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Amorphous Hydrogenated Carbon Films with Diamond-Like and Polymer-Like Properties

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Abstract

Results of the study of structural features and optical properties of thin films of amorphous hydrogenated carbon (a-C:H) films prepared by plasma-activated chemical vapor deposition of various hydrocarbon precursors are reviewed. The effect of different factors on the rate of a-C:H films deposition in a DC glow discharge with the magnetron plasma localized near the anode such as voltage, discharge power, gas pressure, relative content of an inert gas in the mixture with a hydrocarbon and other is analyzed. It is shown that the refractive index of a-C:H films can be changed in the interval 2.35–1.55 by increasing the deposition rate and the choice of the appropriate hydrocarbon precursor. The features of the vibration spectra of the diamond-like and polymer-like films are discussed. The correlations of the structural peculiarities and of the optical absorption edge, gap width, and conductivity as well as the absorption spectra in visible region and the ratio of the fundamental bands in Raman scattering spectra are estimated. Examples of using the optical properties of the a-C:H films are given.

Keywords: a-C:H films, deposition, refractive indexes, vibration spectra, optical gap

1. Introduction

Interest in the study of thin films of amorphous hydrogenated carbon (a-C:H) obtained by a plasma-activated chemical vapor deposition (CVD) is maintained for several decades. The reason for this is the possibility of variations in the properties of the films in a broad interval from diamond-like carbon up to polymer-like films. This opens up great opportunities for their practical application. The glow discharge plasma is produced with RF-biased in [1–6] or DC in [7–9] diode-type systems. The efficiency of gas ionization can be improved by placing a grid

negatively biased with respect to the RF plasma near the substrate in [10], by using a magnetic field perpendicular to the RF plasma electric field in [11], and also by using a dual microwave electron cyclotron resonance RF plasma by applying an independently controlled RF substrate bias voltage in [12].

In this chapter, the results of the study of the structural features and optical properties of thin films prepared by CVD process in a DC glow discharge with the magnetron plasma localized near the anode are discussed. The effect of different factors on a rate of a-C:H films deposition such as voltage, discharge power, gas pressure, relative content of an inert gas in the mixture with a hydrocarbon and other is analyzed. Ellipsometry method was used for a comparative analysis of optical constants of a-C:H films prepared from different precursors. Features of the vibration spectra of a-C:H films according to their refractive index are discussed. The correlation of the absorption bands in the visible region of the spectra with of the optical gap and the Raman scattering spectra of the a-C:H films are explained. Examples of the use of diamond-like and polymer-like properties of the a-C:H films are shown.

2. Deposition of films in a DC glow discharge

2.1. Experimental setup for plasma-activated CVD

The a-C:H films are prepared by the method of CVD of hydrocarbons in the DC glow discharge using magnetron plasma localized at the anode in a quasi-closed volume [13]. The schematic representation of the device for the deposition of a-C:H films is shown in **Figure 1**.

Figure 1. Schematic of the CVD device on DC with magnetron plasma: 1—localized plasma; 2—glow discharge plasma; 3—permanent magnet; 4—cathode; 5—anode; 6—additional electrode; 7—substrate holder; 8—vacuum chamber; 9—current leads; and 10—valve.

Localized plasma (1), produced by crossed magnetic and electric fields, sustains a glow discharge in volume (2). We used annular permanent magnet (3) and two planar annular electrodes: anode (4) and cathode (5). The magnetic field intensity near the cathode surface was about 600 G. Additional electrode (6) and substrate-carrying electrode (7) were mounted

on glass cylinders with a diameter of about 130 mm. The cylinder walls confine the plasma inside the quasi-closed volume of the vacuum chamber. The ring-shaped gap between the magnet and the cathode is used as a gas inlet. Such a design of the device provides uniform gas distribution and efficient gas consumption, as well as reduces the film contamination by foreign impurities. Cathode (4) and anode (5) are placed in the neighborhood of the permanent magnet to provide maximum intensity and uniformity of the magnetic field in the crossed field region. The spacing between cathode 4 and substrate holder (7) is about 50 mm in the absence of the additional electrode. This electrode is placed 30 mm away from the cathode.

