Journal Name RSCPublishing

ARTICLE

Study on morphology and shape control of volcano-shaped patterned sapphire substrates fabricated by imprinting and wet etching

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012, Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Volcano-shaped patterned sapphire substrate (VPSS) was fabricated by imprinting lithography and wet etching to enhance the light output of the device. The hexagonal arrangement patterns with different orientation to the crystal one were imprinted to the sapphire substrate. As the etching time increased, the pattern with a crater in its center was changed from a truncated triangular pyramid to a truncated hexagonal pyramid with the symmetrical sidewall facets. Small craters surrounded by three $\{1\bar{1}08\}$ facets 3-fold or 6-fold symmetrically appeared at the boundaries with neighbor pyramids. The mechanism of sapphire wet etching for VPSS was correlated to thermodynamics limits and SiO_2 mask pattern. The as-fabricated VPSS with slanted angle 34.3° and 69.9° was supposed to enhance the internal quantum efficiency (IQE) and light extraction efficiency (LEE) of GaN-based LED.

Introduction

Patterned sapphire substrate (PSS) has been widely used to improve the light output power in GaN-based light emitting diode (LED) since 2000 [1,2]. The shape of pattern, usually inverted pyramid [3,4], pyramid [5] or hemispheroid [6], affects the internal quantum efficiency (IQE) and light extraction efficiency (LEE) of LED to some extent. It was reported that the LEE of a GaN-based LED grown on a volcano-shaped patterned sapphire substrate (VPSS) was better than that grown on a hemispherical PSS due to more faceted sidewall and large lateral overgrowth area[7]. Formerly, photolithography [7], focused ion beam (FIB) and colloidal monolayer templating strategy [8] were used to fabricate VPSS. However, the morphology of the pattern is easily affected by fabrication process of conventional photolithography under sub-micron scale. FIB is the most precise but also the most expensive and time-consuming method, which is unsuitable for commercial manufacturing. The process of colloidal monolayer templating strategy is complicated and difficult to control, which makes it difficult to apply in large scale wafer [8]. Therefore it is of great significance to seek a low-cost, high efficiency method for large scale VPSS manufacturing.

At present, dry and/or wet etchings are the main methods to transfer the PSS pattern onto the sapphire substrate. Sapphire surface will be damaged due to the ion bombardment during dry etching, which can be avoided by wet etching. The mixture solution of H_2SO_4 and H_3PO_4 are generally used for wet etching sapphire substrate at the temperature above 200 ^oC. The reaction products from H_3PO_4 and sapphire are solvable, while those from H_2SO_4 and sapphire are insolvable [4,9,10]. Aota et al thought that the step flow reaction with/without the impurities might control the pattern shape of PSS [9]. The insolvable products would block the step, which led to reducing down of the step flow reaction. H_3PO_4 was beneficial to the step flow reaction since the products were solvable. It indicates that the etching facets are not only determined by surface atoms and bond structure for a certain crystallographic plane [11]. Furthermore, the different etching facets were also controlled by the rectangular masks with different orientations[12]. It seems difficult to obtain a specific crystallographic plane by wet etching using H_3PO_4 and H_2SO_4. On the other hand, the slant angle of the etching facet is one of the most critical factors for the improvement on LEE [7] and IQE [13] of LEDs. Many etching facets are reported on different crystallographic planes under different etching conditions, including R-plane and R-like planes [3,9,13], N-plane and N-like planes [4,5,9] and some other planes [14,15,16]. The higher Miller-Bravais indexes of the etching facets obtained by above researches indicate the complications of the wet etching and crystal plane calibration. These complications make it difficult to control the shape of VPSS.

The purpose of PSS is to utilize slanted planes to scatter the light and reduce internal reflection, therefore improving light extraction. It is believed that slanted angle and fill factor are important parameters.[17] Illumination intensity will reach its maximum when the slanted angle is around 33° [17,18]. Besides, light extraction can be enhanced monotonously with increasing fill factor because of the increasing of PSS area. On the other hand, the crystal quality is efficiently improved by reducing the threading dislocation and residual strain in the epitaxial GaN layer when the PSS is applied. However, some results have shown that GaN nucleation just happened on C-plane rather than the pattern surface using the cone-shaped PSS fabricated by dry etching. [19,20] In recent researches, growth mechanism was totally different for PSS fabricated by wet etching. Truncated pyramid PSS with GaN buffer gathering near its ridges showed the 3D growth mechanism of GaN.[21] To sum up, the optimized pattern of the PSS is a critical factor for the enhancement of light output power in GaN-base LED.

