Effects of Tungsten Metal Coatings on Enhancing the Characteristics of Ultrananocrystalline Diamond Films

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Nucleation of diamonds on Si substrates was pronouncedly improved by pre-coating a thin tungsten film on the substrates, which is attributed to the enhancement on the formation of the W−C phase in the tungsten silicon interface. The fact that the W coating can enhance the generation of the W−C phase for the W/Si substrate is ascribed to the fast accumulation of carbon species in the W layer, which, in turn, is consequence of the limit volume for carbon inward diffusion. On the contrary, the carbon species can diffuse into the bulk W materials continuously, resulting in a markedly slower rate of accumulation for carbon species and thus delaying the formation of diamond nuclei.

1. Introduction

Diamond films have been investigated extensively for device applications owing to their unique properties.[1] An increasing effort has been devoted to fabricating diamond films. However, the drawbacks of the conventionally synthesized diamond films are that they contain micrometer-sized grains, faceted granular structures, and very rough surfaces. Such kinds of diamond films are not suitable for fabricating devices directly. Reducing the grains of diamond to render the film's surface to a very smooth level, while maintaining the excellent physical and chemical properties of the films, are necessary for practical applications.[2,3]

Because of their high surface energy, diamonds generally are difficult to form continuous films with smooth surfaces on silicon substrates. Therefore, the formation of densely packed diamond nuclei is necessary to grow uniform films on Si substrates. The bias-enhance nucleation (BEN) and ultrasonication process are frequently used for increasing the nucleation density of diamond on silicon substrates. Although the BEN process can enhance the formation of diamond nuclei efficiently,[4,5] it can only be applied on conductive substrates and is of limited use on insulating substrates. In contrast, the ultrasonication process, which ultrasonically abrades the substrate with diamond powder slurry, is a simple and effective technique inducing the diamond nuclei on the Si substrates. But the number density of nuclei formed by the ultrasonication process in diamond methanol slurry is not sufficient for growing diamond films with nanosized grains, ultrananocrystalline diamond (UNCD) films; that is, when the substrates were ultrasonicated in nanodiamond slurry, the nucleation was

enhanced, but large clusters of diamonds were formed preferentially and were distributed scarcely. Such a phenomenon usually results in numerous voids in the UNCD-to-Si interface (figures not shown)[6] and leads to poor UNCD-to-Si adhesion. Modification on such a process by pre-coating either a carbonaceous layer[7−9] or a metallic layer[10−13] has been utilized to further improve the nucleation for diamond films. However, the detailed mechanism is not clear.

In this study, for increasing the nucleation density of diamonds so as to grow the UNCD films, a thin W layer was pre-coated on Si substrates. The mechanism, by which such a W coating modifies the nucleation of diamond growth was investigated by examining the detailed interaction of these metallic layers using X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS).

2. Experimental Section

N-type Si (100) substrates were first cleaned with acetone and were then e-beam evaporated or RF sputter-coated (50 W, 8 Torr) with a thin layer (∼300 nm) of W, which are designated as W_a and W_b coatings, respectively, and the corresponding substrates are designated as W_a/Si and W_b/Si substrates, respectively. The metal-coated substrates were ultrasonicated with diamond powder (∼4−10 nm) slurry for 30 min using methanol as the solvent. The diamond powder residues on the substrates were removed by ultrasonically cleaning with methanol, followed by drying with blowing nitrogen gas. The nucleation and growth of UNCD films were preceded by the microwave plasma enhanced chemical vapor deposition (MPECVD) process using a 2.45 GHz microwave source (IPLAS Cyrannus). The reaction gas was mixture of 1 sccm methane and 99 sccm argon, with 120 Torr total pressure. The microwave power was 1200 W, and the reaction times were 10, 20, 30, and 180 min.

The morphologies of the as-nucleated substrates and the UNCD films were examined by FE-SEM (JSM-6500F). The crystalline structure and surface chemistry of metallic layer,

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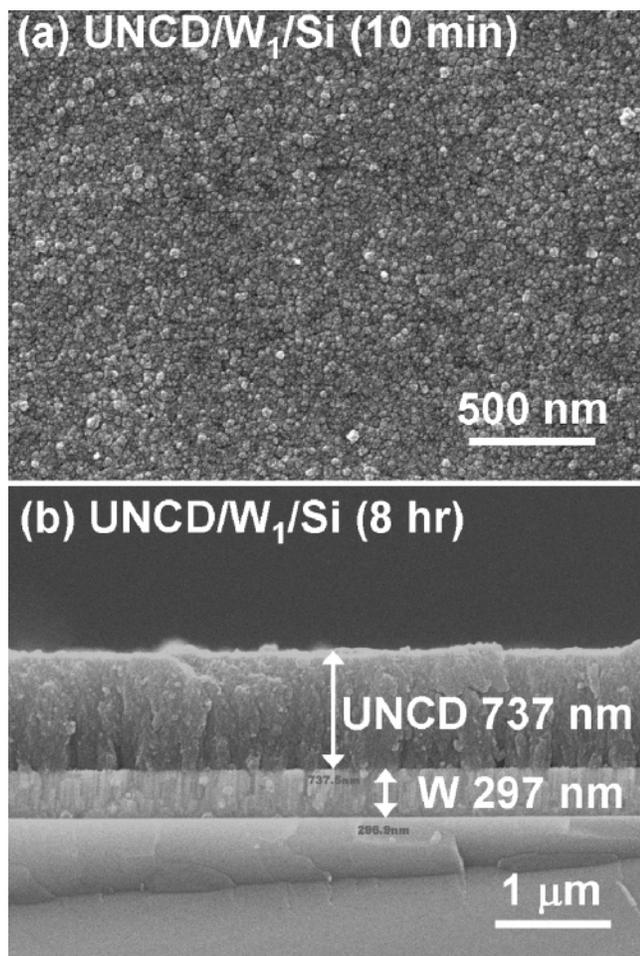∥ MEMS Institute, National Tsing-Hua University.
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Figure 1. (a) SEM micrographs of UNCD nuclei formed by the MPE-CVD process for 10 min on W-coated Si substrates (W_a/Si) and (b) the insets show the corresponding cross-sectional micrograph of UNCD films grown on pre-nucleated substrates by the MPE-CVD process for 8 h (the W layer was prepared by the e-beam evaporation process).

