

Pre-nucleation techniques for enhancing nucleation density and adhesion of low temperature deposited ultra-nanocrystalline diamond

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Abstract

Effect of pre-nucleation techniques on enhancing nucleation density and the adhesion of ultra-nanocrystalline diamond (UNCD) deposited on the Si substrates at low temperature were investigated. Four different pre-nucleation techniques were used for depositing UNCD films: (i) bias-enhanced nucleation (BEN); (ii) pre-carburized and then ultrasonicated with diamond powder solution (PC-U); (iii) ultrasonicated with diamond and Ti mixed powder solution (U-m); (iv) ultrasonicated with diamond powder solution (U). The nucleation density is lowest for UNCD/U-substrate films ($\sim 10^8$ grains/cm²), which results in roughest surface and poorest film-to-substrate adhesion. The UNCD/PC-U-substrate films show largest nucleation density ($\sim 1 \times 10^{11}$ grains/cm²) and most smooth surface (8.81 nm-rms), whereas the UNCD/BEN-substrate films exhibit the strongest adhesion to the Si substrates (critical loads= ~ 67 mN). Such a phenomenon can be ascribed to the high kinetic energy of the carbon species, which easily form covalent bonding, Si–C, and bond strongly to both the Si and diamond.

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1. Introduction

The unique combination of physical and chemical properties of artificial diamond films has drawn much attention among researchers for many potential applications. However, large roughness of microcrystalline diamond films makes them inapplicable in some specific applications. Recently, ultra-nanocrystalline diamond (UNCD) films with very smooth surface have been synthesized by using CH₄/Ar-plasma and the detail formation mechanism of UNCD from CH₄/Ar-plasma has been reported [1,2]. Recent researches demonstrated promising potential for the applications of UNCD films on bio-sensors [3], field emission devices [4,5], bio-medical devices [6] and MEMS devices [7]. In the applications such as micro-electro-mechanical system (MEMS) and packaging/passivation for IC devices, good adhesion between the diamond films and Si substrate is also an important requirement beside the capability of growing the films

at low temperature (<600 °C). Ultrasonication [8], carbide-metal addition [9], pre-carburized [10], and bias-enhanced-nucleation (BEN) method [11–13] are the most effective techniques used for enhancing the nucleation of diamonds. These substrate pretreatment processes, which markedly affect nucleation behaviors for diamond films, are expected to influence profoundly the film-to-substrate adhesion. However, how does these processes alter the film-to-substrate adhesion is still not well understood. Therefore, we systematically investigated the relationship between nucleation pretreatment process for depositing UNCD films and the film-to-substrate adhesion properties.

2. Experimental

In this study, the UNCD films were grown in IPLAS CRYNNUS 2.45 GHz microwave plasma enhanced chemical vapor deposition (MPECVD) system with 1500 W microwave power, 150 Torr, 1% CH₄/Ar reacting gases ratio, ~ 400 °C substrate temperature and 3 or 6 h deposition time. Four pre-nucleation techniques were used for forming diamond nuclei. The Si substrates were either (i) ultrasonicated with diamond powder

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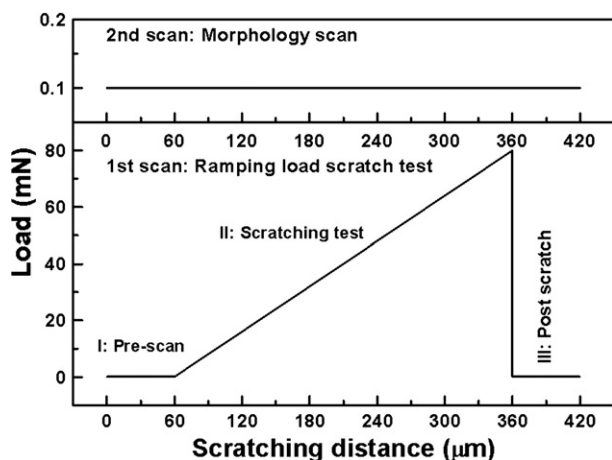


Fig. 1. The schematics showing the nano-scratch test procedure for evaluating the adhesion of UNCD-to-Si substrates.

solution, designated as U-substrates; (ii) ultrasonicated with diamond and Ti mixed powder solution, designated as U-m-substrates; (iii) pre-carburized with CH_4/Ar plasma and then ultrasonicated with diamond powder solution, designated as PC-

U-substrates; (iv) bias-enhanced nucleation process, designated as BEN-substrates. Surface morphology of samples was examined with a field emission scanning electron microscope (JEOL 6010). Crystal quality of UNCD films was investigated by Raman spectroscopy using 514 nm argon laser beam (Renishaw). Surface topography and roughness were measured with atomic force microscopy (PARK).

