Comparative photoemission study between nanocrystalline diamond films and nanodiamond layers

Velardi L[1], Massaro A[1], Senesi G S[1], Nitti M A[2], De Pascali G[2], Melisi D[2], Valentini M[2], Valentini A[2] and Cicala G[1]

[1]*CNR-IMIP Bari, Via Amendola 122/D, Bari, Italia, email: luciano.velardi@le.infn.it*
[2]*Dipartimento di Fisica, Università degli studi di Bari, Via Amendola 173, Bari, Italia*

Abstract

Diamond films exhibit interesting properties, such as a wide bandgap (5.5 eV) and very low electron affinity which favours the electron photoemission. Diamond based cold photocathode is well known and demonstrated, due also to its chemical stability and mechanical robustness.
In this work, a comparative study on photoemission of nanocrystalline diamond (NCD) film and nanodiamond (ND) layers obtained by microwave plasma enhanced chemical vapour deposition and pulsed spray technique, respectively, is presented and discussed evidencing advantages and drawbacks. The first technique permits to obtain thin NCD films at high deposition temperature (650-900 °C) with excellent homogeneity and adhesion; whereas the second one allows to deposit thin ND layer at a temperature of 120 °C with poor adhesion and low uniformity. Both NCD film and ND layers have been characterized by Raman spectroscopy, atomic force microscopy (AFM) and photoemission measurements.

Introduction

Diamond represents a material with superior properties such as chemical and mechanical stability under harsh environment conditions, heat dissipation properties and radiation hardness. Its wide band gap (5.5 eV) corresponds to the energy of ultraviolet photons and makes diamond films very attractive as sensors in UV detection[1]. For these reasons, poly- and nano-crystalline diamond (PCD and NCD) films are suitable for the production of efficient UV photocathodes [2-5] with stability higher than that of conventional materials such as CsI[6].

One of the most important parameters that governs the efficiency of a photocathode is the photoelectron escape probability which is related to the surface work function and electron affinity. In diamond, negative electron affinity (NEA) can be achieved via surface plasma hydrogenation process, so that the vacuum level is lowered below the conduction-band minimum, thus promoting the electrons emitted from the surface [7].
In this work we present a study on the quantum efficiency (QE) of photocathodes based on NCD diamond film grown by microwave plasma enhanced chemical vapor deposition (MWPECVD)[8] and nanodiamond

(ND) layers deposited at low temperature by pulsed spray technique[9]. All the samples were characterized by Raman spectroscopy and atomic force microscopy (AFM) analysis.

Materials and methods

NCD deposition. The deposition of NCD film (about 3 μm thick) was carried out in a home-made cylindrical stainless steel MWPECVD reactor, Astex-type. The NCD film was deposited on a p-doped silicon substrate 2 cm × 2 cm in size, pretreated ultrasonically for 1 h in an ethanol suspension of diamond powder (40–60 μm). The gas mixture used was $CH_4/Ar/H_2$ (1/89/10 %) and during the deposition, the working pressure, the microwave power and the total flow rate were held constant at 140 mbar, 950 W and 100 sccm, respectively. The nucleation time, the thickness and the deposition temperature were monitored in situ and in real time during the process by the pyrometric interferometry (PI) technique using an infrared and non-contact pyrometer (Williamson Pro9240).

ND layers production. ND layers were produced by means of the pulsed spray technique. A natural nanodiamond powder (grain size of 250 nm) was used: ElementSix (ES), Figure 1.

Figure 1. Photo of the 250 nm ElementSix nanodiamond powder.

An amount of 30 mg of powder was dispersed in 30 ml of the apolar solvent 1,2-dichloroethane (DCE) by sonication for 30 min by a Bandelin Sonoplus HD2070 system. Immediately after, the dispersion was sprayed by an ultrasonic atomizer on p-doped Si substrates (previously cleaned for 5 min in isopropyl alcohol by ultrasound bath). The time duration of the spray pulse (t_s) was set at 15 ms and the time between two pulses, evaporation time (t_e) was 2 s. During the deposition the substrates were heated at 120 °C, in order to evaporate easily the DCE solvent.

