Transactions of the Materials Research Society of Japan 30[1] 287-290 (2005)

Fabrication of Diamond Nano-whiskers by Reactive Ion Etching

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Diamond whiskers were fabricated by means of reactive ion etching in radio frequency plasma reactor. Metal particles were coated onto diamond films to serve as micro-masks before etching. Etching processing was performed using O_2/Ar plasmas, with an emphasis to elucidate the effects of reacting gas on the fabrication of diamond whiskers. The results showed that the population densities and distributions of diamond whiskers dependent on the volumetric ratio of O_2 to Ar. Raman spectroscopy was carried out in order to determine the bonding structures of the whiskers. It has been found that the whiskers were still diamond after etching. Field emission characteristics of the whiskers were also inspected.
Key words: diamond films, whiskers, reactive ion etching, plasma

I. INTRODUCTION

Diamond has drawn a great deal of attentions because of its outstanding properties such as extremely high mechanical hardness, high thermal conductivity, chemical inertness, the smallest coefficient of thermal expansion, and negative electron affinity characteristics [1]. All these properties are advantageous to various applications [2]. Recently, the negative electron affinity characteristics of diamond films are considered to be highly promising for applications in electron field emission devices [3]. But the key point remains how to achieve an efficient electron field emission [4]. It has been reported that the electron field emission will be enhanced at the micro-tips of diamond [5]. Therefore, fabrication of sharper field emission tips is still a challenge issue. Among the various approaches, reactive ion etching (RIE) is considered as an efficient method to sharpen diamond micro-rods [6]. In this paper, a novel method for fabrication of nano-whiskers by reactive ion etching in O_2/Ar plasmas was reported. Metals served as masks were coated on diamond surfaces during the etching process. Furthermore, a comparison of the morphologies of diamond surfaces before and after etchings demonstrated that the properties of whiskers were dependent on the reacting gas. Field emission characteristics of the whiskers were also examined and a low turn-on field was obtained.

2. EXPERIMENT DETAILS

N-type Si (100) substrates were abraded with 5-12 μm diamond grits in ultrasonic agitator for 30 min in order to enhance diamond nucleation before deposition. Polycrystalline diamond films were deposited onto Si substrates using a microwave plasma chemical vapor deposition (CVD) reactor system ASTeX (AX-6350). The deposition process was carried out under pressure of 124 torr, microwave power of 5 kW, and flow rates of 25 and 475 sccm for CH_4 and H_2, respectively. During the deposition, the substrate temperature was kept at 900-950 ℃, monitored by a spot thermometer. After the diamond films grew to 3 μm in thickness, Al particles were coated on them for 10 min using a DC sputtering device (SANYUDENSHI, SC701HMC Quick Coater). The etching process was performed for 60 min in a self-assembled radio frequency (RF) plasma reactor with frequency of 13.56 MHz. The chamber pressure was maintained at 22 Pa. Reacting gases were introduced through a mass flow controller. In this study, the gas compositions examined were O_2 (10 sccm)/Ar (90 sccm), O_2 (20 sccm)/Ar (35 sccm), O_2 (100 sccm), and Ar (100 sccm). RF power was 100 W, corresponding to a DC self-bias voltage of -510 V for each sample. The substrate temperature was kept below 200 ℃ using a water cooling system. Raman spectroscopy was performed in order to examine the property changes of the diamond films. The samples were also inspected

using an S-3000N scanning electron microscope (SEM). XPS was used to analyze the surface components after etching.

3. RESULTS AND DISCUSSION

Figures 1-3 present the SEM images of the diamond surfaces after 60 min etching. From the top views, whiskers were found in each sample. An interesting phenomenon was that the distribution of whiskers was not random. Fig. 1(a) illustrates the result for etching in O_2/Ar plasma with 10% O_2 (vol/vol). Whiskers with 150 nm diameter and 200 nm height formed only at the grain boundaries, suggesting that the whiskers may form preferentially at the grain boundaries between diamond

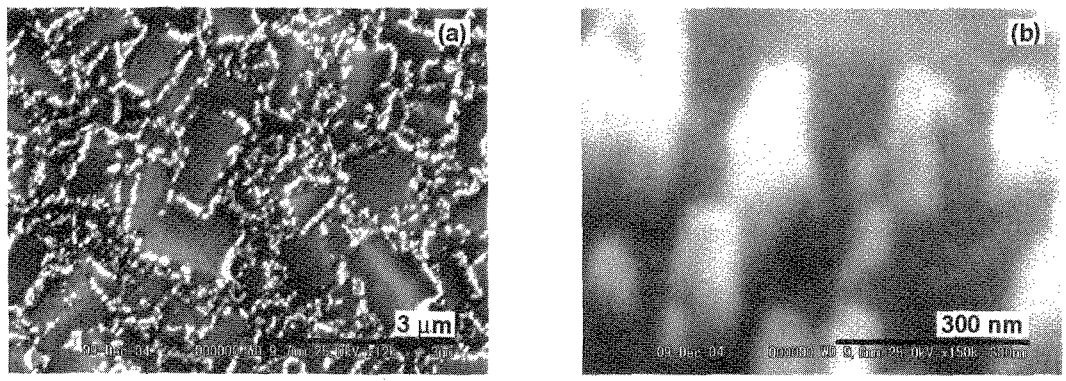

Fig. 1. SEM images of diamond whiskers obtained from etching in O_2 (10 sccm)/Ar (90 sccm). (a) top view, and (b) perspective view.

