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Controlled fabrication of periodically high-aspect ratio CVD-diamond nanopillar arrays by pure oxygen etching process



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ABSTRACT

The CVD (Chemical Vapor Deposition) diamond nanopatterning has been a great challenge due to its superhard property and chemical stability as well as rough surface, especially for fabricating high aspect ratio nanostructures such as nanowires and nanopillars. In this work, we report an approach to fabricate directly periodic high-aspect-ratio nanopillar arrays on the rough CVD-diamond film by e-beam lithography (EBL) and inductively coupled plasma (ICP) etching method. The as-fabricated diamond nanopillar arrays have a controllable aspect ratio and tunable period with good repeatability and uniformity, and the highest aspect ratio of above 10 with 200 nm in diameter can be obtained. This result relies on reduced grain size of CVD-diamond and a special treatment process of the mask-patterning and then effective etching control. The fabrication process does not rely on a thick hard mask layer, but uses a just few nanometers of metal to improve mask adhesion. Masking is also improved by adjusting the growth process of diamond film to make its surface as smooth as possible. Such development of CVD-diamond nanopillar fabrication process, especially having ultrahigh aspect ratio, will likely impact the application of CVD-diamond nanostructure based nanoscale sensors, nanoelectronic devices, and NEMS/MEMS manufacturing.

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1. Introduction

Among diamond family, the CVD-diamond holds an important position because it possesses not only the excellent diamond nature intrinsic property but also high production rate, which can be easily prepared by CVD methods, such as the hot filament chemical vapor deposition (HFCVD) and microwave plasma chemical vapor deposition (MPCVD) [1–8] However, the application range of the CVD-diamond is still very narrow at the present, and some potential have not been fully utilized. It is well known that the nanomaterial and nanodevice can hardly do without modern micro/nano-fabrication technology, and thus it is necessary for the CVD-diamonds to adapt to the standard micro/ nanofabrication method and further widen their application area. For the fabrication of CVD-diamond micro/nano-structure, the rough surface is the greatest difficulty, and moreover, there are some problems including the mask-patterning, interfacial adhesion, removing contamination, uniformity and repeatability to deal with [9,10]. Owing to the above problems of fabrication process, the standard micro/ nano-fabrication method has not been widely used in the CVDdiamond patterning. The methods reported at the present to form CVD-diamond micro/nano-structure include mostly the templated etching [11], metal-hard-mask etching [12] and random maskless etching [13], corresponding to the diamond nanostructures such as nanohoneycomb, nanopillars and nanocones. However, these nanostructured CVD-diamonds are almost random and disorganized, and thus as-reported methods need to face some problems to be resolved, such as large-scale fabrication, periodic patterning, and uniformly controllable fabrication [14,15]. In addition, it is also reported that the metal hard-mask patterning is fabricated by lithography technology for CVD-diamond periodic structure [13], but the complicated metal-mask process, large-size structure morphology controllability and contamination still need to be further improved, and particularly nanostructured CVD-diamond with high aspect ratio, periodic arrays and controlled morphology has rarely been reported so far.

In this work, we report an approach to fabricate directly periodic high aspect ratio nanopillar arrays on the rough CVD-diamond film by the e-beam lithography (EBL) and inductively coupled plasma (ICP) etching method. A grain size of CVD diamond can be controlled by proper growth conditions to reduce the effect of the rough surface on the nanofabrication process. Only a photoresist-mask step makes the whole fabrication process become simple and efficient. Particularly, a special treatment process of the mask-patterning and then effective etching control to overcome the difficulties of the rough surface and mask adhesion, and the whole fabrication process has not adopted

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metal hard mask in addition of only a very thin transition Ti layer for enhanced adhesion. The as-fabricated diamond nanopillar arrays have a controllable aspect ratio and tunable period with good repeatability and uniformity, and the highest aspect ratio of above 10 with 200 nm in diameter can be obtained. This nanofabrication approach enables CVD-diamond material to have a good compatibility with standard semiconductor microfabrication technology and helps promote wide application of nanostructured CVD diamond.

