Fabrication and transfer printing of periodic Pt nanonetwork gratings

Cite as: AIP Advances 10, 035214 (2020); https://doi.org/10.1063/1.5143772
Submitted: 08 January 2020 . Accepted: 28 February 2020 . Published Online: 13 March 2020

Miao Yu, Li Li, Xiaomin Wu, Yingying Song, Jinyun Liu, and Zuobin Wang
Fabrication and transfer printing of periodic Pt nanonetwork gratings

Cite as: AIP Advances 10, 035214 (2020); doi: 10.1063/1.5143772
Submitted: 8 January 2020 • Accepted: 28 February 2020 •
Published Online: 13 March 2020

Miao Yu, Li Li, Xiaomin Wu, Yingying Song, Jinyun Liu, and Zuobin Wang

AFFILIATIONS
1 Ministry of Education Key Laboratory for Cross-Scale Micro and Nano Manufacturing, Changchun University of Science and Technology, Changchun 130022, China
2 International Research Centre for Nano Handling and Manufacturing of China, Changchun University of Science and Technology, Changchun 130022, China
3 College of Artificial Intelligence, North China University of Science and Technology, Tangshan 063210, China
4 IRAC and JR3CN, University of Bedfordshire, Luton LU1 3JU, United Kingdom

ABSTRACT
Metal nanonetworks are applied in various applications, such as biomedicine, bionic materials, optical materials, and new energy materials. Here, periodic variable-sized Pt nanonetwork gratings (PtNGs) are fabricated on the surface of a Pt/Si substrate with single pulse two-beam direct laser interference lithography. The fabricated PtNGs are transferred onto the surface of a glass substrate with polymethyl methacrylate as the transfer mediator. Exposure with different film thicknesses, contrasts, and intensity distributions of the laser interference spot is analyzed, and the formation of nanopatterns is explained. Results show that with the change in the thicknesses of the Pt film, the exposed structures present Pt nanoparticles (PtNPs), Pt gratings, and PtNGs. The morphology and the feature size of the PtNGs are influenced by intensity distributions and the contrast of the laser interference spot significantly.

© 2020 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5143772

I. INTRODUCTION
Metal nanonetworks are applied in various applications, such as biomedicine, bionic materials, optical materials, and new energy materials. Transparent electrodes, noble metal catalysts, biomedical materials, and biosensors, due to their optical, structural, mechanical, and catalytic properties. These properties are sensitively influenced by the structural parameters of the nanonetworks. For example, the size and shape of noble metal catalysts are closely related to their catalytic performances and the material cost. For transparent electrodes, the structural parameters of well-designed networks can balance light transmission and electrical conductivity. In biomedical materials, compared to the conventional metal surface, metal and metallic oxide nanonetworks can improve the growth of the human cell in vitro and in vivo. Hence, a high-throughput method for preparing metal nanonetworks with highly controllable structural parameters will promote research and applications in many fields.

Various methods have been developed to fabricate metal nanonetworks, such as the chemical method, electron beam lithography, and electrospinning process. Among them, the chemical method is simple. However, the prepared nanonetworks are disordered, the process is uncontrollable, and the chemical reagents will pollute the environment. With regard to electron beam lithography, structures are ordered and the feature size can be lessened into several nanometers, but the method is too slow and preparation should be carried out on a flat and smooth substrate. Electrospinning is a powerful method for the fabrication of polymers, metals, and metallic oxide nanonetworks, it can be used in mass production over large areas, but the nanonetworks are irregular, and it has restrictions on the type of the material.
In this paper, we show the ability of two-beam laser interference lithography (LIL) with a single pulse to produce Pt nanonetwork gratings (PtNGs) on the surface of a Pt/Si substrate with controllable parameters. In addition, the PtNGs can be transferred onto the surface of a glass substrate using polymethyl methacrylate (PMMA) as the mediator. Exposure experiments with different Pt thicknesses, contrasts, and intensity distributions are performed. With the different thicknesses of the Pt film, various nanostructures can be obtained including Pt nanoparticles (PtNPs), Pt gratings (PtGs), and PtNGs. The contrasts and the Gaussian intensity distributions of the laser interference spot will lead to variations in the morphology and the feature size of the PtNGs. By spin coating and lift-off PMMA, the PtGs are transferred from silicon to glass. This preparation method is high-throughput with controllable structure parameters and they can be transferred onto arbitrary substrates. It has important application prospects in broad fields.

