



Improved nanodiamond seeding on chromium by surface plasma pretreatment



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ABSTRACT

Surface pretreatment by gas discharge plasmas of N₂, O₂ and CF₄ is studied for enhanced diamond nucleation on Cr surfaces. The seeding density following the interaction of water-dispersed nanodiamonds (NDs) and the Cr surface is enhanced due to chemical modification of a surface. The surface that is untreated or pretreated with N₂ plasma possesses a suppressed electrostatic attraction of NDs, while the pretreatment with O₂ or CF₄ plasmas render a strong electrostatic attraction and high seeding density. Finally, by this method thin nanocrystalline diamond films are achieved on Cr surfaces after O₂ and CF₄ plasma pretreatments.

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Diamond being a superior material due to intrinsic properties [1] is gaining more importance for device fabrications [2] and applications in conjunction with various materials, e.g., refractory metals [3], piezoelectric [4], and biological materials [5], therefore, stimulating investigation of diamond growth on various substrates. Chromium, the refractory metal that is important for industry and microelectronics, has a potential to be used as contact material [2], and thus spurs the investigation of the interfacial properties [6]. Zan et al. suggested that Cr can be used as wetting layer between Au and graphene, due to Cr's ability to catalyze dissociation of C–C bonds which leads to higher formation rate of Cr clusters on graphene than Au, and thus gives better electrical contacts [7]. However, diamond synthesis on many materials is challenging due to the harsh environment of the chemical vapor deposition (CVD) method, i.e. the high temperature hydrogen rich plasma influences the substrate interface via chemical reactions and thermally activated diffusion processes. Generally, the formation of carbides is advantageous and plays a key role for the diamond growth on non-diamond substrates [8]. For instance, spontaneous diamond nucleation on carbide forming substrates, e.g., Si, Mo, and W, is up to two orders of magnitude higher than on the substrates, which do not form carbides, e.g., Cu and Au [9]. This difference is linked to the fast carbon in-diffusion and supersaturation [10,11]. For instance, a thin TiO₂ layer was used

to nucleate diamond films on optical fiber, here the ability of TiO₂ to be converted to TiC was exploited in order to facilitate diamond growth [12]. The formation of TiC in amorphous TiO₂ layer during the early diamond growth had been studied in details, though, its precise role remains unclear [13]. However, without artificial substrate pretreatment step, e.g., colloid based pre-seeding, the incubation times to achieve the supersaturated nucleus are too long for practical use [14]. The surface pretreatment with colloid of nanodiamond (ND) is an established approach, which leads to high seeding densities ($\sim 10^{11}$ seeds/cm²) and is prerequisite to achieve thin and smooth nanocrystalline diamond (NCD) layers [15,16]. Ali et al. showed that Cr can be used as interlayer on copper, which does not form carbides [11]. Here, the substrate was biased to enhance diamond nucleation and allowed successful NCD growth. Recently, Bujinsters et al. investigated the use of transition metals (Cr, Mo, Nb, Ti, V, W) for obtaining smooth and dense NCD films by hot-filament CVD, where notably colloid based ND seeding on Cr yielded rather low density of $\sim 3 \times 10^9$ cm⁻² and consequently led to longer growth times and worse diamond quality [17]. Recently, an alternative approach that employ opposite charge bearing ND's and water soluble polyelectrolytes e.g., polycationic polymer (PDDAC) or polyanionic polymer (PSS) deposited on the substrate surfaces were successfully demonstrated as another route to improve ND seeding, even on 3D objects [18,19]. In this communication, we demonstrate that seeding density is improved on Cr surface using colloid based ND seeding after pretreating the surface with O₂ or CF₄ gas discharge plasmas. Consequently, short microwave plasma

