Original Article

Thermo-optical properties of hydrogenated amorphous carbon and nitrogen-modified carbon layers from in situ ellipsometric studies

Janusz Jaglarz\textsuperscript{a}, Katarzyna Dyndal\textsuperscript{b}, Katarzyna Tkacz-Śmiech\textsuperscript{c,*}

\textsuperscript{a} Cracow University of Technology, Al. Jana Pawła II 37, 31-864 Kraków, Poland
\textsuperscript{b} AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland
\textsuperscript{c} Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland

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Hydrogenated amorphous carbon and nitrogen-modified carbon layers, respectively a-C:H and a-C:N:H, were fabricated by plasma-assisted chemical vapor deposition and subjected to ellipsometric measurements in the temperature range 25 ÷ 300 °C. The results show that the layers are metastable and above 200 °C they undergo a transformation from dielectric to a more stable semiconducting structure. It is confirmed by a rapid drop of the optical gap (from 2.3 eV to 1.2 eV for a-C:N:H; from 2.4 eV to 1.8 eV for a-C:H) and an increase of refractive index, n, and extinction coefficient, k. The changes are permanent, followed by hydrogen/nitrogen release as it results from the investigation of Fourier transform infrared spectra.

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1. Introduction

During the last decades, there has been an increasing interest in studies on carbon and nitrogen-modified carbon layers. The main reason for this is the possibility to use them in a variety of applications as protective and functional coatings. Such layers have some extreme properties similar to those of diamond that are achieved in isotropic thin layers. Carbon layers have been found to be useful in many engineering and biomedical applications [1]. The most common are the ones that exploit their low friction and high wear resistance, e.g. in optical windows, magnetic storage disks, car parts and microelectromechanical devices [2].

A family of carbon layer materials includes the amorphous carbon (a-C) and hydrogenated alloys (a-C:H) of various fractions of sp\textsuperscript{2} and sp\textsuperscript{3} phases [3], optionally modified with nitrogen. The tetrahedral amorphous carbon (ta-C and ta-C:H) contains increased fraction of sp\textsuperscript{3} hybrids. All of them are often referred to as diamond-like carbon, DLC. The term diamond-like has been established to point out three common properties: high hardness, low substrate temperature during the layer deposition and an amorphous or nanocrystalline structure [4,5]. The DLC layers exhibit chemical inertness for corrosive chemicals, organic solvents, acids and bases. Due to a combination of good mechanical and chemical properties, as well as good infrared transmittance, DLC coatings also play a significant role in optical systems [1,6,7]. They have been also found to have an extremely low dielectric constant that makes them promising materials for interconnect structures.

\textsuperscript{*} Corresponding author.
E-mail: smiech@agh.edu.pl (K. Tkacz-Śmiech).
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Nitrogen incorporation into carbon layers brings changes to the properties [3,8–10]. The most notable is a reduction of stresses that results from the clustering of the $sp^3$ phase, and hence an improvement of an adhesion [11]. The research on nitrogen-modified carbon has started since Liu and Cohen’s [12] prediction of stability of the $C_3N_4$ phase of the bulk modulus and hardness higher than those of diamond. As a result of numerous experiments, the amorphous nitrogen-modified carbon layers, which are of interest in their own right, have been obtained [13–15]. They show good tribological properties which let them to be applied as protective coatings for hard disks, read heads and medical devices [16,17].

It is convenient to classify the amorphous nitrogen-modified carbon into four classes of coatings, namely

- a-C:N, mainly $sp^2$ bonded,
- ta-C:N mainly $sp^3$ bonded,
- a-C:N:H of moderate $sp^3$ content,
- ta-C:N:H with high $sp^3$ content and low hydrogen content.

The nitrogen-modified carbon can be modified by changing nitrogen fraction. An effect of $N$ content on the structure and chosen properties of nitrogen-modified carbon were studied by Ferrari et al. in [13].

Various deposition techniques can be applied to manufacture the amorphous carbon and nitrogen-modified carbon. Historically, the first DLCs were produced by Aisenberg and Chabot [18] with the use of the ion beam deposition technique. The mass selected ion beam deposition (MSIB) [19,20] can be applied to ensure the controlled deposition of ion species of well-defined energies. The mostly applied laboratory deposition process is implemented by using r.f. PACVD, 13.56 MHz (radio frequency plasma-assisted deposition) with the substrate placed either on anode or cathode [21]. The properties of the layers are affected by several parameters, e.g. a composition of the reactive gas mixture, pressure of the gases in the reactor chamber, temperature and r.f. power [22].