II. EXPERIMENTAL SECTION

A. Laser interference lithography

PtNGs were structured by two-beam direct LIL with a high power pulsed Nd:YAG nanosecond laser (Innolas Splitlight 2000) at the wavelength of 1064 nm and pulse duration of 7 ns. The spot diameter of the laser was about 6 mm. P-type polished Si (100) substrates were cleaned three times of each type solution using acetone and ethanol rinsing in an ultrasonic cleaner, and each ultrasonic process took 5 min. The Pt film, as the superlens, was deposited on the surface of the Si substrate with different thicknesses ranging from 5 nm to 60 nm using an ion sputtering coater (Q150T, Quorum Technologies), the surface of the film is uniform. The thickness of the film was detected and controlled by a film thickness monitor. The schematic of the two-beam LIL system is shown in Fig. 1(a). One laser beam was split into two beams by a beam splitter with the same intensity. The split beams were reflected to one point by mirrors and realized the interference pattern at one point. The incident angles were varied from 3.4° to 7.6°. The polarization angles were 0° and 90°. The periods were varied with the incident angles. The voltages were varied from 500 V to 620 V and single laser energies were varied from 30 mJ to 160 mJ. The energy was detected by using a digital laser power meter. The laser power was controlled by altering the voltage and half-wave plate, and the polarization angles were altered by polarizers. A scanning electron microscope (SEM, QUANTA FEG 250) was used to take the images and all the experiments were performed in a clean-room environment. Figure 1(b) shows the SEM image of PtNGs and the enlarged image, and the embedded image on the left-hand side of (b) is the simulated intensity distribution of two-beam laser interference by MATLAB. The interference patterns were structured directly by two-beam LIL with a single pulse. The SEM image of the detailed fracture surface of the exposed PtNGs is shown in Fig. 1(c).

B. Mediated nanotransfer printing

The fabricated PtNGs are transferred onto the surface of a glass substrate by the mediated nanotransfer printing technique. In the transfer process, PMMA was used as the transfer mediator material. As shown in Fig. 1(d), the Pt film was deposited on the surface of the Si substrate, and the PtNGs were structured by two-beam LIL. PMMA (AR-P 672.03, Mw = 950 K, 3 wt.%)) was spin coated onto the

FIG. 1. (a) Schematic of the two-beam LIL system. (b) SEM image of PtNGs and the enlarged image; the embedded image on the left-hand side of (b) is the simulated intensity distribution of two-beam laser interference. (c) SEM image of the detailed fracture surface of PtNGs. (d) Processing step diagram of exposure and transfer printing of periodic PtNGs with the PMMA mediator.
surface of the fabricated sample at 2000 r/s for 30 s. The thickness of the PMMA film was about 170 nm. The sample was baked in a drying oven at 25 °C for 60 min and on a hot plate at 115 °C for 15 min, and the thin PMMA film embedding the PtNGs was obtained. Then, the sample was put into a beaker containing KOH solution (5.6 g KOH in 100 ml water) and immersed in an oil bath pan at a constant temperature of 80 °C. The immersion time depends on the separation speed of the Pt film. The sample with the separated film was put into a container filled with water, and the separated film was peeled off and fell onto the surface of the glass substrate. For the transferred PtNGs, the PMMA film was on the top of the gratings. In order to obtain the PtNGs, the transferred sample was
put in a plasma cleaner for 35 min and the PMMA film was wiped off. Thus, the PtNGs could be successfully transferred onto the target substrate.

III. RESULTS AND DISCUSSION

Exposure on the Pt/Si substrate with different film thicknesses was performed. As shown in Figs. 2(a)–2(c), with the increase of the thickness of the Pt film, the structures show differences. With the change in thicknesses of the Pt film, the exposed structures present PtNPs, PtGs, and PtNGs, and the thickness of the Pt film is 5–30 nm, 20–40 nm, and 30–60 nm, respectively. Under the above conditions, with a higher energy of the exposure laser, Si gratings could be obtained as shown in Fig. 2(d).

In this work, the formation of nanopatterns is realized by two-beam direct LIL. Due to the interaction between the high power laser pulse and the metallic film, when the absorbed energy of the exposed regions is higher enough to reach the threshold value of the target material, structures are formed after melting and solidification. As shown in Figs. 3(a)–3(c), the Pt film is exposed as nanonetworks, the morphology of the nanonetworks can be explained by the dewetting process of the film. The Pt film is melted and dewetted into uniform nanonetworks at a lower temperature of LIL, and then solidified when the temperature decreased. In Fig. 3(b), the formation of the PtNPs can be explained by Ostwald ripening. For the exposure on the surface of the Pt/Si substrate, the Pt slab layer can be used as the superlens in LIL, which can significantly enhance the energy around the interface, we denote it as superlens-enhanced LIL (SELIL). The dewetted film presents as sub-wavelength patterns owing to the existence of the surface plasma polaritons (SPPs). Rayleigh–Taylor instability exists in the process of SELIL, and due to the diamagnetic drift of the hot plasma in the magnetic field, there will be charge accumulation between the peak and trough of the disturbance when the disturbance occurs on the boundary between the plasma and the vacuum. The electric field generated by this accumulation makes the trough deeper and the peak higher. Plasma surface fluctuations intensify. This makes the grooves deeper and the wave crest higher. It can be seen from the patterns, as shown in Fig. 2(d). The PtNGs were formed during the exposure process, the heat of the Pt film was absorbed by Si and reached the melting point, and higher energy makes Si gratings exposed. The advantage of the Pt/Si substrate is that it enables the ability of LIL to get Pt nanopatterns accompanied with Si gratings on the surface of a high reflectivity substrate easily and efficiently. At a higher laser intensity, Pt nanowires, PtNPs, and Si gratings are formed. Moreover, the nanopatterns can be realized by single pulse exposure that can avoid the influence of an unstable laser source. PtNPs can be used for the application of photocatalysis and the Si gratings can be used as the mask of the imprinting and also as the substrate of dual-layer metal gratings.

