

Enhanced nucleation, smoothness and conformality of ultrananocrystalline diamond (UNCD) ultrathin films via tungsten interlayers

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Abstract

Extremely smooth (6 nm RMS roughness over $4\ \mu\text{m}^2$), thin (100 nm), and continuous ultrananocrystalline diamond (UNCD) films were synthesized by microwave plasma chemical vapor deposition using a 10 nm tungsten (W) interlayer between the silicon substrate and the diamond film. These UNCD films possess a high content of sp^3 -bonded carbon. The W interlayer significantly increased the initial diamond nucleation density, thereby lowering the surface roughness, eliminating interfacial voids, and allowing thinner UNCD films to be grown. This structural optimization enhances the films' properties and enables its integration with a wide variety of substrate materials.

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Reducing the roughness of diamond thin films is a critical requirement for a range of applications including novel integrated electronic devices, micro- and nano-electromechanical systems (MEMS/NEMS), wear-resistant low friction coatings, and bio-devices [1,2]. Although diamond thin films possess outstanding electrical, mechanical, and thermal properties, the intrinsically high surface roughness is undesirable [3]. Ultrananocrystalline diamond (UNCD) is a form of diamond thin film characterized by 3–5 nm diameter pure diamond grains and atomically abrupt (<0.2 nm) grain boundaries with a mixture of carbon bonding configurations [4,5]. The fine grain size is a result of the high

renucleation rate during growth using hydrogen-poor, argon-rich microwave plasma discharges [6]. Compared to conventional microcrystalline diamond films, UNCD films are inherently much smoother (typically 20 nm RMS roughness over a $4\ \mu\text{m}^2$ area), independent of film thickness [7]. Nevertheless, it should be possible to improve on this by reducing the surface roughness to UNCD's intrinsic grain size. Nanocrystalline diamond films (grain sizes 10–100 nm) deposited using an enhanced nucleation method and a modified growth chemistry [8] achieve low surface roughness. However, as these films get thicker, the grains coarsen, and thus they become rougher.

Several methods have been used to reduce the roughness of diamond films, such as chemical mechanical polishing [9,10], substrate biasing [11,12] and altering the deposition parameters during growth [13]. Most of these methods are cost-prohibitive and can worsen the film properties. There

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remains a need to reproducibly deposit extremely smooth, conformal, continuous, high quality diamond films of arbitrary thickness.

The nucleation and initial growth of diamond films have been widely investigated [14,15] and different seeding techniques have been established to enhance nucleation and film continuity [16]. Typically, the substrate is ultrasonically treated in an organic suspension of nanometer-sized diamond (ND) particles prior to diamond film growth, resulting in high nucleation densities (10^{11} sites/cm²) [16] even at low temperatures [17]. The new nucleation process (NNP), or ‘Rotter nucleation technique’, yields extremely high nucleation densities [8]. However, it involves an extra plasma exposure step separate from film growth, which also involves high substrate temperatures (800 °C). Bias [18] and chemical methods [19] have not been widely standardized. Thus, there is an urgent need for a reproducible seeding technique that enables uniform and continuous diamond coatings on complex shapes.

Metal interlayers have been used to promote adhesion of diamond thin films [16]. Deposition on carbide-forming materials promotes adhesion, while deposition on steel,

copper, or non-carbon affinity materials, which are carbon-dissolving materials, leads to poor adhesion and non-uniformity [16,20]. However, no previous studies on the effect of metal interlayers on nucleation, conformality, and roughness have been reported. Here, we examine the effect of a W film interlayer on the UNCD film roughness and initial nucleation density.

UNCD films were deposited on bare and W-coated Si wafers at 800 °C at a power of 1200 W using a commercial microwave plasma system. The deposition parameters were: argon: 49.2 sccm; methane: 0.8 sccm; pressure: 200 mbar; deposition time: 20 min. Prior to UNCD growth, the wafers were seeded by immersing in an organic suspension of ND powder in an ultrasonic bath [17].

