High aspect ratio submicrometer two-dimensional structures fabricated by one-photon absorption direct laser writing

Mai Trang Do, Qinggele Li, Thi Thanh Ngan Nguyen, Henri Benisty, Isabelle Ledoux-Rak, Ngoc Diep Lai

High aspect ratio submicrometer two-dimensional structures fabricated by one-photon absorption direct laser writing

Mai Trang Do · Qinggele Li · Thi Thanh Ngan Nguyen · Henri Benisty · Isabelle Ledoux-Rak · Ngoc Diep Lai

Abstract We have demonstrated a simple technique, based on a combination of a low cost one-photon elaboration method in a very low absorption regime (LOPA) and a tightly focusing optical system, to fabricate submicrometer 2D and 3D structures. A simple continuous-wave laser at 532 nm with only a few milliwatts allowed to fabricate high-aspect-ratio 2D pillars arrays in a commercial SU8 photoresist. The diameter of pillars is about 300 nm and the aspect ratio is as high as 7. This direct laser writing technique based on the LOPA approach is potentially a breakthrough: it is very simple, compact and low cost, while it allows to achieve the same results as those obtained by the two-photon absorption technique.

1 Introduction

Nano-fabrication based on far-field techniques has been studied since over two decades in the wake of microelectronics technology. Thanks to a high numerical aperture (NA) objective lens (OL), a coherent light beam for resist exposure can be tightly focused within a useful spot size approaching the diffraction limit, 0.61 λ/NA, where λ is the incident wavelength. Two different mechanisms, namely one-photon (OPA) and two-photon absorption (TPA) (Denk et al. 1990), can be used.

For thin film applications, the OPA excitation employing a simple and low cost laser in the UV range can be used (Rensch et al. 1989; Kuehne et al. 2009), and can somewhat extend the capability of traditional incoherent UV lithography. But for truly three-dimensional fabrication, the TPA technique is usually preferred (Cumpston et al. 1999; Kawata et al. 2001; Deubel et al. 2004; Haske et al. 2007; Farsari and Chichkov 2009). It demands an expensive pulsed infrared (λ = 800 nm) laser source (femto- or picosecond) to ensure a high peak intensity and very localized exposure.

However, it should be borne in mind that resist exposure is also per se a highly nonlinear process. Indeed, it is shown in Fig. 1 that there exists a dose threshold above which the polymerization process can be 100 % completed. An example of this fabrication condition is the use of interference technique with a low power continuous-wave laser to fabricate two- (2D) and three-dimensional (3D) structures (Campbell et al. 2000; Wang et al. 2003; Lai et al. 2005). Hence, the exposure localization by TPA is not essential to resolution. Rather, a genuine analysis reveals that the linear absorption is the true limiting factor of current OPA. But then, the absolute value of this absorption is commonly chosen as high (>100 cm^{-1}) in order to perform exposure efficiently with modest laser powers and quick scans.

In this work, we demonstrate a new way to benefit from the advantages of the OPA excitation technique, by using a simple, low-cost one-photon elaboration method operating in a low absorption regime, to achieve 3D fabrication as resolved and agile as in the case of TPA.

M. T. Do · Q. Li · T. T. N. Nguyen · I. Ledoux-Rak · N. D. Lai (✉)
Laboratoire de Photonique Quantique et Moléculaire, UMR 8537 CNRS, Institut D'Alembert, Ecole Normale Supérieure de Cachan, 94235 Cachan Cedex, France
e-mail: nlai@lpqm.ens-cachan.fr

T. T. N. Nguyen
Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

H. Benisty
Laboratoire Charles Fabry de l'Institut d'Optique, UMR 8501 CNRS, Université Paris-Sud, 91127 Palaiseau Cedex, France