The cathode was under the ground potential. The substrate holder was either negatively biased with a DC power unit or under the ground potential. The additional electrode was used as a substrate holder when a-C:H films were deposited at a glancing angle in [14]. The vacuum chamber was evacuated to $1\text{--}5 \times 10^{-3}$ Pa by a rotary backing pump and a turbo-molecular pump. When the voltage is applied to the electrodes, the high-density toroidal plasma arises as a result of the effective electron capture by a magnetic trap, followed by gas ionization in the discharge gap between the anode and the substrate holder. Ion collisions with the solid surface confining the plasma generate extra electrons which also take part in gas ionization. a-C:H films were deposited on polished copper and glass substrates covered by thin conducting and semiconducting layers. This device allows the deposition of films with a thickness nonuniformity of not more than 20% on substrates of diameter up to 100 mm. Dependences of the ion current I through substrate holder vs. acetylene pressure P in the vacuum chamber in **Figure 2** are shown the effect of the localized plasma generated in the region of the crossed electric and magnetic fields.

Figure 2. Dependencies of an ion current on the substrate holder vs. a pressure in the vacuum chamber. Glow discharge is sustained by the localized plasma (*a*, *b*) and without it (*c*). $U = 600$ (*a*), 800 (*b*), and 1200 V (*c*).

When the plasma is sustained by the plasma localized in the device, the ion current varies only slightly with the gas pressure (varying from 0.01 to 0.04 Pa) at a constant voltage U (curve *a* and curve *b* in **Figure 2**). An increase in the voltage from 600 to 800 V leads to a twofold increase in the current through the substrate holder. In the absence of the permanent magnet, the glow discharge was initiated at a higher pressure, 0.06 Pa (curve *c* in **Figure 2**), and at a higher

voltage, 1200 V. In this case, the ion current depends more strongly on the gas pressure and increases with it. In comparison with standard diode-type systems, this device has a wider pressure range from 0.004 to 0.1 Pa and greatly extends the range of operating conditions for the deposition of a-C:H films in glow discharge plasma. The discharge power dissipated by positive ions at the substrate holder can vary between 1.2 and 44 W.

2.2. Factors governing the rate of a-C:H film deposition

Chemical reactions and physical processes at the surface of a-C:H films during their deposition in a low-temperature hydrocarbon plasma were considered in terms of the adsorbed layer model in [15]. This model assumes that CH_3 plasma radicals are physically adsorbed on the surface and then pass into the chemisorbed state as a result of cross-linking due to energetic ions. The surface coverage depends on the number of surface states and surface temperature. When a-C:H films are deposited with the described device, their surface is continuously bombarded by positive ions whose energy depends largely on the voltage. The ion energy may be high enough to consolidate the condensate either by cross-linking or by decomposing weakly bound particles with subsequent surface diffusion and desorption of the decomposition products. The balance of the processes conducive to film deposition and etching defines the deposition rate. The film deposition rate can also be varied by properly selecting the glow discharge parameters (gas pressure, ion current to the substrate, and voltage), which control the number of ions and their energy.

The deposition rate was defined as the ratio of the a-C:H film thickness to the deposition time. The thickness was measured by an MII-4M (Russia) micro-interferometer with an accuracy of 10%. The thickness of a-C:H films was found to be 0.1–0.3 μm . As the voltage increases from 700 to 1300 V, the deposition rate varies from 0.25 to 2 $\text{\AA}/\text{s}$. The rate r of film deposition on the surface of the glass substrates in the acetylene plasma as a function of the voltage is shown in Figure 3.

Figure 3. Rate of a-C:H films deposition on the glass substrates vs. the voltage.