2. Experimental details

The whole fabrication process of CVD-diamond nanopillar arrays includes the growth of CVD-diamond thick-film, the mask-patterning of EBL and ICP etching process. Firstly, the silicon substrate is ultrasonically pretreated for 30 min in the diamond powder solutions, and then the CVD-diamond film samples are grown on the silicon substrate by HFCVD system, in which the distance between the tantalum filament and substrate is kept at 1 cm. During the growth process, the mixture gas of CH₄ and H₂ with the flow ratio of 5:100 is used, and the chamber pressure is maintained at below 20 Torr. After the growth duration of 10 h at the filament temperature ~1800 °C, and a thickness of CVD-diamond film is corresponding to about 10 μ m. A grain size with less than 1 μ m in the CVD diamond sample can be obtained by properly increasing the flow ratio of CH₄ and decrease chamber pressure to reduce the surface roughness of CVD-diamond films.

Before EBL process, the clean step and photoresist spin-coating for the sample are carried out. The sample with 0.8 cm \times 0.8 cm in size is cleaned by the acetone, alcohol and deionized water about 5 min in turns to remove the dirty substance on the surface of the sample. After a drying, a metal transition layer with several nanometer thicknesses is coated on the sample by sputtering and then is annealed at 450 °C. Next, the photoresist (HSQ type) is spin-coated on the sample with a spinning speed of 3500 r/min for 1 min, and then heating step is done at the temperature 110 °C for 1 min. The thickness of HSQ photoresist is kept at about 200 nm.

The EBL system(JBX-6300FS of JEOL) is used for mask-pattern with an accelerating voltage of 100 kV and the exposure dose of 2400 μ c/cm². After EBL process, as-formed HSQ mask-patterns are treated by RIE (CHF₃: Ar = 50:5 sccm, the power of 150 W, gas pressure of 30 mTorr, etching duration of 20 s) to remove the residue of photoresists and Ti transition layer for better resolution.

Finally, the CVD diamond samples with HSQ mask-pattern are etched by ICP etching system (Plasmalab80Plus of Oxford Instrument)

to fabricate the nanopillar arrays. During ICP etching process, the mixture gas of O_2 and Ar with flow ratio: O_2 :Ar = 30:10 sccm is used as etching gas, and the ICP power is varied in the range of 400 to 1000 W. Besides, the RF power and DC-bias is fixed at 100 W and 300 V, respectively, and the chamber pressure is maintained at 10 mTorr. The etching time is changed from 2 to 12 min to obtain the diamond nanopillar with high aspect ratio.

In addition, the morphologies of as-fabricated CVD-diamond nanopillar arrays are characterized by scanning electron microscope (SEM) of the FEI Helios 600i Focused-ion-beam system and the 3D surface analyzer (Bruker Contour GT) based on the white light. A JY-T64000 three grade Raman spectroscopy system is used to detect the bonding states of the CVD-diamond sample by 532 nm laser excitation wavelength.

3. Results and discussions

The fabrication processes for CVD-diamond nanopillar arrays are illustrated in Fig. 1, including the CVD growth and control of grain size of diamond films, pretreatment process and HSO patterning by EBL, after treatment process and ICP etching. Firstly, a reduced surface roughness of CVD-diamond films is papered by controlling the grain size of CVD diamond films at optimized growth conditions for next microfabrication process. Fig. 2 shows the characterization of the morphology and bonding states of as-grown CVD diamond films. Fig. 2a displays an SEM image of diamond film grown on a low pressure, some continuous surface protuberance composed of small grain clusters can be observed without any large visible grains, which is relatively smooth in contrast with usual CVD diamond film due to reduced grain size. Fig. 2b shows the cross-sectional morphology of as-grown diamond film, in which the columnar structure and column boundaries can be clearly seen, along with an interface between diamond films and silicon substrate.

The 3D morphology using surface analyzer based on the white light is displayed on Fig. 2c, which is corresponding to a SEM image of Fig. 2a, having an average surface roughness of ~187 nm in such large area of 62.22 μ m × 46.67 μ m that can exactly reflect the real morphology of the as-grown diamond film.

Raman spectroscopy is an effective tool to characterize CVD diamond film due to its good distinguishing ability for the different allotropes of carbon. Fig. 2d shows Raman results by 532 nm laser excitation wavelength for CVD diamond samples. There are many peaks appearing in the Raman spectrum, in which two main broad peaks centered at



Fig. 1. Schematic of the fabrication processes for CVD-diamond nanopillar arrays mainly including CVD, EBL and ICP process.



Fig. 2. CVD diamond film characterizations: SEM images (a) surface morphology and (b) cross-sectional morphology; (c) 3D morphology using surface analyzer based on the white light, (d) Raman spectrum of as-grown CVD diamond film sample. The scale bar is 5 μ m.

