

CHEMICAL PURIFICATION AND CHARACTERIZATION OF DIAMOND NANOPARTICLES FOR ELECTROPHORETICALLY COATED ELECTRODES

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Received: May 18, 2005

Abstract. Synthetic diamonds nanoparticles can be produced either by detonation or by chemical vapor deposition (CVD) techniques. Trinitrotoluene (TNT) detonation yields, among other carbon structures, diamonds nanoparticles with diameters in the range from 2 to 10 nm. Purification of nanoparticle diamond (NPD) is important because small amounts of graphitic impurities and other carbon structures in diamond can alter its most important properties. We carried out chemical purification of commercially available NPD by refluxing in aqueous HNO_3 and characterized the samples by spectroscopic and surface techniques before and after purification.

As a first step in the preparation of electrodes for electrochemistry, we have electrophoretically deposited thin, highly uniform layers of controlled thickness (1–8 μm) on silicon substrates using the purified NPD and have characterized them by scanning electron microscopy (SEM). Such structures could also be used in many other applications.

1. INTRODUCTION

Diamond is appreciated and valued due to its intrinsic properties, including exceedingly low reactivity (high chemical inertness), low background current, and wide electrochemical potential stability range. These make it a very interesting material for study, as well as an attractive material for industrial applications [1].

Purity is very important in diamond; presence of any impurity can alter the intrinsic diamond properties. A useful example is the doping of diamond with boron or other dopants, which allows its use in electrical and electrochemical applications. However, the presence of graphitic or amorphous carbon impurities tends to degrade the superior prop-

erties mentioned. This is also true for nanoparticle diamond (NPD, 2-10 nm, also called ultradisperse diamond or UDD), typically produced by detonation of a carbon source such as charcoal with an explosive such as trinitrotoluene (TNT). Its narrow size distribution is also a characteristic of diamond particles found in meteorites and protoplanetary nebulae. Although various techniques have been examined, treatment in hot aqueous acid solution is effective.

The properties and behavior of NPD are being studied recently, because they can differ from those of larger size (μm); they are true nanoscale materials. One of the more potentially useful characteristics is the extremely high surface, which, together

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with the highly specific nature of the surface functional groups [2], makes NPD an attractive candidate for a catalyst or electrocatalyst support material.

In the present work, in addition to the chemical purification [3], we have examined electrophoretic deposition (EPD), which is a very simple, powerful and useful technique to obtain the desired thin film structure. This technique has been applied in the fabrication of films by deposition of powders from suspensions to produce thin films and coatings on various substrates [4,5].

The product of the purification process was characterized by XRD, XPS, Raman spectroscopy and TEM techniques. The electrophoretically deposited NPD layers were characterized by scanning electron microscopy (SEM).

2. MATERIALS AND METHODS

Chemical Purification. The NPD sample (high-purity UDD, 2-10 nm particle size) was provided by the Alit Company (Kiev, Ukraine). The purification was carried out in a reflux system, in which two grams of NPD were boiled for 42 hours at $\sim 130^\circ\text{C}$ in nitric acid (4 M). The samples were then filtered and washed with nanopure water to neutral pH and then washed with methyl alcohol. This specific method has previously been successfully used for the purification of carbon nanotubes [3]. After this procedure, the sample was characterized by Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM), the latter in a Zeiss 200-kV instrument.

Electrophoretic Deposition. Electrophoretic deposition was carried out with the use of an in-house constructed Teflon cell, in which the silicon wafer substrates were mounted securely, and a medium-voltage power supply EC135-90, E-C Apparatus Corporation. Both NPD samples used (purified and non-purified, Alit Company, Ukraine, 2-10 nm particle size) were mixed with isopropyl alcohol to prepare suspensions (0.1% and 0.5%); these were sonicated for 30 min before the electrophoretic deposition. Into the EPD cell were mounted two electrodes, cut from highly boron-doped silicon wafers (100) (cleaned in piranha solution $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2, 3:1$); these were immersed in the suspension. The deposition process was carried out in constant voltage mode at room temperature. The applied voltages used were between 240 and 300 V. After EPD, the samples were dried at 105°C for 30 min to remove

solvent traces. The thin, uniform layers ($\sim 1\text{-}10\ \mu\text{m}$) obtained were examined with SEM (JEOL 5800 LV scanning microscopy, the samples were coated with a gold layer to avoid charging).