2 Proposal of LOPA microscopy

In an optical microscope system, the propagation of light towards the focusing region is described by a nonlinear wave equation for the optical electric field (Gu 1996). For a high NA OL, the light intensity at the focusing region can reach $\approx 10^7$ W cm^{-2} with a milliwatt of a continuous-wave laser, and about 10^{12} W cm^{-2} with a milliwatt (average power) of a femto-second laser. However, the use of such microscope system with a continuous laser is not possible for 3D addressing until now. Indeed, in this simple estimation, we do not consider the absorption effect of the target material. In practice, continuous-wave lasers are preferred for OPA elaboration with the scope that the resist absorbs most photons entering in it. The light intensity then exponentially decreases along the propagation direction and for thick resists, fewer photons may reach the focus, or the actual intensity becomes quite weak. The actual intensity at the focusing spot depends on the absorption of the material at the excitation laser wavelength. Most OPA technique, however, employ a laser beam whose wavelength is close to the peak absorption band of the material in order to optimize the excitation efficiency. Therefore the intensity drops very quickly when it propagates through, say, a few microns of the material, and even vanishes at the focusing region if it is located deeply inside the material.

We therefore propose to use a new method in which the target material presents an ultralow absorption coefficient

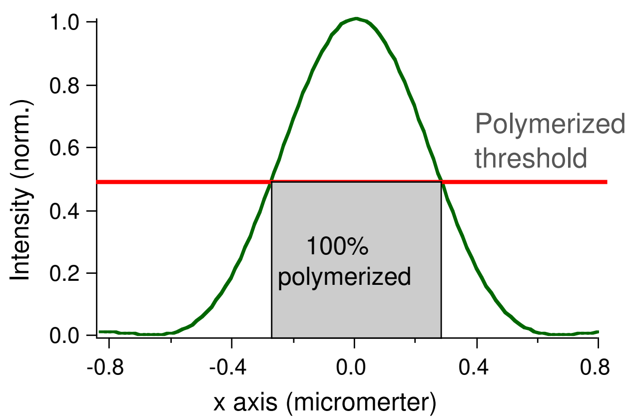

Fig. 1 Photon induced polymerization of negative resist. There exists a dosage threshold above it the polymerization process is 100 % completed