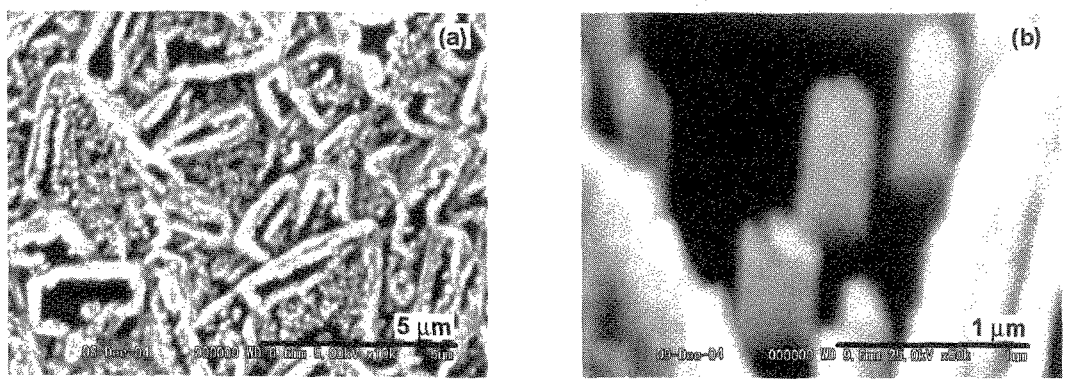

Fig. 2. SEM images of diamond whiskers obtained from etching in O_2 (20 sccm)/Ar (35 sccm). (a) top view, and (b) perspective view.

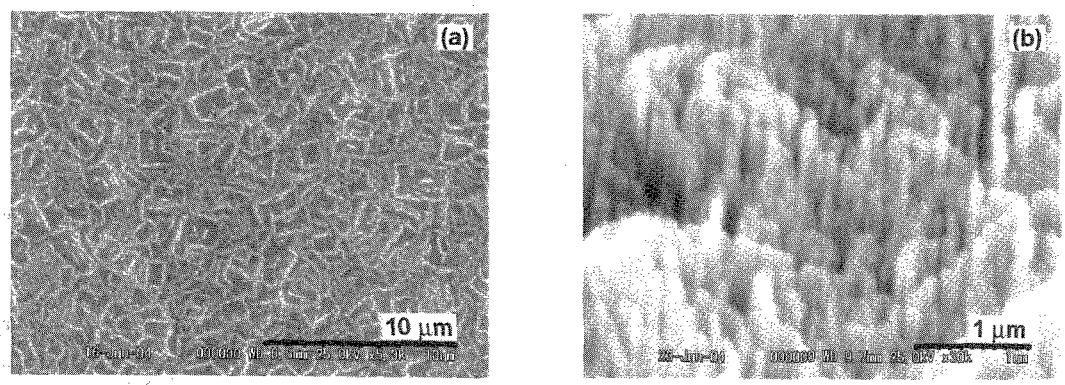

Fig. 3. SEM images of diamond whiskers obtained from etching in O_2 (100 sccm). (a) top view, and (b) perspective view.

crystals. This can be explained, most probably, by the presence of non-diamond sp^2 inclusions (e.g., graphite) [7]. However, with increasing O_2 concentration (O_2: 36%), the roots of the whiskers extended gradually into the diamond grains, as shown in Fig. 2(a). It could be noticed that the height of the whiskers remarkably increased to 900 nm. The population density of whiskers increased with the concentration of O_2. When O_2 ratio approached to 100%, the whiskers had high population density (about 40 μm^{-2}), as shown in Fig. 3(a). The average diameter of the whiskers reduced to 100 nm with a height of 1 μm. In inert gas Ar (100 sccm), whiskers could not be formed on the surfaces after etching.

In general, there were two processes during the RF plasma etching [8]. Pure Ar plasma only caused physical bombardment etching which could explain why whiskers could not be obtained in pure Ar. The diamond surface would be polished completely if the RF power was higher enough. However, the etching process was different in Ar and O_2 mixture plasmas. Whiskers obtained in the latter plasmas could be ascribed to the processes of ion-enhanced chemical etching and physical bombardment etching. O_2 would dissociate into O radicals accompanied by the formation of volatile products of CO and CO_2 [9], while Ar would contribute to bombarding the diamond surface. In the case of pure O_2 plasma, although O_2 contributed to both physical and RIE etchings, the latter effect was apparently predominant [10-11].

