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Spectroscopic ellipsometry characterization of nano-crystalline diamond films prepared at various substrate temperatures and pulsed plasma frequencies using microwave plasma enhanced chemical vapor deposition apparatus with linear antenna delivery

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ABSTRACT

A series of nanocrystalline diamond (NCD) films were deposited by a custom made microwave plasma enhanced chemical vapor deposition apparatus with linear antenna delivery at different substrate temperatures (520–600 °C) and pulsed plasma frequencies (2.7–14.3 kHz) in a hydrogen rich working gas mixture of $H_2/CH_4/CO_2$. Films were deposited onto naturally oxidized Si wafers pre-seeded with nanodiamond particles. Spectroellipsometry characterization of the NCD films was carried out considering various model structures (single and bi-layer models) and various NCD optical constant parameterizations (Tauc–Lorentz and effective medium approximation with different non-diamond component representations). It has been shown that substrate temperature can be lowered with a simultaneous increase in pulsed plasma frequency while still providing high quality NCD films with non-diamond component fraction in the bulk layer of about 5% (identically estimated by ellipsometry and Raman spectroscopy). Films' thickness and their surface roughness were found consistent with atomic force and secondary electron microscopies. Among various NCD structure models the most appropriate has been selected.

1. Introduction

Various carbon-related nanostructures are now studied due to their promising properties and broad range of applications. Chemical vapor deposition (CVD) grown diamond films belong to this family of materials and have been already used for example in micro-electromechanical systems [1], as biological platforms [2,3], electrodes [4], as tribological and biocompatible coatings on orthopedic and vascular implants [5] etc. To further broaden the range of applications and to facilitate mass production, the elevated deposition temperature (higher than 800 °C) of CVD diamond films must be substantially decreased. Diamond film properties that are important for device performance, such as optical transparency, electrical conductivity, and surface roughness are strongly dependent on film morphology. Nanocrystalline diamond (NCD) films prepared by microwave plasma enhanced chemical vapor deposition (MW PECVD) with crystallite sizes below 100 nm show low surface roughness, high optical transparence in VIS and tailored electrical conductivity by B doping [6–8]. Precise characterization of NCD films helps to understand the different role of deposition parameters with respect to plasma chemistry and hence to find routes to decrease deposition substrate temperature while keeping diamond quality of the films high. Among various characterization techniques such as Raman and IR spectroscopy, secondary electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry is often used because it is sensitive to depth variation of optical film properties from which also other important physical parameters (as for example surface roughness, film thickness, B doping, and diamond and non-diamond volume fraction) can be determined. However, spectroscopic ellipsometry is an indirect method and therefore, a reliable model structure including appropriate parameterization of optical properties of studied sample is required to obtain correct results.

The structure of NCD films deposited by MW PECVD onto substrates pre-seeded by nano-diamond (ND) particles has been, due to NCD's promising applications, intensively studied [9–11] and the main growth stages are now generally accepted. In described technique diamond growth starts on seeded ND particles, which is as opposed to other seeding techniques, where nucleation centers are produced typically by mechanical scratching of the substrates surface. The small crystallites

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or grains increase in volume and then coalesce at a certain distance from the substrate. When the film is totally closed, the grains continue to increase in volume following van der Drift growth where the larger grains suppress the growth of their smaller neighbors [12]. This type of growth typically results in columnar film structure. The size of the grains increases with film thickness (together with surface roughness) and when its average diameter surpasses about 100 nm the film becomes microcrystalline rather than nanocrystalline.

Various types of characterizations and their combinations aim to precisely determine structure defects of NCD film and its relation with the deposition process. The most researched parameters, which define overall NCD film quality are the content of non-diamond phase, void components in the film (and its distribution over the film thickness), the thickness at which nucleation grains coalescence and film surface roughness.

So far, many different approaches (model structures) in the literature have been proposed for NCD film spectro-ellipsometric characterization. NCD dominantly consists of ordered sp^3 hybridized carbon in the form of crystalline grains but also disordered sp^3, sp^2 and sp^1 hybridized C are present mainly in grain boundaries and at the interface layer. Quantitative evaluation of the diamond/non-diamond fraction is among the most searched parameters. But unfortunately, different forms of carbon bonds and the degree of disorder in non-diamond component of NCD films make it difficult to precisely model non-diamond optical properties and hence only approximate methods are available.

Frequently used is effective medium approximation (EMA) [13] where NCD is considered as an effective medium of components representing dominant diamond phase and small fraction of non-diamond components and finally voids. The diamond phase is often represented by optical constants of monocrystalline diamond and non-diamond components by optical constants of glassy carbon [10,14,15] or different forms of amorphous carbon [16]. Diamond phase parameterized by Tauc–Lorentz formula can be also found in the literature [15]. Another approach (different from EMA) is parameterization of NCD effective optical constants by Lorentz [17], Tauc–Lorentz [18] or modified Sellmeier [19] dielectric functions. The early stage of growth, i.e. before coalescence of grains, is often reported as a seed layer in contrast to the bulk layer which is formed after grains coalesce. Different stages of NCD film growth including the seed layer, grain coalescence, the bulk layer and surface roughness are usually accounted for by a multilayered model.

