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ICP etching of polycrystalline diamonds: Fabrication of diamond nano-tips for AFM cantilevers

H. Uetsuka *, T. Yamada, S. Shikata

Diamond Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Japan

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Abstract

Diamond nano-tips for measurements of living-cell activities have been fabricated from polycrystalline diamond/Si substrates using an inductively coupled plasma reactive ion etching (ICP-RIE) system. Mixtures of O_2 and CF_4 gas in a plasma was used as etching atmosphere. The etching properties of polycrystalline diamond film have been characterized. During etching of polycrystalline diamond, unintentional nano whiskers were formed due to the inhomogeneity of chemical bonds at grain boundaries. Finally, nano-tips longer than 10 μm and with an apex radius below 50 nm without nano whiskers have been realized.

Keywords: Polycrystalline diamond; Nano-tip; ICP etching; Nano-cell mapping; AFM

1. Introduction

During recent years great progress has been achieved in nano-biotechnology. Especially, the investigation of living-cells has attracted significant attention. Here, a large number of fluorescent markers have been widely used for detection of cell behaviour, however, only information about concentration and position in cells are obtained. On the other hand, 'nano-cell mapping' will be one of the most promised technologies to detect cell activities in living-cells. Fig. 1 shows a concept of nano-cell mapping where spatio-temporal phenomena are traced taking place in inner-cell regions or inter-cells regimes. Here, thin tips are inserted into living-cells. Chemicals such as proteins, DNAs, antibodies, amino acids etc. attached to the tip can be injected into the cell or bio-molecules can be captured from the cell. Furthermore, biological response can be investigated during applying mechanical, irradiative, and electric perturbation to living-cells using specially modified nano-tips. The driving tools of atomic force microscope (AFM) cantilevers are available for precise control of tip positions (Fig. 1b). Nano-tips required for nano-cell mapping should be of high rigidity, should show a high aspect ratio (diameter of tip apex $<$400 nm, tip length$>$6 μm), be conductivity, biocompatibility, and of low invasiveness [1]. Features of diamond such as rigidity, chemical stability, biocompatibility, and bio-functionability [2,3] are much more favourable for such applications than those of Si which is however widely used for AFM tips. The conductivity of diamond can be easily controlled by doping. This can be very beneficial for diamond tips to be used for electrical or electrochemical treatments. Inductively coupled plasma reactive ion etching (ICP-RIE) is a suitable technology for fabrication of such tip structures with short processing times because of the high-plasma density and an independent control of ion flux and ion energy. There are several reports about diamond etching by ICP-RIE to improve etching rate and anisotropy [4], for field emitters [5], for micro-lenses [6], and for fabrication of tip structures [7,8]. However, all these studies have been performed on single crystalline diamond.

In this paper, micro electro mechanical systems (MEMS) techniques like monolithic processes including photolithography and ICP-RIE have been applied in order to develop commercially-available fabrication method for diamond nano-

* Corresponding author. 1-1-1 Umezono, Tsukuba, 305-8568, Japan. Tel.: +81 29 861 5080x55102; fax: +81 29 861 2771.
E-mail address: hiroshi.uetsuka@aist.go.jp (H. Uetsuka).

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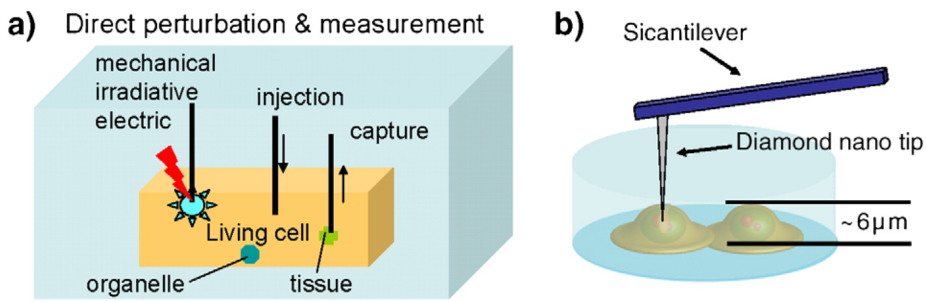

Fig. 1. The concept of 'nano-cell mapping' is shown. Goals are the measurement of signals caused by stimulation of cells using inserted tips. Injection and capture of bio-molecules are also an objective.

