Electrochimica Acta 246 (2017) 68–74

Contents lists available at ScienceDirect

Electrochimica Acta

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

Probing the flat band potential and effective electronic carrier density in vertically aligned nitrogen doped diamond nanorods via electrochemical method

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ARTICLE INFO

Article history:
Received 24 January 2017
Received in revised form 4 June 2017
Accepted 5 June 2017
Available online 6 June 2017

Keywords:
diamond nanorods
reactive ion etching
nitrogen doping
mott schotkky analysis

ABSTRACT

One-dimensional diamond nanorods (DNRs) were fabricated from nanocrystalline diamond films using a facile combination of microwave plasma enhanced chemical vapor deposition and reactive ion etching (RIE) techniques. Structural and electrochemical properties of undoped and nitrogen doped DNRs were thoroughly investigated. A cyclic voltammetry study revealed the increase in density of charge carriers when doped with nitrogen. Mott Schottky analysis was implemented for the quantitative determination of the flat band potential, effective density of charge carriers and energy band diagram, which revealed that the undoped sample exhibit *p*-type behavior, whereas the nitrogen doped sample showed *n*-type behavior. Defect related damage due to graphitization and hydrogen termination in the undoped DNRs (during RIE) was correlated with the *p*-type conductivity. Nitrogen doping induces n-type conductivity and enhances effective density of charge carriers.

1. Introduction

Doped diamond films are used in electronic and electrochemical sensing application for long due to their biocompatibility, chemical inertness, long term stability [1]. The electrochemical analysis suggest that the surface chemistry and electrical conductivity of this material highly depend on the dopant as well as surface pretreatment [2–4]. Conventionally, boron doped diamond film is used extensively in electrochemical detection techniques [5,6]. However, the difficulty in surface modification and unsatisfied selectivity of boron doped diamond films, sometimes restrict its usage in electrochemistry [7]. Electrochemical properties of *n*-type diamond films have gained increasing attention recently for their excellent sensing ability [8,9]. Diamond is often doped with phosphorus, nitrogen etc. to make it *n*-type [2,10]. Recent reports also showed that nitrogen doped nanodiamond films have been used successfully for the simultaneous detection of biological specimens [7,11].

Generally, one dimensional (1D) nanostructures possess high surface-to-volume ratio and tunable electron transport properties due to their quantum confinement effect. In two dimensional thin films, accumulation of charge carriers occurs only on the surface, whereas, the charge accumulation or depletion in the 1D nanostructure takes place in the "*bulk*" structure, thus giving rise to large changes in the electrical properties that permits the detection of small entities [12,13]. Zinc oxide nanowires, silicon oxide nanowires, carbon nanotubes, conducting polymers nanowires, metallic nanowires are the nanostructures used extensively in electrochemical studies [14–16].

Nanostructures of extremely hard and chemically inert materials such as diamond have been obtained by top-down methods e.g. reactive ion etching (RIE) process and also by bottom-

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http://dx.doi.org/10.1016/j.electacta.2017.06.030
0013-4686/

up approaches [17–19]. Shiomi et al. reported the fabrication of porous diamond nanofilms by RIE using oxygen gas [20]. Nanostructured honeycomb diamond films were synthesized by etching diamond through porous anodic alumina mask [21]. Moreover, diamond nanopillar arrays were produced using self-aligned Au particles as the etching mask in a biased assisted RIE with H_2/Ar plasma [22]. It was reported that nitrogen doping in diamond nanowire films enhanced the electrochemical performance [4,7,11]. The superior current density in cyclic voltammetry was postulated due to nitrogen incorporation and increase in grain boundaries of the nitrogen doped sample. However, the exact reason for the superior electrochemical performance of N-doped diamond is not completely clear.

In this work, we have fabricated diamond nanorods (DNRs) from nitrogen doped nanocrystalline diamond films *via* a combination process of microwave plasma enhanced chemical vapor deposition (MPECVD) synthesis for the growth of diamond films and RIE process using O_2 gas for fabricating DNRs. To understand the role of nitrogen doping on electrochemical properties of nanodiamond materials, an extensive electrochemical analysis was carried out on undoped and N-doped DNRs electrodes. The chemical response and the role of surface functionalization were investigated by cyclic voltammetry (CV) analysis. The energy band levels were drawn and the density of charge carriers was calculated using electrochemical Mott-Schottky analysis. The uniform and increased edge planes and N-doping in DNRs were associated with the enhanced defect density of states and was correlated to the boosted current density and carrier density. The study also provided a better understanding about the kinetics of electron transfer. To check the suitability of the electrode as a sensor, the detection of caffeine was performed using square wave anodic stripping voltammetry (SWASV).

