Appl Phys A (2010) 100: 177–180
DOI 10.1007/s00339-010-5732-y

Applied Physics A
Materials Science & Processing

Minimum spacing between suspended nanorods determined by stiction during two-photon polymerization

Mao-Zhu Sun · Yan Li · Hai-Bo Cui · Hong Yang · Qi-Huang Gong

Received: 3 February 2010 / Accepted: 23 April 2010 / Published online: 12 May 2010

Abstract The influence of stiction on the minimum spacing between suspended nanorods fabricated by femtosecond-laser-induced two-photon polymerization has been investigated. The minimum spacing is predicted based on a theoretical model calculating the adhesion length of a nanorod pair, which is in good agreement with the experimental results for suspended nanorods with feature size of around 200 nm. This is helpful for the polymerization of three-dimensional functional nanostructures.

1 Introduction

A femtosecond-laser-induced two-photon polymerization (TPP) is a powerful tool for the fabrication of 3D nanostructures. Various micromachines and microdevices, such as three-dimensional photonic crystals, have been demonstrated [1–5]. To further shrink the device size, higher resolution and smaller spacing are always appealing. On the one hand, much attention has recently been paid to improve the spatial resolution. The feature size of suspended nanorods is reduced to ∼20 nm using excitation wavelength of 800 nm [6–8]. On the other hand, the reduction of spacing has not been taken much into account though it is a challenge to the successful polymerization of a functional nanostructure, for example, in the fabrication of woodpile photonic crystals for visible wavelength [9–15]. In fact, the minimum spacing is not only dependent on the feature sizes, but also limited by the inevitable stiction problem that results from the capillary, electrostatic, van der Waals forces during the fabrication and the developing process. When the suspended nanorods are close enough, surface tension pulls the nanostructure towards each other as the liquid is dried. The structure may adhere permanently. In order to reduce the release-related stiction problem, several special processes, for instance, supercritical drying with CO_2, freeze-drying sublimation, the surface roughening process, and chemical modification of the surface, have been reported [16–19].

Since the stiction can cause severe distortion, the spacing between neighboring polymerized nanostructures should be wide enough to ensure the expected configuration. The phenomenon has been studied in fabrication of structures with microscale feature sizes. With the reduction of the feature size down to tens of nanometers, deformation of the nanorods is seriously detrimental to the performance and reliability of the device. It is therefore important to characterize the stiction to provide a better design for the nanostructures.

In this paper, the influence of the stiction on the minimum spacing between suspended nanorod pairs fabricated by TPP is presented. The length of the nanorod was set by the distance of two anchor supports while the width was changed by varying the incident laser power or the scanning speed of the laser focus. The minimum spacing is found to be determined by the stiction and can be predicted based on a theoretical model calculating the adhesion length, which is in good agreement with the experimental results for suspended nanorods with feature size of around 200 nm. This is helpful for the polymerization of three-dimensional functional nanostructures.

M.-Z. Sun · Y. Li (✉) · H.-B. Cui · H. Yang · Q.-H. Gong
State Key Laboratory for Mesoscopic Physics and Department of Physics, Peking University, Beijing 100871, China
e-mail: li@pku.edu.cn
Fax: +86-10-62756567

Q.-H. Gong
e-mail: qhgong@pku.edu.cn

2 Experiments

Figure 1a shows the schematic setup for the fabrication of nanorod pairs between two parallel rectangular supports by TPP. A liquid resin SCR500 was dropped on a cover glass that was mounted on a piezostage with a precision of 1 nm. The laser beam from a mode-locked Ti:sapphire oscillator with a center wavelength of 830 nm, a pulse width of 120 fs, and a repetition of 80 MHz was focused into the sample by an oil immersion objective lens with numerical aperture of 1.45. A set of two galvanometer mirrors and the piezostage were used for scanning the laser focal spot in x–y and z direction, respectively. A CCD camera mounted behind a dichroic mirror was used for real-time monitoring of the polymerization process. After irradiation, the sample was developed in ethanol to wash out the unpolymerized liquid resin. Then the fabricated solid nanostructures were analyzed by scanning electron microscopy (SEM).

