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# The parametric study of carbon nanotips grown by MWPECVD with controllable sharpness using various metallic catalysts

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**Abstract**

A parametric study for growing vertically aligned carbon nanotips utilizing microwave plasma enhanced chemical vapor deposition was presented. The effects of process parameters including process time, microwave power and applying bias were discussed. The height of nanotips was affected by the microwave power and process time. The growth of rod-shape or tip-shape structure depends on the microwave power. The high microwave power is favorable for growing rod-shape structure which results from the faster diffusion of carbon atoms in the metallic catalysts under high temperature. The sharpness of carbon nanotips seem possibly to be controlled by varying bias voltage. These carbon nanotips exhibit the characters of high number density and well vertical alignment. Furthermore, we demonstrated that the growth of carbon nanotips by different metallic catalysts, such as Au, Pt, Ag and Si, could be chosen for applying in various regions.


*Keywords:* Carbon nanotips; Sharpness-controllable; MWPECVD

## 1. Introduction

For the past decades, numerous researchers devoted their attention and efforts on carbon related materials, such as diamond film [1], carbon nanotips [2], and filamentous carbon which includes carbon nanotubes [3], nanowires [4] and nanorods [5]. In particular, the carbon related materials with high aspect ratio are widely applied in industrial region. The sharp carbon related nanomaterials such as carbon nanotips, carbon nanocones and carbon nanohorns were utilized as field emitters and catalyst supports [6–8]. Either the geometrical advantage or the well electron conductivity is considerable for electrical devices. However, physical [9] and chemical [10] etching technologies were often used to fabricate most of the sharp carbon related nanomaterials. The complicated and expensive fabricating processes are ineligible for a widespread use. In order to reduce the costs and shorten fabricating processes, the synthesis of sharp carbon related nanomaterials by self-assembled bottom-up method is essential for a variety of application.

In this work, we present a bottom-up method for fabricating carbon nanotips instead of the traditional etching method. The figure and sharpness could be controlled by varying the process parameters. These carbon nanotips with high aspect ratio are suitable for the electron field emitting application. Besides, the synthesis of carbon nanotips via different metallic catalysts to meet the need of other industrial areas is demonstrated. Transitional metals, such as Au, Pt, Ag and Si, are used to grow carbon nanotips which exist on the top of the nanotip. This tip growth model is desirable for the application of sensors [11].

## 2. Experimental details

The synthesis of carbon nanotips was achieved by microwave plasma enhanced chemical vapor deposition with DC bias. The metallic catalysts including Au, Pt and

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Ag were first deposited on p-type silicon (100) wafer separately with a thickness of 5 nm by e-beam evaporation. Next, the catalysts deposited wafer was put on a molybdenum holder in a quartz tube for growing carbon related nanomaterials. Methane and hydrogen were introduced to the tube for reactive gas species with flow rate of 20 and 100 sccm, respectively. The base and working pressure in this work were respectively $10^{-3}$ and 1 Torr. Additional biases ranged from −100 V to −250 V were applied during the experiment to enhance the growth of tip-shape carbon nanomaterials. Before growing carbon nanotips, hydrogen plasma pretreatment was performed for nucleating the nanoparticles and clearing the native oxide of Si wafer. The experimental parameters of this work are bias voltage, microwave power, and reaction times. The investigations of surface morphologies and interior structures were relied on scanning electron microscope (JOEL 6500) and high resolution transmission electron microscope (Philips Tecnai-20). Bonding structure of carbon nanotips was investigated by Raman spectroscopy (Jobin Yvon Lab-RAM HR) with a 632.8 nm He–Ne laser.

