

Laser Micro-Raman Spectroscopy of CVD Nanocrystalline Diamond Thin Film

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Abstract— Laser micro-Raman spectroscopy is an ideal tool for assessment and characterization of various types of carbon-based materials. Due to its special optical properties (CrN) coated stainless steel substrates. NCD films have been investigated by laser micro-Raman spectroscopy. The fingerprint of diamond based materials is in the spectral region of $1000\text{-}1600\text{ cm}^{-1}$ in the first order of Raman scattering spectrum. By using of Gaussian peak fitting, characteristic peaks in the micro-Raman spectrum of NCD films including diamond peak (D), NCD features, a vibrational density of states (VDOS) in the ultra-nanocrystalline diamond (UNCD) clusters, graphitic (G) band and disordered (D) band can be assigned. These peaks and bands can be broadened, shifted in the spectral region or may be eliminated from the spectra due to NCD films grain sizes, synthesis conditions and other surface effects on the crystals. The increasing grain sizes to about 100 nm and faceted grains as the most important parameters can promote the diamond Raman signal, eliminate the VDOS, UNCD and even NCD features in the Raman spectrum.

KEYWORDS: FESEM, HFCVD, micro-Raman, NCD film, CrN coated steel.

I. INTRODUCTION

Laser micro-Raman spectroscopy is an ideal tool for assessment and characterization of various types of carbon-based materials [1], such as graphene, carbon nanotube [2], nanocrystalline diamond (NCD with the grain sizes less than 100 nm) and ultra-nanocrystalline diamond (UNCD with grain sizes less than 10 nm) powders [3][4], NCD films [5], microcrystalline diamond films,

single crystal diamond [6], single crystal graphite, polycrystalline graphite, and diamond-like carbon [7]. Indeed, this kind of spectroscopy is sensitive, nondestructive, fast and useful measurement tool based on laser-matter interaction [8]. However, some parameters such as phase purity, the crystalline quality of chemical vapor deposition (CVD) diamond films has been almost characterized by Raman spectroscopy [8].

The hot filament chemical vapor deposition (HFCVD) or hot wire chemical vapor deposition (HWCVD) is one of the best coating systems for thin film diamond synthesis in the world which uses a high temperature filament in the vacuum chamber. More detail about this system can be found in many publications and in a short description it has a gas feeding part, vacuum chamber, power supply, filament or wire arrangement, substrate holder, substrate heater, cooling system, vacuum pump and vacuum gauge, thermocouples, touch screen HMI/PLC and many other parts.

Nanocrystalline diamond (NCD) thin films were prepared by CVD as a high-tech coating inherits some properties from bulk diamond [3][9]. NCD films can be used in many applications such as optics, electronics [10] and photonics due to special physical [11], optical [12], and electronic properties [13]. The most important applications of NCD films include biomedical applications [14][15], microwave and IR windows, nitrogen-vacancy single photon sources [16][17], coherent anti-Stokes Raman scattering [18], color centers in

nanodiamonds [19], UV sensors, and many other applications [20][21][22]. However, NCD thin films as a most important diamond based material in many applications need a fast and easy characterization method such as laser micro-Raman back-scattering evaluation [23][24]. However, there are many different aspects in the micro-Raman spectra of the single crystal diamond and nanocrystalline diamond films [25]. NCD films can be synthesized by means of CVD method on various types of substrates [26][27]. In this paper, some practical details in the laser Raman spectra of CVD NCD thin films has been shown.

II. EXPERIMENTAL PROCEDURE

In the experimental process, NCD thin films have been synthesized on stainless steel and chromium nitride (CrN) coated stainless steel substrates. The substrates were cut into specimens around 10 mm×10 mm in size. Then, they ultrasonically cleaned in the acetone bath and dried. In order to perform diamond coating, the samples have been polished to an acceptable surface finish. NCD films have been growth by means of our HFCVD system as shown in Fig. 1.



Fig. 1. The HFCVD system in the real experiment condition for synthesis of NCD film.

