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Enhanced diamond nucleation on copper substrates by employing an electrostatic self-assembly seeding process with modified nanodiamond particles

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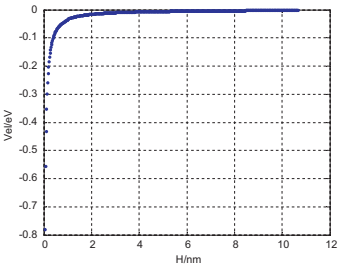
HIGHLIGHTS

- Surface modification and fractionalization prepared a nanodiamond colloid.
- Two-dimensional self-assemblies of nanodiamond seeding without any contaminations.
- The seeding process was revealed from the nonlinear Poisson–Boltzmann theory.
- The interaction energies between ND particle and Cu substrate were calculated.
- High quality of 800 nm thick continuous diamond film was deposited in 60 min.

GRAPHICAL ABSTRACT

By adopting the nonlinear Poisson–Boltzmann theory, the electrostatic energy in the seeding process was calculated, where a_2 = 25.3 nm, and the measured zeta potentials of ξ_1 = −41.5 mV, ξ_2 = 70.7 mV for nanodiamond particles and copper substrate, respectively, at pH 6.7, are used in the analysis. As the curve shown, when the distance between nanodiamond particles and copper substrate decreases, the value of the electrostatic energy exponentially increases.



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ABSTRACT

Nanodiamond seeding is a well-established approach to enhancing the nucleation density in chemical vapor deposition (CVD) diamond growth. However, the effects of nanodiamond seeding are highly dependent upon the dispersion properties of nanodiamond particles, the solvent and the interaction between nanoparticles and substrate surfaces. Surface modification and fractionalization were employed to improve the dispersion of nanodiamond particles and separate those particles into a more narrow range of particle size. Mono-dispersed nanodiamonds with a ζ-potential and average particle size of −41.5 mV and ∼25.3 nm, respectively, were then obtained. They can be charged on copper substrate without any contaminations. Two-dimensional self-assemblies of nanodiamond seeding were actualized. The density and homogeneity of nanodiamond particles which act as pre-existing sp^3 seeds shorten the incubation time of diamond nucleation to less than 30 min. High quality of 750 nm thick continuous diamond film was deposited on copper substrate in 60 min. Furthermore, we calculated electrostatic interaction energy between nanodiamond particle and copper substrate by using the nonlinear Poisson–Boltzmann theory, and discussed interaction energy of nanodiamond-Cu substrate and nanodiamond–nanodiamond in the seeding process.

1. Introduction

CVD diamond deposition on non-diamond substrates requires surface treatment in order to achieve a high nucleation density [1]. One of the most widely used approaches is seeding the substrate with diamond particles dispersed in an appropriate solvent

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accompanied by ultrasonic agitation [2–4]. Nanodiamond (ND) particles have been shown to provide the highest nucleation density as compared to ultrasonic treatment with particles of larger size [4]. Furthermore, ND seeding can cover complex surfaces, including porous structures [5] and 3D nano/micro-electromechanical systems (N/MEMS), avoid inducing mechanical damage and provide high precision during creation of seeded patterns on the substrate [6]. Girard et al. [7] reported that nanocrystalline diamond films of 70 nm thick had been obtained by electrostatic grafting of ND on cationic polymer-coated silicon substrate.

On one side, ND particles, produced from carbon-containing explosives, have a nano-scaled diameter. They can easily aggregate during synthesis and subsequent treatments, especially when added into a variety of solvent. Consequently, further deagglomeration and dispersion are necessary [8,9]. On the other size, ND seeding is a complicated system since it involves ND particles, dispersion solvent and the substrate. Though mono-dispersed ND is adopted, larger aggregation still forms during drying process, which may originate from the mismatch of surface properties between ND particles and the substrate or low dispersion stability of ND colloid. The uneven seeding will decrease seeding density and damage the homogeneity of diamond film.

Mendes de Barros et al. [10] have compared the effects of several dispersion liquids on diamond seeding from five key liquid properties such as: dipole moment, density, vapor pressure, surface tension and viscosity. The results identified that n-hexane and n-pentane are the most suitable liquids. Shenderova et al. [11] demonstrated that combination of dimethyl sulfoxide (DMSO) and alcohol as seeding solvent allowed the removal of the solvent without damaging the uniformity of ND seeds after they distributed over a substrate.

Therefore, in order to achieve homogenous seeding in CVD diamond growth, ND surface chemistry, colloidal stability, the interaction energy between ND particles and the substrate are needed to be overall investigated.

