OBSERVATION OF ENHANCED RAMAN SPECTRA ON THIN LAYERS OF NANOCRYSTALLINE DIAMOND

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1. Introduction

The very effective method of surface enhanced Raman spectroscopy (SERS) has been developing through the late 70's until now. The technique has been continuously used not only for the background suppression in Raman spectra [1] but also for enhancing those Raman peaks which can be measured but are of low intensity [2]. SERS needs an active substrate to work properly and analysis on active substrates requires a liquid sample. Therefore the technique is used rather in chemical analysis than in solid state analysis. The physical principles of enhanced Raman scattering are based on localized plasmon resonances. Proper conditions for plasmon excitation are easily met in noble metals like silver or gold in the visible region [3]. As a consequence, substrates based on nanostructured silver or gold surface can be used as active substrates.

On the other hand, thin diamond layers are considered to be prospective in microelectronics and nanoelectronics. Detection of a relatively thick layer (a few micrometers) of artificially made diamond by Raman spectroscopy is simple and yields significant Raman spectra. However, by decreasing the layer thickness there is a continuous loss of the diamond peak intensity [4]. Problems with enhancing the Raman spectra in solid state can be avoided by applying an active layer directly on top of the investigated layer. Since nanocrystalline diamond exhibits natural surface roughness, localized plasmon resonance can occur.

In this contribution we measured Raman spectra of a nanocrystalline diamond layer grown by hot filament chemical vapour deposition and compared them with the spectra taken from the samples decorated with silver. Also we discuss some aspects of the enhancement of the diamond peak, e.g., the impinging beam intensity loss as well as scattered light intensity loss during the propagation through the silver layer and diamond band intensity dependence on the thickness of the silver layer.

2. Experimental details

Diamond layers were grown on a monocrystalline silicon (100) substrate by hot filament chemical vapour deposition. Before the growth, the silicon substrate was sonicated in isopropylalcohol and consecutively in deionised water. The substrate was nucleated by a suspension of water and diamond powder. During the growth, hydrogen and methane were employed as precursors in 300:1.5 ratio given in sccm.

Raman spectra were acquired using a laser beam focused on the surface of the diamond layer. For spectra acquisition dispersive Jobin Yvon Labram 300 apparatus equipped with a 633 nm excitation line and grating monochromator with 1800 grooves/mm

was used. A laser power of 17 mW and a 100× objective were employed. The charge was collected during 3s accumulation time in 100 acquisitions. The confocal hole and slit were maintained at their maximum apertures.

Thin silver films of various thicknesses were evaporated on diamond layers in vacuum conditions. The thickness of evaporated layer was measured directly during the evaporation by quartz crystal. Silver was of analytical grade of purity (99.99%) and purchased from Sigma. To evaluate the changes in the measured Raman spectra, consecutive measurements were performed in the same conditions as in the previous case. In both cases (undecorated and silver covered diamond layers), the morphology of prepared samples was investigated by scanning electron microscope Jeol JSM 7500 F.

