THE OPTICAL SPECTRA OF CARBON-BASED THIN FILMS MEASURED BY THE PHOTOTHERMAL DEFLECTION SPECTROSCOPY (PDS)

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Abstract

Our photothermal deflection spectroscopy (PDS) setup allows to measure simultaneously the absolute values of the optical transmittance T, reflectance R and absorptance A spectra of thin layers on glass substrates in the spectral range from ultraviolet to near infrared light with the typical spectral resolution 5 nm in the ultraviolet, 10 nm in visible and 20 nm in the near infrared region. The PDS setup provides the dynamic detection range in the optical absorptance up to 4 orders of magnitude. Here we demonstrate the usability of this setup by comparing the optical absorbance on a series of the carbon layer and nanocrystalline diamond (NCD) thin layers deposited on glass substrates by using the magnetron sputtering and the microwave based surface wave-discharge in linear antenna chemical vapor deposition (CVD) processes, respectively. The defect-induced localized states in the energy gap are observed in all carbon layers as well as in NCD.

Keywords: nanocrystalline diamond, amorphous carbon, magnetron sputtering, CVD, optical spectroscopy

1. INTRODUCTION

Amorphous carbon coatings show excellent tribological properties, whereas the nanocrystalline diamond (NCD) layers exhibit an extraordinary variety of surface properties such as high or low electrical conductivity, positive or negative electron affinity, hydrophobicity or hydrophilicity and tunable chemical reactivity1. In the magnetron sputtering process used for carbon coating, a graphite target (cathode) plate is bombarded by the positively charged energetic Ar+ ions generated in a glow discharge plasma situated in front of the target. The bombardment process causes the removal, i.e., sputtering, of carbon atoms, which then condense on a colder substrate as an amorphous thin film in a process called physical vapor deposition. Secondary electrons are also emitted from the target surface as a result of the ion bombardment, and these electrons play an important role in maintaining the plasma2.

In the microwave plasma enhanced chemical vapor deposition (MW CVD) the substrate is exposed to hydrogen rich plasma where the precursors such as methane and carbon dioxide react and/or decompose on the substrate surface to produce the nanocrystalline diamond deposit. The volatile by-products are also produced, which are removed by gas flow through the reactor chamber. The ionization of the precursor gases by the microwave absorption play an important role in maintaining the plasma3.

The NCD layer consists of a closely packed polycrystalline material with grain size below 100 nm and tetrahedrally bonded amorphous carbon located at grain boundaries4. It is widely accepted that in tetrahedrally bonded amorphous carbon (a-C) π-bonded carbon atoms cause the formation of a π-π* pseudogap, emerging about midgap in between the σ+σ* bands and dominating the optical absorption in visible and near UV spectra range5. The similar shape of the optical absorption in the infrared and visible spectral regions is observed also in the polycrystalline diamond layers scaling with the content of amorphous carbon phase in grain boundaries6. On the other hand, the sp3 bonds occur not only in crystals with long-range order, but also in diamond-like amorphous solids where the atoms are in a random arrangement. In this case the bonding extends not in a long-range order over a large number of atoms. The bond types have
a considerable influence on the optical properties of amorphous carbon films. If the sp\(^2\) type is predominant the film will be less transparent then if the sp\(^3\) type is predominant.

In this paper we shown the similarity of the NCD optical absorption spectrum resembling closely the amorphous carbon coatings prepared by the hydrogen-free magnetron sputtering of graphite target in Ar plasma.

2. EXPERIMENTAL

The hydrogen-free carbon coatings on low alkaline borosilicate glass Corning 7052 were deposited at various sample holder temperatures in the magnetron sputtering process using graphite target in the deposition system shown in Fig. 1. The residual pressure (vacuum) was 0.01 Pa, the Argon pressure during sputtering was 1.2 Pa (flow 7.3 sccm). The voltage between target and substrate holder was 550 V and the DC current 0.1 A. The temperature of the resistively heated substrate holder stage, placed 5 cm from the target, was regulated from 100°C up to 450 °C.

