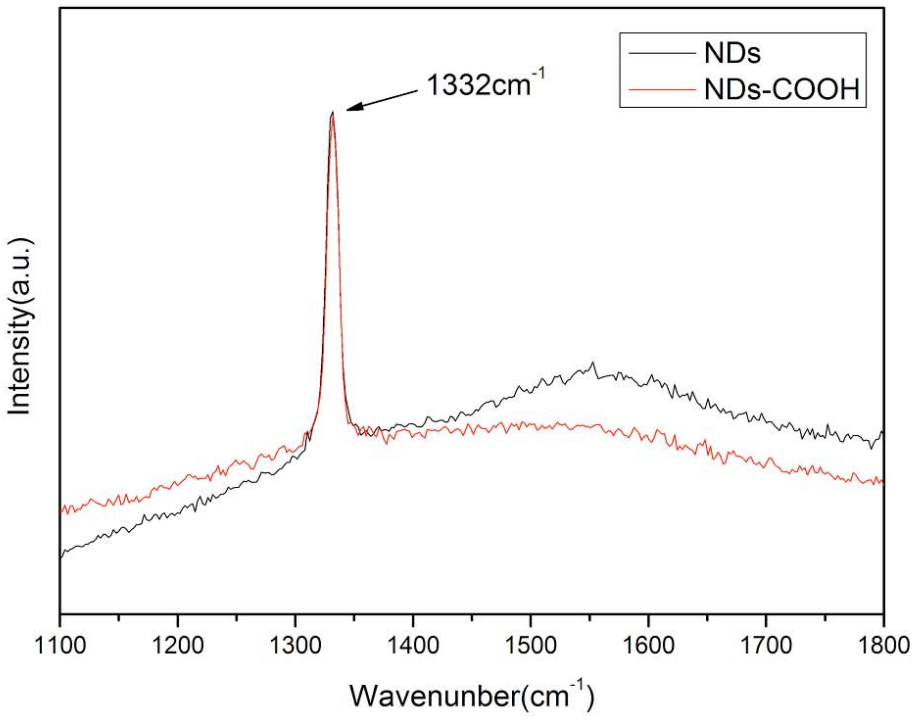


Figure 5 (a) Raman and (b) PL spectra of NDs before and after acid treatments.

(a)



(b)

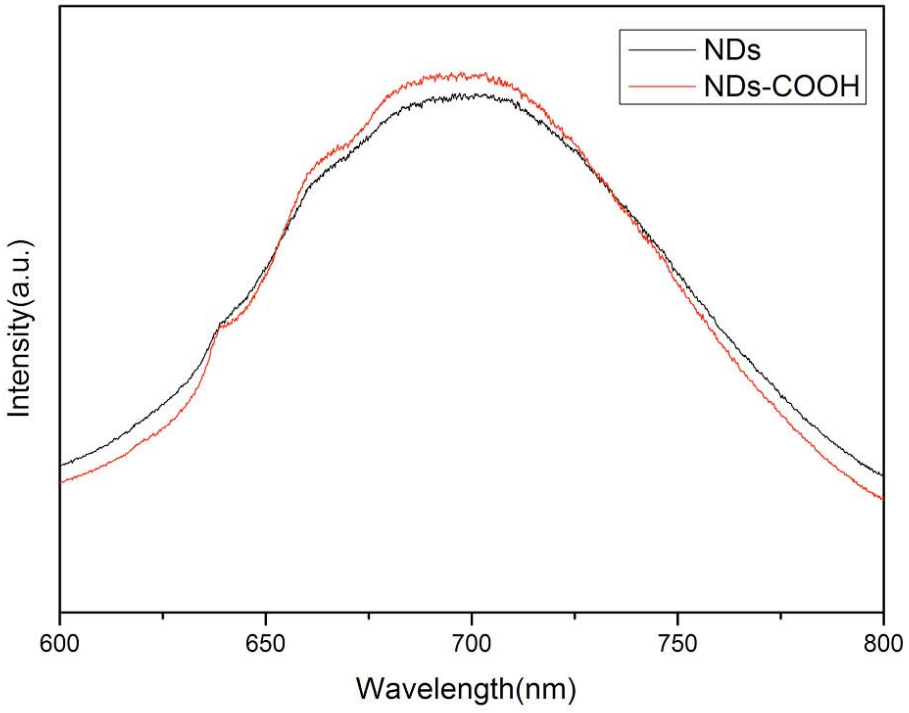


Figure 6 (a) Raman and (b) PL spectra of pattern-in and pattern-out area.