~1360 and at 1550 cm⁻¹ can be seen, belonging to the D and G peaks characteristic of disordered sp²-binded carbon [16]. In addition, a sharper diamond peak centered at ~1332 cm⁻¹ can be distinguished from the broader graphitic D peaks (~1360 cm⁻¹), which is associated with small quantities of microcrystalline diamond [16]. In particular, two well-defined peaks at 1135 and 1480 cm⁻¹ can be often observed in the nanocrystalline diamond (NCD) films as weak shoulders, which have been attributed to trans-(CH)_x (trans-polyacetylene) at grain bound-aries [17,18].

However, these two features in the our diamond sample are obviously different from the reported Raman results of NCD films, having relatively high-intensity, in which the independent characteristic peak at 1135 cm⁻¹ is more prominent, indicating an increase of the amount of grain boundary materials. Overall, the Raman spectrum of our CVD diamond films is consistent with that of the typical NCD films.

Although the grain size in the CVD diamond sample can be reduced to several hundred nanometers in order to diminish the influence of rough surface on the micro/nanopatterning process, the good adhesion between the photomask and CVD diamond film is still a more important part. Here, HSQ photoresist mask instead of the usual metal-mask is used for nanopatterning process by EBL, because the HSQ process is cost-effective and fewer steps in fabricating the diamond nanopillar compare with metal-mask process. In addition, the materials of HSQ composed of silicon dioxide are ideal masks and sacrifice layers during O_2 etching process due to its inertness for the O_2 . At the same time, HSQ is also easy to be removed in comparison with the metal-mask. Before HSQ spin-coating on the diamond films, several nanometer thick Ti films are coated firstly on diamond films and then annealing treatment at 450 °C, which can be used as a transition layer to enhance the interfacial adhesion between the HSQ mask and diamond films. After above pretreatment process, HSQ dot-shaped mask-nanopatterning with different diameters and periods are fabricated by EBL process, showing a much desired effect in uniformity and repeatability, in which the dot-pattern array is changed from 200 nm to 500 nm in diameter and from 500 nm to 2 µm in period. Fig. 3a and b displays the different effects for HSQ mask nanopatterning with and without pretreatment process, which demonstrate that Ti nanolayer and annealing can assure the complete nanopatterning on the diamond films sample with little peeling off. After EBL process and before ICP etching to transfer the HSQ nanopatterning, a short-time aftertreatment by using RIE is needed to remove the residual HSQ photoresist to protect the uniformity of nanopatterning. A short-time aftertreatment RIE cleaning is needed to remove the residual HSQ photoresist and Ti layer between HSQ pillars to protect the uniformity of nanopatterning and increase resolution.

During ICP etching, two kinds of etching gas of O₂ and Ar can be chosen for rapidly reactive etching process. The mixture gas of O₂ and Ar with flow ratio of 30:10 is used to increase the effect of etching due to a reactive etching combined with a physical etching, but the addition of Ar gas also can result in the formation of some small cones around the diamond nanopillar arrays, as shown in Fig. 3c. The reason is that Ar contribution is mainly physical bombarding that strengthens random etching effect, which can lower the etching selectivity rate from 9:1 to 4:1. In addition, but the addition of Ar gas has also caused a prominent cone-liked shape in the top of nanopillar and not enough vertical profile of pillar side-wall, which is related to an etching damage to as-patterned HSQ-masks induced by Ar physical etching. Therefore, the etching process of a pure O₂ gas should be the best way to obtain diamond nanopillar, which can increase the etching selectivity rate to a range from 10:1 to 15:1 that mainly depends on the factors of pillar's density and height, Fig. 3d shows a uniform diamond nanopillar arrays fabricated by using pure O_2 etching, having a perfect vertical profile, high aspect ratio and pillar density, which can be tuned by mask-patterning and etching conditions.