Two large parallel cuboid supports were first fabricated as anchors on the cover glass substrate along the y direction and then several nanorod pairs were scanned at the height h in the x direction. The length l of nanorods was determined by the support distance. When the spacing $2d$ between the pair nanorods was shorter than a critical value named as minimum spacing, the stiction caused the nanorods to adhere to each other. In experiments, the rod length, width, and the spacing were systematically changed to determine the allowable minimum spacing. Figure 1b shows the SEM image of four nanorod pairs with length of ~4 μm and width of ~200 nm fabricated at the height of ~3 μm. The spacings are ~650, 600, 550, 500 nm from left to right, respectively. It can be clearly seen that the nanorods adhered to each other when the spacing was smaller than 550 nm, mainly resulted from the stiction.

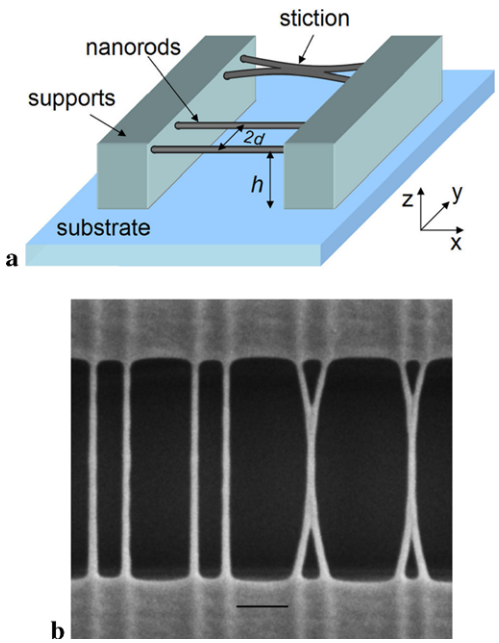

Fig. 1 **a** Schematic setup for the fabrication of suspended nanorod pairs. Nanorod pairs with spacing $2d$ are scanned at the height h from the substrate between two supports with a distance of l. **b** SEM image of four nanorod pairs with length of 4 μm and width of ~200 nm fabricated at the height of 3 μm. The spacings are 650, 600, 550, 500 nm from left to right, respectively. Scale bar: 1 μm

3 Results and discussion

After the polymerization, an unpolymerized resin has been cleaned by ethanol solvent. In the developing process, a capillary force may be strong enough to cause the adhesion and collapse of polymerized structures. To analyze the stiction influence on the minimum spacing, a theoretical model [16–18] is adopted as shown in Fig. 2. The original length and width of rods are denoted as l and t, respectively. The adhesion length is defined as $2x_s$. The displacement of the rod is

$$u(x) = d\left(1 - \left[(x - x_s)/(l/2 - x_s)\right]^2\right).$$

To calculate the adhesion force, one should consider the total energy $U_t = U_e + U_{sl} + U_{sc}$ stored in the system. The total energy of the system comes from three major sources: the elastic energy U_e of the deformed polymer rods, the solid–liquid surface energy U_{sl} stored in wetted areas, and the solid–solid surface energy U_{sc} stored in the contact areas. Since the two rods under consideration are identical, one only have to solve the stored energy for one rod. From Euler's approximation, the elastic energy of one beam under deflection can be written as $U_e = (EI/2)\int_{-l/2}^{l/2}(d^2u/dx^2)^2\,dx$, where E is the Young's modulus of polymer, and I the moment of inertia of the