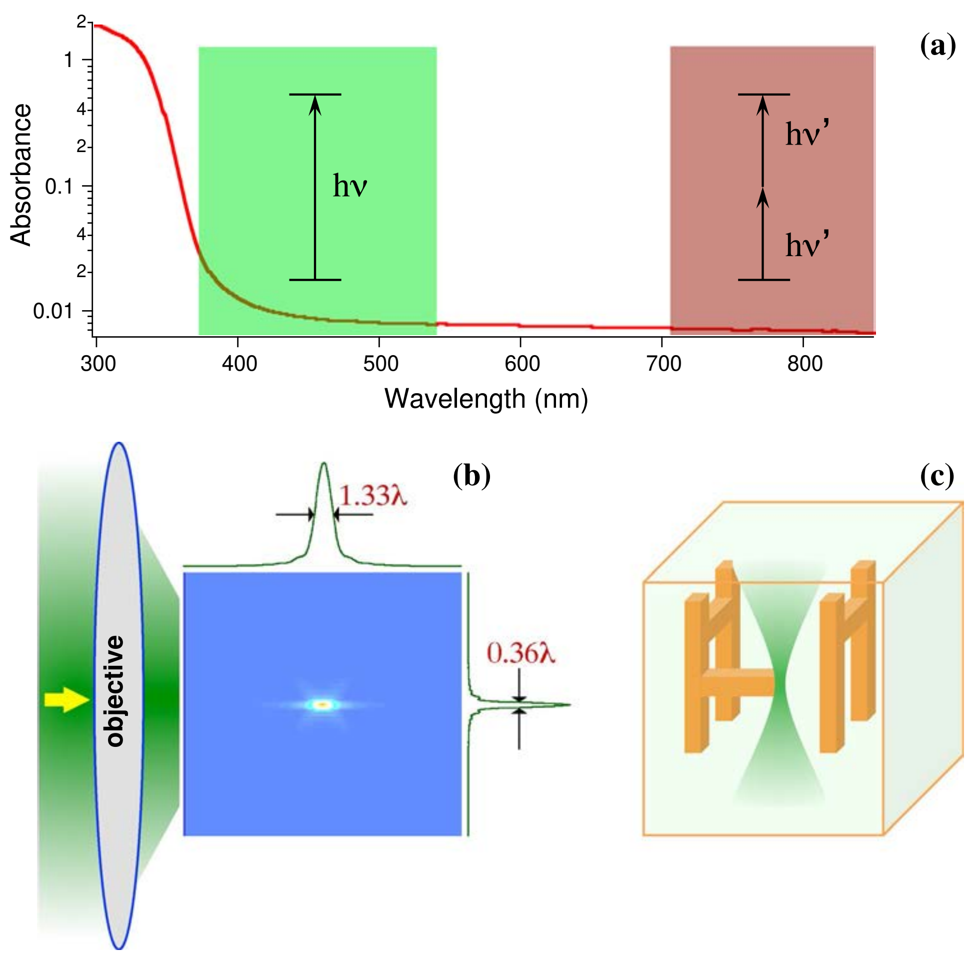

Fig. 2 **a** Absorption spectrum of a commercial SU8 photoresist, plotted in logarithmic scale, and illustration of low one-photon and two-photon absorption in corresponding ranges of wavelengths. **b** Tight focusing of a green laser beam into SU8 photoresist by using an objective lens of NA = 1.3. Simulation of intensity distribution at the focusing spot using vector Debye method, taking into account the material absorption ($\sigma = 723$ m^{-1}). The *two curves* represent the intensities distributions along transverse (*x*- or *y*-axis) and longitudinal (*z*-axis) directions, respectively, at a 10λ depth. **c** Illustration of the direct laser writing technique based on low absorption and high focusing effects

at the excitation laser wavelength. In this case, the light intensity distribution remains almost the same as in a transparent material, and the light intensity is increased by a ten million times at the focusing spot. Although the absorption is ultra weak, the effective photo-induced effect in focusing region is therefore comparable to that obtained at the maximum absorption wavelength with moderate intensity, as in the case of interference technique (Campbell et al. 2000; Wang et al. 2003; Lai et al. 2005). We apply this idea to fabricate submicrometer 2D and 3D photonic structures, and we denote this new technique LOPA (low one-photon absorption) DLW (direct laser writing).

3 Fabrication of submicrometer structures by LOPA based direct laser writing

To demonstrate the LOPA DLW technique, we consider a commercial photoresist, SU8 (Chem. Corp.), and a very popular continuous laser source emitting at 532 nm. SU8 is a standard photoresist commonly used for fabrication of 3D structures by the TPA base DLW. Figure 2a shows its absorption spectrum. We can see that the SU8 photoresist absorbs very weakly at the wavelength range around 500 nm. We have determined experimentally the absorption coefficient of SU8 at 532 nm to be about $\sigma = 723\ \mathrm{m}^{-1}$. We also investigated the point spread function of a high NA OL taking into account the absorption effect of the material in which the light propagates, by using the vector Debye approximation method (Richards and Wolf 1959). The most oblique part of the wavefront arriving at the focus indeed corresponds to quite longer oblique optical path in the resist for these large NA, about twice longer. Hence the need to check the point spread function under those conditions. Figure 2b shows the intensity distribution at the focusing region of an OL of NA = 1.3 (oil immersion), when a laser beam at 532 nm propagates in SU8 photoresist. In the presence of a very low absorption coefficient, the focal spot pattern and intensity remain almost the same within 300 μm depth inside the material. The typical size of the focal spot (diffraction limited for NA = 1.3) is $\simeq 0.4\ \lambda$ (transverse) and $\simeq 1.33\ \lambda$ (longitudinal), where $\lambda = 532$ nm. According to the polymerization threshold condition shown in Fig. 1, the light intensity must be high to compensate the low absorption effect. This condition can then only be satisfied at the focus of the high NA OL. Of course, the operating power should not be too high (just a few milliwatts is enough, as experimentally confirmed) to limit the 100 % polymerization within the focal spot. By moving this focal spot, as illustrated in Fig. 2c, we can then fabricate almost any 2D and 3D structures, especially those with modest fractional exposition.

