Pulsed laser deposition and ellipsometric study of hydrogenated and hydrogen free amorphous carbon films

PhD Dissertation
thesis points

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Introduction

Thin films are present in our every day life as an invisible but integral part of it. In lack of them the scratching of our data storage disks would be unavoidable, our plastic glasses could be damaged during a simple every-day cleaning and the transparent coversheet above the code reader of the cash desk would be damaged frequently. Beyond these examples from our every day life thin films are often applied in the industry (e. g. microelectronics, glass techniques, optics, tool engineering, automotive industry) and also in space research. Industry utilizes a remarkable amount of amorphous carbon films, since these type of films are not only transparent in the visible domain, but also hard and wear resistant. These excellent properties arise from the special features of their crystalline counterparts, i.e. diamond and graphite. The characteristics of the films can be tuned in a wide range via the modification of the deposition conditions, the type and amount of the doping materials. Therefore the deposition of amorphous carbon films and the investigation of their characteristics is a living research area of material sciences.

Literature and aims

Pulsed laser deposition (PLD) is frequently used to fabricate thin films in laboratories. During PLD the thin film is built from a plume generated with laser pulses. The properties of the film are determined by the composition and energy of the plume, which can be controlled relatively easily by tuning the deposition condition (e.g. wavelength and duration of the laser pulse, chemical composition of the applied background gas). It is known

from the literature that PLD can be applied to produce not only hydrogen free but also hydrogenated amorphous carbon films when depositing in hydrogen containing background gases or ablating hydrogen containing targets. However the deposition process in hydrogen containing ambient has not been yet clearly understood. Furthermore the effects of laser pulses shorter than nanoseconds are not known when ablating hydrogen containing targets. *For that reason I have aimed at depositing hydrogen free and hydrogen containing amorphous carbon films in hydrogen containing background gases, and from hydrogen containing targets. A further object was to determine the film properties and to investigate the correlation of the properties with the deposition conditions.*

According to the application field of the films – e.g. covering of glass surfaces with transparent wear resistant coatings – a critical parameter of the layers is their optical properties in the visible domain. One of the most adequate methods for measuring the optical properties is spectroscopic ellipsometry, of which application enables non-destructive determination of the film thickness, refractive index and extinction coefficient. From the measured ellipsometric data the optical data can be determined by a modelling procedure. The optical properties might slightly depend on the applied model. *Hence a further object of my research was to explore how the optical properties of amorphous carbon films depend on the ellipsometric model, and how these optical properties are connected to the other physical and chemical characteristics of the films.*

Methods

Films were deposited by PLD. Sample series were produced by ablating graphite and glassy carbon targets with an ArF excimer laser in increasing pressure hydrogen and methane atmospheres. Sample series were deposited also from glassy carbon and polymer targets at different power densities utilizing the ns pulses of ArF and KrF excimer laser and the sub-ps pulses of a hybrid excimer-dye laser system.

The compositions of the layers were determined with Rutherford back-scattering spectrometry (RBS) and elastic recoil detection analysis (ERDA). RBS and ERDA measurements and the evaluation of the measurements were performed in the Research Institute for Particle and Nuclear Physics of the Hungarian Academy of Sciences. The carbon bonding structure of the samples was investigated with Raman spectroscopy. The Raman spectra of the films were recorded with the Renishaw micro-Raman spectrometer of the Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences. The carbon-hydrogen bonds within the samples were explored by the means of Infrared spectroscopy. These measurements were carried out with the BIO-RAD Fourier transformation spectrometer of the Physical Chemistry Department of the University of Szeged, and with the Bruker IFS-28 Fourier transformation spectrometer of Research Institute for Solid State Physics and Optics. The hardness of the samples was determined with the UMIS, CSIRO nanoindenter of the Department of General Physics, Loránd Eötvös University. Optical properties were investigated with spectroscopic ellipsometry. For these investigations a Woolam M2000F rotating compensator ellipsometer was used operating at the Department of Optics and Quantumelectronics, University of Szeged.

New scientific results

I. Hydrogen free and hydrogenated amorphous carbon films were deposited by ablating high purity graphite targets in hydrogen ambient of different pressure (pH2). It was established that three different type of amorphous carbon films can be deposited at the applied laser fluence values and target – substrate distances when varying the pressure.

At low pressures (pH2 <<10-1 Pa) hydrogen free diamond-like films are formed, which contain high amount of sp3 hybridized carbon atoms. The hardness and density values of these films are close to that of diamond, while their Young modulus and band gap value is high. Both the high value and the dispersion of their refractive index resembles that of diamond [1].

At medium pressures (pH2 ~ 1 Pa) hydrogenated graphite-like carbon films can be deposited. The bonding structure of these films is determined by the sp2 hybridized atoms appearing in the structure. With increasing pressure the density, Young modulus, band gap values and refractive index of the films decreases. The dispersion of their refractive index also changes; it shows the characteristics of graphite [1].

At high pressures (1 Pa << pH2) the deposition of hydrogenated polymer-like films can be achieved. These films contain high amount of hydrogen and sp3 hybridized carbon atoms. The density, hardness, Young's modulus and refractive index decrease while their band gap increases with the further increase of pressure [1].