During pure O_2 etching, ICP power is a major factor to impact the etching rate. Fig. 3e gives the dependence of etching rate on the ICP power. It can be seen that the etching rate increases nonlinearly with ICP power, but although a high ICP power (1000 W) can improve greatly the etching rate, it can also increase the chance in lateral etching, which can lead to spindle-shaped structure with a small diameter in the top and bottom, as shown in the inset of Fig. 3e. Through comparing different ICP powers, the 700 W is confirmed to be an optimal ICP power for etching diamond nanopillars. In addition, the etching time determines the aspect-ratio of diamond nanopillar under optimal



Fig. 3. HSQ mask nanopatterning by EBL on the diamond (a) before and (b) after pretreatment, and the scale bar is 1 µm. The effect of gas composition on the etching results: (c) O₂: Ar = 3:1 and (d) pure oxygen etching at ICP power of 700 W, and the scale bar is 0.5 µm. (e) The etching rate changes with the ICP power and (f) the dependence of diamond nanopillar height on etching time, in which two insets correspond to the sample morphology of the highest value, and the scale bar is 1 µm and 0.5 µm, respectively.

etching conditions. Fig. 3f displays the dependence of the nanopillar height on the etching time, and we can see that the nanopillar height increases with etching time and reach the maximum at etching time of 6 min shown in the inset of Fig. 3f. But when the etching time is extended to more than 6 min at ICP power of 700 W, the nanopillar height is decreased due to an excessive etching that causes the damage and even disappearance of mask-nanopatterning, and meanwhile it can cause the formation of a tubular structure on the nanopillar top. With further etching, the top of diamond nanopillar can be etched out and even broken off when the etching time exceeds 10 min.

Taken all together, an optimized etching condition can be obtained, including the ICP power of 700 W, RF power of 100 W, and pressure of 10 mTorr under pure O₂ etching circumstance, which can be helpful to fabricate uniform diamond nanopillar arrays with the high aspect ratio and good vertical in a reasonable etching time (~6 min). By above etching condition, CVD diamond nanopillar arrays with different diameters and periods can be controllably fabricated, as shown in Fig. 4a-f. The left side of Fig. 4 shows three overhead-views of nanopillar arrays with different periods (2 µm, 1 µm and 0.5 µm), and the right side displays the lateral-views of nanopillar arrays with different diameters (300 nm, 300 nm and 200 nm), which has an one-to-one correspondence with left side. From the overhead-view, the cross section of asetched nanopillar keeps good rotundity and uniformity. A smooth side-wall and high aspect ratio can be observed from the right lateralviews of diamond nanopillar. Among these as-etched diamond nanopillars, Fig. 4f shows the highest aspect ratio of above 10 with a diameter of 200 nm and the height of above 2 µm. It is worthy to note that diamond nanopillar arrays with a small period and high density are easier to be controllably fabricated than that with big period. At a larger spacing between the pillars it is difficult to obtain diamond pillars with a good vertical profile. This may indicate that lateral etching is enhanced with a higher local flux of oxygen radicals, which is reduced when closely packed pillars provide a higher local surface area.

When the diamond nanopillars with small period are over-etched slightly, a special nanostructure with hollow tube around a cone can be formed at the top of diamond nanopillars, as shown in Fig. 5a. This hybrid nanostructure composed by the nanotube and the nanopillar is very interesting and there may be some potential application. It can be seen that with further etching along the drawing arrow in Fig. 5a, the centered cone is etched out to form a single tubular nanostructure. The main reason to form the special structure may be the charging effect in the brim of diamond pillar top, and the different dielectric constant of HSQ and diamond results in the charge accumulation in the brim, which lowers the etch rate and forms gradually the tube structure. In addition, we find that the change of etch time, power and pattern diameter can impact their structural parameter, such as the tube length and cone height and even thickness of the tube-wall. However, it is hard for this special structure to control safely these structural parameters. For this nanostructure, the floor area is presumably continuing to etch down with extended time, and so the tube etch rate when the tube section is lost must be higher than the floor etch rate. More probably the tubes etch through at some midpoint and just fall away. Fig. 5b shows the morphologies of broken-up nanopillar under excessive etching, in which the inside wall of tubular structure on the top of diamond



Fig. 4. SEM images of as-fabricated CVD diamond nanopillar arrays with different periods and diameters. Overhead-view of diamond nanopillar with the periods of (a) 2 µm, (b) 1 µm and (c) 0.5 µm; which is one-to-one corresponding to the lateral view of the nanopillar with diameters of (d) 300 nm, (e) 300 nm and (f) 200 nm with the highest aspect ratio of above 10, respectively. The scale bar is 1 µm.



Fig. 5. Morphological changes of CVD diamond nanopillar structures from (a) tubular nanostructure on the top to (b) broken-up nanopillar under an excessive etching.

nanopillar can be observed clearly, which provides a strong evidence for the formation of hollowly tubular nanostructure on the top of diamond nanopillars. Therefore, the etching effect should be carefully controlled by adjusting the etching parameters to obtain desired nanostructure and avoid the nanostructural damage due to excessive etching.