before and after the nucleation process, were examined by X-ray diffratometry (XRD, Rigaku) and X-ray photoelectron spectroscopy (XPS, PHI-1600), respectively. The structure of the UNCD films was monitored by Raman spectroscopy (Renishaw) using 625 nm lasers and NEXAFs using synchrotron radiation. The adhesion between UNCD and Si substrate was estimated by a ramping-load-scratch-test using a commercial nanoindenter instrument equipped with a nanoscratch option (MTS). The present test employed a Berkovich diamond tip oriented in the face-forward mode.[14,15]

3. Results and Discussion

Figure 1a shows that the diamond nuclei formed readily and are densely populated on the tungsten-coated Si substrates. The grains remain very small despite the 8 h MPECVD process. This is mainly due to the low activation energy for the formation of sp^3 bonds from C_2 species induced by Ar plasma.[2] The cross-sectional image shown in Figure 1b indicates that the UNCD films grown on these pre-nucleated substrates are quite dense. The thickness of these films grown on W_a/Si is 737 nm for 8 h of MPECVD, which corresponds to a growth rate of 92.1 nm/h for UNCD on W_a/Si substrates. Such a growth rate is much higher than that of UNCD on Ti-coated Si substrates, which is 78.5 nm/h.[6]

Figure 2a illustrates the Raman spectra of UNCD films grown by MPECVD for 8 h on W_a/Si substrates (spectrum I). The films
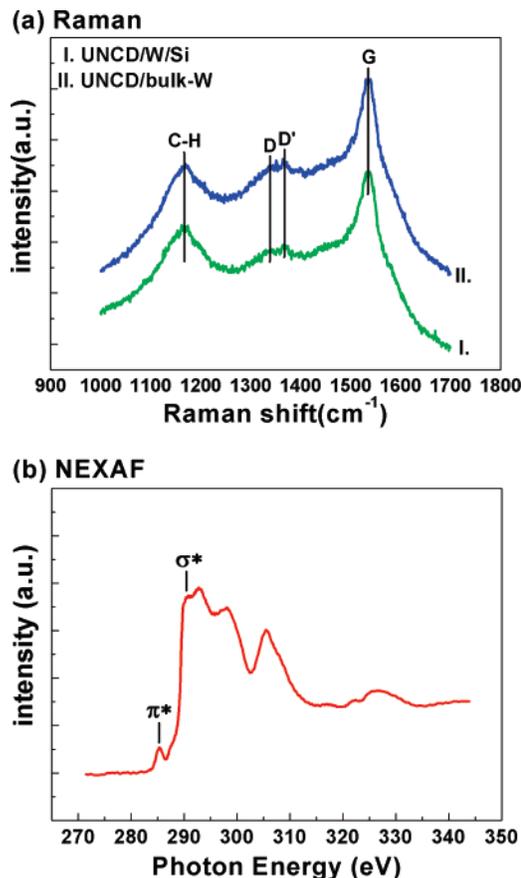

Figure 2. (a) Raman spectra for UNCD films deposited on (i) W-coated Si substrates (W_a/Si) and (ii) bulk W substrates, and (b) typical NEXAF profiles for UNCD films. The MPECVD process was performed using CH_4 (1.0 sccm)/Ar (99 sccm) plasma at room temperature for 8 h, and the W layer was prepared by the e-beam evaporation process.

contain a D band at 1330 cm^{-1} and a G band at 1540 cm^{-1}, typical Raman peaks for carbon related films, and a C$-$H band at 1140 cm^{-1} and a D′ band at 1360$-$1400 cm^{-1}, assigned to *trans*-polyacetylene.[16] The Raman resonance peaks are broad, which is ascribed to the small grain size of the UNCD films and the presence of *trans*-polyacetylene.[16] To unambiguously identify the nature of C bonds in these films, NEXAFs with synchrotron radiation was used. A typical NEXAF spectrum is shown in Figure 2b, displaying a sharp rise near 289.7 eV and a deep valley near 302.5 eV (labeled as $\sigma*$ band). These results confirm the sp^3-bonded nature of the UNCD grains. The small peak near 285.0 eV indicates that a small proportion of graphite phase coexists with the diamond in these films.