3. RESULTS AND DISCUSSION

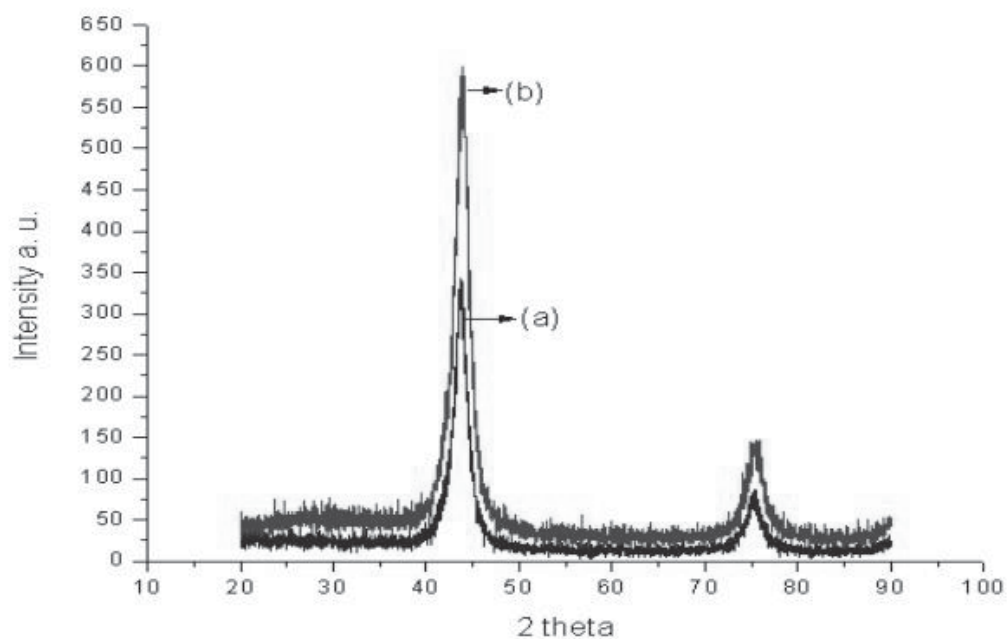
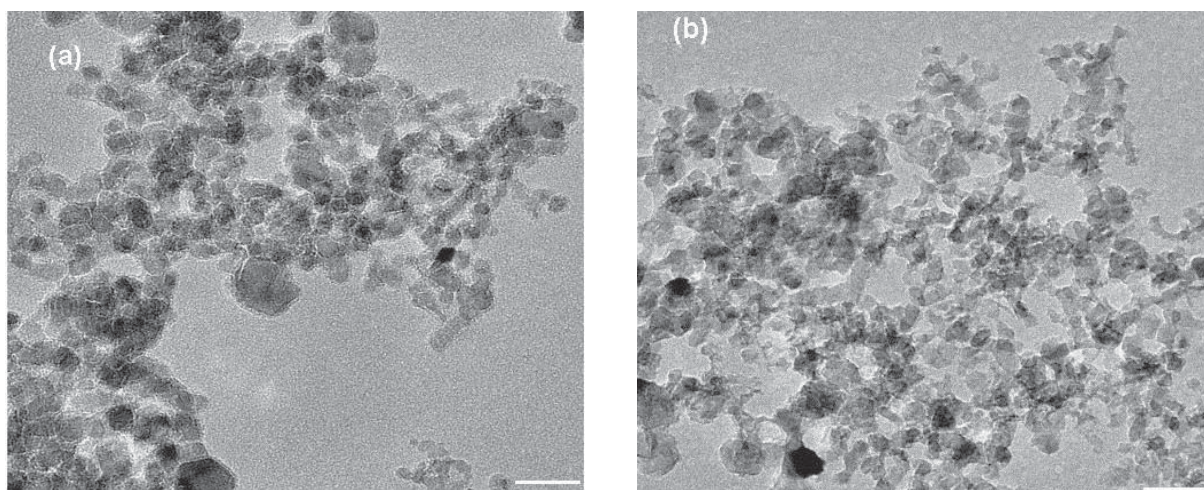
The purification process produced significant differences with some of the characterization techniques but not others. The most noticeable difference was observed in the XRD patterns (Fig. 1); the difference between the intensities of the peaks corresponding to the (111) face of diamond ($2\theta = 43^\circ$) was clear: in the purified UDD sample, the intensity was high, which indicates a higher degree of crystallinity, the purification process must have removed non-diamond material or diamond of lower crystallinity. For the non-purified sample, the peak height was relatively small, indicating a lower purity. The Raman and XPS (not shown) analyses do not show very noticeable differences in the spectra; however, in some areas, the TEM images for the non-purified NPD (Fig. 2a) show greater agglomeration and in other areas a thin layer of either amorphous carbon or graphite covering the diamond nanoparticles. In other areas, the diamond particles were clean and well separated, as they were in the purified sample (Fig. 2b); this is consistent with the XRD results.

We have found that the EPD technique is the most suitable for the preparation of highly uniform, adherent NPD layers on silicon substrates. It is also possible to control the thickness of the deposited layers over the range from 1 to $8\ \mu\text{m}$ by varying the deposition conditions (voltage, time, concentration). The deposited layers were characterized with SEM. The SEM images (Fig. 3) show the uniformity of the deposited layers, with constant thickness and absence of holes or cracks. Two samples were used: non-purified UDD and purified UDD ($\text{HNO}_3, 4\text{M}, 130^\circ\text{C}$). For the purified sample, with the conditions shown, we were able to achieve the thinnest deposited layer ($\sim 1\ \mu\text{m}$). For other sets of deposition voltages and times, the thicknesses ranged up to $8\ \mu\text{m}$ (see Table 1).