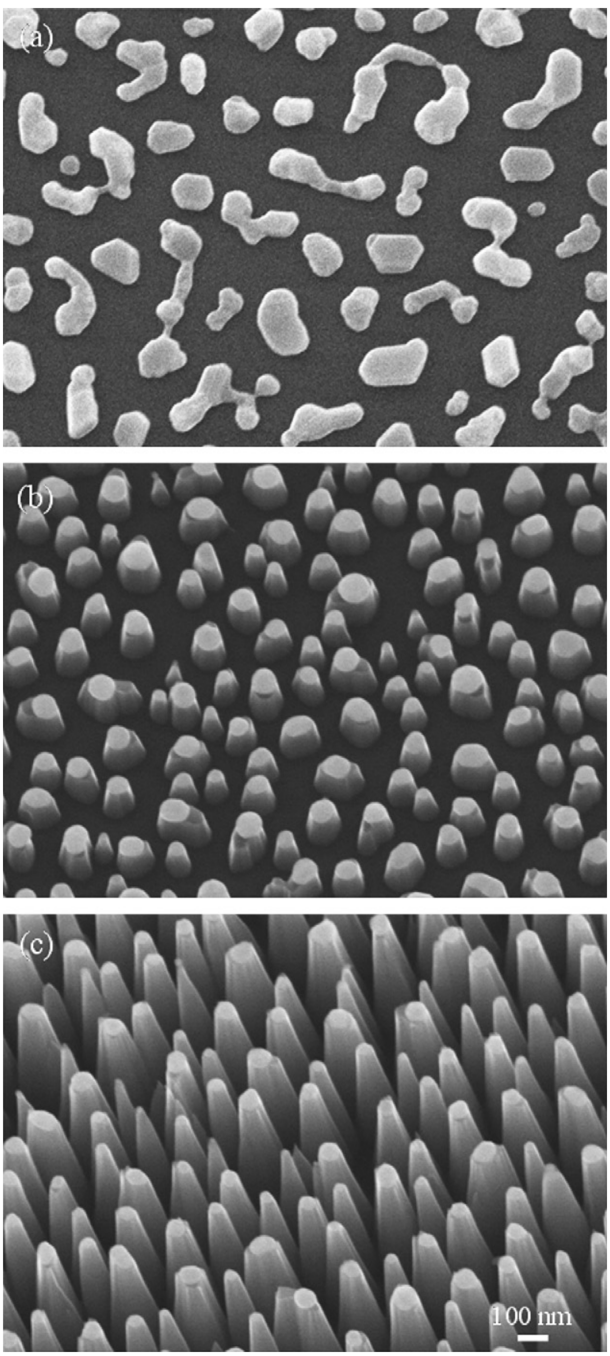


Fig. 1. SEM micrographs of carbon nanotips grow for: (a) only, pretreatment (b) 5 min and (c) 10 min.

## 3. Results and discussion

SEM micrographs of carbon nanotips under different growth time are shown in Fig. 1. Fig. 1(a) depicts the nucleation of gold nanoparticles from gold layer under the hydrogen plasma treatment for 10 min. Fig. 1(b) and (c) present the images of cone-shaped carbon nanomaterials grown under the condition of microwave power 300 W and bias −100 V for 5 min and 10 min, respectively. The lengths of carbon nanotips are ranged from tens of nanometer to hundreds of nanometer, which depends on the growth time and microwave power. The temporal effects of nanotips height under different power are presented in Fig. 2. From Fig. 2, it can be found that the height of carbon nanotips dramatically increase with increasing growth time and saturate even under different microwave powers. The saturation of height might be attributed to the deactivation of gold nanoparticles. The deactivated gold nanoparticles could not catalyze the growth of nanotips. Therefore, the plasma etching rate will higher than the growth rate, which resulted in the shrink of height. However, the higher microwave power will improve the activity of catalyst which results in the slower saturation of nanotips. Another effect of microwave power is the shape of carbon nanostructures. Fig. 3 shows the relationship between the shapes of carbon nanomaterials and microwave power.