To understand how the W_a metal coatings enhance the formation of diamond nuclei on Si substrates, detailed reaction processes were examined. XRD patterns shown in Figure 3a reveal that the as-coated W_a metal layers were crystallized with random oriented grains (spectrum I, Figure 3a). These metal layers interact with carbon species in the plasma readily, forming tungsten carbides under MPECVD for 30 min (spectrum II, Figure 3a). Such a characteristic is similar to the behavior of Ti coating; that is, the metal layer is crystalline when as-sputter-coated and forms the TiC phase instantaneously when exposed to carbon-containing plasma.[6] The XPS profiles shown in Figure 3b indicate the evolution of the C1s signals with MPECVD time. This figure reveals that the W$-$C peak coexists with the carbon peak up to 20 min MPECVD time (spectra I$-$III) and were completely overtaken by the C$-$C (284.3 eV) peaks after 30 min of MPECVD (spectrum IV). These observations support

Effects of Tungsten Metal Coatings

J. Phys. Chem. C, Vol. 112, No. 10, 2008 **3761**

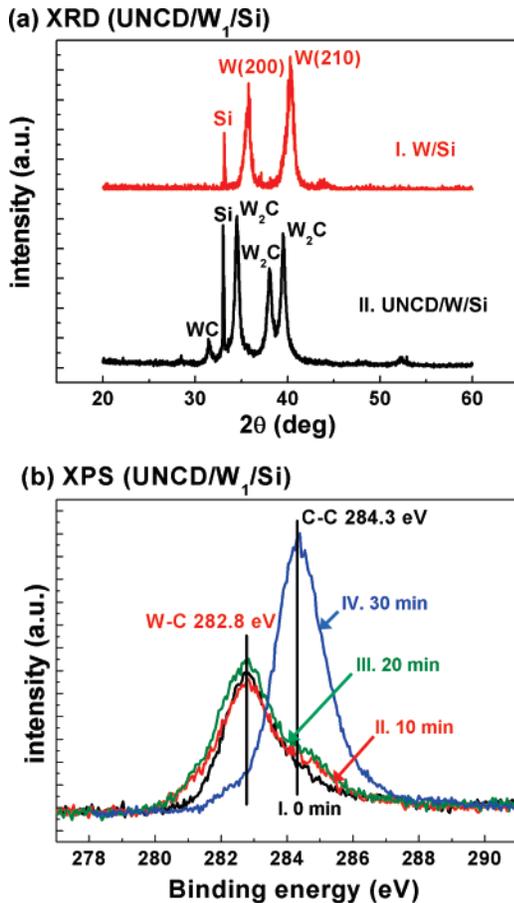**(a) XRD (UNCD/W$_1$/Si)**

(b) XPS (UNCD/W$_1$/Si)

Figure 3. (a) X-ray diffraction patterns of W layer coated on the Si substrate (W$_a$/Si), where XRD-I is the pattern of the as-coated W layer before the nucleation process and XRD-II is the pattern of UNCD after MPE-CVD using CH$_4$ (1 sccm)/Ar (99 sccm) for 30 min; (b) the C(1s)-XPS signal of W-coated Si substrate (C1s-I is the films before the nucleation process; C1s-II, III, and IV are the XPS signals of the films MPECVD for 10, 20, and 30 min, respectively).
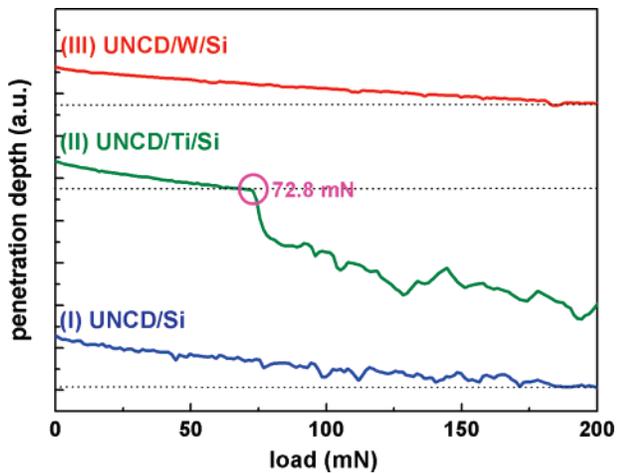

Figure 4. Ramping-load-scratch-test profiles for (i) UNCD/Si, (ii) UNCD/Ti/Si, and (iii) UNCD/W/Si films. The substrates were ultrasonicated using 0.1 μm diamond powders for 30 min and then MPE-CVD for 8 h.