For fabrication, a SU8 photoresist thin film is prepared following a standard process. First, the film is spin-coated on a thin glass substrate to obtain a thickness of about 2 μm. A continuous-wave laser at 532 nm with a moderate power is used as excitation laser source. Figure 3 shows an example of experimental results, imaged by a scanning electron microscope (SEM). The laser power is fixed at 2.5 mW and the laser beam is focused on the interface between the glass substrate and the SU8 photoresist. The sample is then moved in a horizontal plan for fabrication of a 2D structure. For each exposure, a solid structure, called voxel, corresponding to a focusing spot, is obtained. As seen in Fig. 3a, the voxel is represented in the form of an ellipsoid. The voxel size is quite small, 220 nm for transverse direction and 680 nm for longitudinal direction. An array of submicrometer (270 nm-diameter) voxels separated by 1 μm is clearly shown in Fig. 3b. This result is similar to that obtained by using TPA base DLW (Sun

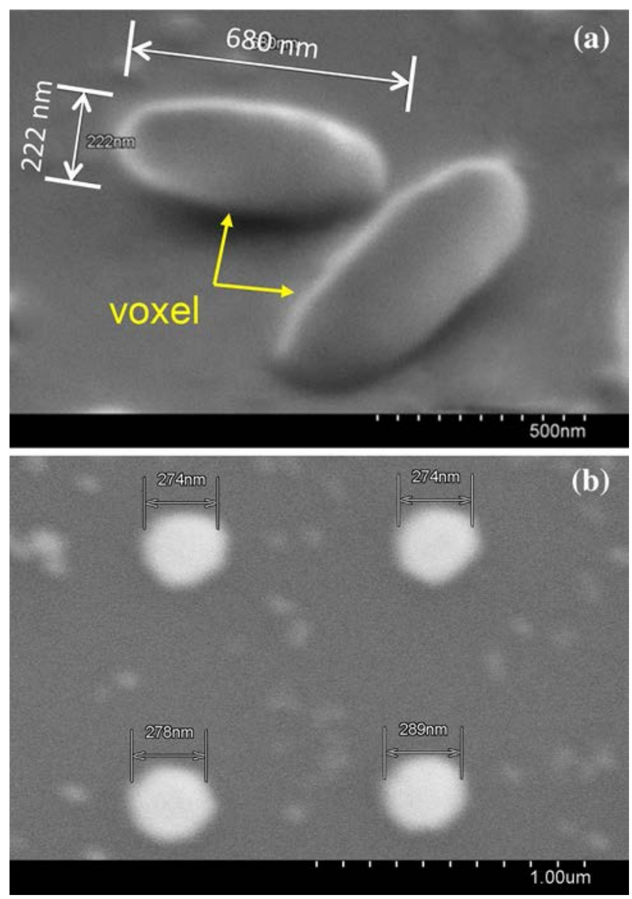

Fig. 3 Fabrication of submicrometer voxels using low one-photon absorption based direct laser writing technique. **a** SEM image of individual voxels (collapsed on glass substrate) fabricated by one exposure of 0.5 s with a modest power, 2.5 mW. **b** SEM image of a voxels array. The voxels are separated by 1 μm, and the voxel size is around 270 nm (exposure time 0.75 s)

et al. 2002). Note that, in the case of TPA fabrication, there exists a first threshold related to intensity, above it two photons are simultaneously absorbed, and a second threshold related to dose, above it complete photopolymerization effect is achieved. In our case of LOPA, there exists only one threshold related to dose, as shown in Fig. 1. However, thanks to a local high intensity of the focusing spot and a control of exposure time, the photopolymerization is only achieved completely in this region. The LOPA DLW therefore allows to create local sub-wavelength structures, and can be used to fabricate 2D and 3D structures.