The chamber was evacuated by means of a vacuum pump. The gas mixture has fed to the chamber by means of digital mass flow controller (MFC, Alicat company) consisting of 6 sccm CH₄ and 150 sccm H₂ gas. The substrate temperature has been controlled by K type thermocouple located to beneath of the substrates. After the synthesis of nanocrystalline diamond thin films, the

morphology, uniformity and grain size characterization have been carried out by means of field emission scanning electron microscope (FESEM), Mira3 Tescan. After that, NCD films have been investigated by laser micro-Raman spectroscopy. The Raman spectra were recorded by Almega Thermo Nicolet Dispersive Raman spectrometer, using Nd:YLF laser at its second harmonic generation at 532 nm. The Raman spectral fingerprint of diamond based material is almost in the spectral region of 1000-1600 cm⁻¹ in the first order of Raman scattering spectra. Accordingly, we have concentrated and analyzed the recorded micro-Raman modes in the mentioned spectral region using a back-scattering micro-Raman spectroscopy setup. It is assigned to crystalline diamond peak with a 4 cm⁻¹ as the resolution for the spectrometer and accuracy in reading the Raman spectra.

III. RESULTS AND DISCUSSION

Figure 2 Shows the FESEM of NCD thin film on the stainless steel substrate. It is completely continuous and almost uniform on the surface.

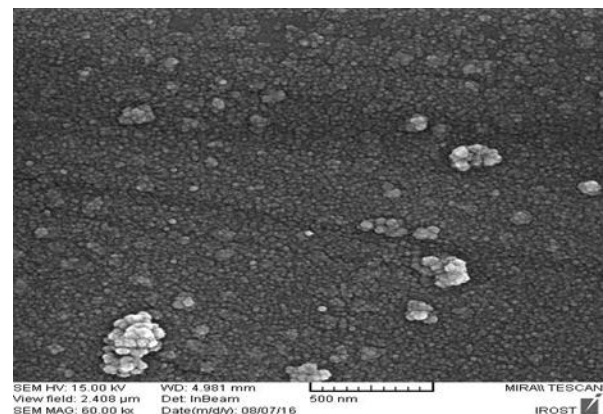


Fig. 2. The FESEM shows NCD thin film as a continuous, uniform and nanometer grain sizes film, sample 1.

However, there are a few aggregations of nanodiamond particles on the film. The aggregations have been shown in 200 nm scale bar of FESEM image in Fig. 3.

The grain sizes have been calculated by means of two analytical software that is common for

SEM image analysis including Measurement and ImageJ. In addition, the software can be employed in manual and automatic modes. In both of them we should calibrate the image by means of FESEM/SEM scale bar on the recorded images and then manually or automatically measure the diameter of particles as line distance. The grain sizes of nanodiamond crystals are calculated in the range of 10 to 35 nm and ballast like.

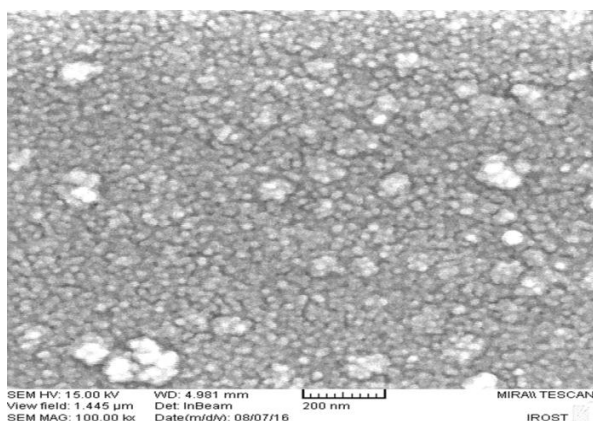


Fig. 3. The FESEM of NCD thin film from 10 to 35 nm grain sizes and ballast like, sample 1.

The other sample with larger grains is shown in Fig. 4. The grain sizes of nanodiamond crystals in this specimen are from 30 to 110 nm. The film is continuous and almost uniform.

