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3D microstructures made of aligned carbon nanotube/polymer composites fabricated by two photon polymerization lithography

Shota Ushiba[1], Satoru Shoji [2], Kyoko Masui [1], Junichiro Kono [3], Satoshi Kawata [1]

[1] Department of Applied Physics, Osaka University　[2] Department of Engineering Science, The University of Electro-Communications　[3] Department of Electrical and Computer Engineering, Rice University
E-mail: ushiba@ap.eng.osaka-u.ac.jp

1. Introduction

Single wall carbon nanotubes (SWCNTs) exhibit ultra-high aspect ratios that can lead to devices and systems with extremely anisotropic mechanical, electrical, thermal, and optical properties if macroscopic ensemble of aligned nanotubes can be made. However, it still remains to be a significant challenge to control the orientation direction of CNTs in 3D structures. Here, we use two photon polymerization (TPP) lithography to fabricate 3D structures containing aligned SWCNTs [1, 2].

2. Results and Discussion

Experiment

SWCNTs are dispersed in an UV-curable monomer. TPP lithography was carried out on the SWCNT-dispersed photo-resin, and SWCNTs were simultaneously fixed in tiny polymer structures. The polarization of laser beam was kept parallel to the *x*-axis. After structures were created, unsolidified resin was rinsed away using acetone, and the structures were then dried. The orientation direction and degree of the alignment of SWCNTs in the obtained structures were investigated using polarized Raman microscopy, with an excitation wavelength of 785 nm.

Results

Nanowires, of which the wire radius is 375 nm, was fabricated by TPP lithography. Polarized Raman microscopy experiment shows that SWCNTs are aligned along the wire. Based on the inspiring result, we fabricated more complex 3D structures with dimensions of 3x6x4 μm^3 (Fig. (a)). This structure is separated into two sections in which the laser scanning directions are orthogonal to each other; the left section is made up of an array of nanowires along the *x*-axis, while the right section is made up of an array of nanowires along the *y*-axis. The width of each nanowire in the structure is around 530 nm. G-band Raman intensity as a function of angle θ between the laser polarization and the *x*-axis is measured from left and right sections (Fig. (b)). For both sections, G-band intensity becomes largest when the polarization is parallel to the scanning direction, while G-band intensity becomes smallest when the polarization is perpendicular. This result clearly indicates that SWCNTs are oriented in the laser scanning direction in each section. Furthermore, the strength of the alignment of SWCNTs is evaluated from the nematic order parameters *S* in a fitting parameter of the fitting curve. From the fitting curve, *S* for the *x*- and *y*-scanning areas is calculated to be 0.2 and 0.1, respectively. The result implies that the polarization of the fabrication laser beam affected the strength of the alignment in the structure.

Discussion

We suggest that the alignment mechanism involves three factors: (1) spatial confinement, (2) volume shrinkage, and (3) optical gradient forces. SWCNTs are spatially confined in nanowires because the typical length of nanotubes was longer than the nanowire widths. Further, the alignment is enhanced by the shrinkage of structures arising from extraction of unsolidified resin during rinse and dry process. Moreover, optical gradient force also contributes to the alignment during the fabrication as the gradient force makes 1D nanostructures align along the polarization direction. All these three mechanisms contribute to the alignment of SWCNTs during TPP lithography.

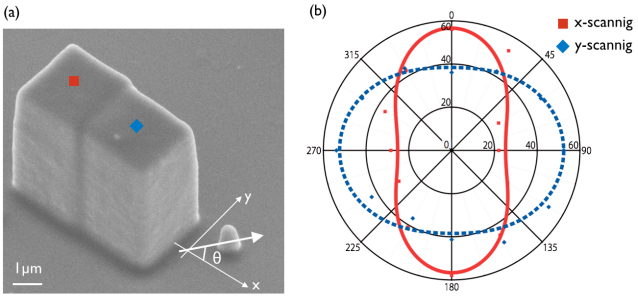

Fig. (a) SEM image of a 3D structure consisting of arrays of nanowires. (b) G-band Raman intensity as a function of polarization angle θ taken from red and blue points in (a).

3. Conclusions

We have developed a technique based on TPP lithography to fabricate arbitrary 3D structures in which aligned SWCNTs are embedded. SWCNTs are aligned along nanowires or laser scanning direction while they are embedded in the structures. The alignment is induced by spatial confinement, volume shrinkage, and optical gradient force. Our method, thus, enables alignment control in any desired directions in arbitrary 3D microstructures.

References

[1] S. Ushiba et al., Carbon **59**, 283 (2013)
[2] S. Ushiba et al., Advanced Materials (2014) (Accepted)