All of above suggested that the density and height of whiskers increased with increasing flow ratio of O_2 to Ar. But their diameters were quite different. It is conceivable that the formations of whiskers could be controlled by changing the concentration of O_2 in the reacting gas.

The metal masks were also critical to inhomogeneous erosion of the diamond films [12]. Since Al was masked on the diamond surfaces before etching, it would react with O_2 to form Al_2O_3 islands on the tops of the whiskers, inhibiting the etching underneath [13]. Other metals, such as Pt and Au, could not react with O_2. But they also could attach to the surfaces, and serve as masks due to their incomparably lower etching rate, comparing to that of the carbon substrate [14]. The remains of metal particles on the top of whiskers after etching were verified by XPS. Thus, the distribution of whiskers also might be controlled by masking metals on the diamond surfaces.

It was necessary to inspect the graphitic transformation of diamond during etching. In order to determine the structures of whiskers, Raman spectroscopy was performed for samples before and after etching. The whiskers were scraped off the substrate and collected on a piece of transparent glass. Scanning electron microscope was used to examine if there were diamond particles mixed with the whiskers. As a consequence, no diamond particles were found in the collected diamond powders. In Fig. 4, the Raman spectrum showed a typical diamond (sp^3 bonding) peak at 1332 cm^{-1} along with a low broad non-diamond (sp^2 bonding) peak at 1580 cm^{-1}. Theoretically, the Raman scattering cross-sections of the graphite should be 50 times higher than that of the diamond. If there were same quantity of sp^2 graphitic carbons, their peaks should be much stronger than that of the diamond. Obviously, for our samples, the diamond peak was much strong than the non-diamond peaks, suggesting that the whiskers had not changed their bonding structures after etching. The presence of a weak graphite peak might be attributed to a small amount of local transformation from sp^3 to sp^2. Most of the bonding structures were kept on sp^3 diamond structures during etching process. Therefore,

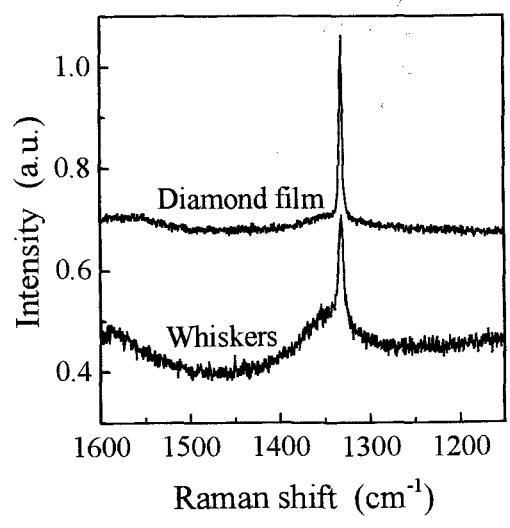

Fig. 4. Raman spectra for the diamond film and the whiskers (Al coated, O_2 100 sccm, etched 60 min).

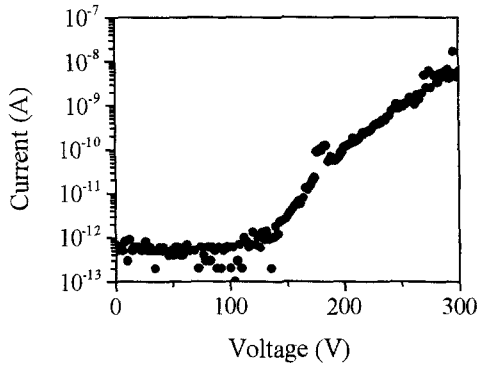

Fig. 5. Current-voltage curve from Al masked diamond whiskers (Al coated, O_2 100 sccm, etched 60 min).

we could conclude that the whiskers were still diamond after etching.

Field emission characteristic of the whiskers which etched in pure O_2 plasma was shown in Fig. 5. Samples after etching were treated in hydrogen plasma for 8 min before the field emission measurement in order to get conductive surface. The field emission measurement system was installed in an SEM observation chamber with a gap size of 10 μm. A turn-on field of 10 V/μm was obtained for the whiskers. It was much lower than the original diamond film of 40-50 V/μm which we measured in other experiments.

4. CONCLUSION

Reactive ion etching in RF plasmas is an effective method to obtain diamond whiskers. Metal masks were important factor for inhomogeneous erosion. The population densities and the distributions of whiskers could be controlled by adjusting the volumetric ratio of O_2 to Ar and by means of metal masks. There were few changes in the bonding structures of the whiskers, and they were still diamond after etching. The turn-on field of the whiskers was as low as 10 V/μm. Therefore, it is possible to use whiskers to cathode emission devices.

ACKNOWLEDGEMENT

This work was partly supported by the Grant-in-Aid for Specific Research of Priority Areas "Generation of Micro-scale Reactive Plasmas and Development of Their New Applications" (#15075209) from the Ministry of Education, Culture, Sports, Science and Technology.

The help with Raman spectra provided by Dr. Kanda is gratefully acknowledged.

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(Received December 23, 2004; Accepted January 31, 2005)