The present research is aimed to study thermal stability of plasma-deposited a-C:H and a-C:N:H layers. The thermal stability is required to acquire the functionality. Accurate data are of obvious interest from both fundamental perspectives and with regard to technical applications. A lack of thermal stability of the hydrogenated amorphous carbon layers at increased temperatures has been revealed by many authors [23–29].

In the studies, various techniques were applied to reveal a change of the properties and structure of the layers during the annealing.

Conway et al. [23] studied hydrogenated tetrahedral amorphous carbon, ta-C:H, fabricated using plasma beam source and subjected to post-deposition annealing. The results confirmed that already at the temperatures less than 300 °C, a short-rate migration of hydrogen and a network reconfiguration started which resulted in defect passivation. At higher temperatures, hydrogen effusion took place. Hydrogen, $H_2$ and hydrocarbons effusion from the hydrogenated amorphous carbon, a-C:H, grown by plasma deposition at various bias voltages was revealed in the studies by Wild and Koidl [24]. The effusion from the a-C:H layers was later confirmed by Ristein et al. [30] and Jiang et al. [31]. The results showed that the mass of the effusing molecules decreased when the layers were deposited at higher bias voltages. Simultaneously, the temperature of the beginning of the effusion increased. Biener et al. [25] studied a structure of ultrathin C:H films obtained using the sputter ion gun. They concluded from spectroscopic investigations that upon annealing, carbon $sp$, $sp^3$, and $sp^2$ groups got destroyed at about 300, 800 and 1100 °C, respectively. The decomposition of these groups was parallel to the effusion of hydrogen and hydrocarbons from the films. Dischler et al. [26] used optical absorption spectroscopy for bonding analysis in a-C:H layers prepared by r.f. plasma deposition from benzene vapor. The authors found that thermal annealing between 150 and 300 °C caused a conversion of weakly bonded hydrogen into normally bonded one. Above 300 °C, the hydrogen effusion and aromatization of the carbon network took place. Up to 75% of the total hydrogen effused in parallel with a decrease of the optical gap from 1.2 eV to 0.17 eV and a change of the $[sp^2]/[sp^3]$ ratio from 2/3 to 1/3.

The result concerning a decrease of the optical gap energy of hydrogenated amorphous carbon was confirmed by F.W. Smith in the optical studies [27]. The a-C:H layers were subjected to reflectance and transmittance temperature measurements. Hence, refractive index, $n$, extinction coefficient, $k$ and optical gap, $E_g$, were determined. It was shown that all optical parameters exhibited a considerable variation with a subsequent annealing up to 750 °C. The optical gap decreased from 2.2 eV to zero, which indicated a development of a graphitic short-range ordering in the layer. At the same time $n$ and $k$ increased.

Contrary to carbon layers, there are only a few results concerning thermal stability of nitrogen-modified carbon, CNx. The CNx films deposited by reactive direct current magnetron sputtering were studied by Hellgren et al. [28] and by Lejeune [29]. The layers were examined with respect to the thicknesses, composition, bonding structure, microstructure, and mechanical properties as a function of annealing temperature and time. The properties were found stable only up to 300 °C. At higher temperatures a nitrogen loss followed by the graphitization was observed.

In this work we show experimental results from the ellipsometric measurements of the optical constants, $n$, $k$ and $E_g$ and thicknesses of hydrogenated amorphous carbon, a-C:H and nitrogen-modified carbon, a-C:N:H, prepared by r.f. PACVD. The parameters were measured in situ with the use of the spectrometric ellipsometry, $SE$, during the post-deposition annealing up to 300 °C, cooling down to room temperature and re-annealing. The $SE$ is a non-destructive method which provides quantitative measures of the parameters related to the structure of the layers. It allows determining refractive and extinction indices and thicknesses of layers by fitting appropriate theoretical model to experimental data. In the method, a change of polarization in the reflection at the surface is measured and hence ellipsometric angles, $\psi$ and $\Delta$, are determined. A typical ellipsometer consists of the light source, polarizer, compensator, analyzer and detector. The sample is placed between compensator and analyzer. The light source emits unpolarized or circularly polarized light that later is polarized by the polarizer. There exists a variety of ways to perform the measurement [32–34]. The null and photometric ellipsometers present general configurations. In the null ellipsometer, the rotational azimuth angle of the polarizer,
compensator and analyzer are adjusted to minimize (“null”) the intensity of the light at the detector. The method can be used in the limited range of wavelengths. The principle of photometric ellipsometry is to vary one or more conditions while measuring the light intensity at the detector. The outputs of the measurement are, in this case, light intensities. Therefore, the retarding element (the compensator) is unnecessary. Due to the possible varied conditions, the basic ellipsometers can be
- rotating polarizer, RPE,
- rotating compensator, RCE,
- rotating analyzer, RAE.