RAMAN analysis. The chemical-structural features of NCD film and ND layers were determined by Raman spectra. The measurements were carried out at room temperature by means of a Raman confocal micro spectrometry apparatus (Labram from Jobin–Yvon Horiba) in the backscattering configuration, using an Ar-ion laser (488 nm).

AFM analysis. The morphological characterization was performed by using a NTEGRA Aura scanning probe microscope (NT-MDT, Zelenograd, Moscow, Russia). AFM images were obtained in ambient conditions and were acquired in non-contact mode.

QE measurements. Photoemission measurements have been carried out in the Vacuum Ultra Violet (VUV) spectral range from 150 to 210 nm. The measurements were acquired in the reflective mode, under vacuum (10^{-5} mbar) and at room temperature (20 ^{0}C). The samples were irradiated with a 30 W deuterium lamp (Mc Pherson TM) coupled to a monochromator for the wavelength selection. The values of photocurrent were assessed through the measurement of the current passing in a grid of wires mounted in front of the sample. The samples were mounted in a multi-wire proportional chamber, not operating in electron multiplication mode.

The absolute QE (in percentage) was evaluated by means of a NIST calibrated

standard Si photodiode, using the following expression:

$$QE(\%) = QE(\%)_{NIST} \frac{I_{sample} - I_{dark,sample}}{I_{NIST} - I_{dark,NIST}} x100$$

where I_{sample} and I_{NIST} are the measured photocurrents of the samples and the NIST, respectively, while $I_{dark,sample}$ and $I_{dark,NIST}$ are the corresponding dark currents.

Results and Discussion

Figure 2 shows the Raman spectra of the ND layer and NCD film. ND layer exhibits the sharp diamond (sp^3 bonded carbon) peak at 1332 cm^{-1} and the weak graphite (sp^2 bonded carbon) band centered at 1574 cm^{-1}.

On the basis of these results the ND layer is classified as rich-diamond ND powder of ElementSix.

The spectrum of the NCD film shows typical features of nanocrystalline type diamond with a less intense diamond peak at 1332 cm^{-1} and different contributions of non-diamond phase, D and G graphite bands (at 1360 and 1550 cm^{-1}, respectively) and transpolyacetylene (t-PA) bands at 1140 and 1480 cm^{-1}.

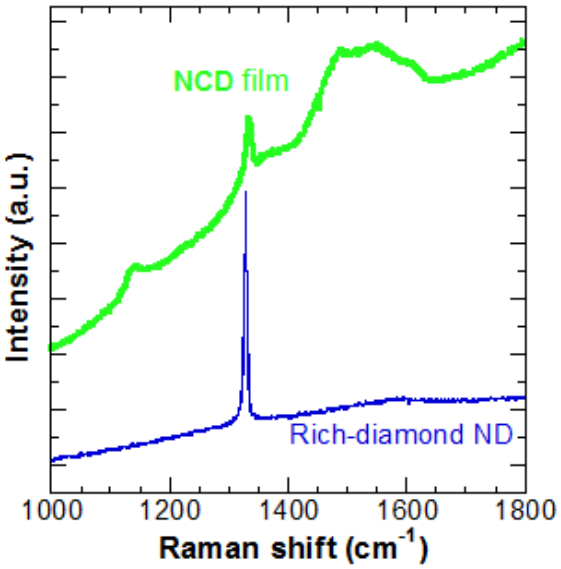

Figure 2. Raman spectra of NCD film and rich-diamond ND layer.

Figure 3 reports the AFM images (10 µm x 10 µm). The morphology of the NCD film (Figure 3a) shows single submicrometric grains with an estimated Root Mean Square roughness (R_{RMS}) of about 60 nm. The image of the ND layer (Figures 3b) shows an irregular morphology of the surfaces (due to the chaotic deposition mechanism of the pulsed spray technique), with corresponding R_{RMS} values of the order of the ND grain size (250-300 nm).