Due to its extreme mechanical, thermal and electrical properties, CVD diamond deposition on copper substrate has attracted many interests. Since copper is immiscible with carbon, graphite layers are needed to be produced as intermediate, which requires a very long induction time (>10 h) [12,13]. This special nucleation kinetics resulted into low nucleation density [14,15].

Because of these factors, ND particles were modified and fractionated to seed the copper substrates. Those ND particles with negative ζ-potential can be charged on copper substrate. This self-assembly method will reach the ideal seeding case: a compact layer of ND particles homogeneously dispersed on the copper substrate. Diamond films deposited later presented high quality with incubation time shorter than less than 30 min.

2. Experimental details

2.1. Surface modification and fractionalization of nanodiamond

ND particles were loaded in the crucible, then put in the stove and heated in air atmosphere within the temperature range of 725–750 K for 30 min. Before taken out for further investigations, the samples were cooled along with the stove under the surrounding room temperature. Following the heat treatment, ND particles were dispersed in de-ionized water using a direct-immersion horn-type ultrasound sonicator (output power of 100–400 W) [16,17]. Then, the ND suspension was further fractionated by a multipurpose refrigerated centrifuge (Thermo Electron Corporation). At the end of fractionation, the supernatant was diluted with an aqueous 0.001 M KCl solution to 0.05 wt% concentration, and subjected to sonication bath to obtain a stable colloid (KCl is an inert electrolyte).

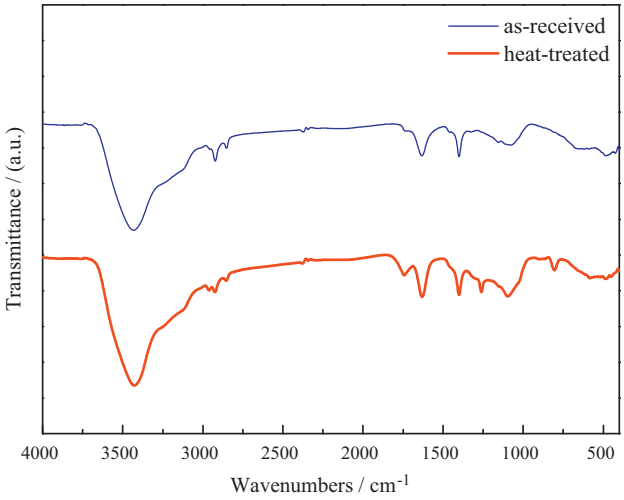

Fig. 1. FTIR spectra of as-received and heat-treated sample.

Fourier transform infrared (FTIR) spectroscopy was introduced to analyze the functional groups on ND surfaces, using the standard technique of KBr-pellet with Nexus 470 (Thermo Nicolet, USA). ND particles were dehydrated before the analysis. Malvern Zetasizer Nano ZS (Malvern Instruments Ltd., UK) was adopted for measurement of the particle size.

2.2. Electrostatic self-assembly seeding

For electrostatic self-assembly seeding, cleaned copper substrates were immersed in the aforementioned colloid for 10 min. The copper substrates taking positive ζ-potentials in 0.001 M KCl solution and ND with negative ζ-potentials facilitate the rapid formation of a nanoseeding layer. The copper substrates were then rinsed in de-ionized water, and blow-dried. After those processes, only those particles which have strong interaction with the substrate were remained.

Electrokinetic measurements of copper substrate and ND particle were carried out in 0.001 M KCl solution with an EKA electrokinetic analyzer from Anton Paar (Graz, Austria) [18]. Hydrochloric acid and sodium hydroxide were used as regulators to modify pH value of the aqueous solution. The zeta-potential values were calculated from the measured streaming potentials by using the Smoluchowski equation.

2.3. Diamond films deposition

Diamond films deposition were carried out in a hot filament chemical vapor deposition (HF-CVD) system which has been described elsewhere [19]. The normal growth conditions were: methane concentration, 2%; hydrogen, 98%; deposition pressure, 3 kPa; substrate temperature, 1023 ± 50 K.

Samples were characterized by field-emission scanning electron microscopy (FE-SEM FEI, Sirion200) and Raman spectroscopy (LabRAM HR800, Ar^+ ion laser operating at 488 nm with an output power of 100 mW), respectively.

3. Results and discussion

3.1. Surface functional groups

The transformation of surface functional groups on ND is shown in Fig. 1. As a result of heat treatment, the FTIR spectrum of ND becomes smooth, confirming higher uniformity in the composition of sample surface. The absorption peak at 1742.60 cm^{-1}