W films were deposited using two methods: RF magnetron sputtering and atomic layer deposition (ALD). ALD offers the advantage of coating complex, non-planar surfaces with monolayer control over the W thickness. Sputtering was carried out using an RF power of 150 W and an Ar flow of 30 sccm at room temperature. The W ALD was performed in a custom apparatus [21] using a previously described method [22] in which tungsten hexafluoride

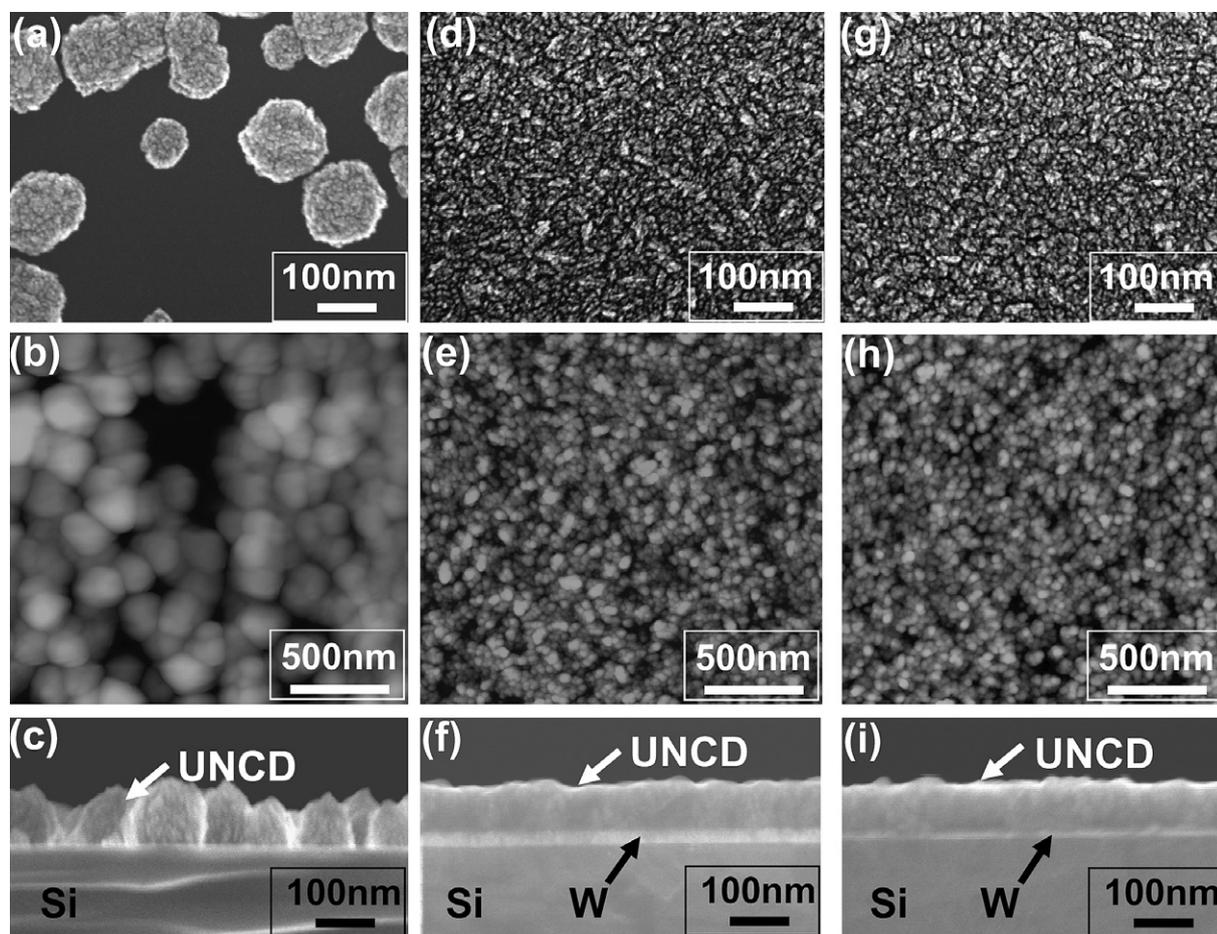


Fig. 1. Plan-view SEM, AFM, and cross-sectional SEM images of UNCD films: (a–c) UNCD deposited without W film added, (d–f) UNCD deposited on a sputtered W film as a seed layer (100 Å thickness) and (g–i) UNCD deposited on an ALD W seed layer (100 Å thickness), respectively. UNCD thickness is 107 nm in (f) and (i), while UNCD thickness is 70 nm in (c). All UNCD films were grown for 20 min under the same conditions. All AFM images are for $2 \mu\text{m} \times 2 \mu\text{m}$ area and the AFM Z range is 150 nm for (b) and 100 nm for (e and h).

(WF₆) and disilane (Si₂H₆) vapors were alternately pulsed through the reaction chamber. To enhance the nucleation of the W, 1 nm ALD aluminum oxide (Al₂O₃) layer was deposited on the Si prior to W growth [23].

UNCD thin films were characterized by scanning electron microscopy (SEM, Hitachi S4700), atomic force microscopy (AFM, Digital Instruments Nanoscope-IV), transmission electron microscopy (TEM, Tecnai 20F ST equipped with a post-column energy filter (GATAN)), and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. TEM cross-sectional samples were prepared by extracting lamella with a thickness in the range of 20 nm using a focused ion beam (FIB, Zeiss XB) and then sputtered with Ar⁺ ions (4°, 1 kV) to remove the FIB-damaged surface layer. NEXAFS spectroscopy was performed in UHV at the Synchrotron Radiation Center (Stoughton, WI) on the HERMON beam line. Spectra were taken in total electron yield (TEY) mode and normalized to the simultaneously-recorded photoinduced current of a freshly coated gold mesh in the beam line.