the assumption that the W–C layer forms instantaneously whenever the W$_a$-coated substrates were exposed to the plasma. Presumably, the diamond nuclei started to form once the W–C layer was generated. The UNCD nuclei completely covered the W$_a$ layer after MPECVD for 30 min with the underlying W–C layer completely covering the Si substrates.
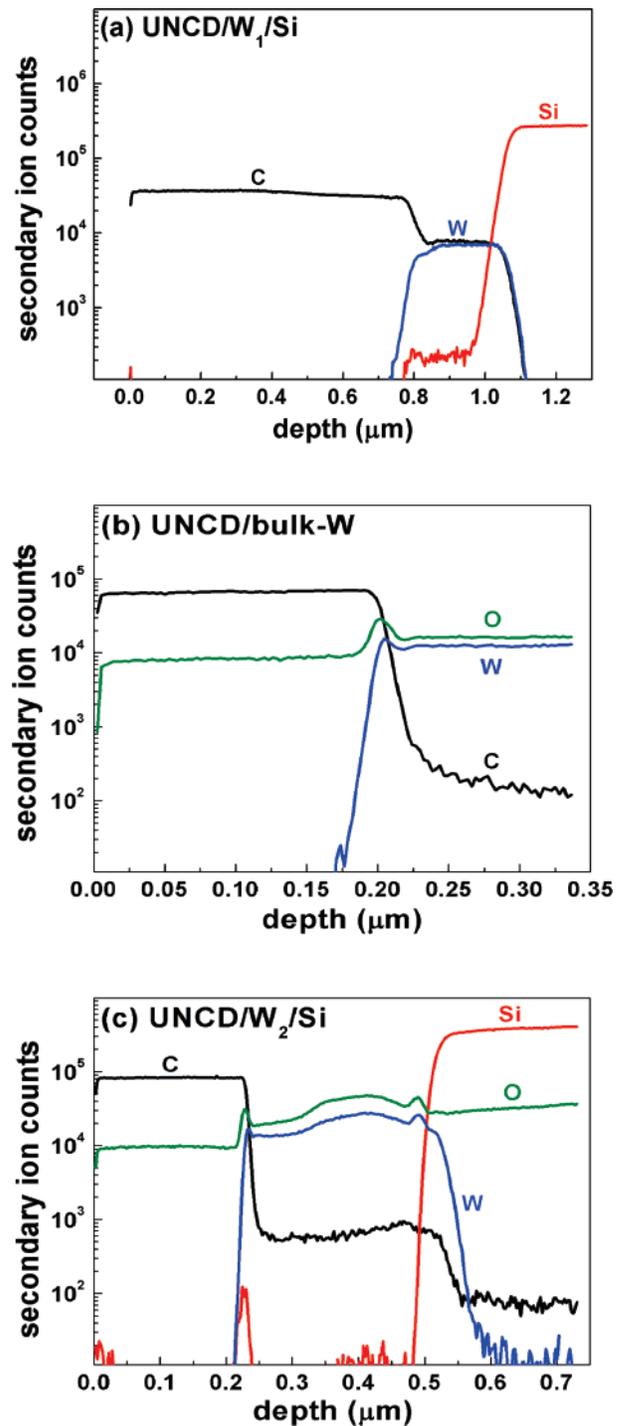

Figure 5. SIMS profiles of UNCD films grown on (a) W$_a$/Si substrates, (the W layer was prepared by the e-beam evaporation process), (b) bulk W substrates, and (c) W$_b$/Si substrates (the W layer was prepared by the RF-sputtering process).

Previous results indicate that, although the Ti coating can also enhance the formation of diamond nuclei very efficiently, it results in a markedly smaller growth rate for UNCD (78.5 nm/h).[6] A probable explanation for such a phenomenon is that the diffusivity of carbon species in Ti metal $((D_c)_{Ti} = 0.7 \times 10^{-8}$ cm^2/s) is overwhelmingly higher than that in W metal $((D_c)_W = 1.0 \times 10^{-13}$ cm^2/s)). Moreover, the TiC layer formed on top of the Ti coating is of lower density ($G_{TiC} = 4.91$ g/cm^3) but contains a higher amount of carbon species (saturated concentration is $C_{TiC} = 0.47$ g/cm^3) compared to those of the W$_2$C phase; that is, $G_{W2C} = 17.2$ g/cm^3 and $C_{W2C} = 0.18$ g/cm^3.
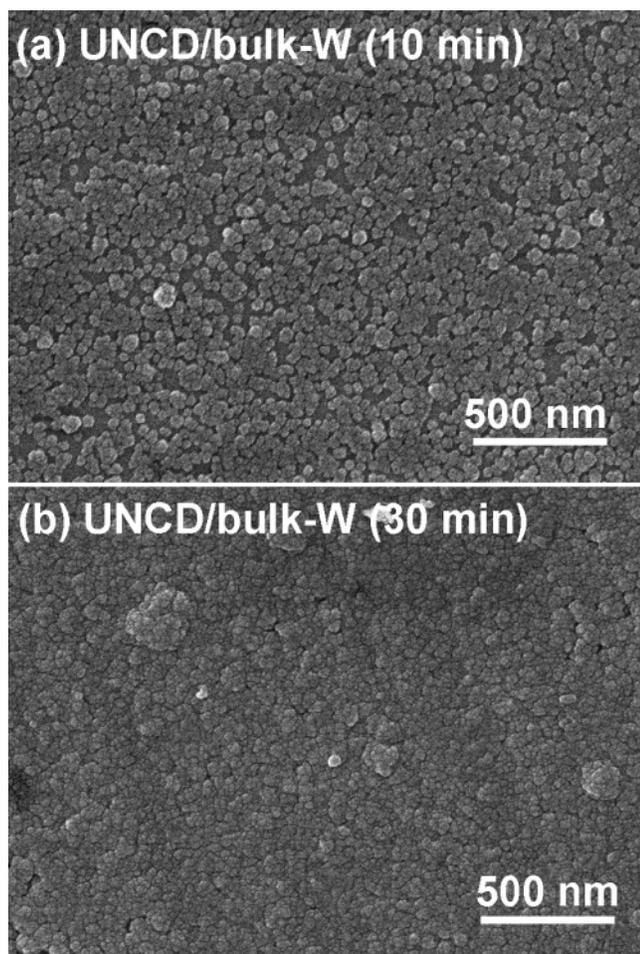
Figure 6. SEM micrographs for UNCD films prepared by the MPECVD process for (a) 10 min and (b) 30 min on bulk W substrates.