![FIG. 2](image1.png)

**FIG. 2.** [(a)–(f)] SEM images of PtNGs distributed in the Gaussian spot of two-beam LIL. (g) Schematic diagram of the Gaussian spot of two-beam LIL and the regions corresponding to the SEM images from (a) to (f). (h) Curves of the structure size of nanonetworks and gratings varied with the laser energy distribution.
Furthermore, we studied the effect of the contrast of the laser interference pattern on the feature of the exposed structures. The contrast is defined as $C = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}}$, where $I_{\text{max}}$ is the maximum intensity and $I_{\text{min}}$ is the minimum intensity of the laser interference spot. The schematic of different contrasts of the laser interference spot is shown in Fig. 3(c). In Fig. 3(c), wave a has the lowest and wave d has the highest contrast orderly. For the line of melting, the intensity is lower than the threshold of the Pt film, and the Pt film will not be exposed. For the intensity between the melting and the boiling, the Pt film tunes to nanonetworks and nanoparticles. For the intensity higher than the boiling, the Pt film will be fully vaporized. The effect of the contrast can be seen in Figs. 3(a)–3(d). For wave a, with the lowest contrast in Fig. 3(e), the Pt film is fully melted and dewetted into Pt nanonetworks as shown in Fig. 3(a). In Fig. 3(b), with the contrast of wave b, Pt nanonetworks are observed in the lower intensity region, while in the higher intensity region, PtNPs exist and a partial Pt film is vaporized. Corresponding to wave c, Pt nanonetworks and PtGs are obtained in the higher and lower intensity regions as shown in Fig. 3(c). For wave d, as shown in Fig. 3(d), the Pt film is vaporized in the intensity region that is higher than the boiling line and the Pt film still exists in the lower region.

As discussed above, the appropriate film thickness and energy control contribute to the formation of the PtNGs. For PtNGs, based on the mechanism of structure formation, the energy difference of a Gaussian intensity distribution on the interference point will lead to the dimension variations of the Pt nanonetworks, gratings, and even the size of the holes of the networks. It can be observed from Figs. 4(a)–4(f) that the representative SEM images of periodic nanonetworks and gratings with different dimensions are presented corresponding to different regions of the laser interference spot, and the feature sizes of Pt nanonetworks and gratings are changed with laser energy. The regions of two-beam LIL corresponding to the SEM images with different feature sizes are labeled in Fig. 4(g). It can be observed in Figs. 4(a)–4(f) that the widths of the Pt nanonetworks are decreased with the increase of laser intensity, while the widths of the PtGs are increased. It can also be observed that the diameters of single Pt nanonetworks are decreased in the higher laser intensity region but increased in the lower region. Figure 4(h) shows the widths of nanonetworks and gratings fabricated by SELIL with different laser intensities. Finally, nanotransfer printing experiments were performed and SEM images of the transferred PtNGs are shown in Fig. 5. With this method, the fabricated PtNGs can be easily transferred onto the surface of any substrate without the restrictions of stacking folds, shapes, and materials.

IV. CONCLUSION

In this work, periodic variable-sized Pt nanonetworks were fabricated via two-beam SELIL with a single pulse and transferred onto the surface of a glass substrate. The formation of nanopatterns was explained by the theories of the dewetting process, Ostwald ripening, and Rayleigh–Taylor instability during the thermal transfer. The morphology and the feature size of the PtNGs were dependent on the thickness of the Pt film, contrast, and intensity distribution of the laser interference spot. The fabricated PtNGs can be transferred onto the surface of any substrate without the restrictions of stacking folds, shapes, and materials, which can be applied in optoelectronics, electronics, and biomedicine.