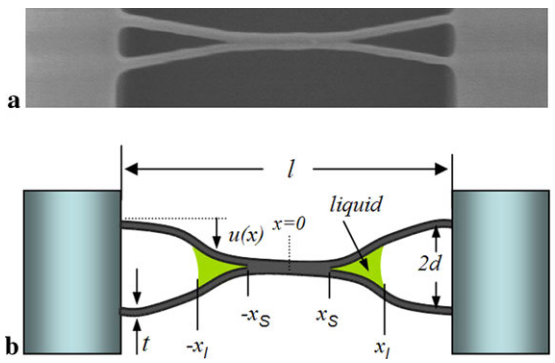

Fig. 2 **a** A SEM image of two adhered nanorods with length of 5 μm, width of 125 nm, and spacing of 700 nm. The adhesion length is ~1.6 μm. **b** Schematic of the model used to calculate the adhesion length $2x_s$. $u(x)$ is the position of the deflected rod. The liquid spreads on the regions $-x_l \le x \le -x_s$ and $x_s \le x \le x_l$. The original length and width of rods are denoted as l and t, respectively. And $2d$ is the spacing between two parallel rods

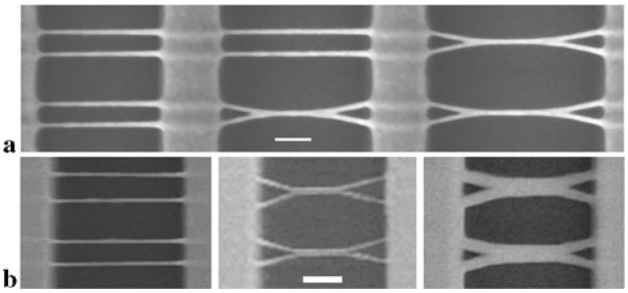

Fig. 3 The dependence of the minimum spacing on the length and width of the suspended nanorod. The spacing between the rod pairs are 650 (*first row*) and 600 nm (*second row*), respectively. Scale bar: 1 μm. **a** The nanorod width is ∼200 nm, the lengths are set to 3.5, 4, 4.5 μm from the left column to the right column. **b** The nanorod length is 3.5 μm, the widths are ∼140, 190, 380 nm from the left column to the right column

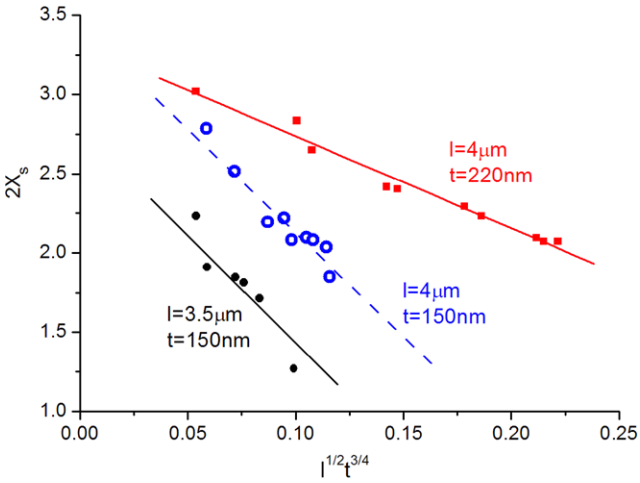

Fig. 4 The adhesion length as a function of $l^{1/2}t^{3/4}$. The *lines* are fitting results

rod. The solid–solid surface energy and the solid–solid surface energy is given by $U_{\mathrm{sl}} = -4\gamma_{\mathrm{l}} w \cos\theta_{\mathrm{c}}(x_{\mathrm{l}} - x_{\mathrm{s}})$ and $U_{\mathrm{sc}} = -2\gamma_{\mathrm{s}} w x_{\mathrm{s}}$, where w is the thickness of the rod, θ_{c} is the contact angle, and γ_{l} and γ_{s} are the surface energy of liquid and solid, respectively.

When the rod is at equilibrium, x_{s} and x_{l} do not change. From the equations above, and let $x_{\mathrm{l}} = x_{\mathrm{s}}$ which means the liquid is totally evaporated, one can derive the adhesion length, $2x_{\mathrm{s}}$, of the drying rods

$$2x_{\mathrm{s}} = l - l_{\mathrm{d}} \tag{1}$$

where the detachment length l_{d} is defined as

$$l_{\mathrm{d}} = \left(\frac{128}{5}\frac{E}{\gamma_{\mathrm{s}}}\right)^{1/4} d^{1/2}t^{3/4}. \tag{2}$$