NCD film (RR130117) was grown at 650°C at pressure 8 Pa from hydrogen-rich gas mixture of methane and carbon dioxide at 650°C on Corning Eagle 2000 glass using the modified commercially available apparatus used for the solar cell technology (AK 400, Roth and Rau, AG). The system employs two microwave generators (2.45 GHz) working at pulse-frequency up to 500 Hz and maximum power up to 4.4 kW in a pulse at each side of the linear conductor located in the quartz tube as well as RF bias (13.56 MHz, 600 W/500 V) to control energy of ions impinging on the substrate surface. The substrate holder stage can be resistively heated up to 800°C and moved up/down to control the distance to the antenna. NCD coatings deposited by linear antenna MW CVD over large area on glass substrates by provide an economical alternative to single crystal diamond showing most of the diamond surface properties.

The photothermal deflection spectroscopy (PDS) is based on detecting the laser beam deflection in the periodically heated liquid. The thin film deposited on non-absorbing glass substrate immersed in non-absorbing liquid is periodically illuminated by the monochromatic light. When the incident light is absorbed in the sample, the heat is transferred to the thermal waves that change the index of refraction of the liquid and deflect the probe laser beam. The amplitude of the oscillation of the laser beam is detected by the position detector and lock-in amplifier referenced to the incident light frequency being proportional to the amount of light absorbed in the sample. To normalize the measured PDS spectra we use a carbon nanotubes (CNT) layer deposited on glass substrate as a highly absorbing reference sample. The PDS setup at FZU AVCR, v. v. i. in Prague, shown in Fig. 2, covers the spectral range 250-2200 nm and consists of the following principal parts:

- 150 W Xe lamp attached to the triple grating monochromator equipped with gratings blazed at 300 nm (600 gr/mm), 750 nm (300 gr/mm) and 1200 nm (150 gr/mm)
- Low frequency mechanical chopper DCH Driver (EOPC)
- The sample/cuvette holder built from Thorlabs 30 mm cage system components
- Helma HEL101-20-40 quartz cuvette filled with 3M™ Fluorinert™ Electronic Liquid FC-72 (perfluorohexane, C\(_6\)F\(_{14}\)).
- Integrating spheres equipped with PbS Amplified Detectors and UV-enhanced Si detectors connected to lock-in amplifiers to detect incident light intensity and transmitted and reflected light
- High Performance JDS Uniphase Helium-Neon Laser 1.5 mW and the 60 mm PCX Lens, 633 nm V-Coat
3. RESULTS

The typical transmittance $T$, reflectance $R$ and absorptance $A$ spectra of hydrogen-free carbon layer sputtered on glass are shown in Fig. 3. The absorptance spectrum measured by PDS is compared with the spectrum 1-T-R calculated from transmittance and reflectance spectra. Fig. 3 shows that 1-T-R is not reliable in the region of weak absorptance in thin film below 1.2 eV as well as in the region above 3.4 eV where the glass substrate absorbs. Above 4 eV the glass substrate absorbs heavily which deteriorates all spectra. The film thickness $d \sim 64$ nm and the index of refraction $n \sim 1.7$ were evaluated from the interference fringes in the reflectance spectra $R$.

In the presence of the interference fringes, it is difficult to evaluate the optical absorption coefficient $\alpha(\lambda)$ of thin films from the transmittance $T$ and reflectance $R$ spectra if the optical function 1–T–R is below 1 %. The PDS measures directly the heat absorbed in the sample and it can detect the optical absorptance $A$ down to 0.01 % providing up to four orders of magnitude dynamic range for the optical absorption measurement of thin film deposited on transparent glass substrates. It is important to note that in our setup all optical spectra are measured simultaneously at the same spot thus avoiding the phase shifts in the interference fringes due to inhomogeneity of the thin film thickness. The optical absorptance coefficient $\alpha(\lambda)$ can be calculated independently for each wavelength $\lambda$ using the commercial thin film modeling software FilmWizard.

