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Enhanced nanodiamond nucleation by surface texturing of Si substrate in SF_6/O_2 plasmas

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SF_6/O_2 plasma surface texturing was employed to pretreat Si substrate for achieving enhanced diamond nucleation density. Surface roughness of the textured Si was found to be strongly dependent on the process pressure and normalized roughness values in the range of 2-16 were obtained. Remarkably enhanced nucleation densities of ~ 10^{10} cm^{-2} compared to conventional mechanical abrasion were obtained after seeding for the surface textured Si substrates. Raman spectroscopy revealed that ultrananocrystalline diamond films with grain size below 10 nm were grown on the surface textured Si.

Key words: Surface texturing, Si substrate, SF_6/O_2 plasma, Nanodiamond nucleation, Nanocrystalline Diamond film, Nucleation density.

Introduction

Nanocrystalline diamond (NCD) films have attracted much attention due to their exceptional mechanical, tribological and electrical properties. Their application fields include nano/micro-electromechanical systems (NEMS/MEMS), surface acoustic wave (SAW) devices, very low friction protective coating, electrochemical electrodes, heat spreaders, and biologically active platforms [1-4]. For example, a hybrid Si cantilever mounted with a very thin NCD coating layer has shown promising sensing properties for chemical sensor applications by utilizing exceptional chemical inertness and biocompatibility of NCD surface [5, 6]. For tribological and NEMS/MEMS applications, surface roughness has a decisive impact on the application of the NCD films. The most critical factor that affects the surface roughness of the NCD film is pretreatment technique for initial diamond nucleation. The purpose of pretreatment process is to generate nucleation sites for diamond film growth since diamond film does not grow readily and uniformly on untreated non-diamond substrates such as Si, SiO_2, Ni, Ti, WC, etc. [7-10] Numerous pretreatment techniques including mechanical abrasion, seeding, carbide interlayer deposition and bias enhanced nucleation have been developed to achieve high nucleation density. Untreated Si surfaces generally present relatively low nucleation density of ~ 10^5 cm^{-2}. On the contrary, scratching the substrates with micrometer-sized diamond particles has been reported to yield enhanced nucleation densities as the large diamond particles chip against the Si surface and small diamond fragments play as nucleation sites [11, 12]. However, conventional pretreatment techniques such as mechanical abrasion and micro-chipping cause considerable surface roughening or defect creation, which is not appropriate for preparing the NCD films with low friction and smooth surface morphology for tribological and NEMS/MEMS applications. Therefore, it is important to find an effective pretreatment technique that can provide high nucleation density and controlled surface roughness over large area. High density plasma etching is a dry processing that can process large area surfaces with high reliability and reproducibility, and it could be an alternative to pretreat non-diamond surfaces for the NCD film growth. In this work, we report a new pretreatment technique consisted of surface texturing of Si substrate in SF_6/O_2 inductively coupled plasmas and subsequent seeding with nanodiamond particles, and high nucleation densities of ~ 10^{10} cm^{-2} were obtained over smooth surfaces.

Experimental

Single crystalline p-type (100) Si wafer of 2.5×2.5 cm^2 was used as substrate. Prior to pretreatment, surfaces of the Si substrates were chemically cleaned in a diluted BOE solution for 1-2 minutes and then washed with acetone and with DI water in ultrasonic bath for 5 minutes, respectively. Two different pretreatment techniques, mechanical abrasion and surface texturing in fluorine-based plasmas, were employed to compare the surface roughness and diamond nucleation density. Mechanical abrasion was performed with diamond suspensions (1 and 3 μm particle size) in a mechanical polisher (Struers RotoPol-25) for 10 minutes. Surface

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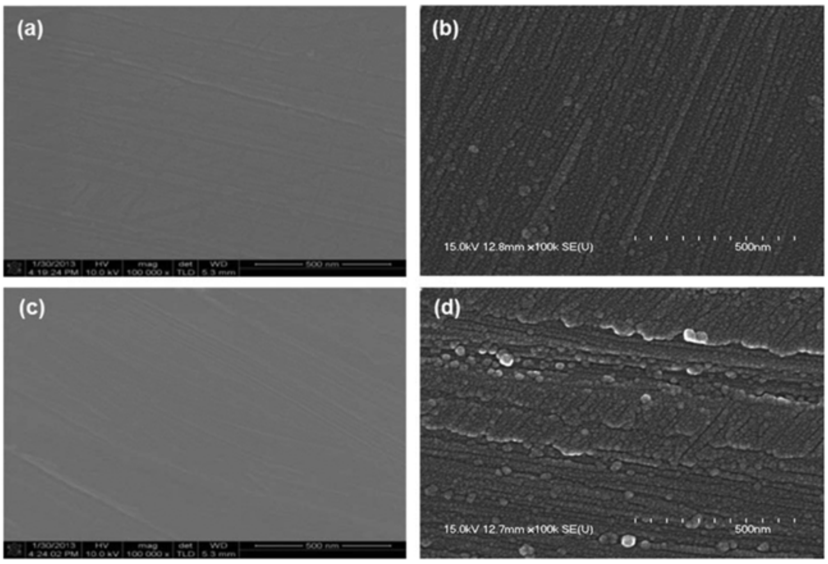