Fig. 1 compares UNCD deposited on plain Si vs. 10 nm W thin films on Si for a short 20 min. deposition time. From plan-view SEM, the films grown using interfacial W (Fig. 1d, g) are much denser and more uniform than those without the W layer, which are discontinuous using this short growth time (Fig. 1a). From AFM, the RMS roughness of the film on Si is 20 nm (Fig. 1b), but is much smoother for UNCD deposited on sputtered W (Fig. 1e, 8.2 nm) and ALD W (Fig. 1h, 6.3 nm). Cross-sectional SEM reveals uniform UNCD films with a thickness of

107 nm when W was used as a seed layer (Figs. 1f, 1i), while UNCD islands (70 nm thickness) are formed without the W layer (Fig. 1c). The reduced roughness of the films on W can be immediately understood as arising from denser and more uniform nucleation, promoting vertical growth vs. an initially three-dimensional growth around fewer nucleating seeds, which is consistent with previous observations of the growth of UNCD colonies about a low-density of seeds [7].

The NEXAFS measurements (Fig. 2a) exhibit the characteristic signature of UNCD [24] and show that the short growth time and the presence of W do not affect the highly sp³-coordinated bonding structure of the top of the films. Therefore, the W interlayer enhances the initial nucleation density which in turn reduces the surface roughness and requires less time (and lower thickness) to produce a coalesced, continuous, high quality film.

In addition to forming uniform, smooth films on planar Si surfaces, ALD W can be used to seed complex shapes such as micro-tip arrays (Fig. 3d). Without a W seed layer, discontinuous UNCD is observed (Fig. 3a). The uniformity improves using a sputtered W layer, but incomplete coverage occurs in shadowed regions (Fig. 3b) since sputtering is limited to the line of sight. A uniform, conformal UNCD film was observed with the ALD W seed layer (Fig. 3c) including shadowed regions.

