Materials Science and Engineering C 43 (2014) 135–144

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Fabrication of planarised conductively patterned diamond for bio-applications

Wei Tong [a], Kate Fox [a,*], Kumaravelu Ganesan [a], Ann M. Turnley [b], Olga Shimoni [a], Phong A. Tran [c], Alexander Lohrmann [a], Thomas McFarlane [a], Arman Ahnood [a], David J. Garrett [a], Hamish Meffin [d,e], Neil M. O'Brien-Simpson [f], Eric C. Reynolds [f], Steven Prawer [a]

[a] School of Physics, University of Melbourne, Parkville, Victoria, Australia
[b] Department of Anatomy and Neuroscience, University of Melbourne, Parkville, Victoria, Australia
[c] Department of Chemical and Biomolecular Engineering, University of Melbourne, Parkville, Victoria, Australia
[d] National Information and Communication Technology Australia, Victoria 3010, Australia
[e] Department of Electrical and Electronic Engineering, University of Melbourne, Victoria 3010, Australia
[f] Oral Health Cooperative Research Centre, Melbourne Dental School, The University of Melbourne, 720 Swanston Street, Victoria 3010, Australia

ARTICLE INFO

Article history:
Received 8 April 2014
Received in revised form 15 May 2014
Accepted 3 July 2014
Available online 10 July 2014

Keywords:
Diamond
Planar
Neural
Biocompatible
Antibacterial

ABSTRACT

The development of smooth, featureless surfaces for biomedical microelectronics is a challenging feat. Other than the traditional electronic materials like silicon, few microelectronic circuits can be produced with conductive features without compromising the surface topography and/or biocompatibility. Diamond is fast becoming a highly sought after biomaterial for electrical stimulation, however, its inherent surface roughness introduced by the growth process limits its applications in electronic circuitry. In this study, we introduce a fabrication method for developing conductive features in an insulating diamond substrate whilst maintaining a planar topography. Using a combination of microwave plasma enhanced chemical vapour deposition, inductively coupled plasma reactive ion etching, secondary diamond growth and silicon wet-etching, we have produced a patterned substrate in which the surface roughness at the interface between the conducting and insulating diamond is approximately 3 nm. We also show that the patterned smooth topography is capable of neuronal cell adhesion and growth whilst restricting bacterial adhesion.

1. Introduction

The use of diamond in microelectronics [1] and in advanced biomedical devices [2–5] has been considered and attempted for many years. Compared with silicon, the standard material of the microelectronic industry, diamond stands out for its mechanical strength, chemical inertness, high thermal conductivity, excellent biocompatibility, high breakdown voltage and extreme working temperatures [1,6–8]. With the development of technology, diamond films can now easily be fabricated onto silicon substrates using chemical vapour deposition (CVD). Here, it is possible to deposit a wide range of diamond films with differing grain sizes depending on the growth conditions elicited by the plasma chamber. The type of diamond films deposited onto the substrate differ according to their grain sizes, and includes polycrystalline diamond (PCD, micro-size crystal), nanocrystalline diamond (NCD, <100 nm) and ultrananocrystalline diamond (UNCD, <5 nm) [9]. As an electrical material, UNCD is attractive as it has the capacity to improve its conductivity by incorporating materials such as boron and nitrogen during its CVD growth. After nitrogen incorporation, the conductivity of UNCD (N-UNCD) can be five orders of magnitude higher than an undoped version of the UNCD (UNCD) [10] due to the increase of sp^2 carbon and the density states associated with π bonding within grain boundaries [11]. This makes N-UNCD promising for applications in electrochemistry and electronics. Moreover, some in vitro studies suggest that UNCD may be as biocompatible as traditional electrode materials (e.g. platinum) and thus N-UNCD offers a possibly more suitable material for the fabrication of biomedical microelectromechanical systems (bio-MEMS) [7,12,13].

The surface roughness of a material is of high importance for a variety of applications including microelectronics and biomedical devices [3,8,14]. The most common microelectronic material, crystalline silicon, continues to be the most optimal material due to its semiconducting properties, low cost and its capacity to routinely product submicron devices. However, crystalline silicon substrates when used for MEMS and NEMS devices suffer from poor mechanical and tribiological properties [15]. Accordingly, diamond based electronics have the potential to fulfil this role. MEMS and NEMS require planar low roughness surfaces. However, to achieve a low surface roughness topography on diamond is challenging. In general, the growth side of the CVD diamond surface is

---

* Corresponding author. Tel.: +61 3 9035 4973.
E-mail address: kfox@unimelb.edu.au (K. Fox).

http://dx.doi.org/10.1016/j.msec.2014.07.016
0928-4931/

rough. PCD diamond is typically rough and UNCD, although somewhat smoother under standard CVD fabrication, remains rough on the micron scale. Therefore, to improve the performance of diamond-based devices for applicability in MEMS applications as well as an electrode device, it is necessary to find an easy and effective way to fabricate planar diamond devices.

Surface roughness of the sample is also a critical component in developing a biologically implantable material. Cell adhesion appears linked to the lateral length scale of a cell relative to the surface roughness of the material it seeks to adhere to as well as the cell surface contact area [16]. This means that cells likely prefer a surface that is either significantly smoother or roughened with troughs magnitudes larger than its cell body size [17–20]. Cell sizes differ from 1 μm to 100 μm depending on the cell type and its biological role. To this end, the optimal surface roughness is tailored to its biological application. Here we seek to fabricate not only a planar device capable of MEMS applications but also a device capable of neural stimulation. Here, the surface must allow for neural population adherence whilst ameliorating bacterial infection. It is well known that smoother surfaces of neural implants are likely preferable to a rougher surface to decrease the likelihood of bacterial adsorption and infection [16].