Fig. 1. SEM micrographs of Si surfaces pretreated with 1 μm suspension (a) before and (b) after seeding, with 3 μm suspension (c) before and (d) after seeding.

texturing of Si substrates was performed in SF_6/O_2 inductively coupled plasmas. Subsequently, the substrates were ultrasonically seeded in the ethanol suspension of 3-5 nm nanodiamond powders for 30 minutes, followed by ultrasonic cleaning in DI water three consecutive times for 1 minute. Nanocrystalline diamond films were grown in a microwave plasma-assisted CVD reactor for 1 h and a mixture of CH_4 and H_2 was used as precursor. During the films growth the fraction of CH_4 was fixed at 2 Vol%. Surface morphology of Si substrate after pretreatment, seeding and film growth was measured by AFM (PSIA SE100) and FE-SEM (Hitachi S4700), respectively. The structural properties of the grown films were characterized by Raman spectroscopy (Thermo Scientific DXR Raman Microscope).

Results and Discussion

Fig. 1 shows SEM micrographs of the pretreated Si surfaces by mechanical abrasion with diamond suspensions and after seeding with nanodiamond powders. It is observed that periodically arrayed scratches are formed on the Si surfaces after mechanical abrasion and AFM measurements revealed that the pretreated Si surfaces show much higher surface roughness values (root-mean-square (rms) roughness 2.26 nm for 1 μm and 3.754 nm for 3 μm suspensions, respectively) compared to the untreated Si (rms roughness 0.27 nm). After seeding, diamond nucleation is observed to occur primarily on the scratches and resultant nucleation densities ~ 10^8 cm^{-2} were obtained.

Fig. 2 presents the AFM scan images of the Si substrates after surface texturing in $18SF_6/9O_2$ ICP discharges and Fig. 3 shows the normalized roughness values as a function of process pressure at a fixed ICP source power (400 W) and rf chuck power (100 W).

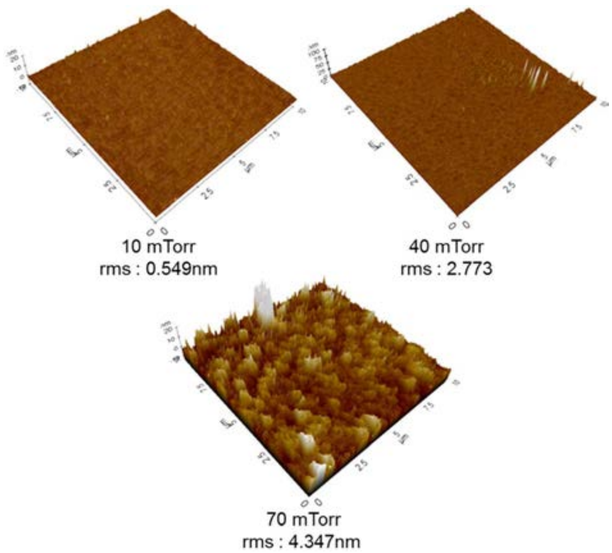

Fig. 2. AFM scan images of Si substrates after surface texturing in $18SF_6/9O_2$ ICP discharges.

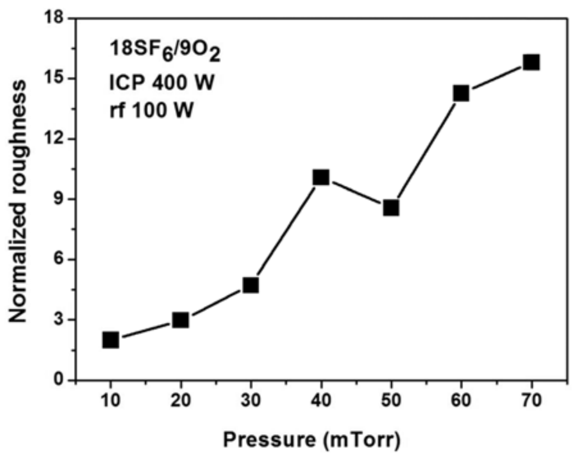

Fig. 3. Dependence of the surface textured Si normalized roughness on process pressure in $18SF_6/9O_2$ ICP discharges.