The adhesion between UNCD and Si substrate was evaluated by a ramping load scratch test technique using nano-indenter instrument equipped with a nano-scratch capability (MTS, USA). The present test employed a Berkovich diamond tip oriented in the face forward mode. The scratch testing procedure is schematically illustrated in Fig. 1. The procedures of the scratch test are: (i) the pre-scan stage, in which the initial surface profile for scratch test was performed by moving the tip under a very small load (0.1 mN) for 60 μm , followed by (ii) the ramping load scratch test, in which the load linearly increased from 0.1 mN to 80 mN, and the tip moved for 300 μm long (from 60 μm to 360 μm) with a scratch rate of 10 $\mu\text{m}/\text{s}$ and, finally, (iii) the post-scratch stage, in which the tip moved further for 60 μm (from 360 μm to 420 μm) with 0.1 mN, and then returned to the original point. The total scratch distance is set to be 420 μm long. During the scratch test, the load and the

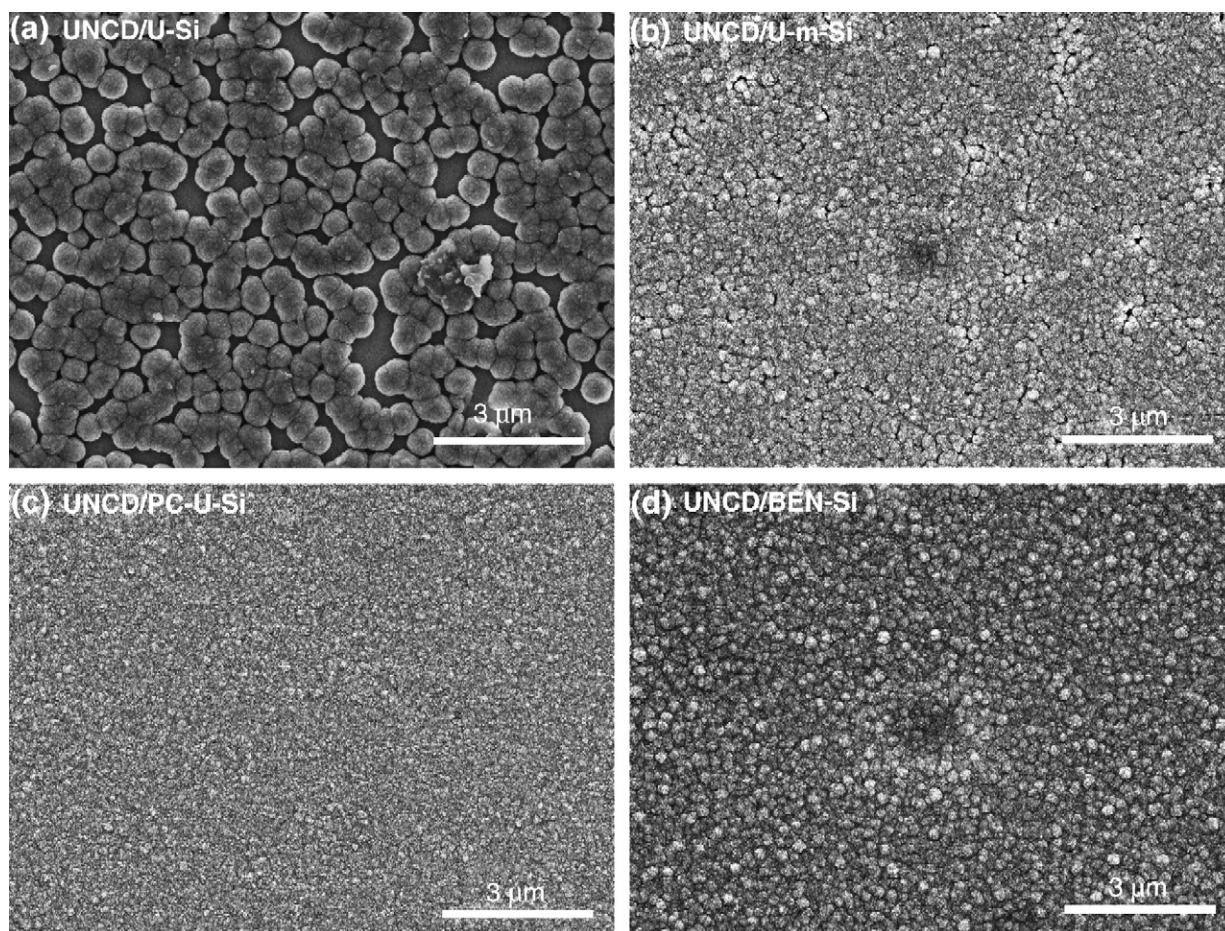


Fig. 2. SEM micrographs of UNCD films grown for 3 h on silicon substrates, which were pretreated by four different nucleation techniques; (a) U: ultrasonicated with diamond powder solution; (b) U-m: ultrasonicated with diamond/Ti mixed powder solution; (c) PC-U: pre-carburized and then ultrasonicated with diamond powder solution; (d) BEN: bias-enhanced nucleation process.