To investigate the Si–W–UNCD interfaces, energy filtered TEM was performed on cross-sectional specimens of UNCD deposited on ALD W. Elemental line-scans with a resolution of 2 nm for Si, W, and C along with a high res-

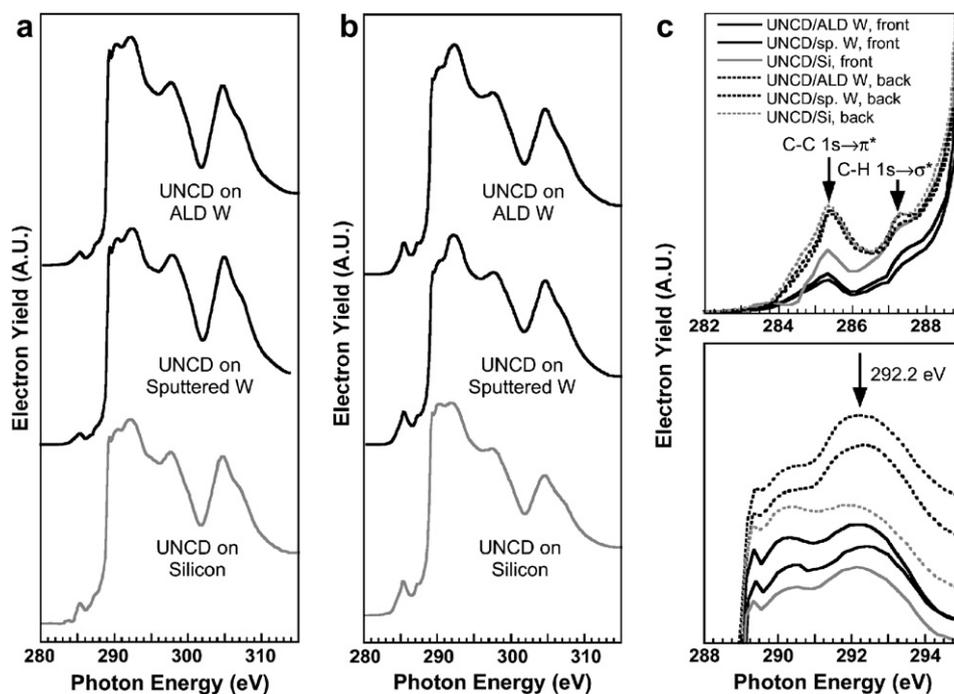


Fig. 2. TEY NEXAFS spectra on the UNCD samples: (a) top sides of the thin samples, (b) undersides of thicker, otherwise equivalent samples and (c) higher magnification of key features in all six samples. The undersides exhibit enhanced sp²-bonded and hydrogenated carbon, and the W-grown samples show a feature at ~292.2 eV that may represent graphitic structure. Note that some of the spectra in the lower portion of Fig. 1 c have been shifted vertically for clarity.

