Vacuum 128 (2016) 80–84

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Short communication

Investigations on etching resistance of undoped and boron doped polycrystalline diamond films by oxygen plasma etching

Dan Liu [a], Li Gou [a, b, *], Junjie Xu [a], Kangning Gao [a], Xing Kang [a]

[a] College of Materials Science and Engineering, Sichuan University, Chengdu, China
[b] State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu, China

ARTICLE INFO

Article history:
Received 17 January 2016
Received in revised form
3 March 2016
Accepted 14 March 2016
Available online 15 March 2016

Keywords:
Diamond film
Boron-doped diamond
Reactive ion etching
Oxygen plasma

ABSTRACT

The reactive ion etching (RIE) technique was used to etch the undoped and boron-doped diamond (BDD) polycrystalline films using oxygen plasma. The effect of boron within the BDD coatings on the morphology was investigated. BDD films exhibited much superior etching resistance than the undoped diamond films, wherein the (111) planes of BDD films were more etching resistant than (100) planes due to much higher boron concentration. However, this is in contradiction to undoped diamond films whose (111) planes were etched more quickly. The results would help to better design a particular and efficient etching method for undoped and BDD films to get a well-patterned microstructures.

Patterning of diamond surfaces by dry etching is a critical step for the fabrication of many diamond-based electronic devices and sensors [1–3]. Reactive ion etching (RIE) of CVD diamond film using pure O_2-based plasma has the inherent advantages of compatibility with lithographic techniques and the ability to produce moderately high etching rate, therefore, it was reported to be the most suitable technique for CVD diamond patterning [4–6].

Diamond doped with boron results in electrically conductive boron-doped diamond (BDD), which is widely used as implantable microelectrode arrays for collecting and monitoring electrical signals [7–10], and wherein microfabrication technology such as RIE has also drawn considerable interest in the field of BDD film patterning. However, in previous RIE works [3,11–15], most studies pay close attention to etching mechanism of undoped diamond with oxygen plasma or the influence of gas pressure and microwave excitation power on the etching rate. O. Dorsch [16] studied reactive ion etching of undoped and boron doped polycrystalline diamond films to form columnar structures, and he has addressed the influence of doping concentration on the formation of columns. Foundational studies of the different etching characteristics of undoped and BDD films would benefit us to understand the significant role of boron in the RIE process, and better design a particular and efficient etching method for these films to get a well-patterned microstructures. In the present study, the effect of boron on the etching performances and the etching mechanisms for undoped and BDD films were proposed.

The undoped and BDD films were grown on intrinsic Si substrates using the microwave plasma chemical vapor deposition (MPCVD) technique. The film deposition was performed at the following parameters: total gas pressure was 4.6 kPa, microwave power 1400 W, 0.56% of methane diluted in hydrogen, temperature ~950 °C and growth time 6 h. In the preparation, boron-doping was achieved by adding trimethylboron (TMB) to the gas mixture and the B/C ratio was 8600 ppm in the gas phase. The prepared BDD films had a metallic-like resistivity of 2.993×10^{-3} Ω cm measured by Hall effect measurements. After film deposition, these CVD films were simultaneously etched in a bell-jar type microwave plasma assisted system for periods of 40, 60, and 90 min. The oxygen contained was excited by a 2.45 GHz microwave plasma. The etching plasma was sustained with a microwave power of 700 W, a process pressure of 800–900 Pa, and the O_2 flow rate of 50 sccm.

The diamond character of BDD film was confirmed by Raman spectroscopy (LabRAM HR, France). Thermogravimetric analysis (TGA) together with differential scanning calorimetry (DSC) (NETZSCH STA 449C, Germany) under flowing air was performed on the undoped and BDD samples (before plasma etching) to investigate and compare the oxidation resistant properties,

* Corresponding author. College of Materials Science and Engineering, Sichuan University, Chengdu, China.
E-mail address: gouli@scu.edu.cn (L. Gou).

http://dx.doi.org/10.1016/j.vacuum.2016.03.012
0042-207X/

samples of ~0.09 cm^2 were oxidized at temperature rate of 10 K/min to 1200 °C. The etched surface morphology changes were observed by scanning electron microscopy (SEM, Hitachi S-4800, Japan).

Fig. 1 displays the Raman spectrum of the undoped and BDD films. Compared to undoped diamond films whose classical diamond peak was around 1333 cm^{-1}, the characteristic peak for diamond (sp^3 carbon) exhibits an asymmetric Fano-like lineshape, downshifts to lower wavenumbers (1301 cm^{-1}) and attenuates. Meanwhile, two broad Raman peaks at 469.1 and 1226.2 cm^{-1} become noticeable for BDD films, and these two peaks are contributed to the locally disordered structures induced by the heavily boron doping [17,18].

Fig. 2 shows TG-DSC curves of undoped and BDD films which were simultaneously oxidized in the same condition. As shown in Fig. 2a, the undoped diamond films begin to loss mass when temperature is below 800 °C, and the mass loss platform between 780 °C and 880 °C is extremely steep. During the mass loss process, chemically activated oxygen particles would firstly convert the diamond into graphitic structure, and then the graphite-like carbons reacted with oxygen in air to release the volatile CO or CO_2 gases. The DSC curve of the undoped diamond film has a sharp peak at 885.2 °C, which is corresponded to the point of maximum slope of mass loss region in the TG curve. When temperature goes up to 1200 °C, the percentage of total mass loss is 4.86%. Compared with Fig. 2a, the onset temperature of BDD film is approximately 830 °C. The mass loss platform is extremely flat and the percentage of mass loss is just 0.94%. Results above demonstrate that the thermal stability or oxidation resistance of boron-doped diamond is much superior to that of undoped diamond.