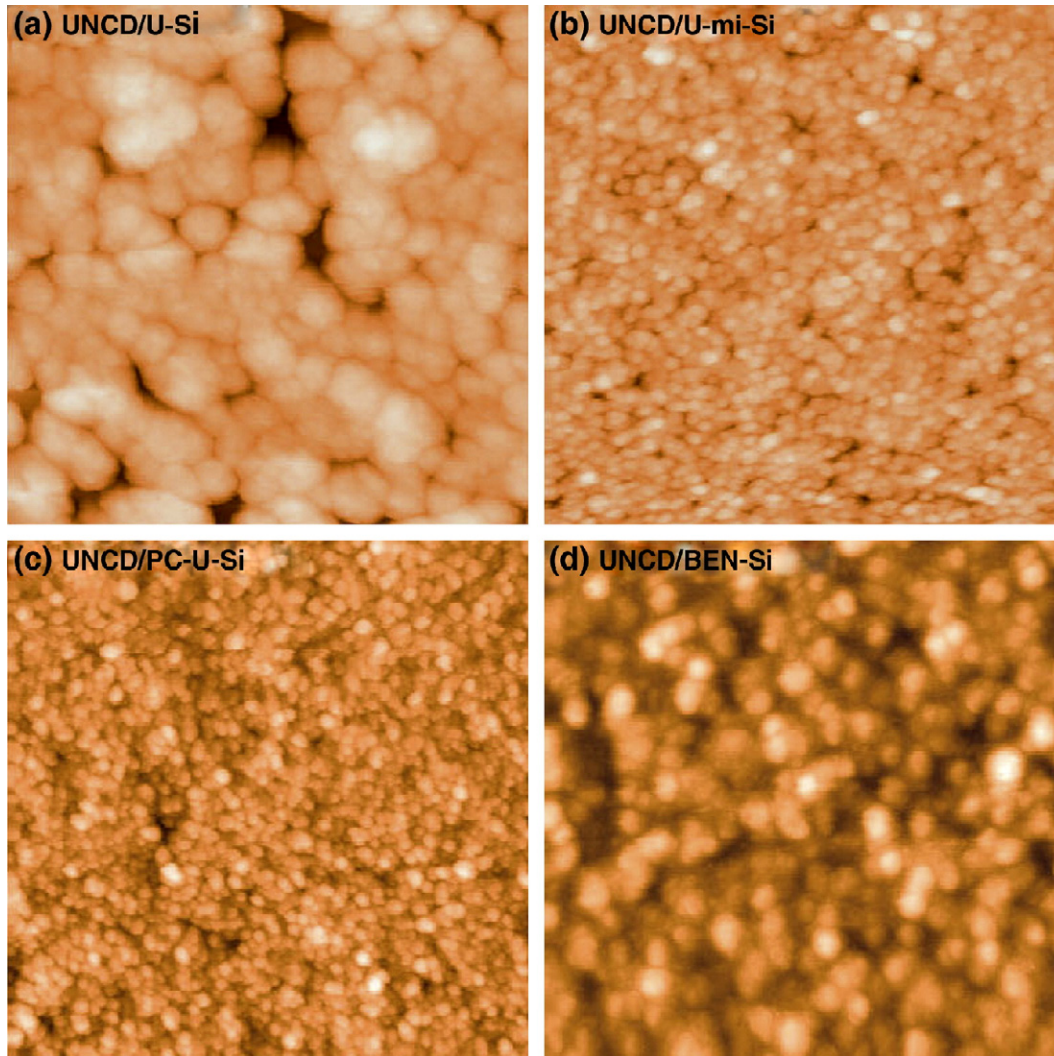


Fig. 3. AFM images of UNCD films grown for 3 h on silicon substrates, which were pretreated by four different nucleation techniques. The surface roughness is (a) U: rms ~ 57.75 nm; (b) U-m: rms ~ 9.12 nm; (c) PC-U: rms ~ 6.61 nm; (d) BEN: rms ~ 10.25 nm.

penetration depth were recorded. The morphology of the scratch profile was examined by the scan tip again with 0.1 mN load after the scratch test.

3. Results and discussion

Fig. 2 shows the surface morphology of UNCD films deposited after different nucleation methods, indicating that all of the UNCD films grown on the U-, U-m-, PC-U- and BEN-substrates are quite uniform. Nucleation density of UNCD, which is determined by density of UNCD clusters, varies with pretreatment methods, and is $\sim 5 \times 10^8/\text{cm}^2$ for U-substrates, $\sim 5 \times 10^9$ grains/ cm^2 for U-m-substrates, $\sim 1 \times 10^{11}$ grains/ cm^2 for PC-U-substrates, and $\sim 1 \times 10^{10}$ grains/ cm^2 for BEN-substrates. Among the 4 nucleation techniques employed, only the PC-U- and BEN-substrates are fully covered by UNCD, forming a continuous film. All of UNCD films possess similar granular structure, that is, they contain grains with a size less than 10 nm, regardless of the pre-nucleation techniques used. It should be noted that, instead of faceted grains comm-

only observed for diamond films grown under CH_4/H_2 plasma, the UNCD films that grow under CH_4/Ar plasma always show smooth surface with roundish diamond grains.