In this work, a novel method based on imprinting lithography and wet etching is presented to fabricate VPSS. The mechanism of wet etching is investigated, and plane indexes of these exposure etching facets in VPSS are determined by a simple method.

Experiment

The VPSS was prepared using imprinting lithography and wet etching. The process is shown in Fig. 1. Commercial cone-shaped PSS, of which the period is 3 μm and the diameter is 2.2 μm, was employed as imprinting stamp. Anti-adhesion treatment was implemented to PSS by spin-coating fluorinated silane on it. 100-nm-thick SiO_2 layer was deposited on the sapphire wafer at 250 ℃ by plasma-enhanced chemical vapor deposition (PECVD), followed by spin-coating resist on the surface. Two-step simultaneously thermal and ultraviolet curing (STU) imprint process was applied by Eitre® 3 Nanoimprinting instrument. The resist accumulated at the edge of the pattern because it was too thin to fill the whole pattern in the intermediate polymer stamp (IPS). When residual resist was removed by O_2 plasma and then SiO_2 was etched by reactive ion etching (RIE) with CHF_3 and O_2, a ring-array pattern of SiO_2 layer was obtained on the sapphire. The sapphire substrate was then wet etched in a mixture of H_2SO_4 (98%) and H_3PO_4 (85%) (H_2SO_4:H_3PO_4 = 3:1, volume ratio) solution at the etching temperatures of 230, 250, 270 and 300 ℃ from 5 to 25 min. Finally, SiO_2 layer was removed by BOE (NH_4F: HF=7:1). The surface of the VPSS was carefully studied by atomic force microscope (AFM, Bruker Dimension Icon with ScanAsyst) and scanning electron microscope (SEM, Nova Nano SEM 430).

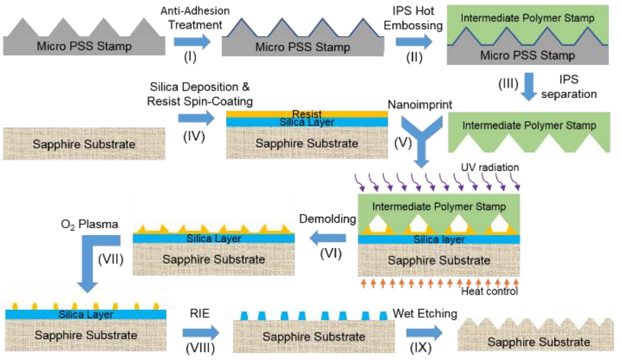

Fig.1. The flow diagram of VPSS manufacturing.

Results and discussion

Fig.2a shows the top-view SEM image of SiO_2 ring-shape masks on sapphire substrate. The period of masks is 3 μm and the diameter is 2.2 μm, which is the same with PSS stamp. The width of the ring increases with the increasing thickness of spin-coated resist. Fig.2b and 2c show the SEM and AFM images of VPSS wet etched in a mixture of H_2SO_4 and H_3PO_4 solution at an etching temperature of 270 ℃ for 15min. The typical VPSS pattern is composed by a truncated pyramid with a crater in its center. It is presented that, three symmetrical facets are formed inside the SiO_2 ring mask. The depth of craters are around 600nm, and they are highly uniform, as shown in Fig 2d.