2. Methods

2.1. Synthesis and material characterization

Two types of nanocrystalline diamond (NCD) films were grown on mirror polished (100) oriented silicon (Si) wafers. Prior to diamond growth, the Si substrates were seeded with a water based colloidal suspension of 5 nm detonation nanodiamonds [23]. On the seeded Si substrates NCD films of 600 nm thick were grown in an ASTeX 6500 series MPECVD reactor. To grow undoped NCD films, a gas mixture of CH_4 and H_2 with flow rates of 3 and 297 sccm (CH_4/H_2 = 1/99), respectively, was excited by 3000 W microwave power. The total pressure in the chamber was maintained at 20 Torr. The substrates were heated due to the bombardment of the plasma species and the growth temperature was estimated to be around 540 °C during the growth of undoped NCD films as measured with an optical pyrometer. For the growth of nitrogen doped NCD films, a gas mixture of CH_4, H_2 and N_2 with flow rates of 18, 267 and 15 sccm ($CH_4/H_2/N_2$ = 6/89/5), respectively, was excited by 3000 W microwave power, and the total pressure in the chamber was again maintained at 20 Torr. The growth temperature during the growth of nitrogen doped NCD films was estimated to be around 650 °C. The surface of both diamond films was then masked using a pseudo-stable suspension containing nanodiamond particles in deionized water. The nanodiamond particles served as etching mask for fabricating diamond nanorods (DNRs) [24]. After masking, the NCD films were etched using the RIE process in O_2 gas at a direct current power of 200 W for 30 min. The obtained DNRs were characterized by scanning electron microscopy (SEM; FEI Quanta 200 FEG microscope), confocal micro-Raman spectroscopy (Horiba Jobin-Yvan T64000 spectrometer) and X-ray photoelectron spectroscopy (XPS; Thermo-VG Scientific

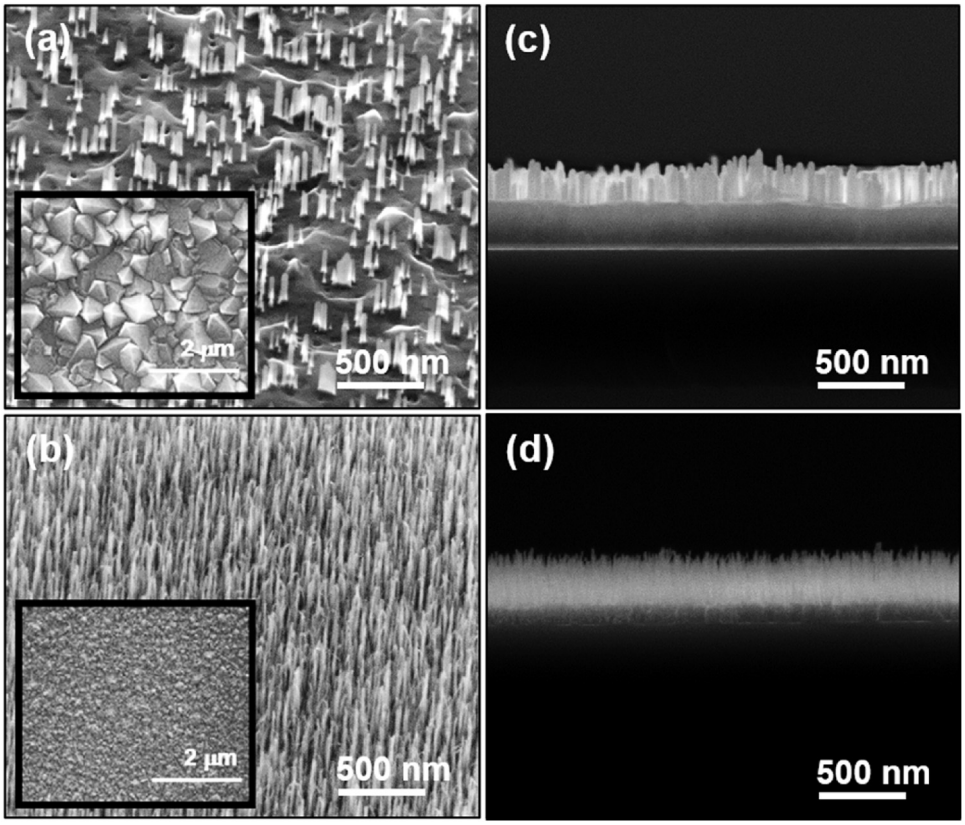

Fig. 1. (a) and (b) Tilt view and (c) and (d) cross-sectional view SEM micrographs of undoped diamond nanorods and nitrogen doped diamond nanorods. The insets of (a) and (b) are the corresponding plane view SEM micrographs of the nanocrystalline diamond films used as starting material.