These factors lead to the phenomenon that, although the carbon species are readily diffused into the Ti layer forming the TiC layer quickly and facilitating the nucleation of diamonds, the Ti layer consumes a pronouncedly larger proportion of carbon. The onset of the formation of diamond nuclei was thus delayed and results in a slower apparent growth rate for the UNCD layer on Ti/Si substrates, as compared to those on W_1/Si substrates.

Pre-coating a W metallic layer (by the e-beam evaporation process) on the Si substrate not only enhances the formation of diamond nuclei but also improves the UNCD-to-Si adhesion. Figure 4 shows the UNCD-to-substrate adhesion measured by the ramping-load-scratch-test technique,[14,15] where the nanoindentation profiles for the UNCD on Ti-coated Si substrates and those on bare Si substrates were also included to facilitate comparison. For the UNCD deposited on bare Si without metal coating (UNCD/Si, profile I), a penetration dip in the ramping-load-scratch-test profile was observed; indicating that the UNCD films were easily detached from the Si substrates. The UNCD/W/Si films possess markedly stronger adhesion (>200 mN, profile III) than the UNCD/Ti/Si (~72.8 mN, profile II) and the UNCD on bare Si substrates. It should be noted that 200 mN is the maximum load provided by the apparatus. The adhesion of UNCD-to-substrate is apparently related to the degree of interdiffusion between layers. To understand the correlation between the two phenomena, SIMS profiles of the UNCD films were examined.

Figure 5 illustrates the SIMS profiles for the 8 h grown UNCD films, indicating the existence of a plateau in the W_a layer, which contains W and C species of the fixed ratio. Such

a phenomenon reveals the formation of tungsten−carbon compound layer prior to the nucleation of diamond grains, which is in accordance with the XRD observation shown in Figure 3a. Detailed analysis on these SIMS profiles reveals that a certain extent of interdiffusion exists between the W_2C intermediate layer with the UNCD layer and the Si substrate. Therefore, the W_2C carbide layer bonds more strongly to the UNCD and Si layers than the TiC layer. Previous studies[6] indicated that the Ti coating forms a complicated intermediate layer, including crystalline TiC and amorphous Ti−Si layers, which bond weakly and thus adhere poorly to UNCD and Si substrates.

The above results infer that to effectively enhance the UNCD to Si adhesion the intermediate layer must be simple in structure and interdiffuse moderately with both the UNCD and Si layers. Moreover, to efficiently induce the formation of diamond nuclei, the metal layer should not dissolve too much carbon so as to form carbide quickly. The implication of this phenomenon is that direct growth of UNCD on the bulk W substrates will be extremely difficult because all of the carbon species will be consumed by the tungsten metal substrates due to high solubility of tungsten to the carbon species. Only when the metallic layer is thin, which limited the amount of carbon dissolved, inward diffusion of carbon species into the metallic layer can be stopped quickly, efficiently inducing the formation of diamond nuclei.

To confirm such a proposed model for the nucleation of diamonds on W−Si substrates, the growth behavior of diamonds on bulk W substrates was investigated. The SEM micrograph shown in Figure 6a reveals that the UNCD grains are not completely covering the bulk W substrates when MPECVD for 10 min, indicating clearly that the nucleation of diamonds on bulk W is not as easy as that on the W_a thin layer. Large proportions of uncoated surface were still present, although the nuclei are still very small in size (~20 nm). It takes 30 min to grow enough UNCD nuclei, fully covering the bulk W substrate (Figure 6b). XRD patterns in Figure 7a indicate that the bulk tungsten is polycrystalline with (110) oriented grains predominating. No W−C phase was observed for all of the MPECVD samples. XPS analyses shown in Figure 7b reveal that for the surface of bulk tungsten only a C1s peak at 284.3 eV corresponding to the C−C bond was observed and no C1s peak corresponding to the W−C bond was detected, regardless of the MPECVD time. Moreover, the W4f peak at 31.5 eV corresponding to the W−W bond and that at 33.6 eV corresponding to the W−O bond are prominent when MPECVD for 10 min (profile I, Figure 7c). The intensities of these peaks decrease pronouncedly when MPECVD for 20 min (profile II, Figure 7c) and are absent when MPECVD for 30 min (profile III, Figure 7c). SIMS analyses (Figure 5b) indicate that carbon contents decrease abruptly across the UNCD-to-W interface. There is no plateau corresponding to the W_2C phase observable, which is in accordance with previous XRD and XPS observations. All of the above observations imply that the diamonds nucleated directly on the W surface without the formation of an intermediate W_2C phase and the proportion of diamond nuclei covering the W surface increases monotonically with the MPECVD period.