II. The microscopic and macroscopic properties of hHydrogen free and hydrogenated amorphous carbons films, deposited from the laser plasma of a glassy carbon disk placed in hydrogen and methane atmosphere of in-

creasing pressure were investigated. It was established that the type of the films changes in a similar way in the increasing pressure of methane and hydrogen atmospheres independently from the chemical composition of the background gas. Regarding the two investigated atmospheres at the applied laser fluences and substrate-target distances the films deposited at low ($p << 1$ Pa), medium ($p \sim 1$ Pa) and high ($p >> 1$ Pa) pressures are diamond-like, hydrogenated graphite-like and polymer-like, respectively. It was established that besides these similarities the films prepared in different background gases differ in their carbon-hydrogen bondings and their thickness. A dominant amount of the bonded hydrogen in the films prepared in hydrogen are localized in sp3–CH2 and sp3–CH sites, while in the films deposited in methane, no such dominance can be observed: the hydrogen bonded in the films are not bond preferentially in these structures. The films prepared in medium and high pressure methane have thicknesses one and a half times larger than that of the film deposited in vacuum, while the films deposited in hydrogen are only 1.2 times thicker than those deposited in vacuum [2].

III. The physical and chemical processes of reactive pulsed laser deposition of carbon based films in hydrogen and methane atmospheres were analyzed. According to the experimental data the different part processes of reactive PLD contribute to the film properties to a different degree when depositing at different pressures. At small pressures where the ambient gas does not significantly influence the expansion of the plasma, the initial velocity of the plasma acquired during the ablation is responsible for the film properties. At medium pressures the film properties are determined by the deceleration of the film building particles due to the interaction of the

plasma and ambient. This means on one hand that the plasma particles are decelerated both in hydrogen and methane ambient and on the other hand that the gas particles containing carbon are accelerated. At high pressures the chemical reactions and the incorporation of the gas particles becomes important. The differences, observed between the films deposited in hydrogen and methane, are explained with the different number of the hydrocarbon radicals formed when carbon particle collide with the hydrogen and methane molecules. The higher thickness of the films deposited in methane gas is described as the consequence of the effective incorporation of the methane molecules [1, 2].

IV. Using lasers operating in the ns and ps time regime with different wavelength, hydrogenated and hydrogen free carbon films were deposited from glassy carbon and polymer targets. It was demonstrated that the volumetric power density – the product of the power density and the absorption coefficient – is suitable to compare and define numerically the different deposition conditions determined by the type of the laser, since it does not only depend on the pulse energy, pulse length and ablated spot's size, but it also takes into account the change in the laser wavelength via the absorption coefficient of the target. It was demonstrated, that from the glassy carbon target regarding the investigated volumetric power densities the most diamond like carbon films could be deposited when using ArF excimer laser, and more graphitic films could be achieved with the KrF excimer laser and the hybrid KrF excimer dye laser system. Regarding the polymer targets it was shown that the density of the films at all volumetric power densities exceeds that of the original target, while the hydrogen and oxygen content decreases compared to the target material. Regarding the

investigated volumetric power densities the films with the highest hydrogen content and band gaps could be deposited with the highest power densities, i.e. with the pulses of the ps laser [3].

V. A number of a-C and a-C:H films have been analyzed with spectroscopic ellipsometry in the 1.24-5 eV range. Three different function based models were used to model the optical properties of the films. The films were compared using three parameters, namely the highest refractive index (nmax), the corresponding photon energy (Emax) derived from their refractive index, and the optical band gap (E04). It was shown that the knowledge of the photon energy dependence of the refractive index in the 1,24 – 5 eV ensures enough information to qualitatively describe the samples. Furthermore it was presented, that although the optical properties of the films derived from ellipsometric measurements may slightly depend on the applied model, the trends derived from the different modeling procedures are the same. When plotting the photon energy corresponding to the maximal refractive index as a function of the maximal refractive index a curved track emerges, while when Emax is plotted against the optical band gap a linear monotone increasing band is drawn out by the data points. In both cases the same types of films occupy different domains, but in the latter case the hydrogen free and hydrogenated graphite-like films and hydrogenated and hydrogen free diamond-like films do overlap. When combining the two diagrams in a three dimensional diagram these overlapping can be resolved. Therefore these type of diagrams behave like a phase diagram for a-C and a-C:H films and can be used to predict the type of the investigated film. The explanation of the optical phase diagram from the point of view of the bonding structure was also given [4].

Publications

Referred articles supporting the thesis points:

[1] Budai J., Tóth Z., Juhász A., Szakács G., Szilágyi E., Veres M., Koós M.
Reactive pulsed laser deposition of hydrogenated carbon thin films, the effect of hydrogen pressure
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[3] Budai J., Bereznai M., Szakács G., Szilágyi E., Tóth Z.:
Preparation of hydrogenated amorphous carbon films from polymers by nano- and femtosecond pulsed laser deposition
Applied Surface Science 253 (19), 8235-8241, (2007)

[4] J. Budai, Z. Tóth
Optical phase diagram of amorphous carbon films determined by spectroscopic ellipsometry
Accepted for publication in Physica Status Solidi C

Further articles:

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Applied Surface Science, 252, 4707-4711, (2006)

[6] Füle M., Budai J., Tóth S., Veres M., Koós M.:
Size of spatial confinement at luminescence centers determined from resonant excitation bands of a-C : H photoluminescence
Journal of non-crystalline solids 352 (9-20), 1340-1343, (2006)

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