Moreover, all the UNCD films show very smooth surface. The detailed morphology of UNCD films was analyzed using atomic force microscopy (AFM) for evaluating the surface roughness. Fig. 3 shows that, for the 3 h-deposited UNCD films, the surface roughness of UNCD/U-substrate films (57.75 nm-rms, Fig. 3(a)) is one order of magnitude larger than other UNCD films (6–10 nm-rms, Fig. 3(b)–(d)), which is, presumably, due to low nucleation density and incomplete substrate coverage of diamond nuclei for the U-substrate. As for the two films grown on high nucleation density substrates that were fully covered by diamond grains, the surface roughness of UNCD/PC-U-substrate and UNCD/BEN-substrate films is 6.61 nm (rms) and 10.65 nm (rms), respectively. The smoother surface of UNCD/PC-U-substrate films is closely correlated with the higher nucleation density of the films. Furthermore, the formation of cauliflower morphology in UNCD/BEN-substrate is also the factor resulting in worse surface morphology of the films.

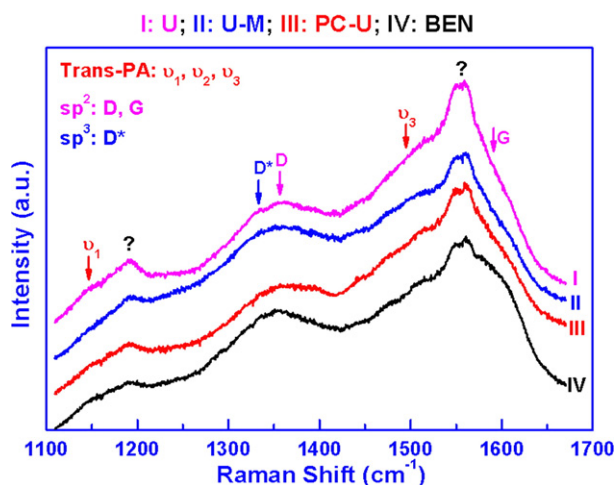


Fig. 4. Raman spectra of UNCD films grown for 3 h on silicon substrates, which were pretreated by four different nucleation techniques; (a) U: ultrasonicated with diamond powder solution; (b) U-m: ultrasonicated with diamond/Ti mixed powder solution; (c) PC-U: pre-carburized and then ultrasonicated with diamond powder solution; (d) BEN: bias-enhanced nucleation process.