This process depends on the sizes and chemical properties of the particles in suspension, including surface functional groups such as hydroxyl groups, ether groups, carbonyl groups and carboxylic acid groups [6]. In general, there is charge on the particle surfaces that can occur due to selective adsorption of ions from the liquid, dissociation of ions from the solid phase into the liquid, and adsorption or orientation of dipolar molecules at the

Table 1. Thicknesses of electrophoretically deposited UDD films on B-doped Si.

Sample	Conc. wt. %	Voltage, V	Time, s	Thickness, mm
Alit (non-purified)	0.5	300	20	8
	0.5	240	10	7
Alit (purified)	0.5	300	20	7
	0.5	245	12	4
Alit (purified)	0.1	260	30	1

**Fig. 1.** XRD spectra of Alit diamond powder: (a) Non-purified, (b) Purified.**Fig. 2.** TEM images of Alit diamond powder: (a) Non-purified, (b) Purified. Both bar scales correspond to 20 nm.

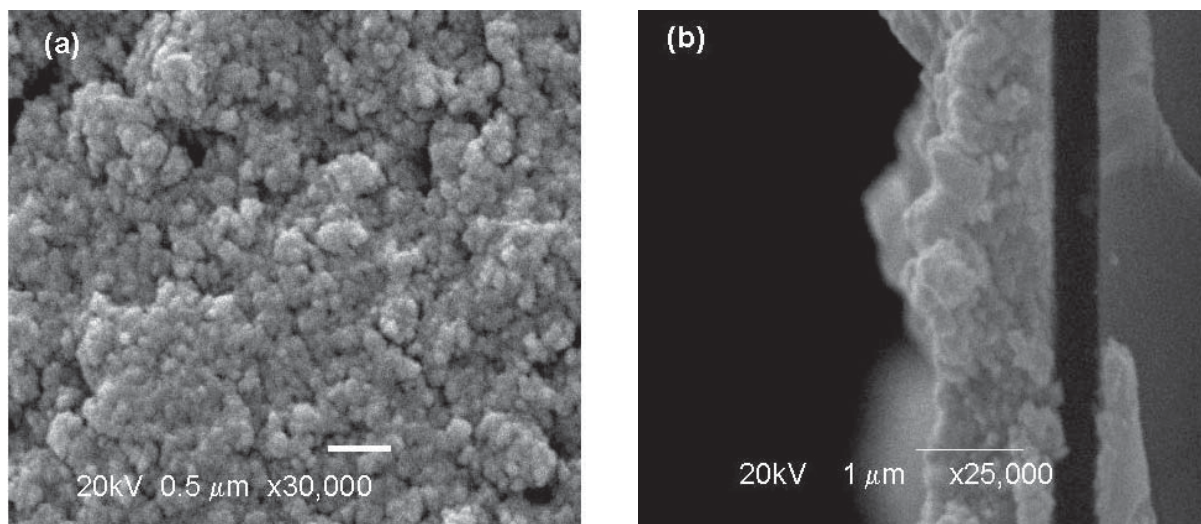


Fig. 3. SEM images of a thin layer of purified NPD electrophoretically deposited: (a) surface view; (b) cross-sectional view. This image shows the thickness of the NPD layer ($\sim 1 \mu\text{m}$) and its conformity with the B-doped silicon wafer substrate. The experimental conditions were: 1% diamond powder suspension; electrodeposition time, 30 s; voltage, 260 V.

particle surface. In the present work, the particles that are deposited are positively charged, because they form on the negative electrode. We are now studying the surface in more detail in order to understand the origin of this charge. In any case, even without this detailed knowledge, the great advantage of this technique is that the voltage, time and suspension concentration can be tuned in order to obtain the desired layer thickness, as is demonstrated with the SEM images.

In continuing work in our laboratory, these deposited layers will be subjected to further procedures associated with making them electrically conductive, so that they can be used as electrodes.

4. CONCLUSIONS

On the basis of the results obtained, we can conclude that the UDD sample, which has already been subjected to stringent purification by the manufacturer, still contains a low level of impurities that can be removed by further chemical purification; good results were obtained with the combination of a concentrated strong oxidizing acid, heat and extended treatment. The treatment time might be decreased if a mixture of acids were used.

The electrophoretic deposition experiments demonstrated that layers of different thicknesses can be obtained via variation of the voltage, time and

concentration of the NPD suspensions. All layers obtained were homogenous in thickness and without cracks or holes. This is a very encouraging result, because these layers, after being subjected to further treatments, can be used as electrodes in a variety of applications such as fuel cells (e.g., direct methanol) or lithium batteries.

ACKNOWLEDGEMENTS

We would like to acknowledge the assistance of members of the Materials Characterization Center, NASA Center for Nanoscale Materials, and the Dr. Gonzalez laboratory facilities all at the University of Puerto Rico, Rio Piedras Campus. The authors acknowledge the financial support from the ARL Collaborative Technology Alliance in Powder and Energy Cooperative Agreement No. DAAD19-01-2-0010 and NASA-URC Grant Number NCC3-1034.

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