ACKNOWLEDGMENTS

This work was supported by the National Key R&D Program of China (Grant No. 2016YFE0112100), EU H2020 Program (FabSurfWAR, No. 644971; NanoStencil, No. 767285), National Natural Science Foundation Program of China (Grant No. 11504030), Jilin Provincial Science and Technology Program (Grant Nos. 20160623002TC, 20180414002GH, 20180414081GH, 20180520203JH, and 20190702002GH), and “111” Project of China (Grant No. D17017).

REFERENCES

1. M. Nafari and J. M. Jornet, IEEE Access 5, 6389 (2017).
2. C. F. Guo, T. Sun, Q. Liu, Z. Suo, and Z. Ren, Nat. Commun. 5, 3121 (2014).
3. K. Yu, B. Park, G. Kim, C.-H. Kim, S. Park, J. Kim, S. Jung, S. Jeong, S. Kwon, and H. Kang, Proc. Natl. Acad. Sci. U. S. A. 113, 14261 (2016).
4. W. C. Records, Y. Yoon, J. F. Ohmura, N. Chanut, and A. M. Belcher, Nano Energy 58, 167 (2019).
5. H. Begum, M. S. Ahmed, and S. Jeon, ACS Appl. Mater. Interfaces 9, 39303 (2017).
6. E. Scavetta, A. Mignani, D. Tonelli, G. Impellizzeri, L. Romano, C. Bongiorno, B. Fraboni, and M. Grimaldi, *Electrochem. Commun.* **30**, 83 (2013).
7. P. V. Kamat, *J. Phys. Chem. B* **106**, 7729 (2002).
8. D. Beydoun, R. Amal, G. Low, and S. McEvoy, *J. Nanopart. Res.* **1**, 439 (1999).
9. J. N. Tiwari, R. N. Tiwari, and K. S. Kim, *Prog. Mater. Sci.* **57**, 724 (2012).
10. S. Santra, A. Das, N. Das, and K. K. Chattopadhyay, *Bull. Mater. Sci.* **41**, 128 (2018).
11. C.-Y. Chiang, S.-H. Chiou, W.-E. Yang, M.-L. Hsu, M.-C. Yung, M.-L. Tsai, L.-K. Chen, and H.-H. Huang, *Dent. Mater.* **25**, 1022 (2009).
12. W.-E. Yang, M.-Y. Lan, S.-W. Lee, J.-K. Chang, and H.-H. Huang, *Nanoscale Res. Lett.* **10**, 167 (2015).
13. I. Jung, H. Y. Jang, I. Moon, and S. Park, *Nanoscale* **6**, 6482 (2014).
14. M. Salvato, R. Baghdadi, C. Cirillo, S. Prischepa, A. Dolgty, V. Bondarenko, F. Lombardi, and C. Attanasio, *Nanotechnology* **28**, 465301 (2017).
15. J. Ahn, C. Ahn, S. Jeon, and J. Park, *Appl. Sci.* **9**, 13990 (2019).
16. M. Arvand and H. A. Samie, *Ionics* **24**, 1813 (2018).
17. R. Yoshikawa, M. Tenjimbayashi, T. Matsuhashi, K. Manabe, L. Magagnin, Y. Momma, and S. Shiratori, *ACS Appl. Nano Mater.* **1**, 860 (2018).
18. M. Arvand and H. A. Samie, *Ionics* **24**, 1813 (2018).
19. R. Yoshikawa, M. Tenjimbayashi, T. Matsuhashi, K. Manabe, L. Magagnin, Y. Momma, and S. Shiratori, *ACS Appl. Nano Mater.* **1**, 860 (2018).
20. B. Zou, Y. Guo, N. Shen, A. Xiao, M. Li, L. Zhu, P. Wan, and X. Sun, *Sensors* **17**, 2954 (2017).

10. D. Wang, Z. Wang, Z. Zhang, Y. Yue, D. Li, and C. Maple, *Appl. Surf. Sci.* **282**, 67 (2013).
21. A. Lasagni and B. Menéndez-Ormaza, *Adv. Eng. Mater.* **12**, 54 (2010).
22. C. Lu and R. Lipson, *Lasers Photonics Rev.* **4**, 568 (2010).
23. L. Jiao, B. Fan, X. Xian, Z. Wu, J. Zhang, and Z. Liu, *J. Am. Chem. Soc.* **130**, 12612 (2008).
24. L. W. Schwartz, R. V. Roy, R. R. Eley, and S. Petrasch, *J. Colloid Interface Sci.* **234**, 363 (2001).
25. J. Ahn, C. Ahn, S. Jeon, and J. Park, *Appl. Sci.* **9**, 13990 (2019).
26. B. Zou, Y. Guo, N. Shen, A. Xiao, M. Li, L. Zhu, P. Wan, and X. Sun, *Sensors* **17**, 2954 (2017).