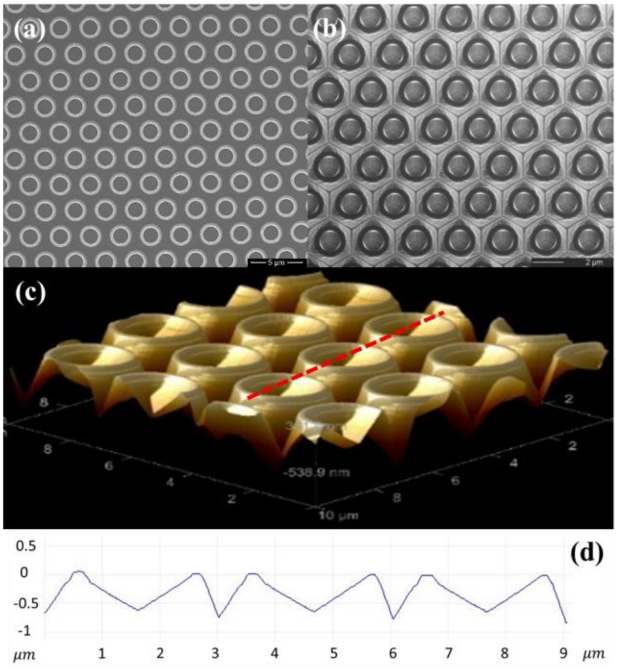

Fig. 2 (a) The top-view SEM image of ring-array SiO_2 mask; (b) the top-view SEM image of VPSS for 15min; (c) AFM images and (d) line profile along the red dash line in (c), including three patterns, shown in bottom of the AFM image. The typical VPSS pattern is composed by a truncated pyramid with a crater in its center.

Fig. 3a and 3b show the SEM images of VPSS wet etched for 5 and 25min under the same condition. The shape of pattern changes from truncated triangular pyramid into truncated hexagonal pyramid with the symmetrical sidewall facets as the etching time increases. At the beginning of wet etching, as shown in Fig. 3a, C-planes 3-fold symmetrically remain at the boundaries with the neighbor pyramids, which would provide more nucleating area for epitaxial GaN. The morphology at the boundaries with the neighbor pyramids is changing with the etching time, as C-plane disappeared, followed a small crater with three new facets, which provides more reflective area and further enhances light extraction. Simultaneously, SiO_2 ring-shape mask is corroded by high-temperature H_3PO_4, resulting in the decrease of the width of SiO_2 mask. In order to investigate the mechanism of wet-etching sapphire, round-shaped SiO_2 mask is also prepared, following by wet etching under the same condition for 25min (called TPSS), as shown in Fig. 3c. The outside morphology of VPSS and TPSS are similar, revealing that the etching processes inside and outside the ring-shape SiO_2 mask are independent.

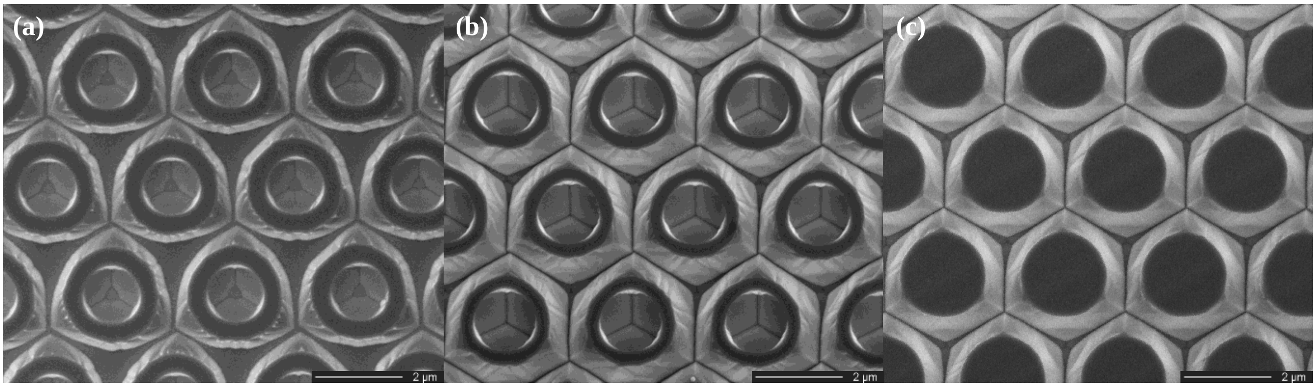

Fig. 3 The top-view SEM images of VPSS for (a) 5min; (b) 25min. The morphology of outside VPSS changes from truncated triangular pyramid into truncated hexagonal pyramid with three symmetrical smooth sidewall facets as the etching time increases. (c) The top-view SEM image of truncated pyramid PSS (TPSS) for 25min. The typical TPSS pattern is a truncated pyramid, which is similar with VPSS.