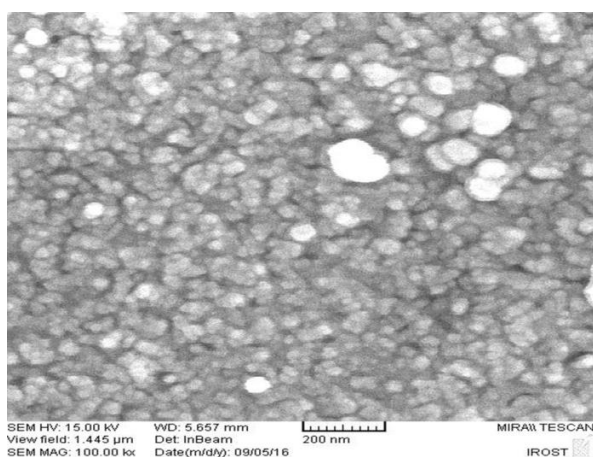


Fig. 4. The FESEM of NCD thin film with grain sizes from 30 to 110 nm, sample 2.

These two NCD films are compared in Fig. 5 as a 3D view. It can be inferred that grain sizes of sample 2 are larger in compare with sample

1. The grain sizes in both samples have a uniform distribution in the nanoscale region.

Also, Fig. 6 indicates the comparison between sample 1 and 2 by plot profile. This analysis has been done for a straight line in the image processing condition of these samples. This plot profile from the left to right side can easily show larger grain sizes for the second specimen.

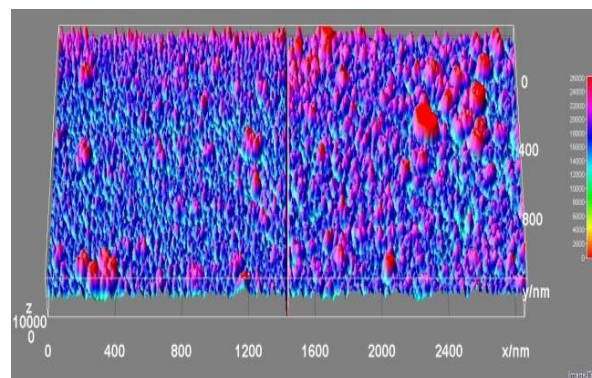


Fig. 5. The 3D view for FESEM images of sample 1 and 2. Two NCD thin films have been inserted to one side-by-side image.

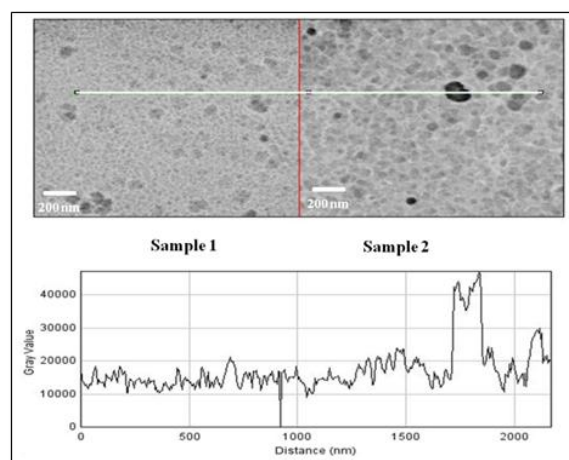


Fig. 6. The plot profile of two NCD thin films under side-by-side FESEM pictures for a straight line show the distance against the gray value in the case of samples 1 and 2.

The surface chemical bonding investigation is one of the most important issues in the field of carbon nanostructure materials. FTIR and UV-Vis analysis data have been discussed in detail for detonation nanodiamond in our previously reported article [28].

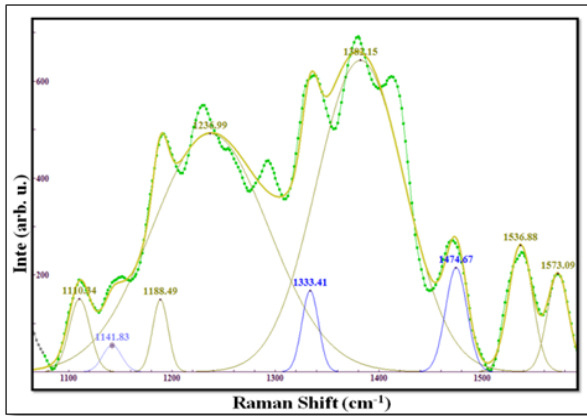


Fig. 7. Micro-Raman spectrum of the NCD film sample 1. The green dotted curve is the original Raman spectrum and it can be deconvoluted to other Gaussian peaks by means of peak fitting method.