Another challenge in fabrication of diamond-based devices is in its patterning. Good patterning technology results in precise patterns as desired and little or no damage to the surface of the substrates. There are two mainstreams of diamond patterning process: bottom-up [21–24] and top-down [25–32]. The first method, the bottom-up approach, uses selective seeding to elicit the deposition of diamond on certain areas. Conventional methods normally involve selective etching of nanodiamonds seeds or selective deposition of other materials, which yields higher nucleation density than the substrate [21,22]. Although these bottom-up methods showed minimal damage to the substrates, the technique is reported to suffer from poor selectivity resulting in the nucleation at undesired areas. The long-term fabrication consequence is that the pattern becomes uncontrollable whereby the expansion of patterns with an increased deposition time changes the size or the shape of the desired patterns. The top-down technique, in comparison, relies on the direct etching of diamond using strong energetic species, such as ion beam [25], lasers [26] and reactive ion etching [27]. Among them, reactive ion etching or inductively coupled plasma reactive ion etching of diamond using oxygen or oxygen mixtures is the most commonly used technique. The basic principle is straightforward, whereby exposed diamond surface is chemically etched by reactive oxygen species in combination with physical etching caused by ion bombardment [29]. Here, the patterns fabricated by dry etching have the merit of precision. However, due to the lack of investigation into the interface between the etching process and the substrate, it is unknown as to whether or not the process is potentially damaging the substrates and accordingly influencing the performance of the fabricated device.

Here, we report the development of precisely patterned monolithic diamond substrates for the use in micro- and bio-electronic applications. Here, we show that a diamond substrate can be developed having a topographically smooth surface whilst also comprising inlaid, precisely patterned conductive features. This planarised substrate was developed using both conductive (N-UNCD) and insulating (UNCD) diamond. The detailed fabrication process is outlined to disclose the growth of diamond by microwave-enhanced plasma CVD, inductively coupled plasma reactive ion etching, a second diamond growth and silicon wet-etching. The resultant diamond surface shared a similar roughness to the sacrificial silicon substrate. The morphology and chemical bonding structures were compared between the smooth diamond fabricated by our method and the as grown diamond surface. Finally, the results of a neuronal cell culture and a bacteria adhesion assay are reported to show the importance of diamond surface roughness and conductivity in its biomedical applications.

The conductive diamond array embedded monolithically in the insulating diamond matrix presented here offers a number of advantages from both the prospective of device processing and biomedical application. It opens the possibility of its integration with other electronic devices using methods such as thin-film processing, where nanometre flatness is critical for achieving high performance devices. Moreover as it will be demonstrated in this paper, the interaction of the smooth conductive/insulating diamond in vivo offers a number of advantages. The planar diamond substrate appears to be an excellent neural biomaterial as the smooth interfacial surface appears capable of supporting both neural cell activity and neurite outgrowth whilst remaining resistant to bacterial activity.

2. Experimental section

2.1. Diamond film deposition

The UNCD film was grown on a 10 mm × 10 mm silicon substrate using microwave-enhanced plasma CVD. Unless specifically mentioned, silicon substrates were cleaned using a tri-alcohol (acetone/methanol/iso-propanol) wash and seeded by ultrasonication of the silicon in a methanol solution comprising 3–5 nm nanodiamonds (Armor, Inc.) for 5 min and rapidly dried by nitrogen gas. The CVD growth conditions differed depending on the type of diamond deposited. UNCD films were grown using a mixture of methane/argon/hydrogen gas in a relationship of 1:79:20. N-UNCD films were grown by replacing the hydrogen with nitrogen such that the gas mixture of methane/argon/nitrogen was 1:79:20. The total pressure of the gas for all diamond growths was kept at 80 Torr and the plasma power used was 1250 W, with the substrate temperature kept at 800 °C. A summary of the samples are outlined in Table 1.

2.2. Low surface-roughness conductive diamond fabrication

For fabrication of the planarised conductive diamond, samples were acquired using the following steps as detailed below and as displayed in Fig. 1.

1) Silicon substrates were first ultrasonicated with acetone, methanol and IPA for 5 min each and rapidly dried in nitrogen gas. Then the silicon substrates were treated with oxygen plasma for 1 min and seeded with nanodiamonds by sonicating in the nanodiamonds/deionised water (DIW) solution for 5 min. The nanodiamonds were previously treated with hydrogen gas in a furnace for 3 h to be hydrogen terminated. The seeding with hydrogen-terminated nanodiamonds ensured a more uniform growth of UNCD. Then UNCD films were deposited onto the seeded silicon substrates for 1 h to get a thickness of about 600 nm.
2) An aluminium hard mask was fabricated on UNCD films by depositing 100 nm of aluminium followed by conventional photolithography. An aluminium etchant of H_3PO_4, HNO_3, CH_3COOH and DIW with a ratio of 80:5:5:10 was used to etch exposed aluminium after photolithography and the photoresist was removed by acetone afterwards.
3) Oxford PlasmaLab 100 ICP-RIE systems were used for diamond patterning. A 15 min cycle of pure oxygen plasma was used for etching

Table 1
Brief description of the samples used in this study.

Abbreviation	Sample Description
UNCD	Insulating ultrananocrystalline diamond (≈0.01 S/cm^2)
N-UNCD	Conductive nitrogen incorporated ultrananocrystalline diamond (≈46 S/cm^2)
$UNCD_G$ or $N\text{-}UNCD_G$	The growth side of the diamond. This is the face of the diamond that was exposed to the CVD plasma during the film deposition.
$UNCD_S$ or $N\text{-}UNCD_S$	The silicon side of the diamond. This is the face of the diamond that was adjacent to the sacrificial silicone substrate during the film deposition. The face is exposed once the silicone substrate is removed via acid etching.