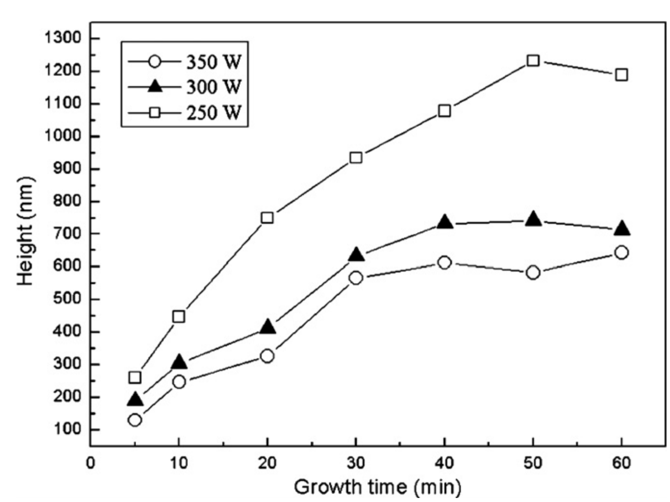


Fig. 2. The relationships between the length of the tips and the process time under different microwave powers.

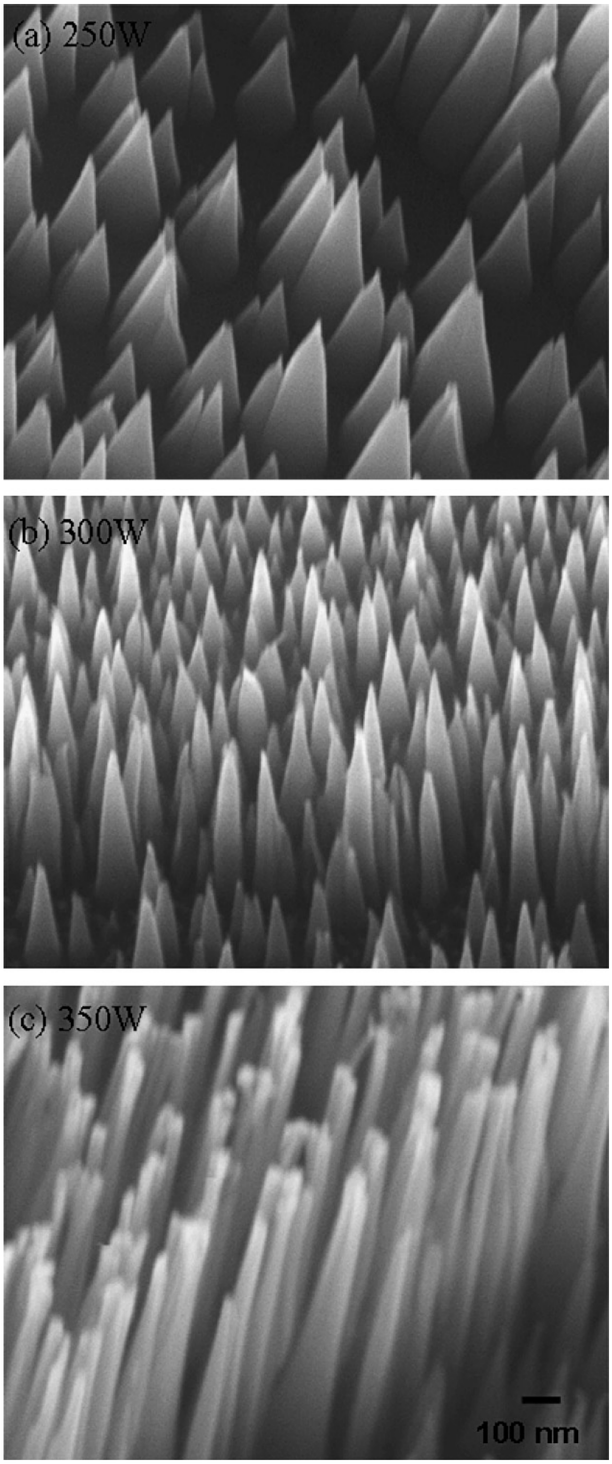


Fig. 3. SEM micrographs of carbon nanotips grow under different microwave powers: (a) 250 W, (b) 300 W and (c) 350 W.