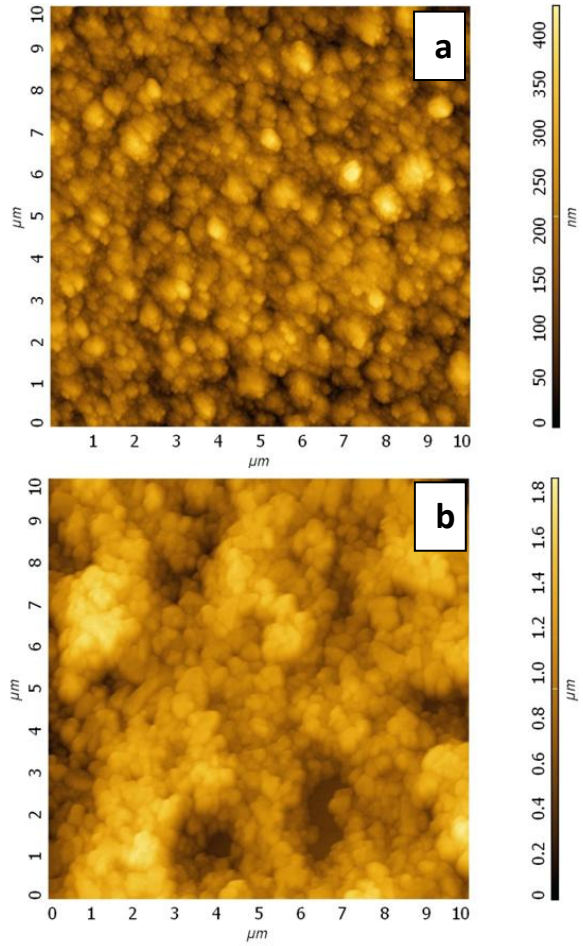

Figure 3. AFM images (10µm x 10 µm) of the samples: (a) NCD film, (b) rich-diamond ND layer.

Figure 4 illustrates the absolute QE trend (%, in logarithmic scale) of the samples, as a function of the wavelength. The absolute QE values estimated at 150 nm, shows a value of 0.6 % for the rich-diamond ND layer and a value of about 3% for NCD film (typical value of PCD/NCD films[3,9]).

These results are of high interest in showing that it is possible to fabricate diamond based

photocathodes in an easy way and at low temperature, thus avoiding the use of the expensive CVD technique.

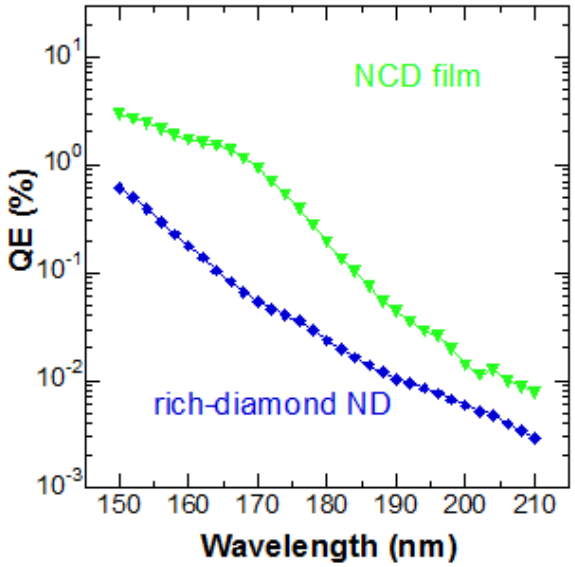

Figure 4. Absolute quantum efficiency (QE, %) of the samples in the UV range from 150 to 210 nm.

Conclusions

The results of this work show how the cheap pulsed spray technique allows to obtain ND layers in an easy way and at low temperature starting from the dispersion of nanodiamonds in DCE solvent, without the use of an expensive MWPECVD reactor.

The QE data show that the ND layer, exhibits a quantum efficiency little low if compared with the NCD film one. However, the disadvantage of photochatodes based on ND layer is its adhesion on the Si substrate, which is not comparable to that obtained with MWPECVD diamond films. This problem can, however, be overcome if the photocathode is packaged or not subjected to mechanical stresses onto its surface.

Acknowledgements

This study was carried out within the framework of the Project PON03PE_00067_6 “APULIA SPACE”, (Italy).

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