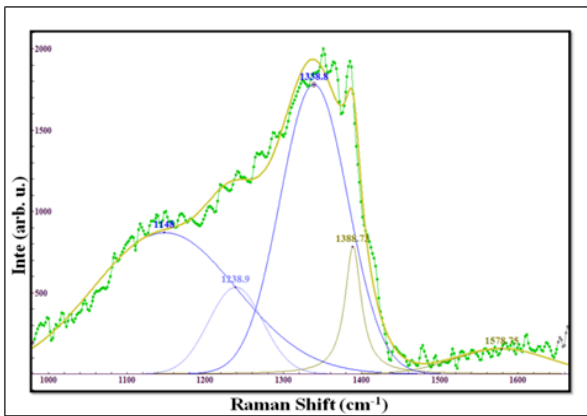


Fig. 8. Micro-Raman spectrum of the NCD film sample 1. The green dotted curve is the original Raman spectrum and it can be deconvoluted to other Gaussian peaks by means of peak fitting method.

In the present manuscript we have focused on the micro-Raman analysis as the most important tools of nanodiamond film characterization. For this purposes, we have investigated the samples 1 and 2 by laser micro-Raman spectroscopy.

On the other hand, XRD analysis of the nanodiamond crystals are essential regarding sp² bonding graphitic ones. However, there is a difference between the XRD of nanodiamond particles and nanodiamond films because of their substrates in thin films. The normal XRD pattern of nanodiamond thin film in thicknesses smaller than 100 nm is not a proper analysis tool and Grazing Incidence XRD analysis is required. Therefore, we have got GIXRD for nanodiamond thin film. The

XRD analysis for nanodiamond particles have been carried out and reported in our previous paper [28].

The comparison made between them can give us some information about the type, grain size and surface structure of the films. In other words, one can be inferred many parameters such as intensity, FWHM, peaks, centers and other useful physical parameters from laser Raman spectrum. The green dotted curve in Fig. 7 is the original Raman spectrum of the NCD film and it can be deconvoluted to other Gaussian peaks by means of peak fitting method with Gaussian sum functions after applying a linear background subtraction. The curve fitting of nanodiamond films are produced from several Gaussian distribution line shapes. It can give us the exact view about each Raman spectrum. It is well known that the Raman active fingerprint mode of single crystal diamond is about 1332 cm⁻¹. For single-crystalline diamond, Raman lines are due to phonon excitation in the center of the Brillouin zone, with $q = 0$ selection rule. This Raman active mode is assigned as D peak or Diamond peak. Two new features around 1150 cm⁻¹ and 1480 cm⁻¹ as NCD features or TPA (trans-polyacetylene) as a major sign of NCD film have been detectable in the Raman spectra [23], [29]. Some asymmetry and broadening due to size and shape of crystals in the layer are common. The Raman spectrum of NCD film is described by selection rule. The relaxation of the selection rule ($q=0$) is the source of new peak appearance in the Raman spectrum of NCD films. It is due to uncertainty in the value of the wave vector that permits the activation of phonons in the Raman spectrum. Also, a broad band is found at around 1200 to 1280 cm⁻¹ that is interpreted as a broadened vibrational density of states (VDOS) of small diamond clusters (disordered diamond mode) or it is vibration modes related to C-C and C-H chain in NCD or Ultra-NCD Raman spectrum [30]. The VDOS is dominated by contributions from the L, 1260 cm⁻¹ and X points, 1175 cm⁻¹, giving rise to the observed broad feature in the region of around 1200 cm⁻¹. In addition, the selection rule corresponds to one sharp Raman line at