When the designed rod length exceeds the detachment length, $2x_{\mathrm{s}} > 0$, stiction will happen. For the given length and width of rods, the spacing should be wider than the minimum spacing to avoid the stiction. The minimum spacing $2d_{\mathrm{m}}$ can be obtained by setting $l_{\mathrm{d}} = l$ or $2x_{\mathrm{s}} = 0$,

$$2d_{\mathrm{m}} = \left(\frac{5}{32}\frac{\gamma_{\mathrm{s}}}{E}\right)^{1/2} l^2/t^{3/2}. \tag{3}$$

From (3), we can see that the shorter the length or the wider the width of the nanorods, the smaller the permitted spacing without stiction. This provides useful information for designing 3D nanostructures. As shown in the following results, the stiction is really the main factor to determine the minimum spacing.

In addition to the material related ratio of E/γ_{s}, the minimum spacing is determined by the length and width of the nanorods. Figure 3 demonstrates the influence of the length or the width of the nanorod, which is good agreement with (2). Figure 3a shows part of a series of nanorod pairs fabricated in three columns with lengths of 3.5, 4, 4.5 μm. The laser power of 10 mW and the scanning speed of 20 μm/s were maintained, so the rod widths (∼200 nm) and the ratio E/γ_{s} were almost the same. For each column, the spacing between the pair rods was decreased from 700 to 450 nm in a step of 50 nm. The stiction occurred when the spacing was close enough and the longer the nanorods, the larger the minimum spacing. When the spacing was 600 nm, the stiction happened for the length longer than 4 μm, but not for length shorter than 3.5 μm. Figure 3b presents the influence of the nanorod width under the same length of 3.5 μm. At the scanning speed of 10 μm/s, the laser powers were ∼9, 10, 12 mW, respectively. The resulted rod widths were ∼140, 190, 380 nm and the ratio E/γ_{s} decreased with the width. It is can be seen that the wider the width, the larger the minimum spacing.

From the fitting of the $2x_{\mathrm{s}}$ versus $l^{1/2}t^{3/4}$, we found the factor $(128E/5\gamma_{\mathrm{s}})^{1/4}$. Then, we obtained the minimum spacing from (3). Figure 4 shows the experimental data of adhesion lengths as a function of $l^{1/2}t^{3/4}$. The black dots, the blue open circles, and the red squares stand for three cases with ($l = 3.5$ μm, $t = 150$ nm), ($l = 4$ μm, $t = 150$ nm), and ($l = 4$ μm, $t = 220$ nm), respectively. The fitting is linear and in accord with (2). The factor $(128E/5\gamma_{\mathrm{s}})^{1/4}$ was almost the same for the nanorod pairs with the same width but with different lengths. Nevertheless, this factor obviously changed with the rod width. For $t = 150, 220$, we got $(128E/5\gamma_{\mathrm{s}})^{1/4} = 16.0, 13.4$. This may be used to measure the E or γ_{s}.

A series of suspended nanorod pairs were polymerized to determine the minimum spacing. The width was changed by varying the laser power or the scanning speed. The length was set by the support distance. The results confirmed the linear relationship between the minimum spacing $2d_{\mathrm{m}}$ and $l^2/t^{3/2}$ as shown in Fig. 5. This provides useful method to

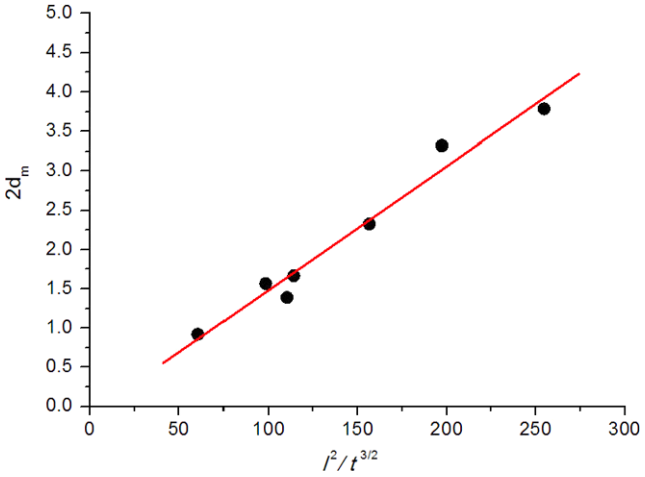

Fig. 5 The minimum spacing $2d_m$ as a function of $l^2/t^{3/2}$. The *line* is the fitting result

determine the minimum spacing to polymerize 3D nanostructures successfully.