The carbon nanomaterials have tip-shape or rod-shape structure which depends on the microwave power. The low microwave power is flavour to form the tip-shape carbon nanostructure instead of rod-shape nanostructure. It could be explained that the high microwave power causes the high reaction temperature and the high decomposition rate of hydrocarbon which might enhance catalytic activity of gold nanoparticles. Moreover, either the inter diffusion or bulk diffusion rate of carbon atoms will increase with the increasing reaction temperature. This might causes the formation of rod-shape of carbon nanomaterials which is similar to vapor–liquid–solid growth mechanism of carbon nanofibers [12]. However, the carbon–gold eutectic point is much higher than carbon–iron. The diffusion of carbon atoms in the gold catalysts is very slow, which results in the formation of "short" carbon nanofibers. Nevertheless, the low microwave power results in the lower activity of gold nanoparticles, which causes the accumulation of amorphous carbon on the outside and the bottom. Moreover, the gold catalysts on the top of the tips act as the protecting mask to prevent the etching of the tip-body. As time goes on, the accretion of carbon atom will continually accumulate in the bottom of the short carbon nanofibers which form in a tip-shape structure. Fig. 4(a) is the TEM image of the metallic catalyst on the top of the tip-like structure. The metallic catalyst which remains on the top of the tip was identified as gold metal by EDX. A TEM EDX spectrum of the tip-body is shown in

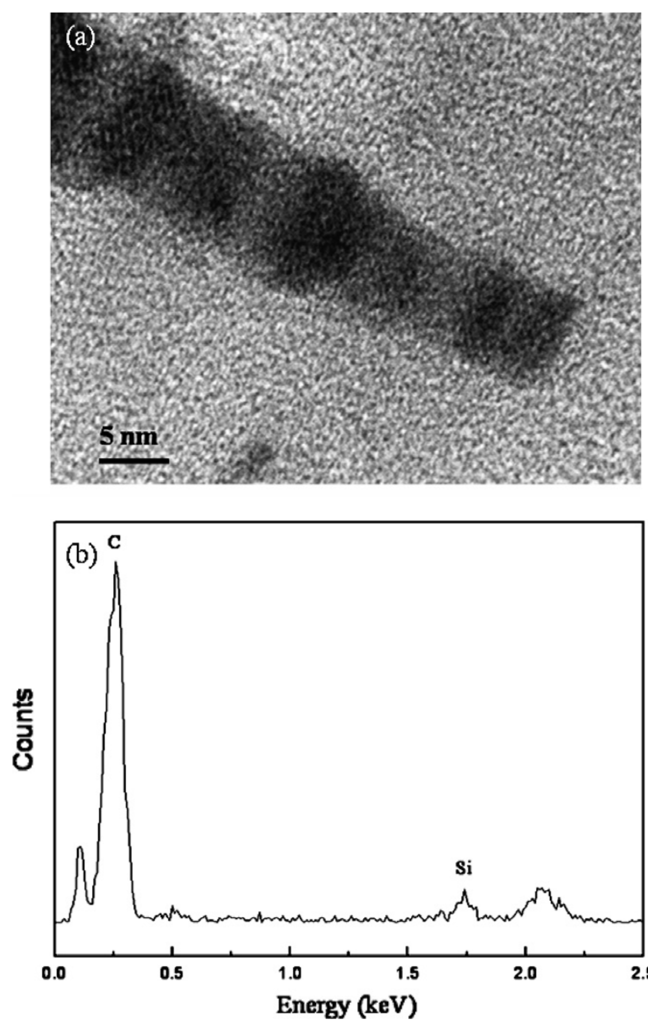


Fig. 4. (a) A HRTEM image of Au catalyst on the top of a carbon nanotip. (b) A TEM EDX spectrum of the tip-body.