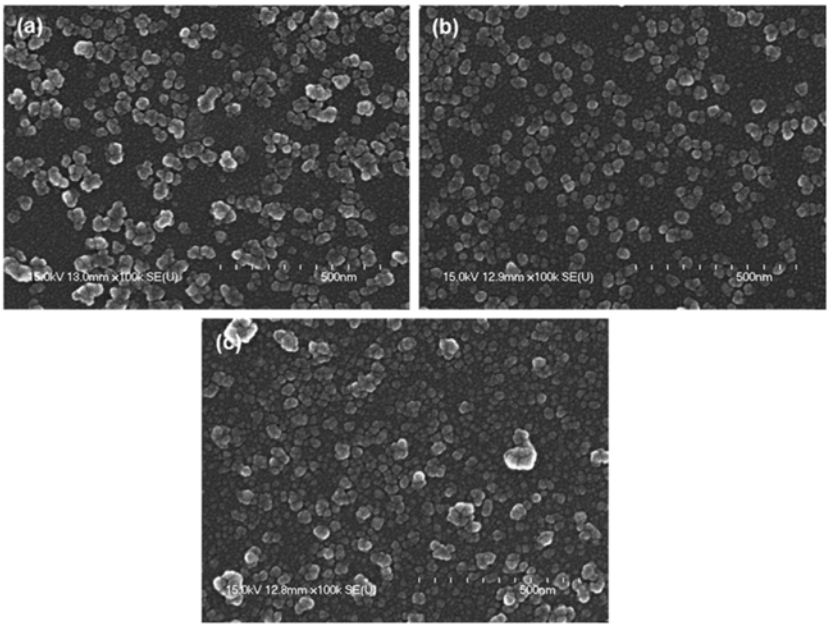

Fig. 4. SEM micrographs of the surface textured Si substrates after seeding (a) 10 mTorr, (b) 40 mTorr, and (c) 70 mTorr.

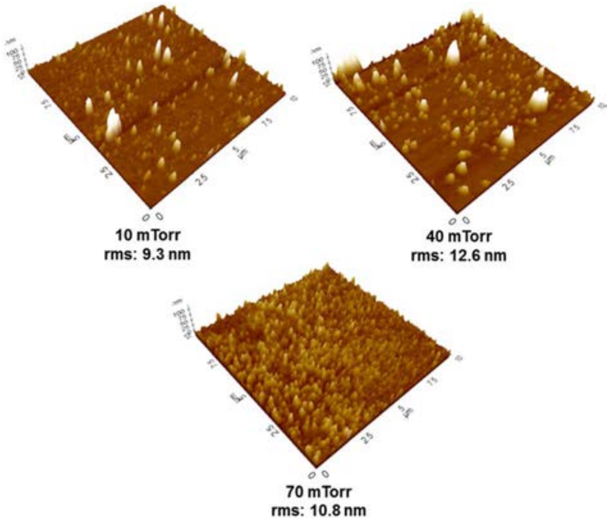

Fig. 5. AFM scan images of the seeded Si surfaces.

Surface roughness of the textured Si substrates shows a strong dependence on the process pressure. The normalized roughness monotonically increases as the process pressure increases due to enhanced chemical reaction between the fluorine radicals and surface Si atoms. These results clearly show that there is a wide process window for controlling the surface roughness of Si with $SF_6/9O_2$ plasma surface texturing. Normalized roughness values in the range of 2-16 were obtained.

SEM micrographs of the surface textured Si substrates after seeding in the ethanol suspension of nanodiamond powders is shown in Fig. 4. The seeded nanodiamond particles exist as aggregates of 20-30 nm in average size and it can be seen that the coverage of Si surface is highly uniform and of high density. Very high nucleation densities in the range of $4.6\text{-}8.0 \times 10^{10}$ cm^{-2} compared to the mechanically polished Si surfaces were obtained.

Fig. 5 shows the AFM scan images of the seeded Si substrates shown in the Fig. 4. The seeded Si surfaces show higher surface roughness values than the surface textured Si substrates shown in the Fig. 2, but maintain relatively smooth surface morphology with surface roughness values in the range of 9.3 to 12.6 nm. Combining the results presented in Fig. 4 and Fig. 5, it is very obvious that the surface texturing of Si substrate in SF_6/O_2 plasmas followed by seeding with nanodiamond powders is a very promising pretreatment technique which leads to remarkably enhanced nucleation densities for nanocrystalline diamond film growth while maintaining relatively smooth surface morphology.

Nanocrystalline diamond films were grown on the seeded Si surfaces presented in the Fig. 4 by microwave plasma-assisted CVD technique and Fig. 6 shows SEM images of the grown NCD films. It is found that well-developed continuous NCD films were formed on the Si substrates in spite of relatively short deposition time (1 h) and the grain size is uniform across the film due to the homogeneous distribution of nanodiamond particle seeds as shown in Fig. 4.