According to the cleaving edge orientation of sapphire substrate (as shown in Fig. 4a), the three symmetric facets in the crater are assigned as $\{1\bar{1}0k\}$ family. On the other hand, the sidewall facets outside the truncated pyramid, although look like 6 fold symmetrical from top view, are also three smooth $\{1\bar{1}0k\}$ facets. In order to determine the value of k, the cross sectional structure of VPSS is also studied along the axis of $[1\bar{1}00]$. As presented in Fig. 4b, the slanted angle of outside facet to C-plane is around 70 ° while the angle of inside facet to C-plane is around 35°. What's more, the angle of the facet of small crater at the boundaries with the neighbor pyramids to C-plane is also around 35 °. The angle, φ, between two crystal planes ($h_1k_1l_1$) and ($h_2k_2l_2$) can be described by [22] (a = 4.759 Å and c = 12.991 Å)

$$\varphi = cos^{-1}\left[\frac{h_1h_2 - \frac{h_1k_2+h_2k_1}{2} + k_1k_2 + \frac{3a^2}{4c^2}l_1l_2}{(h_1^2 - h_1k_1 + k_1^2 + \frac{3a^2}{4c^2}l_1^2)^{\frac{1}{2}}(h_2^2 - h_2k_2 + k_2^2 + \frac{3a^2}{4c^2}l_2^2)^{\frac{1}{2}}}\right] \quad (1)$$

Due to the fact that the angle of $\{1\bar{1}08\}$ facet to C-plane is 34.3 ° and the angle of $\{1\bar{1}0\bar{2}\}$ facet to C-plane is 69.9 °, the facets outside the truncated pyramid are $\{1\bar{1}0\bar{2}\}$ facets while the facets inside the crater are $\{1\bar{1}08\}$ facets. Besides, the facets of small crater at the boundaries with the neighbor pyramids are also $\{1\bar{1}08\}$ facets, as shown in Fig. 4c.

As is well known, the crystal wet etching process is contrary to the crystal growth process, and depends on etching temperature, time, etchant concentration, H_2SO_4/ H_3PO_4 ratio, and so on. The acquired facets are determined by the configuration of surface atoms and the bond structure [23]. The reactions between H_2SO_4/ H_3PO_4 and sapphire are also important [9, 10]. The sapphire etching rate depends on the crystal orientation and decreases in the order of C-plane > R-plane > M-plane > A-plane. The facet with faster etching rate will vanish while the one with slower etching rate will retain [24]. C-planes inside and outside the ring mask vanish gradually since the etching rate of them are fast. While $\{1\bar{1}0k\}$ facets, with slower etching rate, are retained. Truncated triangular pyramid, with three ridges respectively pinch together with ones of adjacent pyramids, firstly appears. The reaction terminates at these intersections as the reaction energy is the same for three ridges of adjacent pyramids. However, the regions at the boundaries with the neighbor pyramids are still C-plane, and wet etching process continues until these three $\{1\bar{1}0\bar{2}\}$ facets conflict at the bottom. There still retains a piece of C-plane when the sidewalls of adjacent pyramids pinch, if the orientation of pattern is not in accordance with the orientation of sapphire substrate. However,