4. Conclusions

We provide a simple and effective approach to fabricate controllably high aspect ratio CVD-diamond nanopillar arrays, and the HSQ photoresist process is used to displace traditionally complicated metallic hard mask process, which simplifies greatly the fabricating steps. Reduction of diamond grain size and a pretreatment along with aftertreatment process have contributed to the solution of the problems for nanofabrication process on the rough surface of CVD-diamond. Under optimized fabrication condition, the CVD diamond nanopillar with different structural parameters and array periods can be successfully fabricated, in which the highest aspect ratio of as-formed diamond nanopillar is more than 10 with a diameter of 200 nm and a height of above 2 µm, and the smallest array period can be controlled in the 500 nm, having a high density of the nanopillars. Further, a diamond hybrid nanostructure of the nanotube on the top of nanopillar has been made to enrich the kinds of diamond nanostructure but the mechanism of tube formation still needs to be deeply considered. Such development of as-proposed fabrication process for high-aspect ratio CVD-diamond nanopillar will promisingly extend the range of application field for nanoscale CVD-diamond.

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References

- [1] J.B. Cui, J. Ristein, L. Ley, Phys. Rev. Lett. 81 (1998) 429.
- [2] J. Ristein, M. Riedel, L. Ley, J. Electrochem. Soc. 151 (E) (2004) 315.
- [3] C.E. Nebel, Science 318 (2007) 1391.
- [4] V. Blank, M. Popov, G. Pivovarov, N. Lvova, K. Gogolinsky, V. Reshetov, Diam. Relat. Mater. 7 (1998) 427.
- [5] L. Tang, C. Tsai, W.W. Gerberich, L. Kruckeberg, D.R. Kania, Biomaterials 16 (1995) 483.
- [6] H.J. Mathieu, Surf. Interface Anal. 32 (2001) 3.
- [7] K.F. Chong, K.P. Loh, S.R.K. Vedula, C.T. Lim, H. Sternschulte, D. Steinmüller, F.S. Sheu, Y.L. Zhong, Langmuir 23 (2007) 5615.
- [8] W. Yang, O. Auciello, J.E. Butler, W. Cai, J.A. Carlisle, J.E. Gerbi, D.M. Gruen, T. Knickerbocker, T.L. Lasseter, J.N. Russell Jr., L.M. Smith, R.J. Hamers, Nat. Mater. 1 (2002) 253.
- [9] M. Liao, S. Hishita, E. Watanabe, S. Koizumi, Y. Koide, Adv. Mater. 22 (2010) 5393.
- [10] C.F. Wang, R. Hanson, D.D. Awschalom, E.L. Hu, T. Feygelson, J. Yang, J.E. Butler, Appl. Phys. Lett. 91 (2007) 201112.
- [11] H. Masuda, M. Watanabe, K. Yasui, D. Tryk, T. Rao, A. Fujishima, Adv. Mater. 12 (2000) 444.
- [12] Y.S. Zou, Y. Yang, W.J. Zhang, Y.M. Chong, B. He, I. Bello, Appl. Phys. Lett. 92 (2008) 053105 (1-3).
- [13] Q. Wang, Z.S. Tian, Y.L. Li, S.B. Tian, Y.M. Li, S.T. Ren, C.Z. Gu, J.J. Li, Nanotechnology 25 (2014) 115301.
- X.P. Wang, L.E. Ocola, R.S. Divan, A.V. Sumant, Nanotechnology 23 (2012) 075301.
 D.B. Seley, D.A. Dissing, A.V. Sumant, R. Divan, S. Miller, O. Auciello, L.A. Lepark, E.A.
- [15] D. Steley, D. Disten, D.A. Fahrner, J.P. Hamilton, M.P. Zach, ACS Appl. Mater. Interfaces 3 (2011) 925.
- [16] J. Birrell, J.E. Gerbi, O. Auciello, J.M. Gibson, J. Johnson, J.A. Carlisle, Diam. Relat. Mater. 14 (2005) 86.
- [17] R. Pfeiffer, H. Kuzmany, N. Salk, B. Günther, Appl. Phys. Lett. 82 (2003) 4149.
- [18] H. Kuzmany, R. Pfeiffer, N. Salk, B. Günther, Carbon 42 (2004) 911.