We note that there are recently two reports about the fabrication of SU8 structures by using a continuous laser at 532 nm (Thiel et al. 2010; Malinauskas et al. 2011), in which the TPA mechanism was used to explain the polymerization of SU8 photoresist. However, according to our analysis, when working with a continuous-wave laser, the LOPA effect is the main reason for the successful fabrication of these reported structures. Indeed, a continuous laser emitting only a few milliwatts ($\approx 10^7$ W cm^{-2}) cannot induce a third-order nonlinear effect, i.e. TPA., which usually requires a high peak intensity such as that from a femtosecond laser ($\approx 10^{12}$ W cm^{-2}). If such a pico- or femtosecond laser at 532 nm wavelength (Malinauskas et al. 2011) can be used, TPA effect may occur, but its efficiency is however too weak as compared with that of the linear absorption even if the OPA coefficient is very low.

In order to fabricate 2D high-aspect-ratio (HAR) structure or pseudo 3D structure, we scan the focusing spot in the vertical direction, i.e. along the optical axis of the OL. Figure 4 shows the theoretical exposure calculation of a string of spots with variable pitch, aimed at forming a submicrometer HAR pillar. When the pitch between two exposures is large, e.g. 1 μm, the focal spots are clearly separated, equivalent to the fabrication of an array of voxels in 3D. When the distance between two exposures is <500 nm, a sub-wavelength continuous and smooth pillar is obtained. This pillar can be as high as the movement of the optical system allows. Note that, because of a linear absorption effect, the intensity (dose) is accumulated when two or multiple exposures are overlapped, resulting in a non uniform pillar between its center and its ends. For fabrication of uniform HAR pillar, the focusing spot should be scanned across the sample as shown in the right side of Fig. 4, where the different iso-intensity contours also suggest a substantial possibility to modulate the final structure diameter.

Figure 5 shows an array of 2D pillars fabricated by LOPA DLW technique. The laser power is kept at 2.5 mW, and the exposure time for each pillar is about 2 s. To form one pillar, the focal spot is scanned vertically across the SU8 film, for a scan range of 5 μm. Clearly, a 2D array of submicrometer pillars is obtained. The transverse size of each pillar is about 300 nm and the height is about 2 μm, as shown in inset of the Fig. 5b. The AR of this submicrometer pillar is about 7, which is comparable to that obtained by the TPA DLW technique (Lee et al. 2004). However, the LOPA DLW technique requires only a very weak power, typically from 2 to 5 mW, of a continuous laser at 532 nm, which presents a great advantage compared with TPA DLW. Note that, pillars with smaller diameter were also fabricated, but they all were collapsed and were washed out upon revelation due to the poor adhesion between SU8 and glass substrate. A promotion layer or another substrate,