For the W_a/Si substrates, the carbon content in the thin W_a layer increased very fast because of the limited volume of the thin films for carbon to inwardly diffuse, which easily induces the formation of the W−C phase, slowing down pronouncedly the inward diffusion of carbon. The carbons accumulate on top of the W−C layer quickly, triggering the formation of diamond nuclei almost instantaneously. As for the case of bulk W
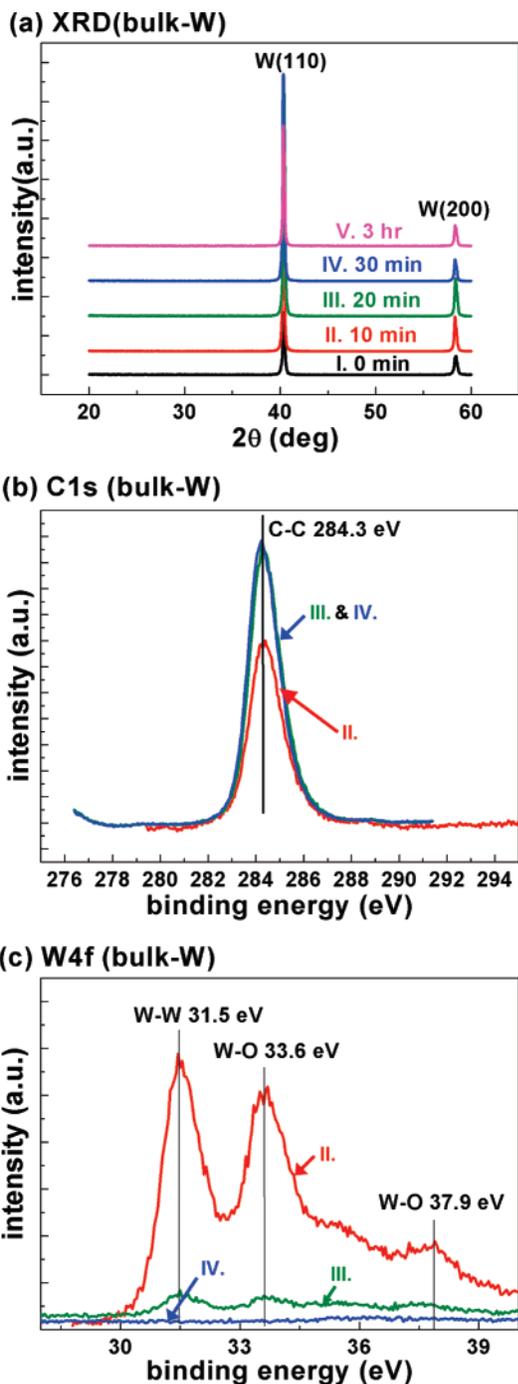
Effects of Tungsten Metal Coatings

J. Phys. Chem. C, Vol. 112, No. 10, 2008 **3763**

(a) XRD(bulk-W)

(b) C1s (bulk-W)

(c) W4f (bulk-W)

Figure 7. (a) X-ray diffraction profiles for UNCD films deposited on bulk W substrates by the MPECVD process for 0−30 min (profiles I−IV) and for 180 min (profile V); (b) C1s XPS and (c) W4f XPS profiles for UNCD films deposited on bulk W substrates by the MPECVD process for 10−30 min (profiles I−III).

substrates, there is no W−C phase formed prior to the nucleation of diamonds. The onset of nucleation of diamonds can be initiated only when the carbon species accumulate on the W surface faster than those inwardly diffusing, rendering the carbons deposited on the topmost surface exceed some critical concentration. Such a process is significantly slower than the in case of W_a thin film coating on Si substrates. Restated, the readiness for the formation of the W−C phase is the prime factor by which the W_a coating facilitates the nucleation of diamonds. However, the slower nucleation rate for bulk W substrates does not degrade the quality of UNCD films. Raman spectra shown in Figure 2a indicate that the UNCD films grown on bulk W
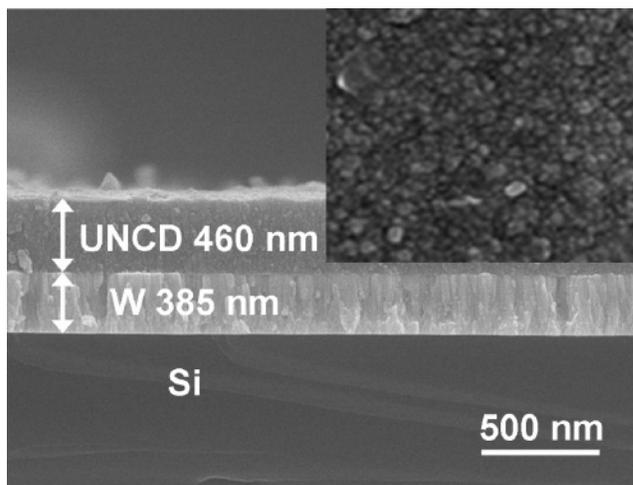

Figure 8. Cross-sectional SEM micrograph of the UNCD films deposited on W_b/Si substrates (the W layer was prepared by the RF-sputtering process) MPECVD for 180 min. The inset shows a plan-view SEM micrograph of the UNCD films.

substrates possess the same characteristics as those deposited on W/Si substrates.