An original solution for the moving conditions was provided by Chen and Lunch [35] who constructed the ellipsometer with the polarizer and analyzer rotating synchronously in the same direction with the speed ratio 1:2. RPAE. This type of ellipsometer was described theoretically in a series of papers by El-Agez et al. [36–39]. The authors presented a mathematical analysis of Fourier transform of the intensity and verified the result experimentally. In [38], they described, in details, the RPAE with polarizer and analyzer rotating in the opposite direction and in [39], the rotating polarizer and compensator ellipsometer, RPCE, with polarizer-compensator rotating with the speed ratio 1:1.

Due to many advantages and variety of solutions, the ellipsometry is becoming one of the most widely used techniques to study layers and surfaces. In [21,22], we used the technique to compare the a-C:H layers deposited by PACVD, 13.56 MHz, at various conditions. Temperature ellipsometric measurements still remain unique. Here, for the first time, we compare, using photometric RAE ellipsometry, the temperature variations of optical constants and thicknesses of a-C:H and a-C:N:H layers, during post-deposition annealing and re-annealing. The results confirm a presence of an irreversible transition between dielectric and semiconducting states observed during the first annealing.

The paper is organized as follows. In the next two sections we present experimental details and present the results from ellipsometric and Fourier transform infrared measurements (FTIR). In the last section we present a short summary and conclusions.

2. Experimental procedure

In this part of the paper, we describe how the layers were deposited and how they were characterized.

2.1. Plasma processes

The amorphous hydrogenated carbon and nitrogen-modified carbon layers were fabricated on Czochralski (001)-oriented silicon by plasma-assisted chemical vapor deposition using radio frequency plasma, 13.56 MHz, r.f. PACVD. The layers were deposited from gaseous methane and, optionally, nitrogen, diluted in argon. Before deposition, the silicon substrates were preliminarily washed in acetone and isopropanol alcohol and then placed in the reactor on the anode and subjected to 10-minute cleaning in argon plasma environment, Table 1. The deposition was started without removal of the sample from the reactor chamber. Here, we present the results for the samples grown at the conditions, as given in Table 1. The layers deposited at these conditions are amorphous and hydrogenated, as our previous results show [21]. Therefore, they are denoted here to as a-C:H and a-C:N:H respectively.

2.2. Methods and apparatus

The atomic structure of the layers before and after annealing was studied by Fourier transform infrared spectroscopy (FTIR), with the use of Bruker Vertex 70 vacuum spectrometer working in a transmittance mode with 4 cm⁻¹ resolution. The 256 scans were obtained for each sample. The atomic force microscopy was used to study the physical state of the layer surface, Bruker AFM MULTIMODE 8 using PeakForce tapping mode with a silicon tip.

The optical characterization of the layers was performed using spectroscopic ellipsometry [21,40-44]. The measurements were made with use of Woollam Co., Inc, M-2000J.A. RAE ellipsometer. The angles Ψ and Δ were measured within 300 ÷ 1000 nm spectral wavelength ranges. The models were fitted to experimental data with the use of Complete EASE 5.0 software.

For thermal ellipsometric studies, the samples were placed into a heating chamber, in an air atmosphere. The ellipsometric angles were measured at the incidence angle of 70°. The chamber is equipped with two windows made of special optical glass (as stated by the producer, Woollam Co. Inc.). The incident and reflected light pass through the window perpendicularly so the aberration is avoided. To remove a moisture, the chamber has been placed into a single stage oil vacuum pump (V-i160SV) pumping with the speed 142 l/min. The achieved vacuum has not been controlled but it should be in the range of 20–30 Pa.

During the measurement, the temperature was increased from 25 to 300 °C and then reduced down to the room temperature in an interval manner as it is shown in Fig. 1. The measurements were made in the stabilization periods. The
annealing procedure was repeated and the final AFM roughness and FTIR spectrum were measured.