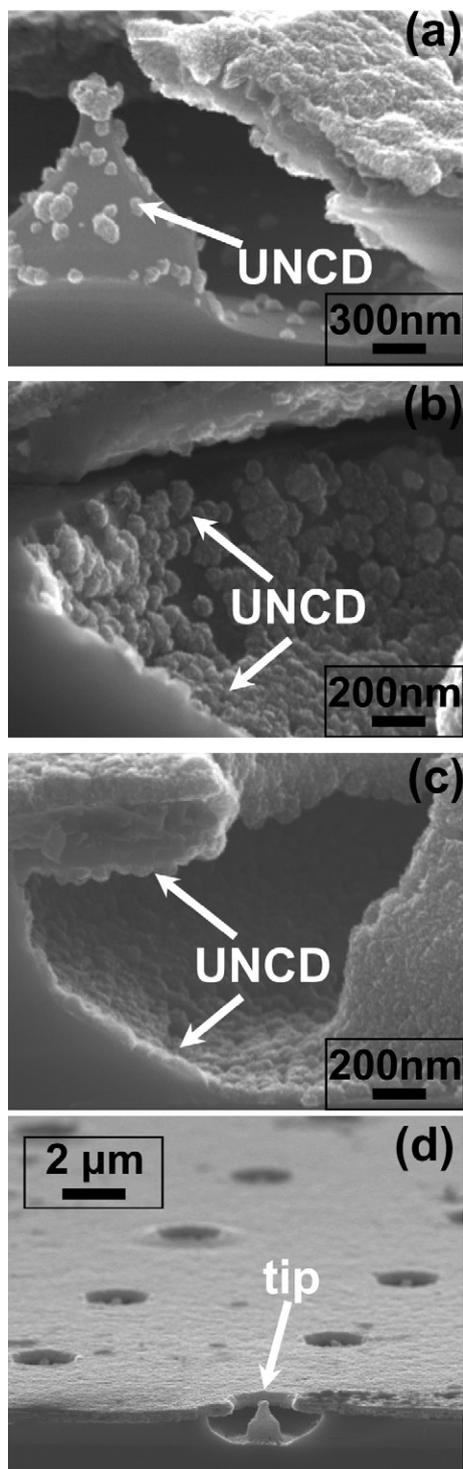


Fig. 3. SEM images of micro tip arrays coated with UNCD: (a) UNCD without any tungsten seed layer, (b) UNCD deposited on a sputtered W seed layer, (c) UNCD deposited on ALD W seed layer and (d) low magnification view of micro tip array.

olution TEM (HRTEM) image are shown in Fig. 4. Elemental scans of O and Al were inconclusive. There is a ~ 3 nm region of predominantly amorphous material between the crystalline Si and polycrystalline W. This amorphous region is thicker than the native oxide of Si (1.5 nm) and the Al_2O_3 ALD nucleation layer (1 nm).

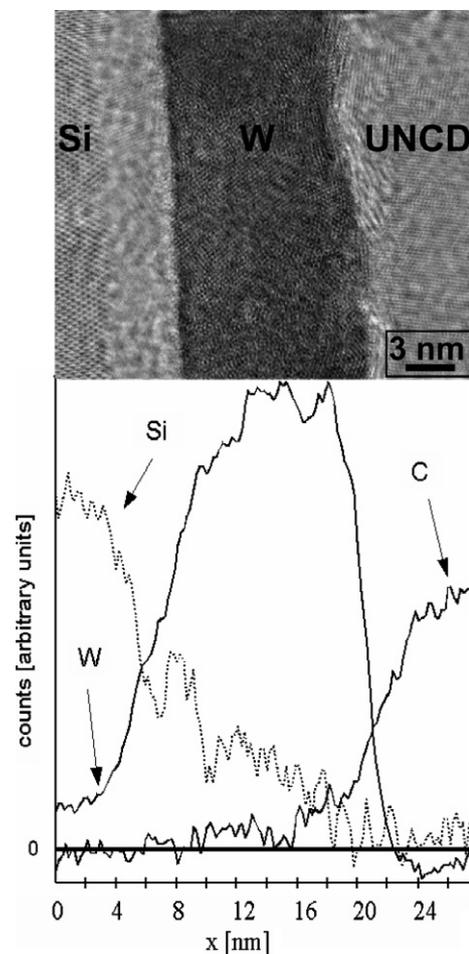


Fig. 4. Cross-sectional HRTEM image and qualitative elemental map of Si (Si-2p edge), W (W-4f edge) and C (C-1s edge) of the UNCD film deposited on an ALD W layer.

However, this region contains appreciable W that may result from W diffusion to form W-oxides and/or W-silicides. The W–UNCD interface is unexpectedly rough considering that AFM analysis of the ALD W films yield ~ 0.8 nm roughness, and this may result from the high temperature MPCVD process, the ultrasonic ND seeding process, or stress- and diffusion-induced interfacial roughening. Significant C is detected in the W layer to a depth of 5 nm. This could be due to tungsten carbide formation or diffusion of C into the nano-crystalline W grain boundaries.