Figure 4 illustrates the effect of surface conductivity on the deposition rate at an acetylene pressure in the vacuum chamber of about 0.05 Pa. For the same discharge power, the rate of film deposition on the surface of a transparent conducting indium–tin oxide (ITO) layer is one order of magnitude higher than that on the surface of a-Si:C:H semiconductor layer with a resistivity of about $10^{12} \Omega \text{ cm}$.

Figure 4. Rate of a-C:H film deposition on the ITO transparent conducting electrode (a) and a-Si:C:H semiconducting layer (b) at the acetylene pressure $P = 0.05 \text{ Pa}$ vs. discharge power N .

Space charge is produced on the substrate surface when it is bombarded by positive ions in a DC glow discharge plasma. Charge leakage from the surface depends on the substrate conductivity, as well as on the thickness and resistivity of the growing film. As the resistivity grows, the critical thickness of the film and the deposition rate decrease. Therefore, the surface conductivities of the substrate and condensate in glow discharge plasma should be considered

Figure 5. Rate of a-C:H film deposition on the copper substrates vs. acetylene volume content in the acetylene–argon mixture.

as important factors affecting the kinetics of a-C:H film deposition. The dependence of the deposition rate on the acetylene volume concentration in a mixture with krypton is shown in **Figure 5** for a constant discharge power of 1.8 W and a pressure of 0.05 Pa.

The addition of an inert gas to acetylene decreases the deposition rate of the a-C:H films on the copper substrates for the same pressure in the vacuum chamber from 4 to 0.5 Å/s. A film bombardment by inert gas ions etches the surface during the condensation and lowers the deposition rate.

3. Optical constants of a-C:H films

The method of ellipsometry enables to investigate the optical constants of thin films in the visible region. Ellipsometric studies have shown that the a-C:H films can have a high refractive index and transparent in the UV–visible range in [16, 17]. The dependences of the optical constants of a-C:H films on the parameters of the condensation process have been established by ellipsometry in [18–21]. The optical constants for the wavelength of 632.8 nm of the a-C:H films obtained by the method described above were determined using LEF-3M ellipsometer (Russia) [21]. The experimental setup consisted from polarizer–compensator–sample analyzer. A dual-zone null method at angles of incidence θ of 50°, 60°, and 70° was used to calculate the ellipsometric parameters. To calculate a refractive index n , an extinction coefficients k , and a thickness d of the films on glass substrates with $n_s = 1.515$ and $k_s = 0$, the homogeneous isotropic layer model was used. The refractive indices and extinction coefficients as a function of the deposition rate of a-C:H films obtained from acetylene, toluene, and octane, as precursors, are shown in **Figures 6** and 7. Increasing the rate of film deposition in plasma from 0.2 to 2.5 Å/s was achieved by increasing the voltage in the range of 700–1300 V.

Figure 6. Refractive index of the a-C:H films obtained from (1) acetylene, (2) toluene, and (3) octane vs. the deposition rate.

Figure 7. Extinction coefficients of the a-C:H films obtained from (1) acetylene and (2) toluene vs. the deposition rate.

The refractive index of a-C:H films obtained from acetylene and toluene decreases monotonically with increasing the deposition rate in **Figure 6**. Decreasing the extinction coefficients for these films can be seen in **Figure 7**. The films obtained from acetylene have the highest refractive indexes $n = 2.35$ and the highest extinction indexes $k = 0.3$ under the deposition rate equal to 0.5 Å/s . For films prepared from toluene, these indexes were equal to $n = 1.8$ and $k = 0.1$ in the same deposition rate. The films obtained from octane under the same conditions have the lowest values of $n = 1.55\text{--}1.6$ and $k < 0.01$ at a wavelength of 632.8 nm , and no dependence on the deposition rate is observed in **Figure 6**. These points to the dependence of the optical constants of the films from hydrocarbon precursors used for their deposition in the glow discharge plasma. It can be concluded that the optical constants of a-C:H films can be varied by changing the deposition rate in the plasma, as well as by selecting the precursor.