The above results imply that once the W−C phase was formed the diamond nucleates instantaneously. The implication of such a phenomenon is that the kinetics for the formation of the W−C phase can be further enhanced had we used a W coating with a higher packing density as the buffer layer. For this purpose, we utilized the RF-sputtering process (50 W, 8 Torr, Ar) to deposit on Si substrates a thin W layer (W_b, ∼300 nm), which is the same thickness as that of the e-beam evaporated W_a layer. The UNCD nuclei also formed easily on W_b-coated Si substrates. The UNCD grains (<10 nm in size) already fully cover the substrates when MPECVD for 10 min (figures not shown), and the grains remain at such a small size even after 3 h of MPECVD (inset, Figure 8). The cross-sectional micrograph (Figure 8) reveals that the interfaces between UNCD films, W_b layer, and Si substrates are very compact and contain no voids. The UNCD films grew to about 460 nm in 3 h, which corresponds to a growth rate of about 153.3 nm/h. This rate is markedly larger than that of UNCD on W_a/Si substrates (92.1 nm/h, cf. Figure 1). Raman spectra of the UNCD/W_2/Si films are similar to the one shown in spectrum I of Figure 2a, and the corresponding NEXAF profiles are the same as those shown in Figure 2b. That is, the characteristics of the UNCD films are not altered by the different nucleation behaviors on the two substrates (W_a/Si and W_b/Si) used for growing the films.

To understand the mechanism resulting in the faster nucleation rate for UNCD due to the presence of the W_b layer on Si substrates (W_b/Si) compared to those on W_a/Si substrates, we also examined the evolution of phases on the surface of W_b/Si substrates using X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS). Figure 9a shows that the as-deposited W layers are crystallized (XRD-I) and MPECVD does not modify such a characteristic (XRD-II to IV). No W−C signal was detected, even after MPECVD for 180 min (XRD-V, Figure 9a) whereas the XRD signal from the silicon substrate is clearly observable (XRD-I to V, Figure 9a).

However, XPS analyses reveal clearly the presence of a C1s peak at 282.0 eV corresponding to carbon in the W−C bond for the films MPECVD for 10 min (profile I, Figure 9b). Detailed deconvolution on this C1s profile reveals the presence of small peaks of the 284.3 eV C1s peak, corresponding to carbons in the C−C bond, which indicate that the nucleation
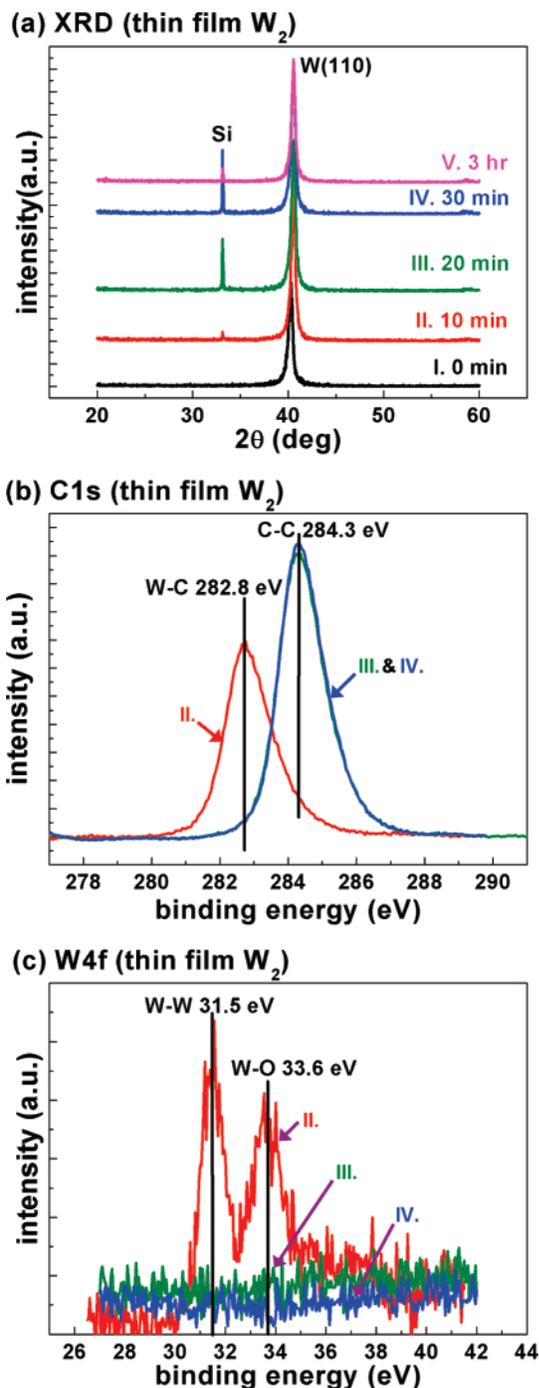
3764 *J. Phys. Chem. C, Vol. 112, No. 10, 2008*

Chen et al.

(a) XRD (thin film W₂)

(b) C1s (thin film W₂)

(c) W4f (thin film W₂)

Figure 9. (a) X-ray diffraction profiles for UNCD films deposited on W_b/Si substrates by the MPECVD process for 0–30 min (profiles I–IV) and for 180 min (profile V); (b) C1s XPS and (c) W4f XPS profiles for UNCD films deposited on W-coated Si substrates by the MPECVD process for 10–30 min, profiles I–III (the W layer was prepared by the RF-sputtering process).