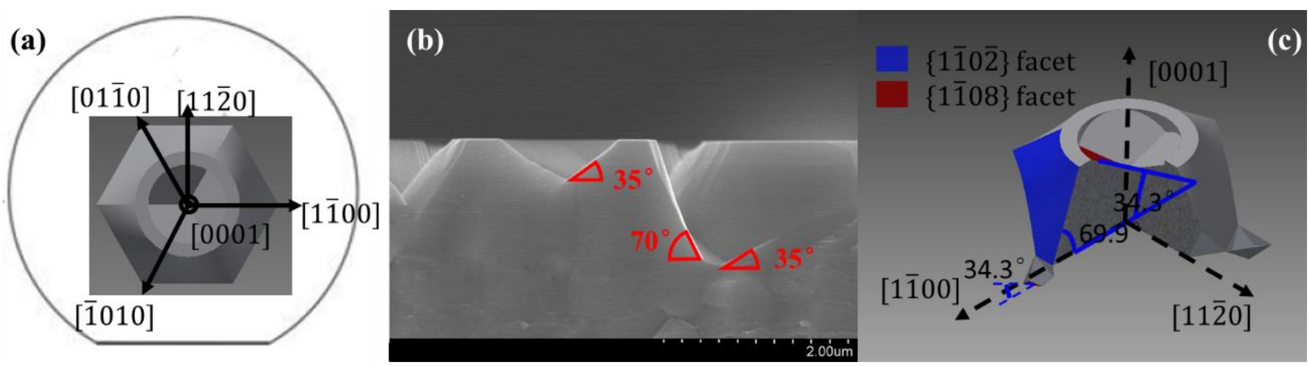

Fig. 4 (a) The relative orientations of VPSS on (0001) plane; (b) cross section SEM image of VPSS; (c) the schematic illustration of VPSS. The facets outside the truncated pyramid are $\{1\bar{1}0\bar{2}\}$ facets and the facets inside the crater and at the boundaries with the neighbor pyramids are $\{1\bar{1}08\}$ facets.

the disappearance of C-planes is no longer in accordance with the original etching way because the sidewalls act as mask just as the ring shape SiO_2 mask. The reaction manner is similar with that inside the crater. That is the reason why small craters with three $\{1\bar{1}08\}$ facets form at the boundaries with the neighbor pyramids. Due to the decrease of the width of SiO_2 mask with increasing time, the volcano overall inward shrinks in order to keep the same k in $\{1\bar{1}0k\}$, resulting in the increase of the area of small crater at the boundaries with the neighbor pyramids.

The formation of the crystallographic patterns can be attributed to the thermodynamics and transportation process in a specific facet. To reveal the reaction mechanism of VPSS, the activation energy is estimated by following Arrhenius equation [25],

$$\log r = -\frac{E_a}{RT} + \log A, \qquad (2)$$

Where, r is the reaction rate, E_a is the activation energy, R is the gas constant, T is the reaction temperature, and A is the reaction frequency factor. Fig.5 shows a plot of etching rate of C-plane outside the truncated pyramid as a function of reciprocal temperature. The log of etching rate can be fitted to a linear curve.

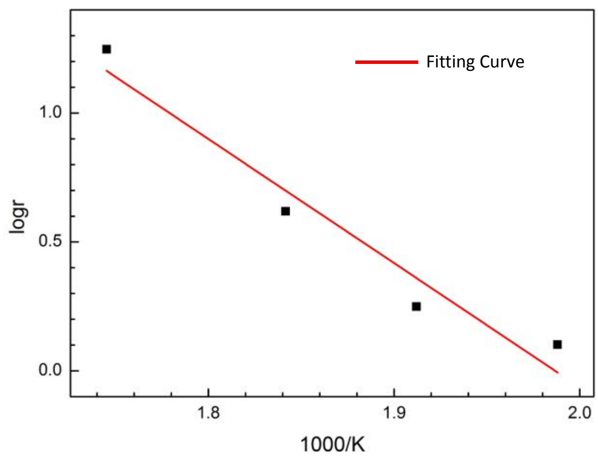

Fig. 5 Semi-log plot of etching rate of C-plane outside the truncated pyramid as a function of reciprocal temperature

The etching rate equation, r, is fitted by

$$\log r = \frac{-4.82\times10^3}{T} + 9.57 \qquad (3)$$

The activation energy of this reaction can be calculated to be 22.00 ± 3.42 kcal/mol, which indicates that the etch process outside the truncated pyramid is reaction-limited [11].This explains why the low index $\{1\bar{1}0\bar{2}\}$ facets form in the sidewall of volcano. However, when the diameter of mask is small, the hole in the mask hinders the transportation of fresh solution to the sapphire surface, resulting in wet etching process deviates from the thermodynamics controlled process [26]. That is why high index $\{1\bar{1}08\}$ facets form inside the crater and at the boundaries with the neighbor pyramids. The activation energy value is a bit more than the pure H_2SO_4 reacted with sapphire [9], and less than the value for $3H_2SO_4$:$1H_3PO_4$ mixture reaction [4]. It also can be attributed to the different masks.