Fig. 3a–d shows SEM images of undoped diamond film etched by oxygen plasma with increasing time. As shown in Fig. 3a and the magnified image in Fig. 3e, after being etched for 20 min, some shallow trenches appear on (111) faces of diamond grains and grain boundaries, however, (100) faces are not eroded. The sides of the shallow trenches within (111) faces are found to be parallel to their crystal edges. As the etching time increased to 40 min, numerous deepening etch pits spread over the entire (111) faces, along with the etched crystal edges of (100) textured surfaces, as we can seen from Fig. 3b. When etching for 60 and 90 min, as shown in Fig. 3c and d, {111} faceted large crystallites are severely damaged and collapsed into a multitude of wreckage of small grains. Meanwhile, some deeper etch pits gradually appear at the corner or center of the (100) faces. From the observation of surface morphology of etched (111) and (100) faces, we can find that the oxidation resistance of (100) faces is far beyond the (111) faces.

As is well known [19,20], the etching characteristics of diamond films in oxygen plasma had found to proceed via a step mechanism, that is, the desorption of original terminated hydrogen from the diamond surface and oxygen atoms saturate the dangling bonds instead, then the highly reactive oxygen atoms chemically react with the diamond film, and finally the oxidative products (CO or CO_2 gases) would escape from the system. In this point, it could be suggested that the different etching behaviors of different diamond crystallographic planes in one film is a result of their different surface conditions, namely the number of dangling bonds on the surfaces which is proportional to the plane atomic density of some certain crystallographic planes. Considering diamond is the face-centered cubic crystal structure and its lattice parameter (a) as 0.3567 nm, the plane density of some certain crystallographic planes can be computed through the relationship: *plane density* $= n/A$, where n is the number of atoms associated with the planes, A is the area of the planes. Thus, the plane density of {111} and {100} facets can be calculated as fellows:

$$\{111\}\ \text{facets}: 2\Big/\left(\sqrt{3}\Big/2 \bullet a^2\right) = 2\Big/\left(\sqrt{3}\Big/2 \bullet \left(0.3567 \times 10^{-9}\right)^2\right) = 1.8152 \times 10^{19}\left(m^{-2}\right) \quad (1)$$

$$\{100\}\ \text{facets}: 2\Big/a^2 = 2\Big/\left(0.3567 \times 10^{-19}\right)^2 = 1.5720 \times 10^{19}\left(m^{-2}\right) \quad (2)$$

Apparently, {111} facets are more reactive since more dangling bonds are revealed on their surfaces. Etching will, therefore, preferentially occur at (111) faces and the higher etching rate would be expected, while etching rate is considerably slower at (100) faces. Similar results was achieved by oxidative etching of (100) textured diamond by P. John [21] and F.K. de Theije [22], who showed that (111) faces etched in dry oxygen are morphologically rough and oxygen would destabilize the surfaces, while (100) faces are strongly stabilized by the adsorption of oxygen. Taking account of this mechanism, the sides of trenches should parallel to the ⟨110⟩ direction which has the highest linear atomic density as shown in Fig. 3e.

The surface morphology of BDD films etched by oxygen plasma

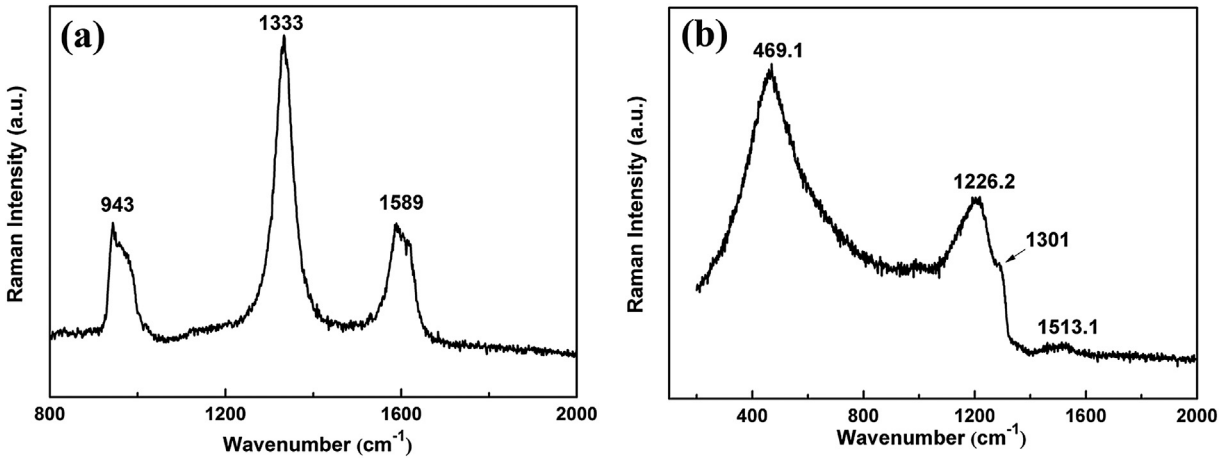

Fig. 1. Raman spectrum of undoped (a) and boron-doped (b) diamond films, $\lambda_{ex} = 632$ nm.