The characteristics of surface morphology are not altered pronouncedly as the films grow thicker. For UNCD films deposited for 6 h after the pre-nucleation process, the surface roughness is 47.49 nm for UNCD/U-substrate, 8.52 nm for UNCD/U-m-substrate, 8.81 nm for UNCD/PC-U-substrate, and 13.23 nm for UNCD/BEN-substrate. The exceptionally large roughness for UNCD/U-substrate can, again, be ascribed to the incomplete coverage of the nuclei. The surface roughness of the other three films is very similar with each other, indicating that the surface of UNCD films has been smoothed out as the films grew thicker. The influence of nucleation density on the morphology of UNCD films becomes less significant.

Fig. 4 shows Raman spectra of UNCD films deposited on silicon substrates pretreated by different nucleation methods. There are four major Raman resonance peaks observed at around 1150 cm^{-1} (ν_1), 1350 cm^{-1} (D), 1480 cm^{-1} (ν_3) and 1580 cm^{-1} (G) in visible Raman spectrum of UNCD films, which are assigned as graphite-like sp^2 -bonding (D & G) and *trans*-polyacetylene (ν_1 & ν_3) [15]. In addition, there are two extra Raman resonance peaks at around 1190 cm^{-1} and 1550 cm^{-1} , which only appear at low temperature deposited UNCD films. The sharp Raman peak at 1332 cm^{-1} is usually not observable for UNCD films, as the Raman signal is much more sensitive to sp^2 -bonded carbon than to sp^3 -bonded carbon. The formation of *trans*-polyacetylene (ν_1 and ν_3) [15] further suppresses the intensity of this peak. Such a phenomenon is in accordance with previously reported results [8,15]. However, this Raman spectroscopy is still a convenient technique for characterizing UNCD films [14]. Fig. 4 infers that all of these UNCD films with different pre-nucleation techniques and different thickness are of similar crystallinity.

Pre-nucleation processes impose pronounced effect on the film-to-substrate adhesion. Fig. 5(a) represents the typical sliding-wear-tracks on UNCD films that resulted from nano-scratching testing procedures. It shows a clear critical point, where the UNCD films start to delaminate from substrate. Fig. 5(b) shows