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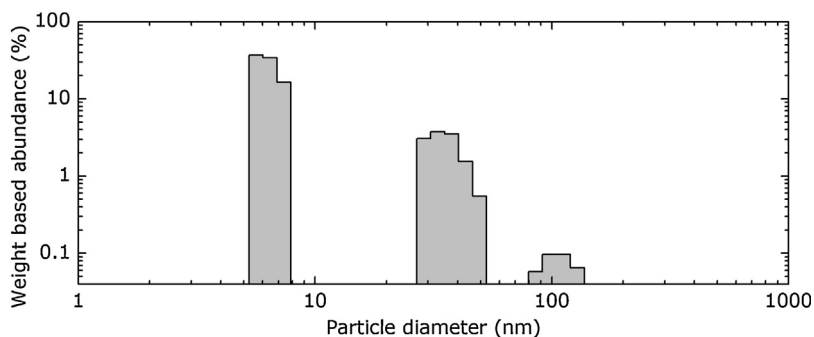


Figure 1. Dynamic light scattering spectrum of the (0.05 wt%) ND particles containing aqueous colloid.

enhanced CVD (MW PE CVD) leads to a thin (42 nm) NCD layers on Cr.

Single crystalline Si (1 0 0) substrates were coated with 200 nm thick Cr layer by DC-pulsed magnetron sputtering. Subsequently, four samples series were exposed for 1 min to different gas discharge plasmas (1.2 Pa): nitrogen (N_2), oxygen (O_2) and tetrafluoromethane (CF_4), respectively, whereas one sample series was left untreated as a reference. Samples were negatively biased keeping constant power of 250 W. Within 5 min after the plasma pretreatment or Cr deposition for the untreated case, samples were immersed into an aqueous ND colloid for 2 min followed by DI water rinsing and drying using a spin-coater. The colloid was prepared from detonation ND powder provided by the NanoCarbon Institute Co., Ltd., and possessed NDs of approximately 7 nm in diameter and the zeta-potential $\zeta = (49 \pm 5)$ mV at pH 4.8. **Figure 1**, shows dynamic light scattering spectrum of the ND particles size distribution.

The surface morphology and the ND seeding density were assessed by a Veeco NanoScope III MultiMode atomic force microscope (AFM). The seeding density was estimated by analyzing height images of $1 \times 1 \mu m^2$ area, where the height baseline was set at 3 nm to ensure that only NDs are visible in the image. This approach was possible due to very smooth Cr surface, measured surface root mean squared value were low for all plasma treated samples ($R_q \leq 0.5$ nm) and the fact that NDs were at least 7 nm in diameter. In order to estimate ND seeding density, single-digit and aggregated particles irrelevant to their aggregation were counted as one seed. Gwydion software were used to process AFM images [20]. Afterwards, the samples were exposed to a $CH_4:H_2$ (3:97) plasma for 3 min in an ASTeX 6500 MW PE CVD reactor in order to enlarge NDs so that they could be visualized by scanning electron microscope (SEM). Later, the same samples were additionally exposed to the CVD plasma for 9 min so that an approximately 42 nm thick NCD layer formed on CF_4 pretreated sample. The estimated NCD film average surface coverage is $(89 \pm 4.5)\%$ and $(92 \pm 4.6)\%$ on O_2 and CF_4 treated surfaces, respectively. Contrary, the non-treated Cr film and N_2 plasma treated Cr yield only $(7.8 \pm 0.4)\%$ and $(8.2 \pm 0.4)\%$ diamond coverage. The thickness was monitored in situ by 405 nm diode-pumped solid-state laser interferometry. NCD films were grown until the first interference minimum was reached. According to the classical thin film interference model this corresponds to 42 nm film thickness when refractive index of diamond, $n(\lambda = 405 \text{ nm}) = 2.461$, is taken [21]. The NCD growth parameters where set-to: 4×10^4 Pa plasma pressure, 3500 W MW power, $750^\circ C$ substrate temperature, and 500 sccm total gas flow. SEM images were obtained with FEI Quanta 200 FEG. The Raman spectra in backscattering configuration of the NCD films were recorded with a Horiba Jobin-Yvon T64000 spectrometer to assess the film quality. The surface chemical composition was determined by X-ray photoelectron spectroscopy (XPS) using a physical electronics (PHI) 5600LS electron spectrometer equipped with an X-ray

source providing monochromatized AlK_{α} photons (1486.6 eV). The binding energy scale has been calibrated by means of an independent Au reference sample setting the Au $4f_{7/2}$ core level to a binding energy of 84.0 eV.

