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Versatile doping technique for diamond by solid dopant immersion during microwave plasma CVD

Takahiro Tamura[1], Takashi Yanase[1], Taro Nagahama[1],Susumu Sato[2], Toshihiro Shimada[1]

[1] Hokkaido Univ.
Division of Materials Chemistry, Faculty of Engineering
Kita 13 Nishi 8, Kita-ku, Sapporo 060-8628, Japan
Phone: +81-11-7706-6576 E-mail: shimadat@eng.hokudai.ac.jp
[2] ARIOS Inc.
Musashino 3-2-20, Akishima-si, Tokyo 196-0021, JAPAN
Phone:+81-42-546-4811

Abstract

We have developed a simple and versatile technique for the growth of doped diamond films by immersing solid dopant source to plasma during plasma CVD. We report detailed characterization of boron doped diamond using X-ray diffraction, Raman spectroscopy, and transport measurement.

1. Introduction

There is an increasing interest for the doping techniques of various elements to diamond, because they will lead to high voltage electronic devices[1], fluorescent biomarkers[2], magnetic sensors[3] and quantum information processing[4]. Popular methods for the doping to diamond are (1) plasma CVD using gaseous compounds of dopants that is introduced to the reaction vessel [5], or (2) ion implantation followed by annealing [6]. (1) has a problem of using toxic gases, whereas (2) has problems of low throughput and not uniform concentration. Since the efficient dopants are still searched for various applications, simple and versatile technique for the doping to diamonds is needed.

In this paper, we propose a technique for the doping to diamond, i.e., immersing solid state compound containing dopant to the plasma during CVD. We demonstrate it for boron doping, with the detailed characterization by x-ray diffraction, Raman spectroscopy and transport measurement.

2. Experimental setup

We used a compact microwave plasma CVD equipment which uses the microwave antenna as the sample holder, which was developed by ARIOS Inc. [7]. We used Si(001) and diamond (001) substrate for the growth. The substrates (3-10 mm) were placed on a molybdenum sample holder after chemical cleaning and further cleaned by H_2 plasma (1000^{o}C, H_2 pressure 6000Pa, microwave power 200W, 6h). The diamond was grown using a mixed gas of methane and hydrogen (CH_4 : H_2 = 1.2% : 98.8%). The plasma CVD of diamond was performed at 1000 ^{o}C and 5500 Pa with 80 sscm gas flow. The growth was typically continued for 24 hours and the thikness of the grown diamond was ~ 30 μm. For the boron doping, a sintered boron rod (diameter 6 mm) was immersed in the plasma with the distance of 30mm, which was varied to search for the optimum parameters. The picture taken during the growth is shown in Fig. 1.

Fig.1 Snapshot of plasma CVD of diamond with immersing a boron rod to plasma

2. Result and discussion

We used glow discharge optical emission spectroscopy (GDOES) to confirm the boron doping. This technique uses etching of the sample by the glow discharge in argon gas, and depth profile of element distribution can be obtained. Boron signal was detected along with strong carbon signal and the ratio B: C was uniform throughout the film thickness.

X-ray diffraction of the film shows the diamond crystal structure of the film without bi products. Figure 2 shows Raman spectra of obtained without (b) and with (a) immersing the boron rod into the plasma. They are substantially different from each other and the Fig. 2(b) agrees well with the spectrum of boron-doped diamond in the literature. It was reported that the Raman peak around 1332 cm^{-1} of diamond is sensitive to the concentration of boron in the diamond [8]. By comparing the shape of the curve, the concentration of the boron is estimated to be around 2 %.

Since B-doped diamond with the high boron concentration exhibits superconductivity [9], we measured the transport properties at low temperature. Figure 3 shows the sheet resistance of the B-doped polycrystalline diamond film grown on Si(001). Four gold electrodes were deposited on the film for the measurement in PPMS (Quantum Design). It shows a sudden decrease below 1.8 K. It is not clear whether it is superconductivity or not because zero resistance was not observed. We consider that this strange behavior of the resistivity is due to the lateral non-uniformity of the dopant concentration due to the geometry of the sample and boron rod, which can be improved.

Since it is expected that any elements can be atomized by immersing them to the plasma as used in GDOES elemental analysis, this technique will be applicable to various elements.

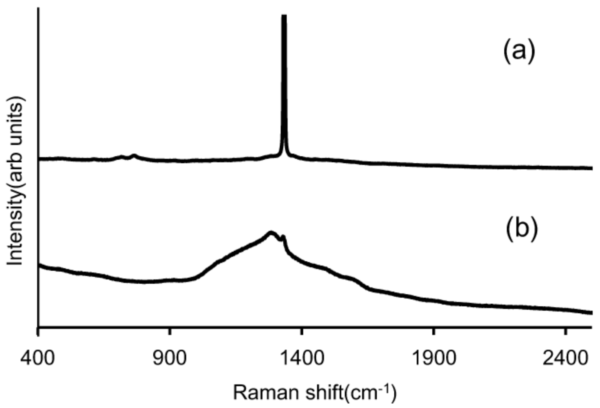

Fig. 2 Raman spectra of diamond films grown without (a) and with (b) the immersion of a boron rod.

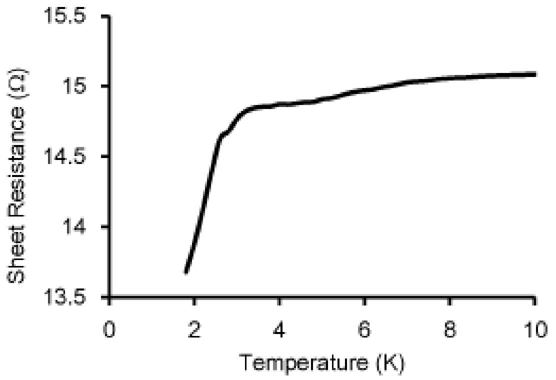

Fig. 3 Transport property of a diamond film grown with boron-rod immersion.

4.Conclusion

We demonstrated a new simple technique for doping various elements to diamond by taking example in boron doping. It does not require toxic gas source but boron concentration up to 2 % seems to be obtained.

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