Investigation on reactive ion etching CVD diamond Film

Choung-Lii Chao^{1a}, Wen-Chen Chou^{1b}, Ta-Tung Chen^{2c}, and Chung-Woei Chao^{2d}

¹ Department of Mechanical and Electro-mechanical Engineering, Tam-Kang University, Taiwan, R.O.C.

² Department of Information Management, Hsing-Wu College, Taiwan, R.O.C.

^aclchao@mail.tku.edu.tw, ^bwcchou@tedns.te.tku.edu.tw, ^c096007@mail.hwc.edu.tw, ^d089009@mail.hwc.edu.tw

Abstract:

Diamond, having many advanced physical and mechanical properties, is one of the most important materials used in the mechanical, telecommunication and optoelectronic industry. It has played an important role for being advanced materials of MEMS devices. In this present study, reactive ion etching (RIE) polycrystalline CVD diamond film was conducted. The etching gases such as O_2 , O_2 / CF_4 , and O_2 / SF_6 were used in the RIE experiments. Experimental results showed that using O_2 can obtained rough etched surface where have uniform and densely sub-micro pillar-like structure formed on the diamond grains. From the Raman spectra analysis and TEM micrographs showed that the etched diamond film surfaces were transformed into graphite and amorphous carbon. In addition to the atmospheric pressure air plasma (APAP) pretreatment was also conducted before RIE process. Using the APAP process seems can help to obtain some cauliflower-like and sub-micro cone-like structures on the RIEed/ O_2 surface. Although RIEed and APAP/RIEed diamond films exhibited similar surface modified layer, their surface morphologies showed very different.

Keywords: atmospheric pressure air plasma, reactive ion etching, CVD diamond

1. Introduction

Diamond has many outstanding physical, chemical, optical, mechanical, and electrical properties [1-2]. Though diamond possesses those excellent properties, the high cost and difficulty in production have limited its industrial applications. At present, using the chemical vapor deposition (CVD) method to synthesis diamond is a rather mature and popular technology. Therefore, several potential applications can be anticipated in electronics, optics, protective corrosion resistant coatings. Owing to the properties of CVD diamond are better than conventional semiconductor materials such as silicon, diamond films have already begun to be adopted as MEMS materials. And the correlative technologies called diamond-MEMS. Today, many semiconductor etching technologies were depended on dry etching, RIE especially. However, diamond etching is a very difficult task due to its hardness and the chemical inertness. Although many RIE researches have been reported, the etching technologies of polycrystalline diamond films seem still immature [3-13]. This paper not only investigated on the surface morphological variation of diamond under different etching gases, but also compared the difference using APAP pretreatment or not. The SEM, TEM micrographs and micro-Raman spectroscopy were used to analyze the morphology and microstructure of the obtained surface.

2. Experimental

The MWCVD diamond specimens were deposited on <100> single crystal silicon substrates and the thickness of as-grown diamond film is $\sim 15\mu m$. The surface morphology and microstructure were measured by scanning electron microscopy (SEM), Micro-Raman

spectroscopy, respectively. Raman spectra were measured at room temperature with an argon ion laser ($\lambda=514nm$) and recorded at relatively low power $\sim 15mW$ on the samples. Fig.1 shows the surface morphology and quality of as-grown CVD diamond in our study.

2.1 Atmospheric pressure air plasma (APAP)

The pretreatment are carried out using the atmospheric pressure plasma equipment which made by Agrodyn Plasma Treat GmbH, Bielefeld, Germany. The working distance between specimen and jet-nozzle was 5 mm (Fig.1(a)). Air was used as the reactive gas under $5 kg/cm^2$ pressure. The specimens were set on an X-Y moving table in order to acquire uniform surface treatment. Plasma was jetted out in the form of straight stream. Treatment time was 30 sec, 1 min and 3 min, respectively.

Fig.1(a) the straight stream atmospheric pressure plasma

Fig.1 (b) the schematic diagram of the RIE apparatus.

2.2 Reactive ion etching

A SAMCO compact reactive ion etching system, operating at 13.56 MHz, was used in this work. Etching was performed under RF power at 150~200 W and the pressure was 1 mTorr. O_2 (50 sccm), O_2/CF_4 (50/10 sccm), and O_2/SF_6 (50/10 sccm) were used as the reactive gas, respectively. Fig.1(b) depicted the schematic diagram of the RIE plasma system. The etching time was 2min, 15min and 25min, respectively.

Those non-treated and etched samples were characterized by SEM (Hitachi S3000N). Crystal structures and the diamond quality were examined by micro-Raman spectroscopy (Renishaw inVia), which were excited with an Ar^+ laser (514nm) focused onto a spot of 3 μm . Fig.2 shows the surface morphology and the quality of as-grown CVD diamond which used in this study.