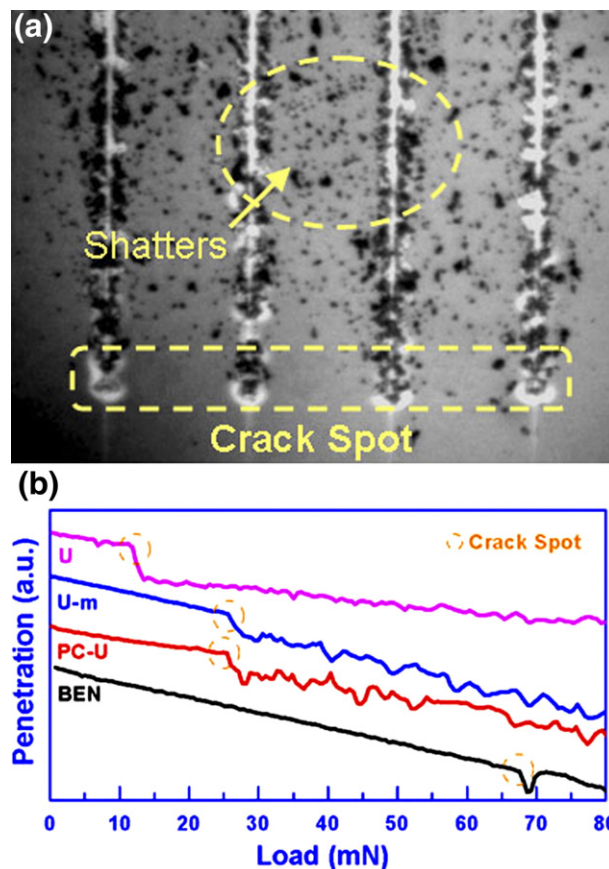


Fig. 5. (a) The micrograph showing the typical damaged image after nano-indentor tip scratching of UNCD films grown on silicon substrate and (b) the penetration curves of the nano-indentor tip scratching along the UNCD films, where (i) U: ultrasonicated with diamond powder solution; (ii) U-m: ultrasonicated with diamond and Ti mixed powder solution; (iii) PC-U: pre-carburized and then ultrasonicated with diamond powder solution; (iv) BEN: bias-enhanced nucleation process.

the penetration profiles of ramping load nano-scratch surface for UNCD films grown on substrates pretreated by different nucleation methods, where the surface penetration is plotted as a function of the applied load. During the nano-scratching test, the Berkovich tip gradually penetrated into the UNCD films due to linearly increasing load. The profile drops suddenly when UNCD films delaminate from the Si substrate. The load at which the Berkovich tip suddenly drops is designated as critical loads (L_c). Table 1 indicates that the critical loads are $\sim 12\text{ mN}$ for

Table 1
The critical loads (L_c) in nano-scratching measurements for the UNCD films grown on Si substrates pretreated by four nucleation techniques

Samples	Critical load (mN)
UNCD/U-Si	12 ± 0.4
UNCD/U-m-Si	24 ± 1.2
UNCD/PC-U-Si	22 ± 2.6
UNCD/BEN-Si	67 ± 0.6

U: ultrasonicated with diamond powder solution; U-m: ultrasonicated with diamond/Ti mixed powder solution; PC-U: pre-carburized and then ultrasonicated with diamond powder solution; and BEN: bias-enhanced nucleation process.

UNCD/U-substrate, ~ 24 mN for UNCD/U-m-substrate, ~ 22 mN for UNCD/PC-U-substrate and is ~ 67 mN for UNCD/BEN-substrate. Contrary to the phenomenon that crystallinity of UNCD films insignificantly changed with the nucleation technique used, adhesion between UNCD and Si substrate varied pronouncedly due to different nucleation methods.

The UNCD/U-substrate films show poorest film-to-substrate adhesion (~ 12 mN) among the four UNCD films, which is apparently due to low nucleation density and incomplete coverage of the UNCD nuclei over Si substrate. In contrast, the UNCD/BEN-substrate films show best film-to-substrate adhesion (~ 67 mN), which is about 3 times as large as that for UNCD/U-m- and UNCD/PC-U-substrate films (22–24 mN). The main factor influencing the adhesion behavior of UNCD films is apparently the bonding strength between UNCD nuclei and Si substrate, since all of UNCD films possess the same granular structure and crystalline characteristics. The stress on the UNCD films induced due to mismatch in CTE is minimal as the films were grown at relatively low substrate temperature (~ 400 °C). In BEN process, the carbon species are accelerated, possessing high kinetic energy and easily form covalent bonding, SiC, when bombarding the Si substrates [16,17], which adhere strongly to the diamond nuclei. The UNCD-to-Si substrate adhesion is thus greatly enhanced. In contrast, in all other ultrasonication processes, the kinetic energy of diamond powders is relatively low and bombardment damage on the Si substrate is relatively mild. An amorphous carbon layer is formed prior to the formation of diamond nuclei. The UNCD-to-Si substrate adhesion is thus inherently low.

4. Conclusion

UNCD films with grain size less than 10 nm were grown on Si substrates pretreated by four different nucleation techniques. Nucleation density between 10^8 and 10^{11} grains/cm² was obtained, which depends on different pretreated process. Using reformed ultrasonication methods, like forming a:C before ultrasonication or mixed Ti and diamond powder suspension solution, can dramatically improve nucleation density and reli-

ability of UNCD nucleation. AFM study revealed that the PC-U-substrate process results in the best surface smoothness for UNCD films (rms 6.61 nm) due to high nucleation density. The nano-scratch examination indicates that the UNCD-to-Si adhesion is best for BEN processed substrate, i.e., the critical load (L_c) for UNCD/BEN-substrate is as high as 67 mN, which is about 3 times larger than other UNCD films grown on ultrasonicated and pretreated Si substrates.

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