4 Conclusion

In conclusion, the influence of the stiction on the minimum spacing of suspended nanorod pairs fabricated by TPP has been investigated. For suspended nanorods with feature size of around 200 nm, the allowable minimum spacing is almost determined by the stiction, which is in good agreement with the prediction based on a theoretical model calculating the adhesion lengths of rod pairs. This provides a way to calculate the minimum spacing of the nanorods and is helpful for the polymerization of three-dimensional functional nanostructures.

Acknowledgements The authors acknowledge financial support from the National Natural Science Foundation of China under Grant No. 10821062, and the National Basic Research Program of China under Grant Nos. 2006CB921601 and 2007CB307001.

References

1. K.S. Lee, R.H. Kim, D.Y. Yang, S.H. Park, Prog. Polym. Sci. **33**, 631 (2008)
2. S.H. Park, D.Y. Yang, K.S. Lee, Laser Photon. Rev. **3**, 1 (2009)
3. S. Maruo, J.T. Fourkas, Laser Photon. Rev. **2**, 100 (2008)
4. S. Kawata, H.B. Sun, T. Tanaka, K. Takada, Nature **412**, 697 (2001)
5. W.H. Zhou, S.M. Kuebler, K.L. Braun, T.Y. Yu, J.K. Cammack, C.K. Ober, J.W. Perry, S.R. Marder, Science **296**, 1106 (2002)
6. H.B. Sun, K. Tanaka, S. Kawata, Appl. Phys. Lett. **80**, 3673 (2002)
7. D.F. Tan, Y. Li, F.J. Qi, H. Yang, Q.H. Gong, X.Z. Dong, X.M. Duan, Appl. Phys. Lett. **90**, 071106 (2007)
8. L.J. Li, R.R. Gattass, E. Gershgoren, H. Hwang, J.T. Fourkas, Science **324**, 910 (2009)
9. K.K. Seet, V. Mizeikis, S. Juodkazis, H. Misawa, Appl. Phys. Lett. **88**, 221101 (2006)
10. T.S. Drakakis, G. Papadakis, K. Sambani, G. Filippidis, S. Georgiou, E. Gizeli, C. Fotakis, M. Farsari, Appl. Phys. Lett. **89**, 144108 (2006)
11. H.B. Sun, T. Suwa, K. Takada, R.P. Zaccaria, M.S. Kim, K.S. Lee, S. Kawata, Appl. Phys. Lett. **85**, 3708 (2004)
12. T.W. Lim, S.H. Park, D.Y. Yang, Microelectron. Eng. **77**, 382 (2005)
13. Y. Li, F.J. Qi, H. Yang, Q.H. Gong, X.Z. Dong, X.M. Duan, Nanotechnology **19**, 055303 (2008)
14. Y. Li, H.B. Cui, F.J. Qi, H. Yang, Q.H. Gong, Nanotechnology **19**, 373504 (2008)
15. A. Ovsianikov, J. Viertl, B. Chichkov, M. Oubaha, B. MacCraith, I. Sakellari, A. Giakoumaki, D. Gray, M. Vamvakaki, M. Farsari, C. Fotakis, ACS Nano **2**, 2257 (2008)
16. C.H. Mastrangelo, C.H. Hsu, J. Microelectromech. Syst. **2**, 33 (1993)
17. D.M. Wu, N. Fang, C. Sun, X. Zhang, Appl. Phys. Lett. **81**, 3963 (2002)
18. D.M. Wu, N. Fang, C. Sun, X. Zhang, Sens. Actuators A **128**, 109 (2006)
19. H.S. Hwang, J.T. Song, J. Micromech. Microeng. **17**, 245 (2007)