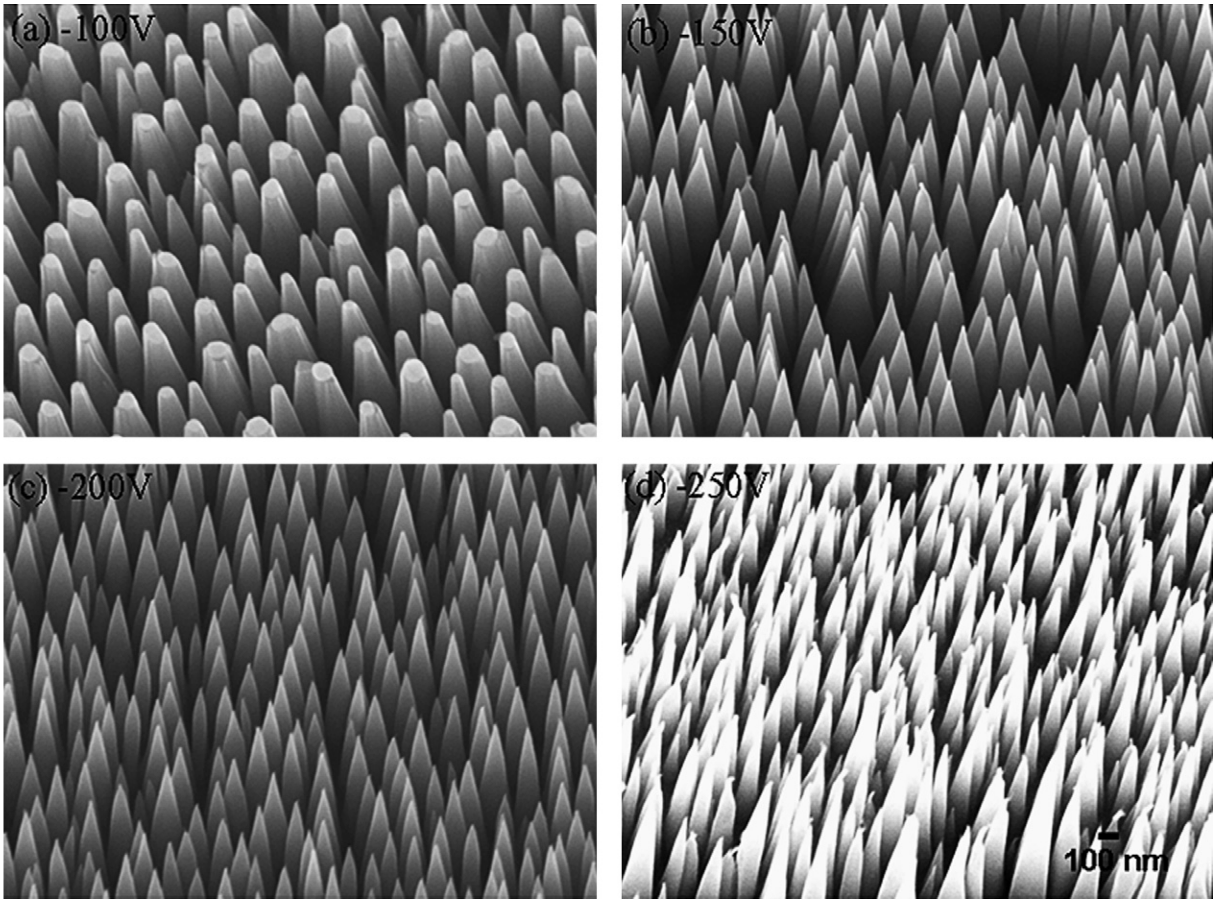


Fig. 5. SEM micrographs of carbon nanotips grow under various applied biases: (a) −100 V, (b) −150 V, (c) −200 V and (d) −250 V.