3. Results

Spectroscopic ellipsometry (SE) measures ellipsometric angles \( \Psi \) and \( \Delta \) that enter a fundamental equation of ellipsometry
\[
\rho = \frac{r_p}{r_s} = \tan(\Psi) \cdot e^{i\Delta}
\] (1)

The fraction \( \rho \) in the above equation is a ratio of the complex Fresnel reflection coefficients of the sample for \( p \) - (in the plane of incidence) and \( s \) - (perpendicular to the plane of incidence) polarized light. The measurement can be performed as a function of wavelength and angle of incidence. The method is highly accurate and does not demand a reference material. Various material parameters can be determined by SE. To extract the respective data, it is necessary to perform a model analysis of \( \Psi(\lambda) \) and \( \Delta(\lambda) \) dispersion dependencies. The appropriate theoretical model allows predicting \( \Psi \) and \( \Delta \) as functions of optical constants and layer thickness. The mean squared error (MSE) is used to quantify a difference between the experimental and predicted data [43].

The hydrogenated amorphous carbon and nitrogen-modified carbon layers, of interest herewith, are dielectric [2,19,21], essentially transparent over the SE measurement wavelength range. For such materials, the extinction coefficient is nearly zero, \( k \approx 0 \). Metals absorb light at all wavelengths, and \( k \neq 0 \). Semiconducting materials present the features of both dielectrics and metals. Due to band gap energies lower than those of dielectrics they absorb short light wavelengths and pass long wavelengths of the light. Many dispersion equations are used to describe optical functions for the transparent and absorbing materials.

In the wavelength range in which the layer is transparent, light can penetrate the layer and it provides thickness information. For the transparent materials, the Cauchy formula is used for spectral dependence of the refractive index
\[
n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}
\] (2)

where \( A, B, C \) are Cauchy coefficients determined by regression analysis and \( \lambda \) is given in \( \mu \text{m} \).

The Cauchy equation assumes \( k = 0 \) and can be applied for dielectrics and organics. It was further developed by Sellmayer [40,43].

In the case of semiconductors, the Cauchy formula is applied for photon energies smaller than absorption edge. However, for small absorption in the layer, the Cauchy dependence may be used. For absorbing layers, the extinction-coefficient dispersion \( k(\lambda) \) is given by the Urbach dependence:
\[
k(\lambda) = \alpha e^{(E - E_0)}
\] (3)

where \( E \) is the photon energy and \( \alpha \) - an amplitude, \( \beta \) - an exponent factor, \( E_0 \) - band gap of layer.

Eq. (3) describes a small exponentially decaying absorption below the band gap characteristic for many amorphous materials [44].

When the material becomes absorbing, the Cauchy equation cannot be used. The common models for absorbing materials are oscillator and b-spline models. The b-spline models are advantageous when describing complex optical dependencies.

In oscillator models, one of which is applied herewith, the optical constant peaks appearing at resonant frequencies are described using various oscillator equations. The simple oscillators are Gaussian’s, Lorentz’s and harmonic’s. A simple Gaussian oscillator describes the absorption shapes by 4 parameters, i.e. center energy (related to the resonant frequency), amplitude, broadening and offset shifting [41,42]. A few asymmetric oscillators have been proposed for the amorphous materials with the band gap and no absorption at lower energies, including Cody-Lorentz, and Tauc-Lorentz models. A very useful parameterization of the optical functions of amorphous dielectrics and semiconductors was proposed by Jellison and Modine [45]. The model is referred nowadays as the Tauc-Lorentz’s as it is based on the combination of the Tauc absorption edge [46,47] and oscillator broadening as given by the Lorentz oscillator [48].

The Tauc model predicts the absorption coefficient \( \alpha = 4\pi f R / \lambda \), \( f = c/\lambda \), (c - velocity of light in vacuum) as
\[
\alpha = M^2 \frac{(\hbar \omega - E_{Tauc})^m}{\hbar \omega}
\] (4)

where \( M \) contains all constants of simple Gaussian’s. The energy \( E_{Tauc} \) is the Tauc gap energy which is a measure of the bandgap in the amorphous materials. The power \( m \) depends on whether the material is crystalline (\( m = 3/2 \)) or amorphous (\( m = 2 \)).

According to the Tauc’s relation, the plotting of \( (\hbar \omega)^1/m \) versus the photon energy \( \hbar \omega \) is linear in a certain spectral region. The extrapolation of this straight line intercepts the \( (\hbar \omega) \)-axis to give the value of the energy gap [49,50].