4. Vibration spectra of the a-C:H films

Infrared spectroscopy is widely used to study the optical absorption and structural features of a-C:H films in [22–29]. However, this method is not sufficiently sensitive for systems composed of a-C:H films and semiconductors with high refractive indices (Si and Ge) due to the significant interference effect. Comparative analysis of the IR spectra of multiple attenuated total internal reflection (MATIR) in the range $4000\text{--}1000 \text{ cm}^{-1}$ was performed in [30]. The use of the MATIR method excludes the influence of the interference effect and makes it possible to record the vibration spectra of thin a-C:H films. A single-crystal germanium prism, which provided 12 reflections of IR radiation from a plane surface at an angle of 45° , served as the MATIR element. **Figure 8** shows the IR spectra of a-C:H films with the refractive index $n = 2.3\text{--}2.4$. These films were obtained from toluene (1), octane (2), and cyclohexane (3) vapors at pressures of $0.01\text{--}0.03 \text{ Pa}$ and discharge powers of $10\text{--}13 \text{ W}$. It should be noted that the spectra of diamond-like C:H films obtained from various hydrocarbons have similar IR spectra in **Figure 8**. **Figure 9** shows the IR spectra of a-C:H films with the refractive indices $n = 1.64$ and

1.55, which were prepared at a vacuum-chamber pressure of ~ 0.3 Pa and a discharge power of 2 W from toluene (1) and octane (2) vapors, respectively.

Figure 8. IR spectra of the diamond-like a-C:H films prepared from vapors of (1) toluene, (2) octane, and (3) cyclohexane.

Figure 9. IR spectra of polymer-like a-C:H films prepared from vapors of (1) toluene and (2) octane.

As can be seen from **Figures 8 and 9**, an increase in the power by a factor of 5 (from 2 to 10 W) leads to significant changes in the IR spectra of the a-C:H films. The higher the discharge power, the higher the energy of the positive ions and their effect on the deposition process increase. The four functional branching structures are formed during the deposition of diamond-like films by decomposition of hydrocarbons in glow discharge plasma in the interaction of ions with the surface of the growing film. There are the stretching vibrations of C–H groups, carbonyl groups, single (C–C) and double (C=C) bonds, and bending vibrations of C–H groups

in the spectra in **Figures 8** and **9**. In addition, weak peaks at 2100 and 1900 cm^{-1} (**Figure 8**) and 2080 cm^{-1} (**Figure 9**) due to the stretching vibrations of the $\text{C}\equiv\text{C}$ bonds are observed in the spectra. The diamond-like films in **Figure 8** and polymer-like films in **Figure 9** have specific features in the IR absorption spectra. It should be noted that the IR spectra of the diamond-like a-C:H films (**Figure 8**) prepared from different hydrocarbons (octane, toluene, and cyclohexane) do not demonstrate any significant differences. They are similar to the spectra of the a-C:H films prepared from acetylene in [30]. The IR spectra of the polymer-like a-C:H films prepared from toluene and octane (**Figure 9**) are similar to previously measured spectra of polymer-like films prepared from benzene, toluene in [28], and acetylene in [29, 30]. The symmetric (ν^s) and asymmetric (ν^{as}) stretching vibrations and the symmetric (δ^s) and asymmetric (δ^{as}) bending vibrations of aromatic and olefin compounds, which observed in the IR spectra of the diamond- and polymer-like a-C:H films, are shown in **Table 1**.