tips on diamond/Si substrates. Therefore, polycrystalline diamond has been selected as the material of choice taking mass productivity and cost into account. Fabrication of thin diamond tips from single crystalline diamond for electron field emitter devices have been reported in the literature [9,10]. These reports focus on single crystalline diamond while only few etching studies with respect to tip fabrication for electron field emitter have been done on polycrystalline diamond [11–13]. AFM cantilevers with diamond tips have been fabricated using mold transfer technique, where, wet-chemically etched pyramidal holes in Si are used as mold and polycrystalline diamond is then grown into it to obtain pyramidal shaped tips [14–17]. However, this approach is not suitable for the production of thin tips with a high aspect ratio. Focused ion beam (FIB) has been applied to realize inverted conical molds [17]. This technique has also been applied to prepare electron field emitters.

2. Experimental details

Polycrystalline diamond films grown on Si wafer (ϕ 2 in.) by hot-filament chemical vapour deposition (HFCVD) method were mainly used as substrates. Thicknesses of the films were above 15 μm. Single crystalline diamond of Ib(100), homo-epitaxially grown boron doped diamond film on Ib(100), and boron doped polycrystalline diamond (free standing) were also used for comparison of etching rate. In the present study, an ICP etching system (ULVAC 300I) was used to etch diamond substrates. Fast etching rate and verticality of structure are favourably obtained by the etching method. Mixture of O_2 and CF_4 plasma (gas pressure: 0.6 Pa) was used for diamond etching. Typical antenna and bias powers were 1000 and 100 W, respectively. Surface patterning with circler dots was carried out by photolithography technique after Al or SiO_2 film deposition on diamond as hard mask. The detail procedure of sample cleaning and photolithography was stated in the literature [8]. Scanning electron microscope (SEM) and profiler were used to characterize the structure of diamond nano-tips.

3. Results and discussion

The etching behaviour of single crystalline Ib(100) diamond, of boron doped single crystalline films grown on Ib(100) substrates, and of free-standing boron doped polycrystalline films were characterized. Fig. 2 shows the etching rate achieved on these substrates. Here, Al of 100 nm thickness was used as hard mask. Dots of 5 μm diameter were fabricated using photolithography. The etching rates are almost the same with an averaged etching rate of 18.8 μm/h. This result shows that conductivity and crystallinity of diamonds do not affect the etching rate during ICP etching. Please note that the etching rate of the Al hard mask applying identical parameters is 1.6 μm/h which results in an etching ratio diamond/Al of about 12. As shown in Fig. 3, unintentional nano whiskers are generated by this etching. While only a few whiskers can be detected on Ib (100), it seems that much more whiskers are generated on boron doped single crystalline diamond (Fig. 3b). As shown in Fig. 3c and d, the height of all whiskers is lower than that of the nano-tips. The height depends on how thin whiskers are and when whiskers begin to form. Whiskers are generally thinner than tips. The apex of whiskers is easy to etch. Therefore lower whiskers are obtained. There are three types of whiskers. One type arranges along grain boundaries. These whiskers are rather homogeneous in height. They are generated at the same time, maybe at the beginning of the etching process due to the difference in chemical composition of grains and grain boundaries. Second type is the randomly generated whiskers within grains. These whiskers have a variety of heights and widths. These are generated at intrinsic defects in the crystals and micro masks caused by sputtering and re-deposition of hard mask material. The third kind of whiskers is regularly formed in specific grains which depend on surface orientation of the grains. These whiskers are much thinner, and are therefore also lower in height. Etching which prevents the generation of

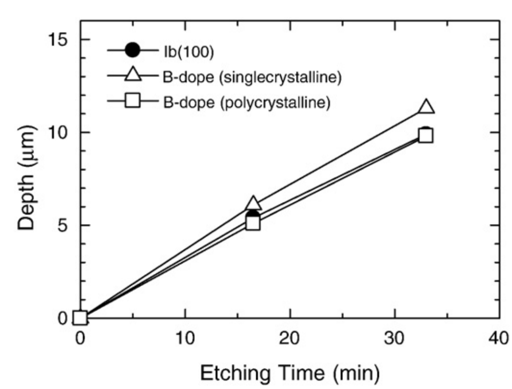

Fig. 2. Etching rates of different diamond substrates.