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Thickness controlled and smooth polycrystalline CVD diamond film deposition on SiO_2 with electrostatic self assembly seeding process

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ABSTRACT

Sub micrometer thick continuous CVD diamond film was synthesized on thermally grown SiO_2 film employing the electrostatic self assembly seeding with nano-meter sized ultra dispersed diamond particles. Hot filament CVD system was used to deposit diamond film. Formation of mono-dispersed and mono-layered nano diamond seeding layer by well-known Electrostatic Self-Assembly method was effective to increase density and homogeneity of seeding particles. Because of high density of uniformed seeding particles, the nm controlled continuous CVD films with the surface roughness of less than 13 nm on silicon oxide without any mechanical damage were obtained. Linear growth rate with short incubation time was also observed. Depending on the film thickness, coloring effect was observed ranging from blue to yellow and orange. There was no visible fringe on the coated surface which affirms the good thickness uniformity.

1. Introduction

Since the first report of the detonated diamond particles [1], there has been considerable effort aimed at applying these unique nano diamond particles as a reinforcing additive for high performance structural composites, drug delivery vehicle for bio-chemical application, and pretreatment agent for diamond nucleation enhancement [2–5]. Although S. Iijima et al. reported direct diamond growth from fullerene particles consist of sp^2 bonding, nano diamond particles have been regarded as a better seeding material than fullerene on account of their sp^3 imbedded structure [6]. Some research groups used these nano diamond particles to enhance the nucleation density of CVD diamond. Although the individual size of the nano diamond particles is normally smaller than 5 nm, as-purchased these particles form a few hundred nanometers to a micrometer sized hard aggregates. Without a hard-aggregate-breaking dispersion process, ultrasonication with nano diamond particles is the same mechanical process as a conventional ultrasonic vibration seeding process with a nano and micro meter sized diamond particle mixture. On the other hand, it is difficult to avoid inducing mechanical damage to the substrate using this process. In acidic solutions, ultrasonic seeding with nano diamond particles to achieve a higher nucleation density has been reported [7]. For a more efficient seeding treatment, the aggregated nano diamond particles should be crushed. The application of high revolution blades is the only known method of effectively disintegrating the hard aggregates by vigorously stirring the micro ceramic beads and nano diamond particle mixtures. Mono-dispersed nano diamond particles through high rpm milling system were recently employed as an ultrasonic seeding process [8–10]. Very fine grain diamond films were successfully obtained on Si and quartz substrate with a high initial nucleation density by this process [11]. A more homogeneous and high density of seeded nano diamond particles are needed to ensure large area uniformity and uniform film growth. To meet this necessity, the well-known and fully developed ESA (Electrostatic Self-Assembly) method was used to prepare a mono-dispersed and mono-layered nano diamond seeding layer. As a dispersion agent of nano diamond particles, strong anionic polymers were added to the nano diamond solution to stabilize the cationic nano diamond surface exposed to the high revolution milling process crushing hard aggregates of nano diamond particles. After this vigorous stirring sequence, the anionic polymer coated nano diamond particles showed good dispersion stability. The polymer/nano diamond colloid has the same characteristics over 2 weeks in an ambient laboratory environment. This anionic polymer/nano diamond conjugates were used as a brick for a layer-by-layer process [12]. A cationic polymer monolayer coated substrate was prepared as a counterpart of this brick. This ESA based nano diamond particle seeding process can be applied to any metallic and ceramic substrates, which have negative or positive charges, with large area uniformity without any mechanical impact on the surface. In this study, this process was used to make an 80 nm–300 nm thick smooth polycrystalline diamond films on a SiO_2 surface. The thickness of the diamond film was controlled by the deposition time. For thickness control, a conventional hot filament CVD chamber was redesigned to

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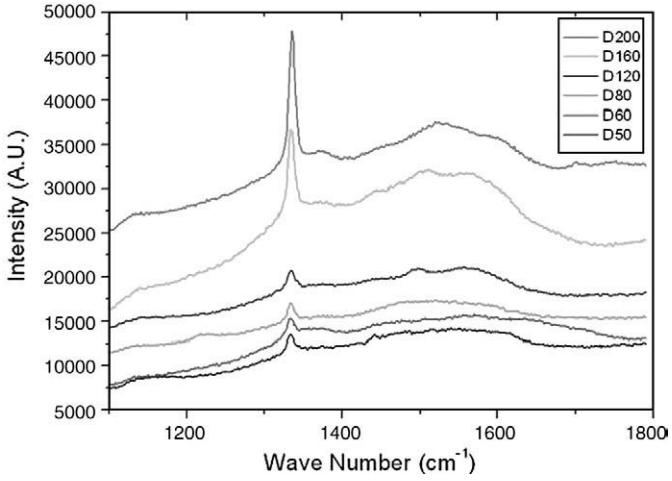

Fig. 1. Raman spectra of polycrystalline CVD diamond films according to the deposition time.

have a low growth rate (~83 nm/h). This low growth rate was attributed to the double wall water cooled cold chamber, shorter gas stream line, and auxiliary cooling system for a colder deposition environment.