Fig. 4(b). The result shows strong signal of carbon on the body of the nanotips. Furthermore, a weak Si signal is also presented in the EDX spectrum of the tip-body, which may be due to the strong ion bombardment from the Si substrate and re-depositing on the surface of nanotips.

The applied bias effect is shown in Fig. 5; each sample was synthesized in the condition of 300 W and 30 min growth. Apparently, when the bias contrarily increases, the tip angle will decrease, namely, it becomes sharper. It could be explained that the higher bias will increase the stronger ion bombardment in plasma system. However, the metal on the top of nanotip could prevent the etching on the topside. As the bias increasing, the metallic mask on the top will gradually lessen due to a strong ion bombardment rate which caused the needle-shape structure. In addition, applying negative bias will promote the growth

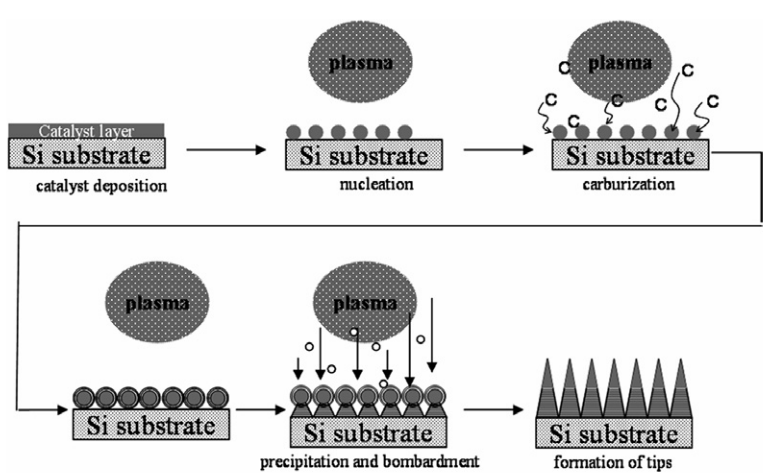


Fig. 6. The possible growth model of carbon nanotips.

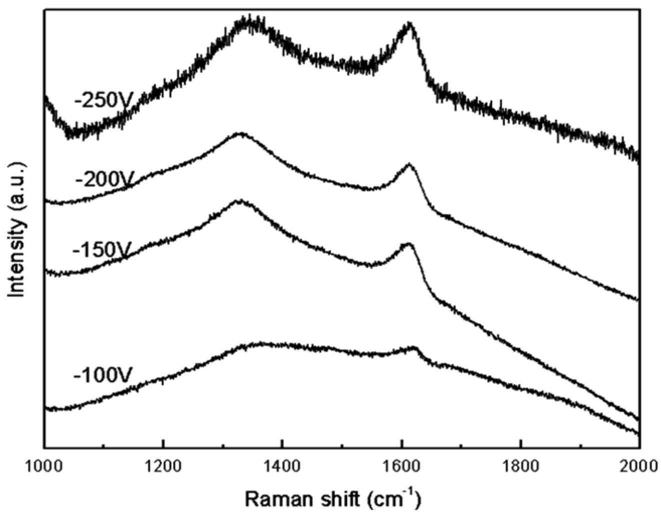


Fig. 7. Raman spectra of carbon nanotips grow under various applied biases.