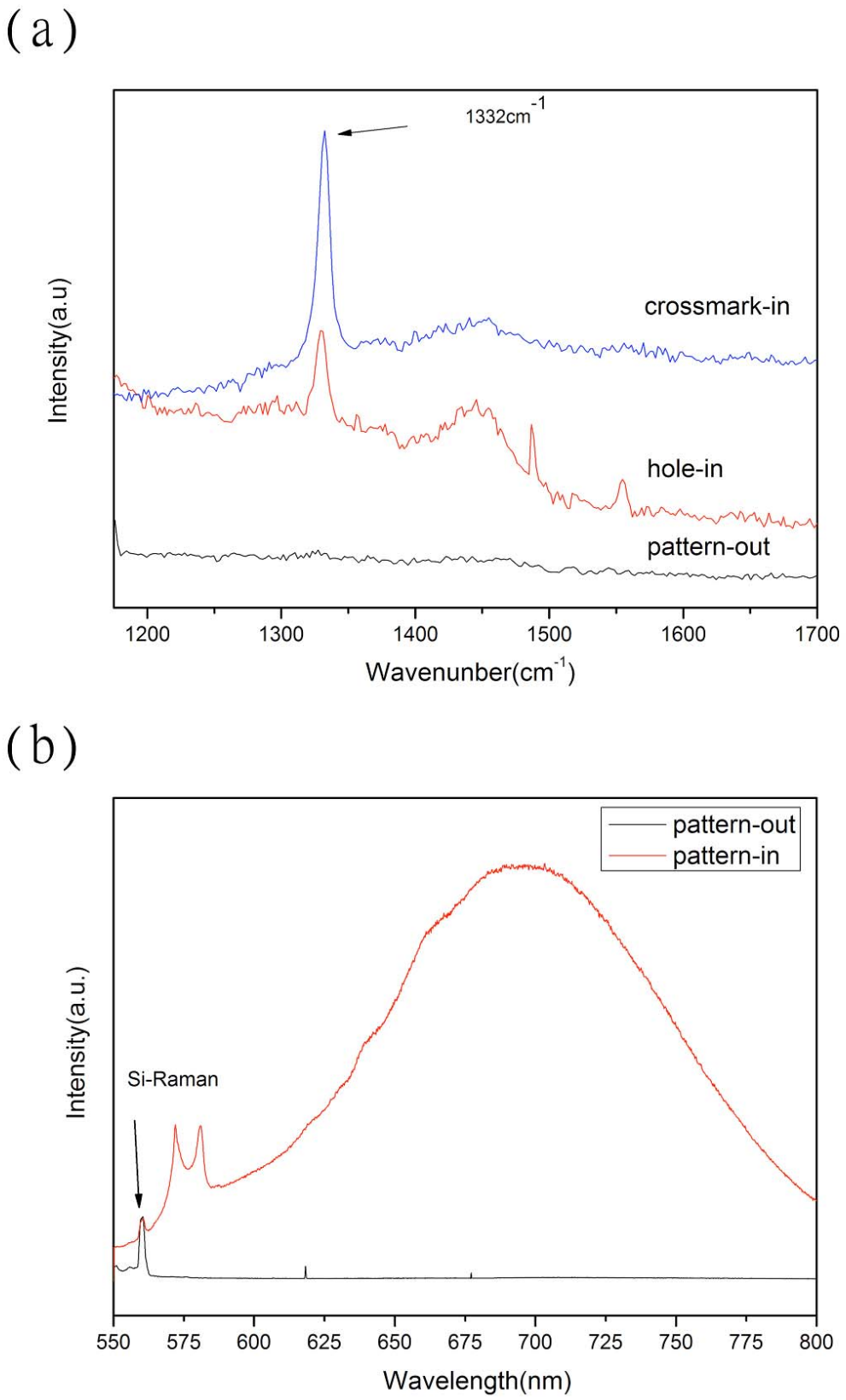
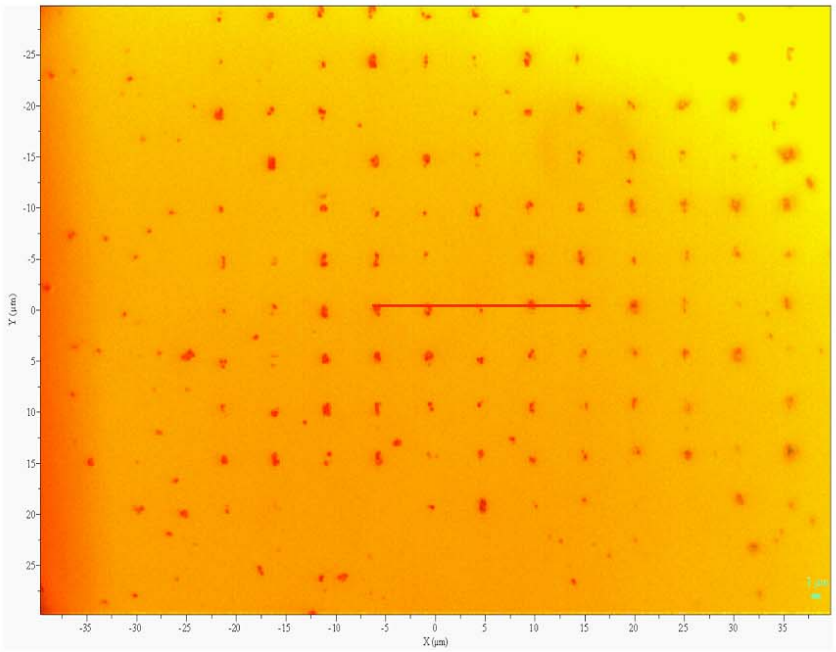


Figure 7 (a) Optical image of the 1D mapping area, indicated by the straight line and (b) image of the 1D Raman intensity mapping.