3.1 Refractive index and extinction coefficient

The Cauchy model was applied to derive refractive indices and extinction coefficients of the a-C:H and a-C:N:H before

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* Standard cubic centimeters per minute.
the post-deposition annealing. Such layers are non-absorbing dielectrics with $k \approx 0$ and $n$ given by Eq. (2). The absorption in the layers subjected to the post-deposition annealing up to $300^\circ$C but measured at room temperature clearly increases. Therefore the Tauc-Lorentz model is more appropriate to fit it to the ellipsometric results. In Fig. 2, the results of fitting the models to experimental data measured before and after the first annealing cycle are shown. A good agreement, additionally confirmed by MSE values (Fig. 6), can be seen.

The dispersion functions of the refractive index, $n(E)$ and extinction coefficient, $k(E)$, derived from $\Psi$ and $\Delta$ for the layers before and after annealing and given as the functions of the photon energy are shown in Fig. 3. Clear quantitative differences are seen. First, the extinction coefficients for the pristine layers, both a-C:H and aC:N:H, are nearly zero in all spectral range (Figs. 3b and 3d). The spectral dependence of refractive indices present normal dispersion typical for transparent dielectric materials (Figs. 3a and 3c).

The optical properties of the layers subjected to the post-deposition annealing are substantially different. Both the refractive indices and extinction coefficients increase in the spectral range 300–1000 nm. The changes are due to an increase of the absorption of the layers. The observed differences can indicate a transformation of the electronic structure of the layers from a typical dielectric to a semiconducting one. It can be parallel with an increase of the densities of the layers due to annealing that explains the rise of the refractive index in accordance with the formula

$$\frac{n - 1}{\rho} = C_{DG}$$

(5)

The above equation is the Gladstone-Dale formula [42,51,52] that relates the average refractive index of the medium, $n$, to its density $\rho$, where $C_{DG}$ is the Gladstone-Dale coefficient.

3.2. Thermal hysteresis of the optical constants

As can be concluded from the comparison of the dispersions of the optical constants of the pristine layers and the layers subjected to the post-deposition annealing, the annealing causes the transformation of the electronic structure of the studied layers. Hence the optical constants change as well.

To describe the transformation precisely, we have recorded the ellipsometric angles during two annealing cycles, i.e. the post-deposition annealing up to $300^\circ$C and cooling down to the room temperature, and the re-annealing. Hence temperature changes of the refractive indices, extinction coefficients of the layers were determined. Here, we show only the data for 633 nm (He-Ne laser), Fig. 4. Thickness variation was also determined and temperature dependence of the optical gap energy calculated. The results are shown in Figs. 5 and 7, respectively.
The results show that when the temperature approaches 200 °C, all the parameters rapidly change in the both layers. A character of the changes suggests that at this temperature, the transformations between dielectric, non-absorbing, and semiconducting, partly absorbing, states take place.

The results for the first heating-cooling cycle present an open hysteresis which means that the observed transformations are due to irreversible processes. After cooling, the initial parameters are not achieved. At the secondary annealing, the layers appear to be thermally stable and the parameters achieved after the first annealing-cooling course are kept.

The changes of the optical parameters are in parallel to a significant decrease of the layers’ thicknesses from about 470 nm before annealing to 225 nm after the first post-deposition annealing and 220 after the second annealing, for both a-C:H and a-C:N:H layers, Fig. 5. This result remains in agreement with the observed rapid increase of the refractive index and indicate a densification of the layers.

To evaluate the quality of the fitting, the mean-square error, MSE, was calculated, Fig. 6. For all fittings, it is lower than 30 which confirms a good quality of fitting with the Cauchy and Tauc-Lorentz models. A worse agreement observed at
increased temperatures can be due to a lack of saturation of the optical properties within the 10 min stabilization period.

Additionally the AFM roughness before and after annealing is clearly below 5 nm, so it doesn’t affect the evaluated optical parameters. The values are $3.12 \pm 0.95$ nm and $2.39 \pm 0.82$ nm, respectively for the a-C:H and a-C:N:H pristine layers, and $3.56 \pm 0.49$ nm and $2.56 \pm 0.75$ nm for the layer after the second annealing cycle.

The dispersion functions of the optical constants at various temperatures were used to calculate the optical gaps. The parameterization was made by fitting the Tauc-Lorentz model for the amorphous solids. The temperature dependence of the Tauc gap is shown in Fig. 7. For both layers when the temperature exceeds 200 °C, a clear decrease of the optical gap is seen. For the a-C:H layer, it decreases from almost 2.4 eV before annealing to 1.5 eV - after annealing. Similarly the band gap of the a-C:N:H layer changes between about 2.3 and 1.2 eV.