of carbon nanotips. Applying bias in MWPECVD to enhance the growth of a series of carbon nanomaterials have been discussed in many researchers [13–15]. The higher tip height will cause the smaller apex angle. The possible growth model of carbon nanotips is demonstrated on Fig. 6. Fig. 7 is the Raman spectra of carbon nanotips synthesized under various applied biases. The first-order of Raman spectrum of carbon nanotips shows two peaks at 1591 $cm^{-1}$ (G line) and 1348 $cm^{-1}$, which are high frequency $E_2g$ first-order mode and the D-line associated with disorder-allowed zone-edge modes of graphite. The Raman spectra reveal that applying a high bias voltage can increase the graphite phase and diminish the disorder carbon phase of carbon nanotips. Pursuant to the consequence above, we can attribute a fact that high ion bombarded rate will diminish the content of amorphous carbon outside the nanotips under high applied bias. Other metallic catalysts, such as Pt, Ag and Si, were used for growing carbon nanotips which are presented in Fig. 8. The metallic layers, except for Si, were first deposited on the Si wafer by e-beam evaporation. The appropriate development condition for growing these nanotips is microwave power 300 W with applying −250 V bias for 30 min. This reveals that the carbon nanotips can be synthesized even using dissimilar metallic catalysts. And, all of the nanotips are tip-grow model, whish can be widely used in many region such sensor and field emission.

## 4. Conclusion

Vertically aligned carbon nanotips were synthesized by microwave plasma enhanced bias assisted chemical vapor deposition. The shape, length and sharpness can be