Fig.2(a) The surface morphology of the as-grown MWCVD diamond, (b) micro-Raman spectrum of the as-grown diamond.

3. Results and discussion

3.1 RIE

According to our previous researches showed the effective parameters of RIE were gas percentage ratios, etching time, and RF power if under the same reactive pressure [14].

Fig.3 shows the SEM micrographs of the RIEed diamond film under O_2 , O_2/CF_4 , and O_2/SF_6 , respectively. Owing to the oxygen ions acted as ideal etching agent with diamond to produce the volatility gas such as CO or CO_2 , the Fig.3(d) revealed a lot of short pillar-like microstructures formed on the diamond grains. On the contrary, Fig.3(b)(c) using mixture gas such as O_2/SF_6 and O_2/CF_4 has not yielded such microstructures. Although there showed different surface morphology, from the Raman spectra proved there have the similar surface modifications existed such as amorphous carbon

and graphite. Fig.4 shows the Raman spectra of these etched diamond films. They all nearly have the same diamond peak (1333 cm^{-1}) and the amorphous carbon phase ($\sim 1500\text{ cm}^{-1}$) band. That is to say diamond grains have been weakening through the RIE process.

For the sake of understanding which gas plays an important role in RIE process, we using pure O_2 , SF_6 , and CF_4 as experimental recipes, respectively. Fig.5 shows the SEM micrographs of the RIEed diamond in pure O_2 , SF_6 , and CF_4 , respectively (30sccm, 5min, 150W). There have distributed many tiny pits on the diamond grain facets when using O_2 as reactive gas. The pillar-like structures seem resulted from these tiny pits when etching time increased. Fig.6 shows the schematic diagram of the micro-pillar structures formed. Comparatively, diamond grain edges/tips became rounded in CF_4 and SF_6 at the same experimental conditions. In the case of mixture gases such as O_2/SF_6 and O_2/CF_4 , there have not appear pillar-like structure. Therefore, it is highly probable that SF_6 or CF_4 can suppress the microstructure formed.

Fig.3 SEM micrographs of the CVD diamond film: (a) etching in O_2 (50sccm, 25min, 200W), (b) etching in O_2/CF_4 (50/10sccm, 25min, 200W), (c) etching in O_2/SF_6 (50/10sccm, 25min, 200W), (d) the magnification of surface morphology of (a).

Fig.4 Raman spectra of the RIEed CVD diamond (25min, 200W, $O_2=50\text{sccm}$, $O_2/CF_4=50\text{sccm}:10\text{sccm}$, $O_2/SF_6=50\text{sccm}:10\text{sccm}$).

Fig.5 The grain facets and edges/tips of the CVD diamond film induced by RIE process (30sccm, 5min, 150W): (a) O₂, (b) SF₆, and (c) CF₄.

Fig.6 Schematic illustration of the micro-pillar structures formed under using O₂ as the RIE gas.

Fig.7 shows the TEM micrographs of these micro-pillar structures. From these pictures can obviously observed the modified layer existed on microstructure surface. And the core of the micro-pillar structure still is diamond structure, which was consistent with the analysis of micro-Raman spectra.

Fig.7 TEM images of these micro-pillar diamond structures.

3.2 APAP/RIE

As we know, surface treatment not only can be used to change the surface properties of material, but also can enhance the surface activities. Therefore, the atmospheric pressure plasma was used in this study and air was used as the pretreatment plasma gas source. Due to oxygen could make diamond surface form pillar-like microstructures, it also was selected as the RIE etching

gas in this section. Fig.8 showed the SEM micrographs of APAPed diamond in 30 sec, 1 min and 3 min, respectively. It is clearly to observe the surface morphology was changed from pyramid-like to the irregular shape as APAP treating time increased. The reason attributed to that using APAP pretreatment not only could activate the CVD diamond film surface but also pre-etch some defects and impurities that existed at diamond grain boundaries.

The micro-Raman spectra of the APAP treated specimens indicated the existence of graphite (~1583cm⁻¹) and amorphous carbon (~1500 cm⁻¹) on the treated surface (Fig.9).

Fig.8 SEM micrographs of APAP pre-treatment CVD diamond film in (a)30 sec, (b)1 min, (c) 3 min.

Fig.9 the micro-Raman spectra in three different APAP pretreatment time

There nearly have not any spectra difference between these APAPed specimens when treating time was increased. It means there have similar surface modified layer formed on diamond grains. The reason can be deduced that the ionized molecules such as oxygen and nitrogen bombarded the diamond grain and made the diamond surface oxidized. Therefore, it is helpful to etch quickly in RIE process when using oxygen.