(a)



(b)

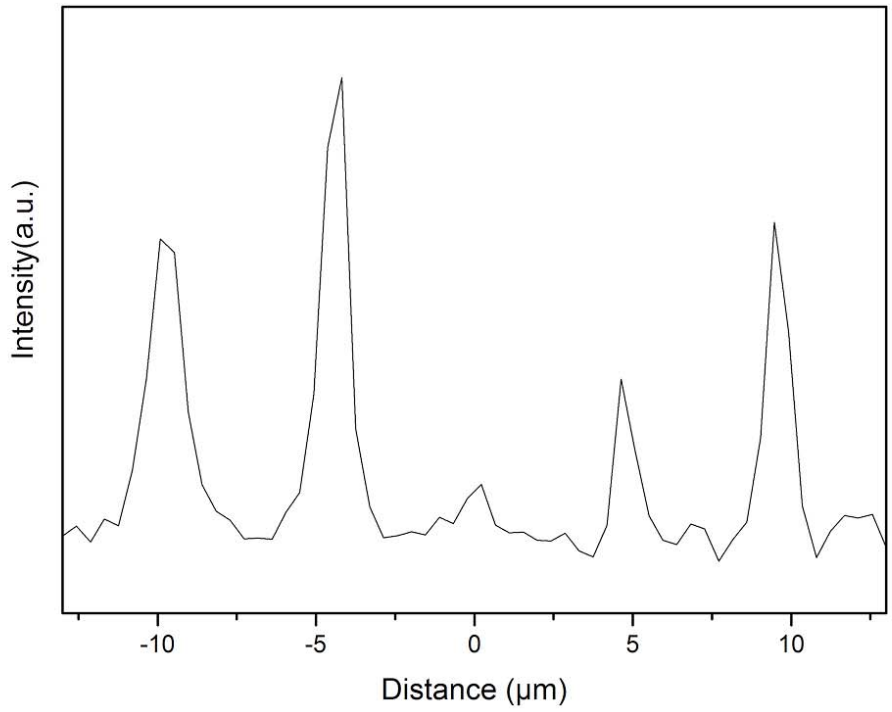
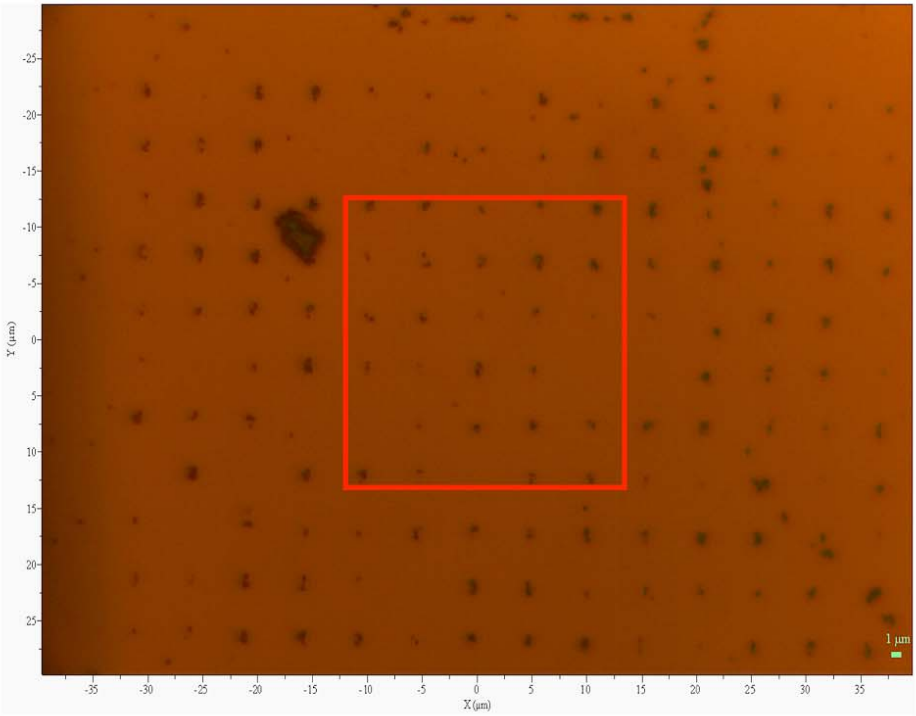


Figure 8 (a) Optical image of the 2D mapping area, indicated by the square and (b) image of the 2D Raman intensity mapping.

(a)



(b)