about 1575 cm^{-1} that is G or graphitic band due to sp^2 carbon bonding states. In polycrystalline graphite, sharp Raman line at 1575 cm^{-1} is broadened and it can also split into two shorter bands in the range of 1530 to 1580 cm^{-1} for c-sp^2 carbon bonding state as graphitic clusters. In addition, in graphitic clusters, an additional peak appears at around 1350 cm^{-1} as D band or disordered band in the sp^2 bonding states. This feature appears in many other carbon-based materials due to sp^2 graphitic bonding states. The intensity of this broad peak scales inversely and proportional with the crystallite size of graphitic carbon clusters. The source of this D band in polycrystalline graphite clusters is breakdown of the $q=0$ selection rule. However, NCD grains in the film as a carbon base material have two essential parts including core structure and surface structure for any grain. The diamond crystals grain in the nanoscale has a high surface to volume ratio. In addition, the grain boundaries as 2D defects in the nanometer size of crystallites have a major role in the back-scattering Raman signals. The core structure of crystal grains is carbon- sp^3 with diamond bonding state while the surface of grains and the grain boundaries have various types of carbons including graphitic sp^2 carbon and clusters in ring and chains shape, sp^1 carbon bonding states, sp^3 disordered carbon bonding states and other mixing carbons. Therefore, the Raman spectrum can give us more information from the surface of grains and grain boundaries in the nanometer-size crystals than the core of crystals. Also, the larger grains have bigger cores and less number of grain boundaries and they can cause increasing the Raman signal from the diamond cores and vice versa for the smaller grains. It means that the most important role in the Raman signals in the case of very small diamond crystals is related to the grains surface and grain boundaries between the clusters. In conclusion, Nanocrystalline diamond can show several peaks and bands. The first one is diamond peak (D peak $\sim 1332\text{ cm}^{-1}$) as a low or high-intensity signals depend on the crystal sizes, the thickness of films, the crystal quality of the core structures, defects in the grains and etc. The second signs of NCD

films are two new features around 1120 - 1180 cm^{-1} and 1480 cm^{-1} as TPA (trans-poly-acetylene) in NCD films. These are the most important sign of the NCD crystals in the Raman spectra and depend on crystal sizes, the wavelength of the Raman laser, NCD film growth condition and etc. The third sign of NCD or UNCD in the films is the shoulder around 1200 to 1280 cm^{-1} disordered diamond or C-C and C-H chain in NCD or Ultra-NCD Raman spectrum. The forth sign of NCD films is graphitic band at around 1530 - 1580 cm^{-1} due to graphitic clusters on the surface and grain boundaries. The other Raman peaks and bands such as disordered graphitic band (D band at $\sim 1350\text{ cm}^{-1}$) can appear on the films, not always. The peak around 1380 - 1390 cm^{-1} is likely due to CH_3 (methyl) as the most species for the diamond growth process.

Table. 1. Assignment of NCD film Raman spectra

Position (cm^{-1})	Raman Mode type	Ref.
1100, 1150, 1190	NCD & UNCD	[3] [20][26] [29] [31] [32] [33] [34]
1200-1250, 1228	VDOS in NCD & UNCD	[6][23] [15][34]
1332	SCD & MCD	[6][30] etc.
(1460-1480)+(1140 to 1160)	to NCD (TPA)	[3] [6] [15] [23] [29][33] [23], [29] [34]
1350	Disordered (sp^2)	[31][33][34]
1500-1550	MCG (G) (sp^2)	[3] [33][34]
1530-1580	G and SCG	[31][15] [33]

Therefore, it is clear that the diamond, NCD, small disordered diamond or UNCD, graphitic clusters and CH_3 species are the presence in samples 1 and 2, but they have differences at the grain sizes and surface structures. The high-intensity diamond peak at sample 2 indicates the larger grain sizes and crystals in this sample. While the high intensities for CH_3 and UNCD peak at sample 1 shows that the diamond crystallites in this sample are so small and non-growth crystals. In both samples, the graphitic clusters have been produced on the surface, but these structures in sample 1 are higher than sample 2 because of the higher surface to volume ratio. Table. 1 can help us for the assignment of NCD film Raman spectra.

After that, the same experiments have been done on the CrN coated stainless steel substrates. The FESEM of NCD thin films on the CrN coated stainless steel are shown as samples 3 and 4 in the Figs. 9 and 10, respectively. Then the micro-Raman analyses of them are shown in the Figs. 11 and 12, respectively.