Fig. 4 shows the optical absorption coefficient of a series of hydrogen-free carbon coatings sputtered on glass substrates for about 20-35 min at various substrate holder temperatures. The growth rate was found to be about 3 nm/min for carbon coatings deposited at and below 300°C and about 2 nm/h for coatings deposited at and above 350°C. From Fig. 4 follows that the defect density of hydrogen-free carbon coatings slightly decreases with increasing substrate temperature up to 300°C, but deteriorates significantly at elevated temperatures above 350 °C on the substrate temperature.

The typical transmittance $T$, reflectance $R$ and absorptance $A$ spectra of as grown NCD layer on Corning Eagle 2000 glass substrate is shown Fig. 5. In the UV region above 3 eV the transmittance and reflectance spectra are deteriorated by the optical scattering, whereas the optical absorption spectrum measured by PDS is much less influenced by the scattering. The film thickness 360 nm and the index of refraction $n \sim 2.4$ were evaluated from the interference fringes in the reflectance spectra $R$. The growth rate was about 20 nm/h. In the case of NCD that is a mixture of diamond and non-diamond phase, it is not possible to calculate the optical absorption coefficient of the non-diamond phase directly from the optical absorptance spectrum without knowing the non-diamond volume fraction. However, since the optical absorption of as grown NCD layer in the red spectra range at 2 eV (620 nm) is about 6 % compared to about 20% in carbon coating deposited at 400°C. Thus, the sputtered carbon layer absorption is about 20x higher then in the as grown NCD layer taking into account the film thickness. We roughly estimate the volume fraction of non-diamond fraction in NCD should be about 5 %. As we have shown in our previous paper, the non-diamond content in NCD located at grain boundaries can be significantly reduced by the post-growth etching and cleaning.9

4. CONCLUSION

Our PDS setup provides a highly reliable simultaneous measurements of the optical transmittance, reflectance and absorptance spectra of thin films deposited on glass substrates in a broad spectral range from UV to IR. The film thickness and the index of refraction are evaluated from the reflectance spectra. The optical absorption coefficient spectra evaluated from the optical absorption provide a tool to estimate the defect density in carbon coatings. In this paper we have demonstrated this concept by comparing the optical absorption coefficient spectra of a series of the hydrogen-free carbon coatings deposited on glass substrates using the magnetron sputtering. Experimental data showed that hydrogen-free carbon coatings exhibit a
characteristic shape in the subgap optical absorption that resembles the optical absorption spectra of NCD films. We suggest the highly defective hydrogen-free magnetron sputtered carbon layer deposited at elevated temperature 450°C to be used as a thin interlayer between NCD and gold contacts to prepare the ohmic electrical contacts for NCD sensors avoiding the unwanted Schottky effect.

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LITERATURE

Fig. 1 The thermal evaporation and magnetron sputtering of the graphite target equipped with turbomolecular pump and Argon gas inlet.
Fig. 2 PDS setup. The sample S is adjusted to be parallel and in the close proximity to the focused probe laser beam monitored by the position detector PD. The transmitted and reflected light is collected by lens L1 and L2 placed behind and in front of the sample and focused into integrating spheres IS1 and IS2. The background spectrum proportional to the incident light intensity is monitored via the beamsplitter B by detectors D1 and D2.
Fig. 3 The typical transmittance $T$, reflectance $R$ and absorptance $A$ spectra of 64 nm thick hydrogen-free DLC layer grown by magnetron sputtering of graphite target in Ar plasma for 30 min at 400 °C on Corning glass 7052.
Fig. 4 The optical absorption coefficient of a series of hydrogen-free carbon coatings deposited on glass substrates by magnetron sputtering at various substrate holder temperatures.
Fig. 5 The typical transmittance $T$, reflectance $R$ and absorptance $A$ spectra of the as grown 350 nm thick nanocrystalline diamond (NCD) layer (prior grain boundary cleaning) grown at 650°C by MW CVD on Corning Eagle 2000 glass.