Fig. 7 shows Raman spectra of the grown films on the Si substrates pretreated with SF_6/O_2 plasmas surface texturing and seeded. The surface textured Si exhibits typical Raman peaks at ~ 1140 cm^{-1}, ~ 1330 cm^{-1}, ~ 1560 cm^{-1}, respectively. The peak at ~ 1140 cm^{-1} indicates that the films grown on the surface textured Si substrates are ultrananocrystalline diamond (UNCD) layer since this peak is attributed to trans-polyacetylene (TPA) present in abundant grain boundaries between nanoscale diamond grains, generally grain size below 10 nm [13, 14]. The Si substrate pretreated at

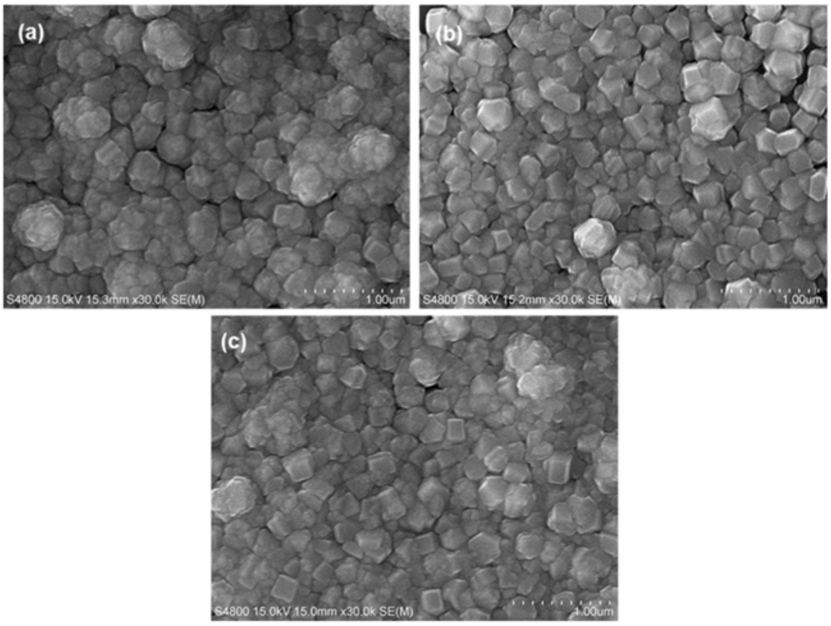

Fig. 6. SEM micrographs of the grown nanocrystalline diamond films (a) 10 mTorr, (b) 40 mTorr, and (c) 70 mTorr.

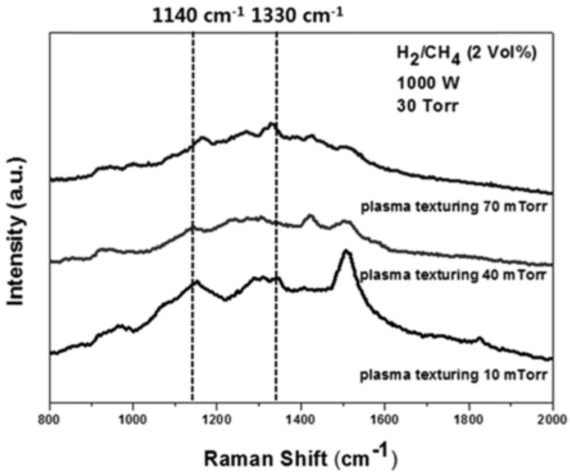

Fig. 7. Raman spectra of as-grown films on the surface textured Si substrate with different process pressure.

10 mTorr condition shows the strongest intensity of 1140 cm^{-1} peak and the Raman spectra also reflect the presence of diamond phase associated with the small peak at ~ 1330 cm^{-1}.

Conclusions

A new pretreatment technique utilizing surface texturing of Si substrate in SF_6/O_2 inductively coupled plasmas and subsequent seeding with nanodiamond particles were employed in this study. It was found that surface roughness of the textured Si substrate is readily controlled by varying the process pressure. The seeded Si surfaces showed that nanodiamond particle seeds were distributed uniformly and of high nucleation densities in the range of $4.6\text{-}8.0 \times 10^{10}$ cm^{-2}. The grown films on the surface textured Si substrate were found to be ultrananocrystalline diamond layer with grain size below 10 nm, which is obvious from the Raman peaks at 1140 cm^{-1}. The surface texturing of Si substrate in SF_6/O_2 plasmas followed by seeding with nanodiamond powders is a very promising pretreatment technique which leads to remarkably enhanced nucleation densities for nanocrystalline diamond film growth.

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