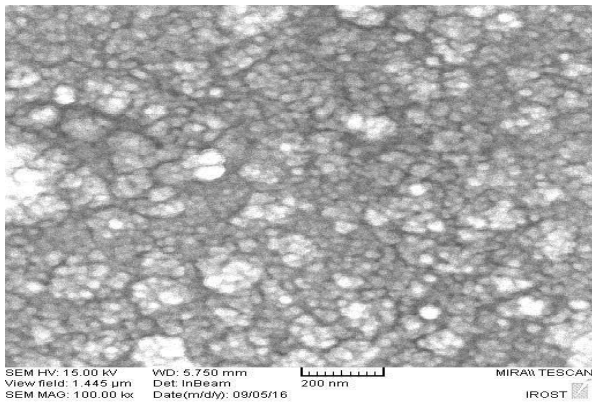


Fig. 9. The FESEM of NCD thin film from 15 to 50 nm grain sizes and ballast like on the CrN coated stainless steel, sample 3.

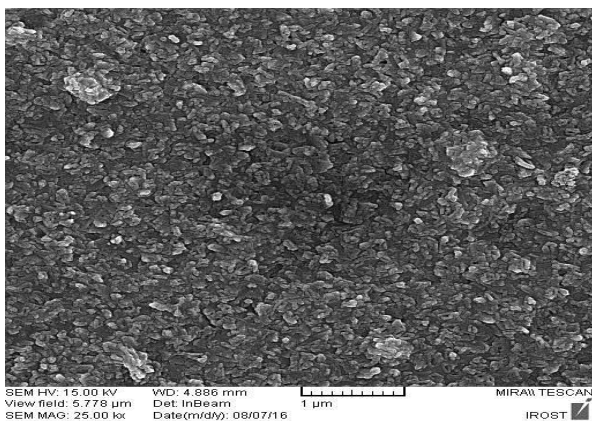


Fig. 10. The FESEM of NCD thin film from 50 to 150 nm grain sizes on the CrN coated stainless steel, sample 4.

Raman signals and they can promote the diamond sharp peak. However, when the diamond grain sizes are less than 100 nm, the NCD, UNCD, graphitic and non-diamond Raman signals will exist definitely on the Raman spectrum. Therefore, it is obvious that the essential features of micro-Raman for NCD films are almost similar for all 4 samples, but their differences are due to several parameters such as $c\text{-sp}^2$ bonding states on the surfaces, the size of crystals that may

affect the surface structures, synthesis conditions for NCD films, the shape of crystallites, etc.

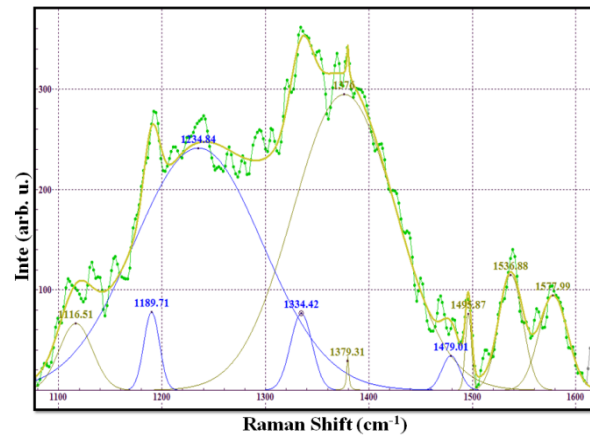


Fig. 11. Micro-Raman spectrum of the NCD film sample 3. The fitting has shown two shoulders at 1149 cm^{-1} and 1471 cm^{-1} as the sign of NCD film.