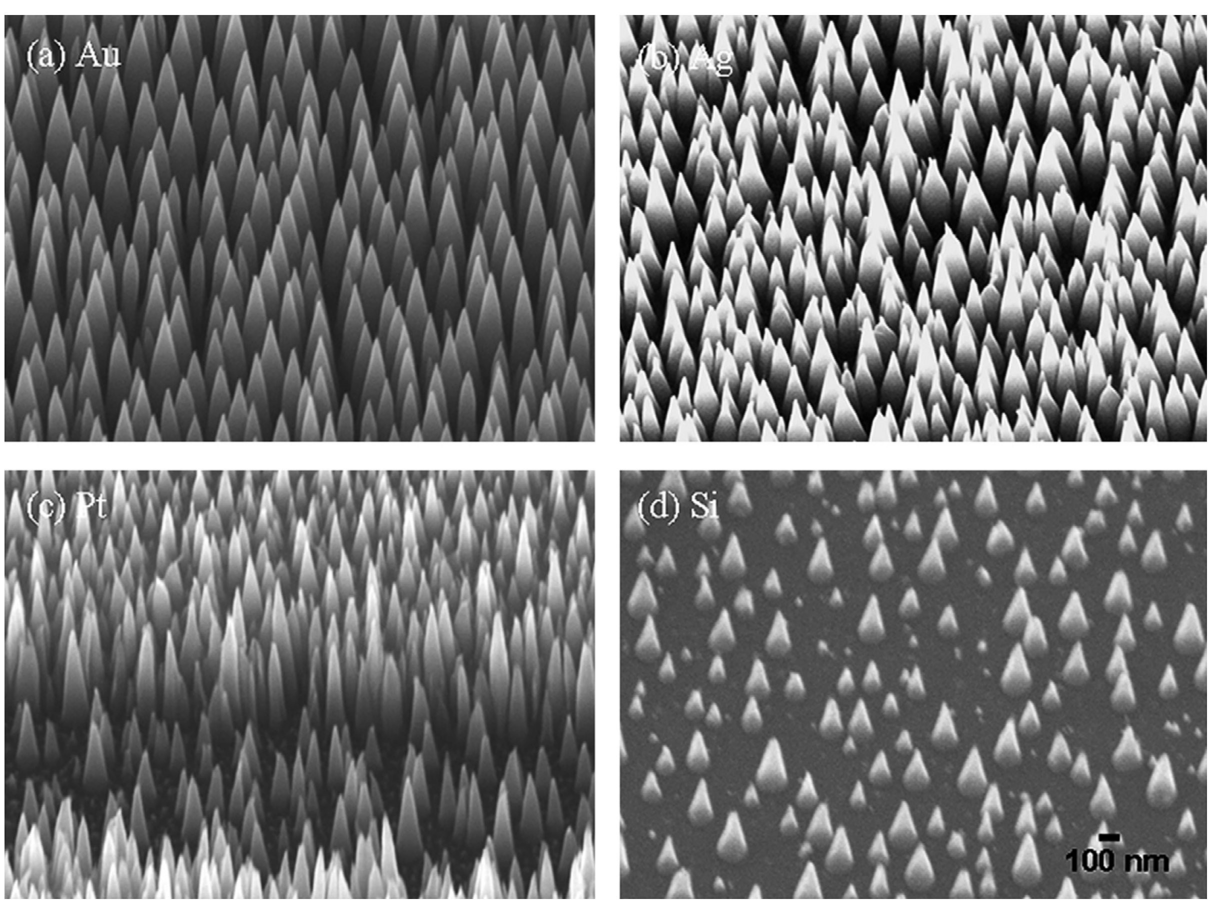


Fig. 8. SEM micrographs of carbon nanotips grow by different metallic catalysts: (a) Au, (b) Ag, (c) Pt and (d) Si.

controlled by adjusting the microwave power, process time and applied bias. The HRTEM image and EDX spectrum show that the metallic catalyst exists on the top of the tip and the nanotip is made of carbon. The possible growth model of carbon nanotips was also proposed. The low diffusion rate of carbon atoms and strong ion bombardment incur the formation of carbon nanotips. Furthermore, we demonstrated the growth of carbon nanotips with different metallic catalysts, i.e. Au, Pt, Ag and Si, which could be chosen for a practical application in various regions.

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## References

[1] X.L. Peng, Thin Solid Films 370 (1–2) (2000) 63–69.
[2] S.D. Johnson, D.G. Hasko, K.B.K. Teo, W.I. Milne, H. Ahmed, Microelectronic Engineering 61–62 (2002) 665–670.
[3] Y. Shiratori, H. Hiraoka, M. Yamamoto, Materials Chemistry and Physics 87 (1) (2004) 31–38.
[4] Xia An, Huizhao Zhuang, Li Yang, Chengshan Xue, Applied Surface Science 193 (1–4) (2002) 87–91.
[5] Yunqi Liu, Wenping Hu, Xianbao Wang, Chenfeng Long, Jinbiao Zhang, Daoben Zhu, Dongsheng Tang, Sishen Xie, Chemical Physics Letters 331 (1) (2000) 31–34.
[6] Z.L. Tsakadze, K. Ostrikov, J.D. Long, S. Xu, Diamond and Related Materials 13 (10) (2004) 1923–1929.
[7] Chun Liu, Zheng Hu, Qiang Wu, Xizhang Wang, Yi Chen, Weiwei Lin, Hai Sang, Shaozhi Deng, Ningsheng Xu, Applied Surface Science 251 (1–4) (2005) 220–224.
[8] T. Yoshitake, Y. Shimakawa, S. Kuroshima, H. Kimura, T. Ichihashi, Y. Kubo, D. Kasuya, K. Takahashi, F. Kokai, M. Yudasaka, S. Iijima, Physica B 323 (2002) 124–126.
[9] G. Kumaravelu, M.M. Alkaisi, A. Bittar, D. Macdonald, J. Zhao, Current Applied Physics 4 (2–4) (2004) 108–110.
[10] Irina Kleps, Anca Angelescu, Narcis Samfirescu, Adriana Gil, Antonio Correia, Solid-State Electronics 45 (6) (2001) 997–1001.
[11] Ying-Hong Liu, Thuc H. Dam, Paul Pantano, Analytica Chimica Acta 419 (2) (2000) 215–225.
[12] Chunxu Pan, Yueli Liu, Feng Cao, Jianbo Wang, Yaoyao Ren, Micron 35 (6) (2004) 461–468.
[13] C.L. Tsai, C.F. Chen, L.K. Wu, Applied Physics Letters 81 (4) 721–723.
[14] C.L. Tsai, C.F. Chen, Diamond and Related Materials 12 (2003) 1615–1620.
[15] Goufang Zhong, Takayuki Iwasaki, Hiroshi Kawarada, Iwao Ohdomari, Thin Solid Films 464–465 (2004) 315–318.