Shown in Fig.10, it can clearly observe the diamond

film surface formed some micro cauliflower-like and cone-like microstructures if APAP pretreatment 30sec and RIE 25 min be used. We inferred that the cone-like structures resulted from the large diamond crystal. The reason could attribute to the surface modified layer on the diamond surface which can be etched easily in the following RIE/O₂ process. Therefore, there only have larger grains to survive. These larger diamond grains continuously were etched anisotropically. Finally the cone-like microstructures formed. In the case of smaller diamond grain would be etched out or formed some cauliflower-like microstructures during the RIE/O₂ process. It can be explained why the cone-like microstructures appear considerable quantities in 3 min APAP pretreatment.

Although the mechanism of activated diamond film by the APAP pretreatment did not to be fully understood, the combined process indeed can promote the diamond weakening quickly. The related research still has to study in the future.

Fig.10 The SEM micrographs of different APAP treatment time (a) 30sec, (b) 1 min, (c) 3 min and combined RIE process O₂ (50 sccm, 25 min, 200W).

4. Conclusions

The APAP can be used in various applications to produce some new functional surfaces. In this study, it has successfully integrated with RIE process. According to present results there have some conclusions: 1. using mixture gas such as O₂/CF₄ or O₂/SF₆ as the reactive gas of RIE, there have not micro-pillar structure appear on diamond facets; 2. using O₂ as the reactive gas some micro-pillar structures formed on diamond grains; 3. these surface modified layers or weakening structures have similar components which composed of graphite and amorphous carbon; 4. comparing pure RIE process with APAP/RIE process can obviously found the surface morphology is very different. The diamond film surface formed some micro cauliflower-like and cone-like microstructures if APAP pretreatment 30sec and RIE/O₂ 25 min be used.

References

[1] Prelas, A.M., Popovici, G. and Bigelow, K.L.

Handbook of industrial diamond and diamond films, Marcel Dekker, Inc., 1998

- [2] Hugh O. Pierson, Handbook of carbon, graphite, diamond and fullerenes properties, processing and applications, Noyes Publications, Park Ridge, New Jersey, U.S.A., 1993.
- [3] Vivensang, C., Ferlazzo-Manin, L., Ravet, M.F., Turban, G., Rousseaux, F. and Gicquel, A. "Surface smoothing of diamond membranes by reactive ion etching process", *Diamond and Related Materials* 5 (1996) 840-844.
- [4] Vescan, A., Ebert, W., Borst, T.H. and Kohn, E. "Electrical characterization of diamond resistors etched by RIE", *Diamond and Related Materials* 5 (1996) 747-751.
- [5] Sandhu, G.S. and Chu, W.K. "Reactive ion etching of diamond", *Appl. Phys. Lett.* 55 (5),31, 1989
- [6] Ding, G., Zhao, X., Yu A., Yang, C., Cai, B., and Yao, X. "Reactive ion etching of CVD diamond films for MEMS applications", *Proc. Of SPIE Vol.4230* (2000) , 224-230.
- [7] Yang, C.S., Ding, G.F., Yao, X., and Zhao, X.L. "The study on mask technology of CVD diamond thin films by RIE", *Proc. Of SPIE Vol.4230* (2000), 218-223-186.
- [8] Ding, G., Yao, J., Yu, A., Zhao, X., Wang, L., and Shen, T. "Patterning of diamond films by RIE and its MEMS applications", *Proc. Of SPIE Vol.4174*, 451-461.
- [9] Ha, S.C., Kang, D.H., Kim, K.B., Min, S.H., Kim, I.H. and Lee,J.D. "Fabrication of gated diamond field emitter array using a selective diamond growth process", *Thin Solid Films* 341 (1999) 216-220.
- [10] Wells, T., El-Gomati, M.M., Wood, J. and Johnson, S. "Low temperature reactive ion etching of silicon with SF₆/O₂ plasmas", 9th International Vacuum Microelectronics Conference, 1996, 349-353.
- [11] Lister, K.A., Casey, B.G., Dobson, P.S., Thoms, S., Macintyre, D.S., Wilkinson, C.D.W. and Weaver, J.M.R. "Pattern transfer of a 23 nm-period grating and sub-15 nm dots into CVD diamond", *Microelectronic Engineering* 73-74 (2004) 319-322.
- [12] Ando, Y., Nishibayashi, Y. and Sawabe, A. "Nano-rods of single crystalline diamond", *Diamond and Related Materials* 13 (2004) 633-637.
- [13] Ando, Y., Nishibayashi, Y., Kobashi, K., Hirao, T. and Oura, K. "Smooth and high-rate reactive ion etching of diamond", *Diamond and Related Materials* 11 (2002) 824-827.
- [14] C.L. Chao, W.C. Chou, K.J. Ma , T.T. Chen, Y.M. Liu, S.W. Huang and H.Y. Lin, "Machining of CVD diamond film by RIE, Laser Ablation and Thermo-chemical Polishing," *Leading Edge Manufacturing in the 21st Century*, October 19-22, 2005, Nagoya, Japan.