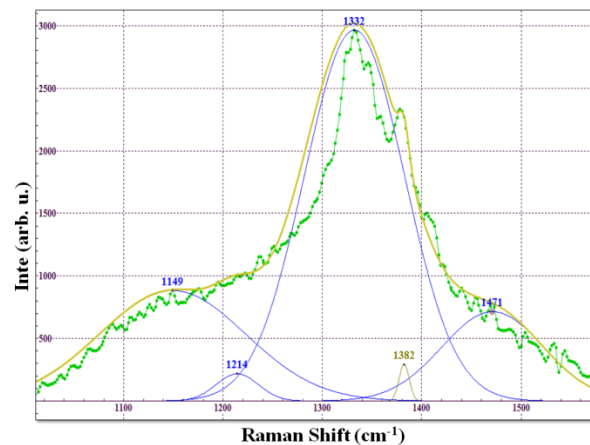


Fig. 12. Micro-Raman spectrum of the NCD film sample 4. The fitting has shown two shoulders at 1149 cm^{-1} and 1471 cm^{-1} as the sign of NCD film.

Similar to the previous micro-Raman spectra, the green dotted curves are the original Raman spectra. By using peak fitting and deconvolution technique, the other peaks can be appeared. The micro-Raman shows the nanocrystalline diamond structure on the CrN coated steel substrates in sample 3. It has 1334 as diamond peak, 1189 and 1479 cm^{-1} due to the main sign of NCD film, 1234 cm^{-1} due to UNCD, 1536 and 1577 due to graphitic sign. The FESEM confirms easily the small grain sizes of this NCD films. While for sample 4, the grain sizes are larger than sample 3. The large crystals have been produced the sharp Raman peak of diamond at 1332 cm^{-1} and

NCD features at 1149 and 1471 cm^{-1} . Therefore, it is obvious that the increasing in the size of diamond nanocrystals to submicron size can eliminate the graphitic and UNCD

IV. CONCLUSION

Nanocrystalline diamond films can show several peaks and bands in the laser micro-Raman spectrum and there are various kinds of bands including diamond peak, NCD peaks or shoulders, D band, G band, and vibrational density of states (VDOS) or disordered small diamond band. The micro-Raman shows the ultra-nanocrystalline diamond structure on samples 1 and 3 while samples 2 and 4 indicate the better NCD Raman signals than two others. Increasing the numbers of fitted peaks in the spectra means that the samples 1 and 3 have small sizes of crystallites, a large number of grain boundaries, higher surface in contact with the grains, un-faceted grains or ballast-like grains and some mixed carbon phases on the surface of crystallites. The low number of peaks in the samples 2 and 4 are due to larger grain sizes, the lower surface to volume ratio in crystallites; lower the surface effects and the better-faceted crystals in NCD films. Also, the CrN coated stainless steel substrate show the better crystallinity of CVD NCD film with larger grain sizes and faceted grains. However, Raman scattering is a surface effect and it cannot penetrate to the deeper layer of films. Therefore, in very small diamond crystals, the most important role in the Raman signals is related to the grains surface and grain boundaries between the clusters. Also, the c-sp² bonding states as non-diamond carbons have large scattering Raman cross sections. In addition, the diamond crystals are transparent for laser Raman interaction while the non-diamond c-sp² bonding states and surface graphitic carbons are absorbencies for laser Raman signals and then they can absorb the photons in the outer layer of films. Therefore, all of these issues are effective on the laser Raman signals and especially can cause to appear some peaks and decrease diamond peaks in Raman spectra. Although, there are significant differences in the Raman spectra in details, but it seems that

the larger grain sizes in NCD films, the higher intensity of the diamond peak in Raman spectrum. Therefore, we can conclude that not only the purity and quality of crystallites can affect on the Raman spectrum of NCD films, but also many other parameters such as grain sizes, the shapes of crystallites, growth process conditions and etc. can affect the micro-Raman spectra. However, there is no doubt that the Raman spectroscopy can be regarded as an ideal tool for assessment and characterization of NCD films.

In conclusion, we can mention the following item as the novelty of the present article:

- a) Raman scattering spectroscopy of NCD films on the steel and CrN substrates have been carried out by means of our patented HFCVD system.
- b) We have gathered and reported all micro-Raman signals of NCD film in the manuscript and have clarified their differences.
- c) Investigation of the nanocrystal and film grain size effect on the micro Raman spectra.
- d) The results of this research indicates the increasing grain sizes to about 100 nm and the faceted grains can promote the diamond Raman signal, eliminating the VDOS, UNCD and even NCD features in the Raman spectra.

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