3. Results and discussion

In Fig. 1 a comparison of samples by scanning electron microscopy is given. Figures show specimens with NCD layer and NCD decorated with silver coatings. In each case the thickness of NCD layer was ~100 nm (the thickness was measured on cross sections by SEM). Figure 1a exhibits fully developed NCD grains varying from few tens of nm to ~150 nm in diameter. In the case of decorated layers, silver was incorporated non-uniformly in the valleys and the hills of nanocrystalline diamond and the surface roughness of NCD layer was rather smoothed than transferred directly on the silver / air interface. As seen in Figs. 1b, 1c, 1d grain boundaries of NCD are successively hiding under evaporated silver layer as the thickness of the layer increases.
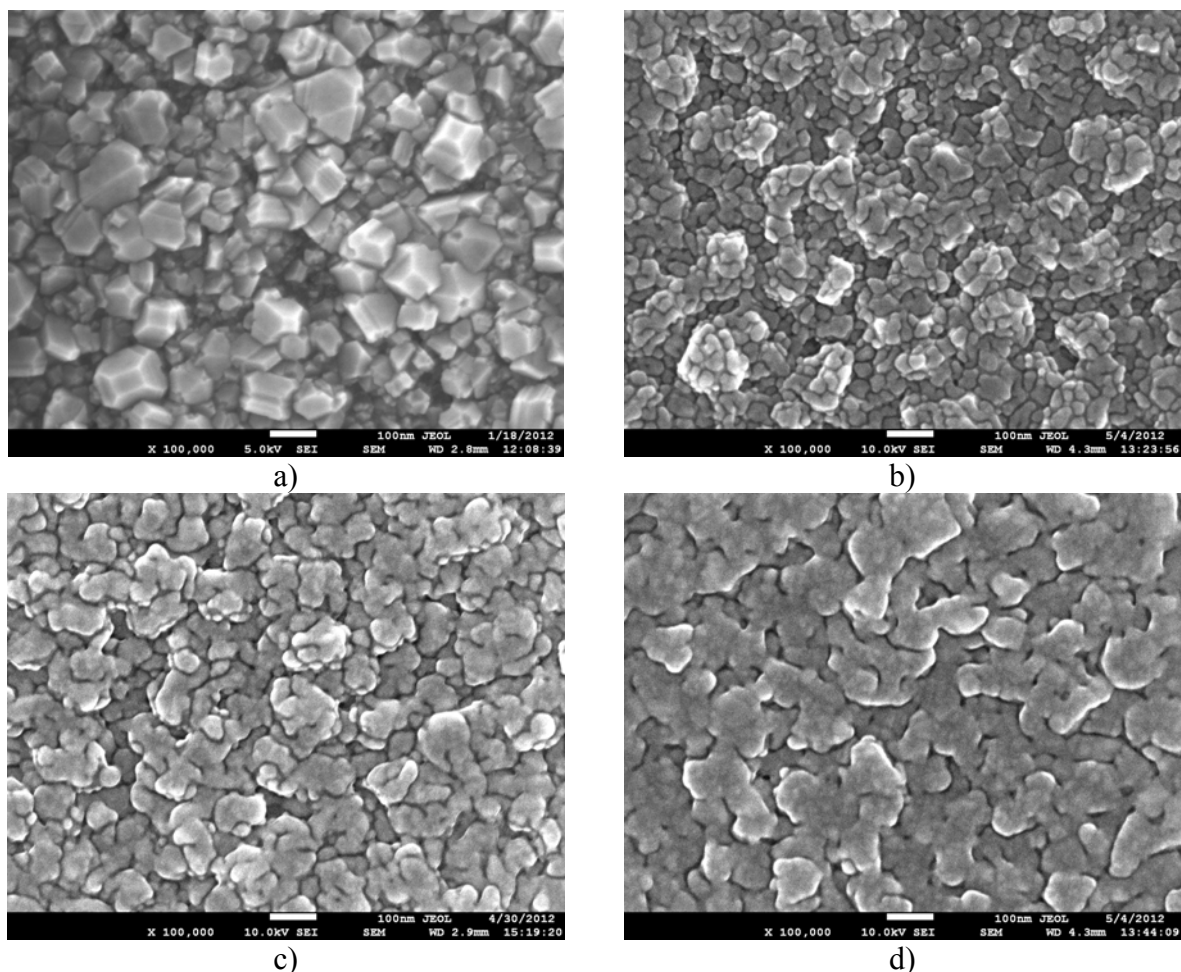

Fig. 1: *SEM images of a) grown NCD layer, b) NCD with 8 nm silver coating, c) NCD with 11 nm silver coating, d) NCD with 14 nm silver coating*

Raman spectroscopy is very sensitive to morphology differences. Nanocrystalline diamond has a slightly different structure to bulk diamond due to the increased surface area . The effect on the Raman spectrum can be dramatic because of phonon confinement [5]. In Fig. 2a the Raman spectrum of the undecorated NCD layer is seen. The spectrum consists of diamond peak (T_{2g}) at $1332\,cm^{-1}$, D band (A'_1) represents sp^3 bonds (tetrahedral configurations) or it may represent disorder in hybridized sp^2 bonds. G band ($\approx 1600\ cm^{-1}$) represents sp^2 bonds (planar configurations) and the maximum at $1543\ cm^{-1}$ bode some sp^3 ordering [6]. The D and G bands form the core of carbon Raman spectrum [6,7]. Except those bands, various defect features can join the spectrum [8]. The amorphous carbon modes are reserved for imperfections and can be used to evaluate the quality of the diamond layer. The lower intensity of such modes and higher intensity of the diamond peak are indicative for an appropriate apparatus setup. Concerning the relative intensities of the diamond and carbon peaks, one may conclude that carbon content is smaller than that of the diamond phase.

