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Superior hardness and Young's modulus of low temperature nanocrystalline diamond coatings

G. Cicala [a,*], V. Magaletti [b], G.S. Senesi [a], G. Carbone [c], D. Altamura [d], C. Giannini [d], R. Bartali [e]

[a] CNR-IMIP Bari, Via G. Amendola 122/D, 70126 Bari, Italy
[b] ALTA S.p.A., via Gherardesca 5, 56121 Ospedaletto (Pisa), Italy
[c] DIMeG-Politecnico di Bari Viale Japigia 182, 70126 Bari, Italy
[d] CNR-IC Bari, Via G. Amendola 122/D, 70126 Bari, Italy
[e] Fondazione Bruno Kessler, Via Sommarive 18, 38123 Povo (Trento), Italy

HIGHLIGHTS

- We produce the hardest NCD coating at the lowest deposition temperature.
- We modify the deposition temperature to tailor the grain size and shape of the NCD coatings.
- We assess the mechanical properties (hardness and elastic modulus) of superhard NCD coating on a soft silicon substrate.

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ABSTRACT

Nanocrystalline diamond (NCD) coatings with thickness of about 3 μm were grown on silicon substrates at four deposition temperatures ranging from 653 to 884 °C in $CH_4/H_2/Ar$ microwave plasmas. The morphology, structure, chemical composition and mechanical and surface properties were studied by means of Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), Raman spectroscopy, nano-indentation and Water Contact Angle (WCA) techniques. The different deposition temperatures used enabled to modulate the chemical, structural and mechanical NCD properties, in particular the grain size and the shape. The characterization measurements revealed a relatively smooth surface morphology with a variable grain size, which affected the incorporated hydrogen amount and the sp^2 carbon content, and, as a consequence, the mechanical properties. Specifically, the hydrogen content decreased by increasing the grain size, whereas the sp^2 carbon content increased. The highest values of hardness (121 ± 25 GPa) and elastic modulus (1036 ± 163 GPa) were achieved in NCD film grown at the lowest value of deposition temperature, which favored the formation of elongated nanocrystallites characterized by improved hydrophobic surface properties.

1. Introduction

The outstanding mechanical properties of diamond have generated and are promoting a renewed interest in the production of synthetic poly- and nanocrystalline diamond (NCD) films [1,2] by chemical vapor deposition (CVD). It is generally believed that the fraction of grain boundaries increases as one moves from single-, to micro- or nano- and ultrananno-crystalline diamond [2], resulting in a high hydrogen concentration (10^{22} cm^{-3}) and sp^2 carbon bonding (5%) [3] which deteriorate the relevant elastic and mechanical properties of diamond. The extent of this deterioration can be monitored, and in some cases reduced, by modifying the experimental deposition conditions. To this purpose, the mechanical properties of diamond films and their dependence on the deposition conditions have been studied and reported in the literature by many research groups.

Wiora et al. [4] have identified correlations among grain size (from 9 to 60 nm), chemical composition and mechanical properties of 6 μm thick NCD films grown by hot filament CVD (HFCVD). Both hardness (H) and Young's modulus (E) were found to decrease from 90 to 65 GPa and from 1050 to 700 GPa by decreasing the grain size.

A similar dependence has been reported by Williams et al. [5] in very thin NCD films (140 nm thick) grown by microwave plasma

* Corresponding author. Tel.: +39 0805929518; fax: +39 0805929520.
E-mail address: grazia.cicala@ba.imip.cnr.it (G. Cicala).

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enhanced CVD (MWPECVD) technique from CH_4/H_2 gas mixture as a function of CH_4 concentration and microwave power density. The decrease of Young's modulus (determined by standard bulging tests) values has been correlated to the reduction of grain sizes and increase of hydrogen and sp^2-carbon content at the grain boundaries.

Xiao et al. [6] have investigated NCD films from $CH_4/H_2/Ar$ (1/5/94%) plasmas at different temperatures (from 800 down to 400 °C) and have found that the hardness (measured by nanoindentation) varies from 100 (value close to that of single crystal diamond) to 57 GPa, and the elastic modulus (measured by nanoindentation and laser wave acoustic systems) from 1040–1020 to 440–700 GPa, respectively. Harder NCD coating is produced at higher temperature because less hydrogen (determined by elastic recoil detection) and sp^2 carbon are incorporated into the grain boundaries (with average and constant grain size of 7 nm).

You et al. [7] have studied the effects of the total gas pressure, deposition temperature (from 550 up to 750 °C) and CH_4 concentration on grain size, surface roughness and hardness of 1.2 μm thick NCD films produced from CH_4/H_2 gas mixture by HFCVD. Specifically, the grain size and the hardness increase by increasing the deposition temperature.

In this study, the mechanical properties of NCD coatings grown on Si substrates via MWPECVD from $CH_4/H_2/Ar$ (1/10/89%) gas mixtures were analyzed by using the nanoindentation technique at penetration depth values ≤10% of the film thickness, following the recommended value of the rule-of-thumb [1,8,9]. The study was focused particularly on the mechanical properties of the coatings (about 3 μm thick) as a function of the deposition temperature, and the obtained results were discussed considering the grain shape and size, orientation, morphology, topography, and chemical-structure of the material.