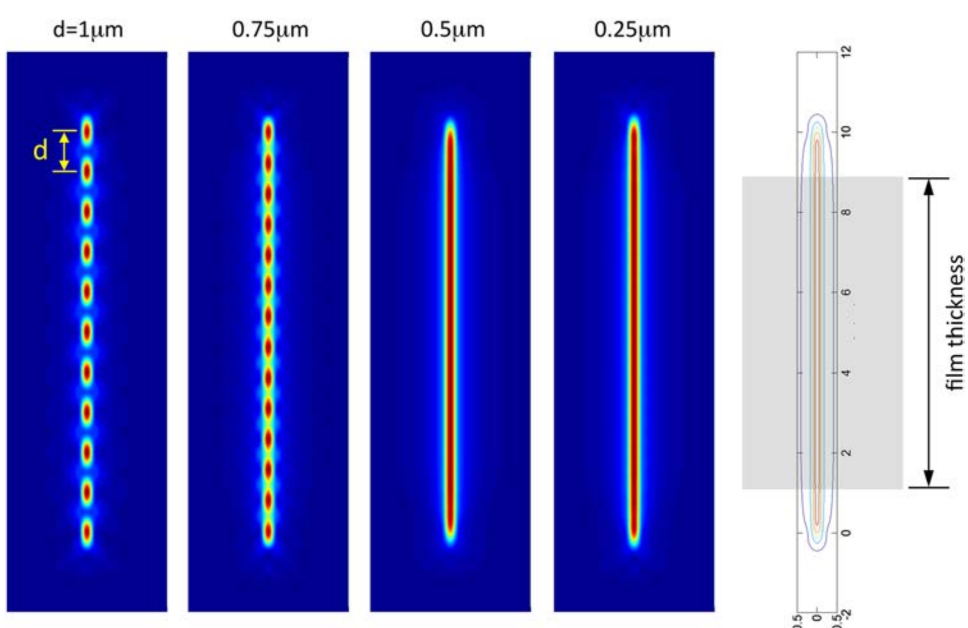

Fig. 4 Theoretical calculation of light pattern created by LOPA technique. The high aspect ratio submicrometer pillars are obtained by addressing multiple focus along the optical axis of the objective lens with a small enough pitch, d. A smooth pillar can be created with d < 500 nm. The uniform pillar can be obtained by scanning vertically the focal spot across the sample, and its size can be controlled by the exposure dose (time and power) as shown in the *right* figure. Simulation of intensity distribution at the focusing region is realized by the vector Debye method, including the absorption of the material ($\sigma = 723$ m^{-1})

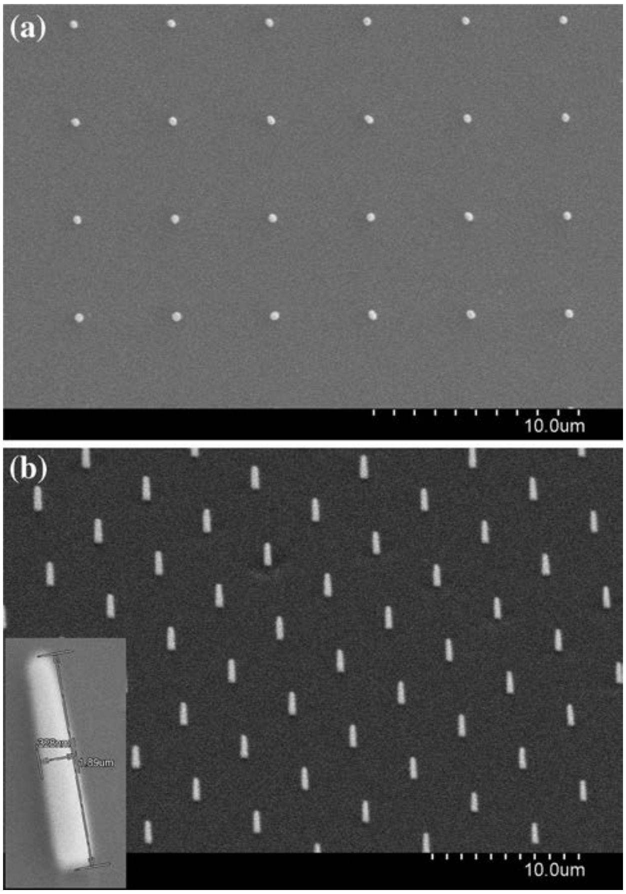

Fig. 5 SEM image of a 2D submicrometer pillars structure, obtained by scanning the focusing spot along the optical axis of the system. **a** *top view*; **b** *side view*. *Inset* shows a magnified image of a single pillar. The transverse and longitudinal sizes of one pillar are about 300 and 2,000 nm, respectively, resulting in a high aspect ratio of about 7. Structure was fabricated with a modest laser power of 2.5 mW, and an exposure time of 2 s per pillar