NEXAFS spectra were acquired from the ‘underside’ of three UNCD films (Fig. 2b) and compared with the spectra from the as-grown top side of the films (Fig. 2c). The undersides were exposed by etching the silicon substrate away with a 1:1 mixture of hydrofluoric and nitric acid. W was also etched using hydrogen peroxide for films grown on W. For these film underside studies, thicker films (~ 1 μm) were grown under otherwise identical conditions to the three thinner films, to allow the released films to be handled. Tungsten carbide exhibits NEXAFS peaks at 284.8 eV, 286.8 eV, 287.8 eV, and 289 eV, all on a broad

edge that spans that range of energies [26]. A peak at 289 eV is impossible to observe in our spectra due to the sharp absorption edge at the same energy in UNCD, as is typical in highly sp^3 -bonded CVD diamond. No detectable peaks are found at the other WC peak energies. Although modest increases of intensity at 286.8 and 287.8 eV compared with the top side spectra are observed for the films grown on W, the same increase is observed for the film grown directly on Si.

More strikingly, an increase in the peak intensities at 285.4–285.5 eV, and at 287.4 eV are observed for all three underside samples compared with the topside. These features correspond, respectively, to the C–C $1s \rightarrow \pi^*$ transition seen in graphite and disordered carbon due to sp^2 -bonded carbon and the C–H $1s \rightarrow \sigma^*$ transition seen on hydrogenated carbon surfaces [27]. The intensities of these features are equivalent for all three underside samples. This suggests that the films exhibit a modest degree of non-diamond, hydrogenated carbon on the underside, consistent with previous observations [7]. The greater degree of sp^2 -bonded carbon on the topside of the Si-grown sample is due to the incomplete coverage of this film.

There is also an increase, relative to its lower-energy neighboring peaks, in the broad peak at ~ 292.2 eV on the underside of both W-grown films, but not for the film grown on Si (Fig. 1b, c, lower). This feature can be attributed to a portion of the C–C $1s \rightarrow \sigma^*$ transitions that are normally observed in graphitically bonded carbon. The sp^2 -bonded carbon on the underside of the W-grown films may be more ordered than the film grown on Si, but further analysis is needed to corroborate this. Spectra obtained at 60° incidence angle showed no significant difference in relative intensities of the π and σ peaks associated with sp^2 -bonded carbon. Thus the sp^2 -bonded carbon present on the underside is not preferentially oriented either in the plane or out of the plane of the films.

Overall, the NEXAFS spectra demonstrate that there is only a small increase in sp^2 -bonded carbon present at the underside of all of the films compared to the top side, including for films grown on W. UNCD nucleation and growth on W does not lead to significant WC formation nor an increase in non-diamond carbon at the UNCD/W interface. Thus, the integrity of UNCD at the film–substrate interface is preserved using the W process, which is a critical feature for applications such as MEMS or NEMS where the film underside may be exposed as part of the device [7].

It is not yet clear why the W interlayers enhance the nucleation of UNCD. Previous experiments with Ti, Cr, and Mo interlayers did not produce similar enhancements [15]. Compared to other metal carbides, WC has a high thermal stability and a thermal expansion coefficient that is closely matched to CVD diamond [25], and these properties may enhance nucleation [15]. No evidence of WC formation is apparent from the NEXAFS data. Being softer than Si, W may enable smaller ND seeds to be embedded in it during ultrasonication, reducing the presence of

agglomerated seeds and leading to denser, finer dispersion. Clearly, physical interactions between the ND seeds and the W surface are involved in the enhanced UNCD nucleation because virtually no UNCD is deposited on Si or W without ND seeding. Further investigations will clarify the possible role of carbide and silicide formation, surface chemistry (of the W and ND particles), effectiveness of particle spreading, and interface roughness in the enhanced nucleation of the UNCD films.

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