It is noticed that the morphology of VPSS is relative with the angle between the orientation of pattern array and the orientation of sapphire substrate. A VPSS with 30° (as PSS stamp is hexagonal symmetry) between the orientation of pattern array and the orientation of sapphire substrate is prepared, called 30VPSS. As presented in Fig. 6, the ridges of truncated triangular pyramid pinch the sidewalls of adjacent one. Wet etching process is asymmetric since the activation energy is not consistent between the ridge and the sidewall of pyramid, leading to the deformation of original truncated triangular pyramid. The regions 6-fold symmetrically appear at the boundaries with the neighbor pyramids in which C-planes change to small craters surrounded by three $\{1\bar{1}08\}$ facets as the etching time increases.

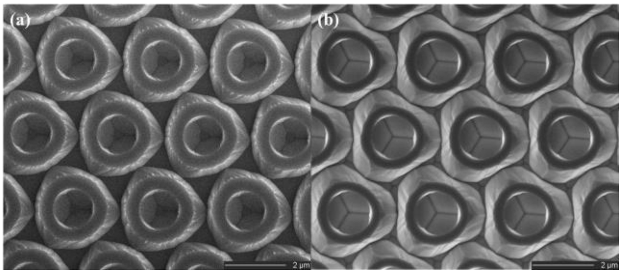

Fig. 6. The top view SEM image of 30VPSS for (a) 5min; (b) 25min. Truncated triangular pyramid deforms due to the inconsistent activation energy between the ridge and the sidewall of pyramid. Small craters surrounded by three $\{1\bar{1}08\}$ facets 6-fold symmetrically appear at the boundaries with the neighbor pyramids

It is notable that the slant angle of $\{1\bar{1}08\}$ family to C plane is about 34.3°. This value is beneficial for the improvement on LEE [7] and IQE [13] of LEDs. The close-packed hexagonal array further enhances the light output because of large fill factor [17]. Besides, top C-planes and sidewall facets outside the truncated pyramid provide more GaN nucleation sites [21], which facilitate the epitaxy of GaN. The etching $\{1\bar{1}08\}$ facets will appear when etched by H_2SO_4/ H_3PO_4 mixture at 270°C and SiO_2 ring mask for enough etching time. The inner diameter confined by masks or outside sidewalls should be about 1.5μm for the conventional 3 μm period PSS stamp. 30VPSS provides more area of $\{1\bar{1}08\}$ facets. If the etchants ratio, concentration, etching mask and etching temperature are changed, other high index etching facets will be produced [9, 10, 16]. The enhancement of light output is under investigated by fabricating GaN-based LED using VPSS.

Conclusions

In summary, a low-cost method combining imprinting lithography with wet etching is used to fabricate VPSS. The etching temperature, etching time, and the ring mask orientation are confirmed to control the shape and the morphology of VPSS. The formation of the crystallographic patterns can be attributed to thermodynamics and surface process in a specific facet, where the truncated triangular pyramid is with a crater consisted of three symmetric facets $\{1\bar{1}08\}$ inside and sidewall facets $\{1\bar{1}0\bar{2}\}$ outside. The LEE of LED using the as-fabricated VPSS may be enhanced due to both more reflective area and smaller slant angle of the sidewall facets.

Acknowledgements

This work was supported by National Key Basic Research Program of China under Grants Nos. 2011CB301905, 2013CB328705, National Natural Science Foundation of China under Grants Nos. 61334009, 60976009, U0834001, and Guangdong Innovative Research Team Program (No. 2009010044).

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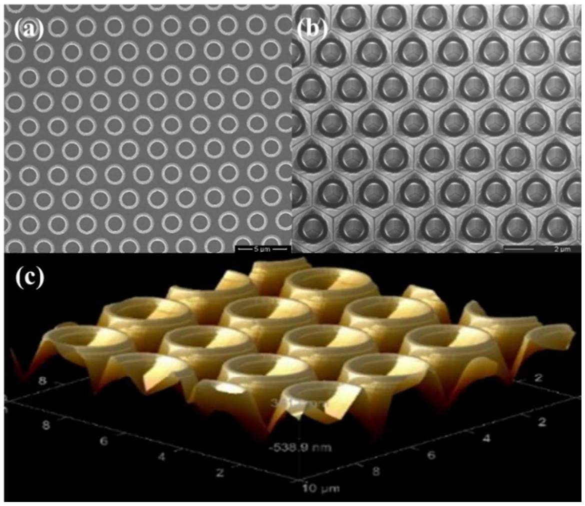

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