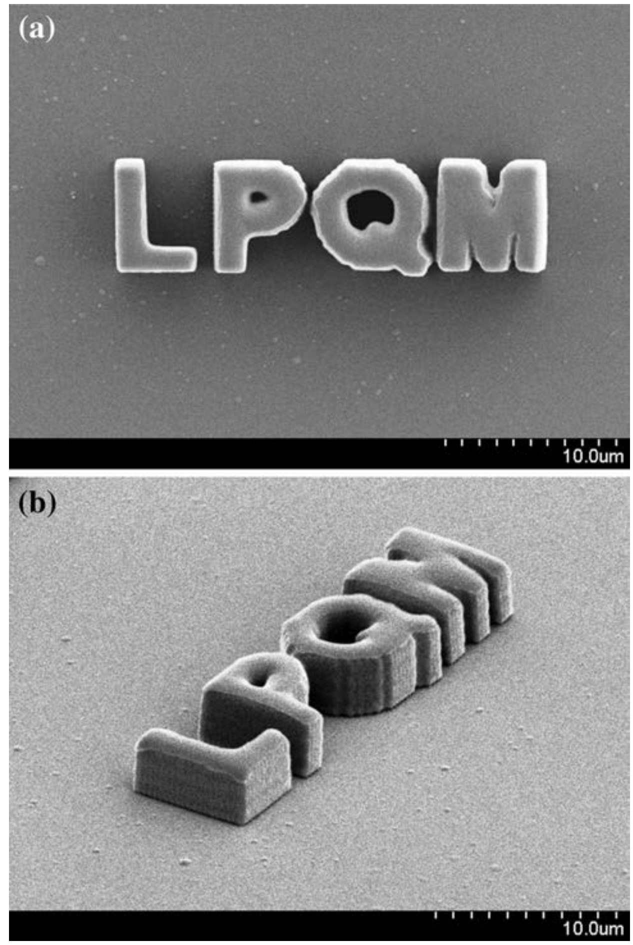

Fig. 6 SEM images of an arbitrary 2D submicrometer structure fabricated by the LOPA based direct laser writing technique. **a** *top view*; **b** *side view*. This structure was fabricated with a laser power of 2.3 mW

such as silicon wafer, could help improving the adhesion of the future nano-pillars fabricated by this method.

In order to demonstrate the versatile ability of the LOPA DLW technique, we fabricated different arbitrary 3D structures. Figure 6 shows a desired structure (letters: LPQM) fabricated with a power of 2.3 mW. The structures are fabricated by scanning the focusing spot in *x*, *y* and *z* axes with a pre-designed pattern. The height of these characters is 7 μm and the width is in between 1.5 and 2 μm, depending on the letter and on the position of each letter. Note that, in this attempt, the width of characters is still thick because of the assembling of multiple walls, i.e. multiple scans in *z* direction for different *x*, *y* positions. We expect a very HAR 2D structures by using a single wall for the formation of these characters, because the adhesion and the rigidity of these structures are much better than those of a single pillar.

Finally, we emphasize that this LOPA technique can be applied for almost any 3D optical addressing. The LOPA DLW could produce any 3D photonic structures, similar to those created by TPA DLW. Furthermore, the use of a shorter laser wavelength (532 versus 800 nm) allows to reduce the voxel size, which is related to the diffraction limit of the optical system. The LOPA microscopy could be used to image submicrometer structures in 3D by using a very modest laser power, which allows avoiding the destruction of studied materials, in particular in biology. Other applications, such 3D data storage, can be also envisaged, because the LOPA allows to minimize the optical system by using a very simple diode laser at suitable wavelengths.

4 Conclusion

We have developed a simple and low cost fabrication technique, based on one-photon absorption phenomena in a weakly absorbing photoresist. This novel technique enables the fabrication of submicrometer high aspect ratio 2D structures. The LOPA DLW requires a very low excitation power, several milliwatts of a continuous laser, but allows to achieve the same results as those obtained by TPA DLW. The LOPA approach opens a new and inexpensive way to address 3D structures, namely 3D fluorescence imaging and 3D fabrication.