After the plasma pretreatments no significant change in surface roughness was observed (**Figures 2(a) and 4**). In the case of O_2 plasma pretreatment, oxygen reactive species facilitates Cr oxidation as the surface of Cr naturally tends to form native trivalent chromium oxide (Cr_2O_3) layer in ambient atmosphere [22]. XPS overview spectra (**Figure 3(a)**) of the as-deposited Cr and N_2 , O_2 , CF_4 , plasma pretreated samples show the appearance of an O 1s signal at a binding energy (BE) of 530.5 eV, which can be associated with a partial Cr surface oxidation arising from the short sample transfer to the XPS system in ambient (few minutes). Here, the O_2 pretreated sample reveals the highest intensity of the O 1s signal indicating that, indeed, the Cr surface after O_2 plasma is extensively oxidized. The detailed inspection of the high-resolution Cr $2p_{3/2}$ signal (**Figure 3(b)**) suggests that the Cr surface after oxygen plasma treatment is composed of trivalent Cr_2O_3 (576.0 eV) [23] and hexavalent CrO_3 (578.4 eV) [24] oxide thus differing from a pure Cr surface (shortly exposed to air) where $Cr(OH)_3$ is observed. This finding is consistent with results of Prysiashnyi where, after treatment with O_2 plasma for 40 s, the surface converted to CrO_3 (~35%), $Cr(OH)_x$ (~10%), and Cr_2O_3 (~42%) [25]. The presence of hexavalent chromium oxide (CrO_3) was not observed before O_2 plasma treatment, thus supporting the idea that O_2 reactive species largely promote oxidation during the plasma exposure. In the case of pretreatment with CF_4 plasma, the surface is susceptible for fluorination [26]. The XPS survey spectrum of the CF_4 plasma pretreated Cr surface (**Figure 3(a)**) indeed shows a very intense F 1s signal, thus providing evidence that the surface is fluorinated. The high-resolution XPS spectrum of the Cr $2p_{3/2}$ core line (**Figure 3(b)**) confirms that the Cr surface after CF_4 plasma pretreatment is dominated by CrF_3 binding energy of 580.9 eV, that is upshifted from the values reported in literature CrF_3 (580.3 eV) [27] and possibly CrF_2 (579.0 eV) [29] which presence is negligible (due to the appearance of rather symmetric CrF_3 line shape), with a small admixture of Cr hydroxide [27]. Mismatch observed for CrF_3 signal can be explained with the fact that CrF_3 is insulating material that slightly charges during photoelectron emission, whereas Cr $2p_{3/2}$ signal position of the native Cr surface well matches the value reported in literature [29]. The high-resolution Cr $2p_{3/2}$ spectrum of the N_2 plasma pretreated Cr surface proves formation of CrN with a small admixture of Cr_2N (**Figure 3(c)**), as a strong N 1s core level intensity can be detected in the corresponding survey spectrum [30,31]. All surfaces furthermore show a small amount of carbon contaminations (C 1s at 284.7 eV) which can be assigned to hydrocarbons that emerge during sample transfer from the plasma chamber to the XPS set-up.

AFM images of ND seeded Cr surface clearly shows that untreated and N_2 plasma pretreated samples yield low seeding densities of $2.4 \times 10^9 \text{ cm}^{-2}$ and $3.3 \times 10^9 \text{ cm}^{-2}$, respectively

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