The observed behavior confirms that above 200 °C the layers undergo the transformations. The electronic structure of the layers change from dielectric to semiconducting. The transformation is irreversible because hysteresis in not closed.

### 3.3. Atomic structure and FTIR spectra

The possible structural changes due to the post-deposition annealing have been revealed by the comparison of the FTIR spectra of the layers before annealing and after two cycles of annealing, Fig. 8. The spectra were recorded at room temperature.

The FTIR spectra of the pristine layers show the features typical for the a-C:H and a-C:N:H layers, deposited with plasma-activated CVD [2,21,22]. Both spectra show the absorption at 2800 ÷ 3000 cm⁻¹ and 1000 ÷ 1800 cm⁻¹. The absorption at 2150 ÷ 2300 cm⁻¹ and at 3250 ÷ 2500 cm⁻¹ is present only in the spectrum of the a-C:N:H layer [11]. The peaks below 1000 cm⁻¹, belonging to the fingerprint region are not shown here.

The band at 2800 ÷ 3000 cm⁻¹ is observed in the spectra of both the a-C:H and a-C:N:H layers. It arises from CH stretching and breaks down into 3 modes assigned to C-sp¹ (≡C-H), C-sp² (≡CH₂) and C-sp³ (≡CH₃). The peaks between 1000 ÷ 1800 cm⁻¹ are due to skeletal C=H and C=C vibrations, characteristic for the a-C:H and a-C:H layers, respectively.

The IR activity at 2150 ÷ 2300 cm⁻¹ is characteristic for the a-C:N:H layers. The absorption is due to vibrations of the C≡N nitrile groups and can be considered an indicator of the nitrogen content in the a-C:N:H layers. The absorption at 3250 ÷ 3500 cm⁻¹, present only in the spectrum of the a-C:N:H layer, can be assigned to the NH terminal bonds and OH from the atmosphere.

The narrow band at about 1100 cm⁻¹ can be assigned to the CO bonds. Such bonds exist at the interface between the carbon from the layer and oxygen from a native SiO₂ thin film, justified by the same intensity in all spectra.

The FTIR spectra of the layers subjected to the post-deposition annealing show differences with respect to the spectra of the pristine layers. The most visible is a decrease of the intensity of the bands at 2800 ÷ 3000 cm⁻¹, assigned to the vibrations of CH₃ groups in both a-C:H and a-C:N:H lay-
ers. Likewise the intensities of the bands at 2150 \(\pm\) 2300 cm\(^{-1}\) and 3250 \(\div\) 3500 cm\(^{-1}\) in the spectrum of the a-C:N:H layer subjected to the post-deposition annealing are lower.

The observed changes confirm a partial release of hydrogen from the terminal CH and NH groups. A release of nitrogen is also possible. Such behavior was previously observed in the a-C:H [23,26] and CN\(_x\) layers [28,29]. The present result is in agreement with a significant thickness decrease.

Summary and conclusions

We present, for the first time, the use of the spectroscopic ellipsometry technique to make the in situ studies of the thermo-optical properties of the a-C:H and a-C:N:H layers. The measurements were carried out during the post-deposition annealing, cooling and during the re-annealing up to 300°C. From ellipsometric study, the temperature dependencies of refractive indexes, extinction coefficients, band gaps and thicknesses of the layers were determined. Due to significant differences between the properties of the layers before and after annealing, the FTIR spectra were also measured and compared to determine the structural changes.

The obtained results show that during annealing, at the temperature approaching 200°C and above the electronic structure of the layers turns from more dielectric to semiconducting, what is confirmed by the rapid decrease of the optical gap and by the changes of the refractive indexes, extinction coefficients and the thicknesses. The values achieved during annealing up to 300°C remain unchanged after cooling which shows the irreversibility of the transformation. The stability of the optical parameters during the re-annealing is also confirmed. The comparison of FTIR spectra of the layers before and after annealing indicates a partial release of hydrogen from both layers and a possible release of the nitrogen from the a-C:N:H layer.

It also manifests itself in decreasing thickness of the studied layers by about half. The release of the elements (H, N) can be accompanied by a partial graphitization of the layers as before shown by Hellgren et al. [28] and Lejeune [29]. The premise herewith can be a rapid decrease of the optical gap.

All the obtained results provide additional arguments for the lack of the thermal stability of the a-C:H layers and we present entirely new results concerning the a-C:N:H layers. We also show, for the first time, that at the re-annealing of both a-C:H and a-C:N:H layers keep their individual properties that are entirely different than those of the pristine layers.

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References


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