2. Experimental

2.1. Sample preparation

Thermally oxidized Si (100) wafer is used as an oxide substrate. Thickness of oxide layer is 1 μm. Nano diamond powder was purchased from JinGangYuan New Material Development Co., LTD. According to the specification provided by the manufacturer, the average size of individual particle is 3.2 nm. However, most of the particles exist as a form of hard aggregate, which are hardly crushed down to smaller particles through common ball milling. Vigorous attrition milling process was employed to crush down the hard aggregates and to coat the nano diamond particles with anionic polymer. Nano diamond particles were mixed with 10 vol.% aqueous PSS (poly sodium 4-styrene sulfonate Mw: 70,000) solution by attrition mill at 1000 rpm for 5 h. After the milling process, cationic nano diamond particles were coated with anionic PSS chain. For the seeding process, cleaned substrate was dipped into 10 vol.% PDDA (poly diallyldimethyl ammonium chloride Mw: 400,000–500,000) aqueous solution for 30 min. Because the silicon oxide wafer bears negative charge, cationic PDDA chain aggregates on the surface of the wafer. To build up PDDA monolayer, D.I. water washing was followed. Through this process, most of the cationic polymers were dissolved out and the inner most layer which has direct electrostatic contact with the substrate was remained. The measured thickness of fully dried PDDA monolayer was 1.5–3 nm. And this substrate was dried with N_2 gas. With the same sequence, Anionic PSS-ND (PSS coated Nano Diamond) particles were densely attached to the cationic surface. Consequently, SiO_2/PDDA/PSS-ND structure was formed on the surface of thermally oxidized Si wafer as a seeding layer. This process was denoted as ESAND (ESA seeding of Nano Diamond). At the early stage of growing process, there was no trace of polymer so that there was only 20 nm–30 nm thick nano diamond particle layer.

The samples were exposed to a hot filament environment of 1% CH_4 in H_2 at a substrate temperature 800 °C. The gas flow rate was 100 standard cm^3/min and chamber pressure 70 Torr. According to the deposition time, we denoted each specimen as D-50–D-200. The number which follows after the hyphen means the deposition time in minutes.

2.2. Measurement

Surface bonding status was analyzed with Raman spectroscopy (Horiba Jobin Yvon's T64000) using 514.532 nm Ar-ion laser for 120 s. For the surface profile investigation, AFM (Veeco's Multimode V) was used. Film thickness and morphology were observed with SEM (Hitachi, S-4300), which is equipped with automatic cross sectional scale measuring software. High resolution SEM (S-4800) and AFM were used to observe the morphology of the nano diamond seeded surface.

3. Results and discussion

3.1. Diamond film quality

From D-50 to D-200, the emerging diamond layer showed a clear sp^3 peak at 1332 cm^{-1}, and a low G peak around 1580 cm^{-1} (Fig. 1).

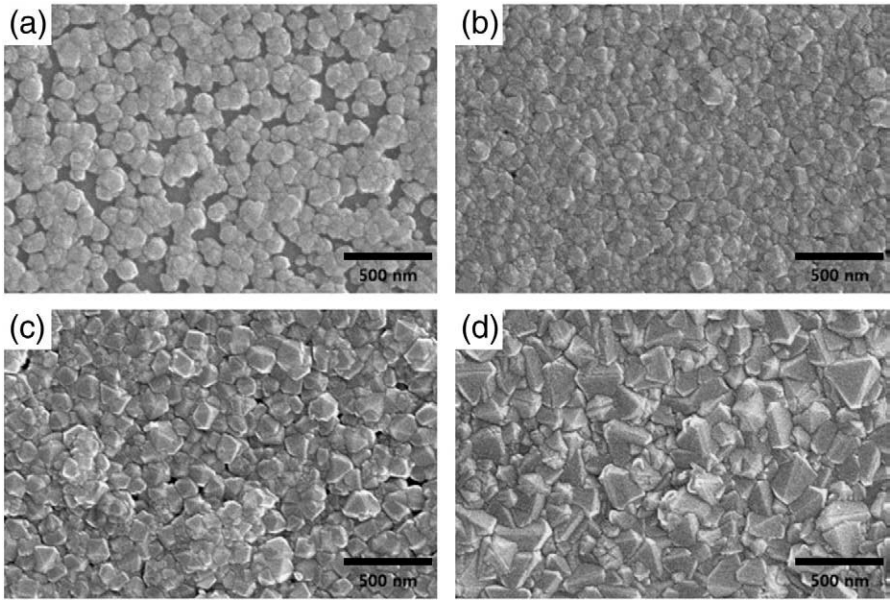

Fig. 2. Surface SEM images of CVD diamond films deposited for (a) 50 min, (b) 60 min, (c) 120 min, and (d) 200 min.