of diamond has already been induced. After 20–30 min of MPECVD, the C1s peak at C−C 284.3 eV completely overtook the W−C 282.8 eV peak (profiles II and III, Figure 9b), suggesting that the diamond nuclei have fully covered the W−Si substrates. In contrast, the W4f profiles shown in Figure 9c reveal the presence of peaks corresponding to W metal, that is, W−W at 31.4 eV and W−O at 33.6 eV, for the 10 min MPECVD samples (profile I, Figure 9c), but not for 20 and 30 min MPECVD ones (profiles II and III, Figure 9c). These W4f profiles, in conjunction with the C1s profiles in Figure 9b, imply that the W−C phase already started to form but partially
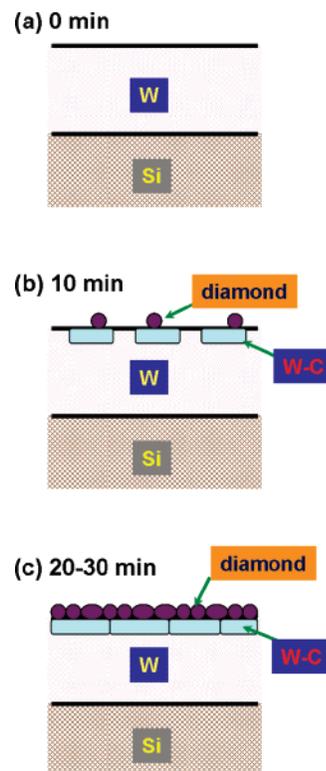

Figure 10. Schematic diagrams illustrating the phase evolution whenever the W−Si substrates were exposed to CH₄/Ar-plasma: (a) as-deposited W coating on Si substrates, (b) formation of W−C phase and diamond nuclei after 10 min MPECVD, (c) formation of diamond nuclei fully covering the W layer as soon as a continuous W−C phase resulted after 20–30 min MPECVD.

covering the substrates for the samples MPECVD for 10 min. Some proportion of exposed W surface still exists. It takes around 20 min MPECVD to form the W−C phase completely covering the W surface. The diamonds nucleated instantaneously once the W−C phase was formed such that, when MPECVD for 20–30 min, the W surface was completely covered with diamond. The W−C layer is much thinner than the W_b layer because the XRD patterns shown in Figure 9a did not detect the presence of the W−C phase.

After MPECVD for 10 min, the W metal peaks (W4f binding energy = 31.4 eV) coexist with W−C phase (C1s binding energy = 282.8 eV) for thin-film W_b Si substrates (cf. Figure 9) and they coexist with the diamond phase (C1s binding energy = 284.3 eV) for bulk W substrates (cf. Figure 7). However, the W4f peaks corresponding to W materials of bulk W substrates is 10 times as large in intensity as those for W_b/Si substrates. It implies that the exposed W surface on bulk W is much larger than that on the thin-film W_b/Si substrate. This is another indication that the rate of nucleation of diamonds on bulk W substrates is markedly lower than that on thin film-W_b/Si substrates. SIMS profiles shown in Figure 5c illustrate an abrupt drop in carbon ion counts in the W_b layer. It should be noted that the C/W ion count ratio (γ value) is around $(\gamma)_{W2}$ = 0.032, which is much smaller than the γ value observed for the W_2C phase in the W_a layer $((\gamma)_{Wa} = 1.0$, Figure 5a). Moreover, this γ value is close to the one in bulk W, which implies that the C/W ion count ratio (γ value) in the W_b layer is approaching the residue value when the inward diffusion of carbon is completely blocked. Such an observation is in accordance with the argument that a thin W−C phase was formed instantaneously as soon as the W_b/Si substrates were

Effects of Tungsten Metal Coatings

J. Phys. Chem. C, Vol. 112, No. 10, 2008 **3765**

exposed to CH_4/Ar plasma and thereby effectively hindered the inward diffusion for carbon.

The phase evolution of the W_b Si substrates subjected to MPECVD is illustrated schematically in Figure 10. This figure indicates that once the W−C phase was formed the inward diffusion of carbons into the W layer is suppressed. The carbons accumulated on the W−C surface very quickly, triggering the formation of diamond nuclei instantaneously (Figure 10b). Full coverage of the diamond nuclei was resulted once the W−C phase completely covered the W layer (Figure 10c). Restated, the RF-sputtered W_b coating results in pronouncedly faster nucleation and growth behavior for UNCD films, compared to the e-beam evaporated W_a coating, not to mention the bulk W. The possible explanation for such a phenomenon is that the W species produced in the RF-sputtering process possess kinetic energy (∼1 eV) at least 1 order of magnitude higher than those produced by the e-beam evaporation process (∼0.1 eV) so that the RF-sputtered W_b films are thus expected to be much denser than the e-beam evaporated W_a films. Therefore, only the outmost surface of the RF-sputtered W_b films forms tungsten carbide. In contrast, the e-beam evaporated W_1 films are loosely packed such that whole films were readily reacting with carbon species and being converted into carbides. It takes longer to convert the W_a films into W−C phase and, thereafter, retards the onset for nucleation of diamonds, resulting in markedly smaller effective growth rates for the UNCD films, as compared to those of W_b films.

4. Conclusions

Well-adhered and uniformly distributed nanodiamond thin films were prepared from tungsten-coated silicon wafers. The nucleation behavior of diamonds on W/Si and bulk W substrates was investigated, and the former was markedly faster than the latter. XRD, XPS, and SIMS analyses imply that this can be ascribed to the formation of the W−C phase on the W/Si substrates, which in turn is ascribed to the fast accumulation of carbon species in the W layer because of the limited volume for carbon inward diffusion. In contrast, carbon species diffuse into the bulk W materials continuously, which slow down the rate of accumulation, therefore delaying the formation of diamond nuclei.

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