One of the goals of this paper is to assess and compare various NCD model structures applied on spectro-ellipsometric characterization of a series of NCD films deposited by an innovative MW PECVD system with linear antenna delivery working in pulsed plasma mode. Another goal is to use the obtained results and elucidate the possible interrelation of two selected deposition parameters, namely substrate temperature and pulsed plasma frequency, and to establish evidence of high quality NCD film deposition with decreased substrate temperature facilitated by the simultaneous increase of plasma frequency.

2. Experimental details

NCD films were deposited onto naturally oxidized Si substrates by a custom made MW PECVD system with linear antenna delivery operating in pulsed plasma mode. Two planar sets of four linear antennas guided microwaves into the deposition reactor where the plasma was ignited in a working gas mixture of $H_2/CH_4/CO_2$ with a fixed volume ratio of 92/5/3. Substrates were seeded before the deposition with monodispersed ND particles (NanoAmando®B) with a surface density of about 10^{10} cm^{-2} and a mean diameter of 4–6 nm. A series of NCD_f^T films were deposited with different substrate temperatures T = 520, 550, and 600 °C, and pulsed plasma frequencies f = 2.7, 4.5, and 14.3 kHz, labeled low, mid, and high, respectively, in the following text. Samples were heated only by the direct interaction with the plasma. Different substrate temperatures were realized by placing the samples at different distances from the antennas. More details about the apparatus can be found in Refs. [20–22].

Ellipsometry parameters Ψ and Δ that represent complex reflectivity coefficient ratio of p- and s-waves, were recorded in the spectral range of 0.7–5.5 eV (225–1769 nm) by a rotating analyzer based ellipsometer (VASE system, Woollam Ltd.). Ellipsometric spectra of three angles of incidence (65°, 70°, and 75°) and 18° incidence reflectance (measured in one beam configuration with the same instrument in spectral range 0.7–3.65 eV) were fitted simultaneously against different sample models discussed in more detail in the next sections.

NCD films were complementary characterized by AFM, SEM and micro-Raman spectroscopy. Atomic force microscopy scans were carried out in semi-contact mode using HA_NC etalon tip with a NTEGRA Prima NT MDT system. Secondary electron microscopy images of grown films were recorded using an FEI Quanta 3D FEG apparatus. Raman spectroscopy was carried out at room temperature using a Renishaw InVia Raman Microscope with the following parameters: excitation wavelength 488 nm (25 mW), ×50 Olympus objective, 65 μm slit width, spot focus, and 2400 l/mm grating.

3. Results and discussion

Various models in terms of complexity could be considered for ellipsometry spectra evaluation. We start with a simple model where the NCD film is approximated by a homogeneous single layer with different representations of diamond and non-diamond components. Here, a limited number of free parameters help to keep their correlations in reasonable limits. In the second step we introduce a more complex bi-layer model of NCD film that aims to account for the presence of the seed and bulk layers. In all models, opaque 0.5 mm thick monocrystalline Si wafer substrate is approximated by c-Si semi-infinitive medium with thin (3 nm) SiO_2 overlayer. Surface roughness was also considered in all models in the form of a two-component (void and bulk layer) Bruggeman type effective medium approximation [13].

3.1. Single layer models

Single layer models shown in Fig. 1 were considered for ellipsometry spectra analyses. Optical constants of c-Si and SiO_2 were taken from the literature [23]. The NCD film itself was approximated with a different representation of diamond and non-diamond components and void consideration. Abbreviations *gc*, *ac* and *v* in the model names indicate the presence of glassy carbon, amorphous carbon and voids, respectively. In the model 5tl optical constants of NCD films are parameterized by Tauc–Lorentz formula.

As it was already mentioned, NCD films consist mainly of sp^3 hybridized C arranged in grains with a diamond crystalline structure. Apart from this dominant phase all possible hybridizations (sp^3, sp^2, and sp^1) might be present at defect sites and are localized mainly in the grain joints and seed layer where the coalescence is reached. The optical constants of a material composed of a host medium filled with different types of inclusions can be approximated by an effective medium theory that takes into account the host and inclusion material optical constants and corresponding filling factors. Therefore, if NCD optical properties are parameterized by EMA with diamond as the host and non-diamond as the inclusion phase, then the non-diamond component fraction could be estimated from spectro-ellipsometric analyses. This approach is applied in the models 1ac, 2gc, 3acv, and 4gcv. Here, the diamond component is represented by optical constants of bulk diamond [24]. However, optical constants of non-diamond phase are not well defined because the exact structure and ratio of sp^1, sp^2, and sp^3 hybridized C in defect sites of NCD is not known. Frequently, the non-diamond phase in NCD is approximated with glassy C where only sp^2 hybridized C is present in a well-defined structure [25] and therefore with well-defined optical constants. Alternatively, instead of glassy C, amorphous C that contains all possible hybridizations of C can be