Acknowledgments This work has been supported by the "Laboratoire d'Excellence NanoSaclay", in the framework of the project "ONE-FAB-3D", and by the "Triangle de la Physique", in the framework of the project "PUTTON". Special thanks are devoted to J.-F. Roch for various equipment helps. M. T. Do and T. T. N. Nguyen acknowledge the fellowship from the Vietnam International Education Development "322 program" and Q. Li acknowledges the fellowship from the China Scholarship Council.

References

Campbell M, Sharp DN, Harrison MT, Denning RG, Turberfield AJ (2000) Fabrication of photonic crystals for the visible spectrum by holographic lithography. Nature 404:53–56

Cumpston BH,Ananthavel SP, Barlow S, Dyer DL, Ehrlich JE, Erskine LL, Heikal AA, Kuebler SM, Lee IYS, McCord-Maughon D, Qin J, Röckel H, Rumi M, Wu XL, Marder SR, Perry JW (1999) Two-photon polymerization initiators for three-dimensional optical data storage and microfabrication. Nature 398:51– 54

Denk W, Strickler JH, Webb WW (1990) Two-photon laser scanning fluorescence microscopy. Science 248:73–76

Deubel M, Von Freymann G, Wegener M, Pereira S, Busch K, Soukoulis CM (2004) Direct laser writing of three-dimensional photonic-crystal templates for telecommunications. Nat Mater 3:444–447

Rensch C, Hell S, Schickfus MV, Hunklinger S (1989) Laser scanner for direct writing lithography. Appl Opt 28:3754–3758

Farsari M, Chichkov BN (2009) Materials processing: two-photon fabrication. Nat Photonics 3:450–452

Gu M (1996) Principles of three-dimensional imaging in confocal microscopes. World Scientific Publishing

Haske W, Chen VW, Hales JM, Dong W, Barlow S, Marder SR, Perry JW (2007) 65 nm feature sizes using visible wavelength 3-D multiphoton lithography. Opt Express 15:3426–3436

Kuehne AJC, Elfstrom D, Mackintosh AR, Kanibolotsky AL, Guilhabert B, Gu E, Perepichka IF, Skabara PJ, Dawson MD, Pethrick RA (2009) Direct laser writing of nanosized oligofluorene truxenes in UV-transparent photoresist microstructures. Adv Mater 21:781–785

Kawata S, Sun H-B, Tanaka T, Takada K (2001) Finer features for functional microdevices. Nature 412:697–698

Lai ND, Liang WP, Lin JH, Hsu CC, Lin CH (2005) Fabrication of two- and three-dimensional periodic structures by multi-exposure of two-beam interference technique. Opt Express 13:9605–9611

Lee C-H, Chang T-W, Lee K-L, Lin J-Y, Wang J (2004) Fabricating high-aspect-ratio sub-diffraction-limit structures on silicon with two-photon photopolymerization and reactive ion etching. Appl Phys A 79:2027–2031

Malinauskas M, Danileviius P, Juodkazis S (2011) Three-dimensional micro-/nano-structuring via direct write polymerization with picosecond laser pulses. Opt Express 19:5602–5610

Richards B, Wolf E (1959) Electromagnetic diffraction in optical systems. II. Structure of the image field in an aplanatic system. Proc Roy Soc A 253:358–379

Sun H-B, Tanaka T, Kawata S (2002) Three-dimensional focal spots related to two-photon excitation. Appl Phys Lett 80:3673–3675

Thiel M, Fischer J, Freymann GV, Wegener M (2010) Direct laser writing of three-dimensional submicron structures using a continuous-wave laser at 532 nm. Appl Phys Lett 97:221102

Wang X, Xu JF, Su HM, Zeng ZH, Chen YL, Wang HZ, Pang YK, Tam WY (2003) Three-dimensional photonic crystals fabricated by visible light holographic lithography. Appl Phys Lett 82:2212–2214