After evaporation of silver on the prepared NCD layers, Raman spectra were collected once more under the same conditions (Fig. 2b). A large increase in Raman signal is obvious from the measured spectra. Tab. 1 clearly shows the enhancement dependence on the thickness of the silver layer as well as maximum enhancement for the 11 nm coating.
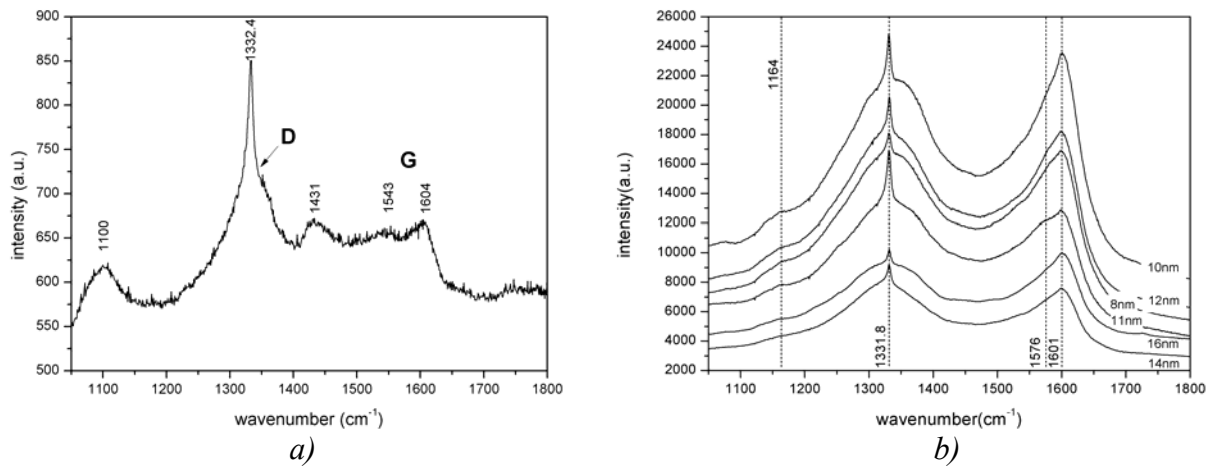

Fig. 2: *Raman spectra collected from a) NCD thin layer surface, integration time 3 s, 100 acquisitions, 100× objective, b) silver decorated NCD layers, integration time 3 s, 100 acquisitions, 100× objective. The right hand side designations stand for the thickness of the silver layer. Spectra were slightly shifted for clarity.*

When evaluating the enhancement factor one has to take into account the intensity loss during the propagation of the impinging beam through the silver layer. Since the absorption is governed by the Lambert-Beer law and, additionally due to reflectance of the interfaces, the impinging intensity (at 633 nm) at any diamond grain is small when compared with an uncoated diamond layer.

Tab.1: *Dependence of the enhancement factor on the thickness of the silver layer*

Silver layer thickness (nm)	8	10	**11**	12	14	16
Enhancement factor	10	24	**26**	14	8	7

The same correction must be added for spreading the secondary signal at 1332 cm^{-1} (691 nm) in opposite directions. Therefore the enhancement of the Raman cross section is much greater than the observed enhancement.

Additionally, considering the impinging beam spot of ~5 μm in diameter, the surface roughness cannot be neglected because of the dimensions of NCD grains and silver flakes. The grains are oriented randomly with respect to the surface plane [9] and the effect of orientation should be incorporated to get a proper reflectivity of the interfaces. The suggested approach should be revised by a more precise research since it is occurring along with (or is completely overbuilt by) localized plasmon resonance effects.

4. Conclusions

The Raman signal arising from a thin NCD layer can be enhanced by a factor of 26 by simple evaporation of silver. The properties of silver coating may be exploited when investigating ultra thin diamond layers. Raman spectra acquired by the classical method on such layers are difficult to obtain when the thickness decreases under the critical level. Furthermore, amorphous carbon is more sensitive to enhancing and can be used as a marker for the growth process adjustment. A drop in the enhancement with increasing the thickness of silver coating suggested by our approach is possible but additional studies are needed for the enhancement process.

References
[1] J. Zhao, R. Tian, J.Zhi: *Thin Solid Films*, **516**, 4047, (2008).
[2] S.T.Chen, et al.: *Diamond and Related materials*, **24**, 161 (2012).
[3] E. C. Le Ru, P. Etchegoin: Principles of surface enhanced Raman spectroscopy and related plasmonic effects, Elsevier, London, United Kingdom (2008).
[4] W. Kulisch, et al.: *Diamond and Related materials*, **20**, 1076 (2011).
[5] M. Roy, et al.: *Diamond and Related materials*, **11**, 1858 (2002).
[6] A.C. Ferrari, J. Robertson: *Philosophical Transactions of The Royal Society London A*, **362**, 2477 (2004).
[7] S. Prawer, et al.: *Chemical Physics Letters*, **332**, 93 (2000).
[8] A. Hu, W.W. Duley: *Chemical Physics Letters*, **450**, 375 (2008).
[9] M. Kadlečíková, et al.: *Microelectronics Journal*, **34**, 1075 (2003).