The hardness and Young's modulus values showed that the temperature decrease has a significant and beneficial effect on the mechanical properties of the material, since it increases the grain size and decreases the hydrogen content (mainly localized at grain boundaries). The novelty of this study is to show that NCD films obtained at the lowest deposition temperature achieve almost the same hardness and elastic modulus of the high quality diamond and NCD films ([2], see also the therein Refs). To the best knowledge of the authors the present study shows for the first time that superior mechanical properties of NCD coatings are obtained at lower deposition temperature in contrast to findings reported in Refs. [6,7].

2. Experimental

2.1. Coating preparation

The NCD films were prepared by means of the MWPECVD technique starting from Ar-rich $CH_4/Ar/H_2$ (1/89/10%) gas mixtures deposited on squared pieces of single crystal (100) p-type silicon wafers of 2.6 × 2.6 cm^2 substrates. Prior to the deposition, the substrate surface was ultrasonically treated in an ethanol suspension containing diamond powders of sizes in the range of 40–60 μm. The working pressure, microwave power and total flow rate during the deposition in $CH_4/Ar/H_2$ plasmas were held constant at 140 mbar, 950 Watt and 100 sccm, respectively. Four values of the deposition temperature were considered (T_D: A – 653 °C; B – 775 °C; C – 833 °C; D – 884 °C). A buffer layer, 500 nm thick, between the Si substrate and the NCD films allowed improvement of the smoothness of coatings. This layer was easily obtained under the typical conditions of microcrystalline diamond growth (gas mixture CH_4/H_2 1/99 sccm; 50 mbar; 1000 W; T_D 825 °C), and was characterized by a nucleation time shorter than NCD films without the buffer layer as monitored through pyrometric interferometry (PI) and described in detail in Ref. [10]. Successively, the deposition was continued on the buffer layer in Ar-rich $CH_4/Ar/H_2$ gas mixture. The surface temperature of the substrate, the deposition rate and the thickness during the deposition process were monitored *in-situ* and in real-time by the PI technique [10] using a dual-wavelength (λ_1 = 2.1 μm and λ_2 = 2.4 μm) infrared pyrometer (Williamson Pro 92 40).

2.2. Coating characterization

All samples were characterized by nanoindentation, X-Ray Diffraction (XRD), Atomic Force Microscopy (AFM), Raman spectroscopy, and Water Contact Angle (WCA).

A nanoindentation tester (NHTX, CSM Instruments) equipped with a Berkovich indenter was used to determine the mechanical properties, in particular H and E of the NCD coatings. The "advanced indentation" testing configuration was used with a constant loading/unloading rate of 94 mN min^{-1} and a maximum load of 47 mN. At the maximum load the indentation process was stopped for 10 s before unloading. The Oliver & Pharr method [9] was utilized to calculate penetration depth, projected contact area, hardness and Young's modulus. A Poisson's ratio of 0.07 was assumed for the elastic modulus calculation. Each measurement consists of a matrix of four indentations carried out at different locations on the surface of each sample and a High Pressure High Temperature (HPHT) single crystal diamond. The nanoindentation tester was calibrated by measurements on fused silica and the elastic modulus was found to be 71.3 ± 1.7 GPa, which is close to the theoretical value (72 ± 2 GPa). Since the sample material (diamond) was the same as the one of the indenter, at the end of the four measurements for each sample, the integrity of the Berkovich indenter was controlled by performing indentations on a reference relatively soft copper sample (H_{Cu} = 1.1 GPa and E_{Cu} = 128.1 GPa) and checking that the shape of the indented footprint was free from imperfections that may be connected to the geometry of the Berkovich indenter. All measurements were done at room temperature in air on NCD coatings as grown without polishing its surface.

The orientation and the crystallite size values were assessed by XRD. Measurements for grain size analysis were performed by using a 12 kW Rigaku Cu rotating anode ($K_{\alpha 1}$ radiation, λ = 1.5405 Å) coupled to a Ge single crystal monochromator and an INEL CPS-120 linear (1D) curved detector that was able to acquire simultaneously over a 120° scattering angle range. The beam size was 0.04 mm × 6 mm at directions parallel and perpendicular to the diffraction plane, respectively. The XRD data were collected at a fixed incidence angle of 28°, which allowed to obtain a similar beam footprint and instrumental resolution function (IRF) for both examined reflections (111) and (220) and for all investigated samples. Further, the angle of 28° lies in between the Bragg angles (θ) of (111) ($2\theta_{(111)}$ = 43.3°) and (220) ($2\theta_{(220)}$ = 75.3°) reflections. Because of this, the lattice planes were probed at approximately the same tilt angle (and almost parallel) to the sample surface. The preferential orientation was investigated by means of a Bruker D8 Discover equipped with a Cu X-ray tube coupled to a Göbel mirror (selecting K_α radiation), an Eulerian cradle, and a scintillation detector.

An NTEGRA Aura scanning probe microscope (NT-MDT, Zelenograd, Moscow, Russia) fully equipped for surface analysis was employed to evaluate the surface topography and the surface root-mean-square roughness (R_{RMS}) values. All AFM measurements were performed in air using the semi-contact mode in order to avoid dragging effects of the analyzed surface. The AFM maps were acquired using commercial, unmodified "golden" silicon probe tips with high resonance frequency. To limit the risk that the measured