Frequency, cm^{-1}	Nature of vibration	Intensity of band	
		Diamond-like films	Polymer-like films
~3400	ν (–OH)		medium
3300	ν ($\equiv\text{CH}$)		low
3100	ν ($=\text{CH}$) aromatic sp^2	low	low
3050	ν^{as} ($=\text{CH}$) aromatic sp^2	low	low
3000	ν ($=\text{CH}$) olefin sp^2	low	low
2920	ν^{as} ($-\text{CH}$) sp^3	high	high
2850	ν^s ($-\text{CH}_2$) sp^3	medium	medium
1900–2100	ν ($\text{C}\equiv\text{C}$)	very low	very low
~1700	ν ($\text{C}=\text{O}$)		high
1600	ν ($\text{C}-\text{C}$) aromatic		medium
1540	ν^{as} ($\text{C}=\text{C}$) polyene	medium	
1450	δ^{as} ($-\text{CH}_3$)		medium
1440	δ ($-\text{CH}$)	medium	
1370–1375	δ^s (CH_3)		medium
1250	ν ($\text{C}-\text{C}$) complex branching	medium	

Table 1. The frequencies, intensities, and nature of the vibrations in the IR spectra of the diamond- and polymer-like a-C:H films in the range 4000–1000 cm^{-1} .

A feature of the IR spectra of these films is the presence of bands at ~1250 cm^{-1} due to the stretching vibrations of $\text{C}-\text{C}$ bonds at the branch points of four functional structures (**Table 1**). This band weakly manifests itself or is almost absent in the spectra of the polymer-like a-C:H films. The spectra of these films show strong absorption bands due to the stretching (~2920 cm^{-1}) and bending (~1450 cm^{-1}) vibrations of CH groups, as well as of carbonyl (~1700

cm^{-1}) and hydroxyl ($\sim 3400 \text{ cm}^{-1}$) groups in [27–30]. The reason of occurrence of the stretching vibrations of carbonyl and hydroxyl groups in the IR spectra is in the chemisorptions of water and oxygen from the environment into micropores of a-C:H films. The porosity of a-C:H films with a low refractive index can be up to 7% as the ellipsometric investigation of the films was shown in [21].

The content of bound hydrogen in polymer films is much more than the diamond-like films. The intensity of the absorption band in the range $3400\text{--}2600 \text{ cm}^{-1}$ in the spectra of the polymer-like a-C:H films (**Figure 9**) is much higher than the spectra of the diamond-like films (**Figure 8**). The correlation between the refractive index of the a-C:H films and the integrated intensity of the band peaked at 2900 cm^{-1} has been shown in [27]. With a change in the refractive index from 1.55 to 2.4, the integrated intensity of the band attributed to the stretching vibrations of the CH groups exponentially decreases by an order of magnitude. Hence, a decrease in the content of bound hydrogen is accompanied by an increase in the refractive index of the a-C:H films, which indirectly proves that the film structure becomes denser.

5. Structural features of the a-C:H films

The known forms of amorphous carbon, including the various modifications of a-C:H, consist of carbon atoms in the sp^3 -state which forms tetrahedral σ -bonds with four neighboring atoms, atoms in the sp^2 -state which forms σ -bonds with three neighboring atoms in a plane, a weak π -bond perpendicular to this plane, and, to a lesser extent, atoms in the sp^1 -state. According to the cluster model for the structure of amorphous carbon developed in [31–34], aromatic graphite π -bonded atomic clusters consisting of sp^2 -states are distributed within a sp^3 -bound matrix. The π -states form a filled valence band, while the π^* -states correspond to an empty conduction band in the optical gap near the Fermi level. In accordance with the cluster model, the width of the optical gap depends on the sizes of the π -clusters and decreases as the fraction of sp^2 -states which form them rises in [34] while the sp^3 -bound matrix determines the tunnel barrier between them in [31]. It has been shown in [35, 36] that there is no difference in the nature of the states below and above the edge of the optical absorption edge and that the density of the π - and π^* -states close to the Fermi 2 eV.

Increasing the hydrogen concentration in an amorphous carbon structure leads simultaneously to a reduction in its equilibrium density and to a substantial change in the character of the clustering. This has been shown by studies of the stability of a-C:H systems and of their atomic and electronic structure as functions of the mass density and concentration of hydrogen using the molecular-dynamic density method in [37, 38]. The extent of the clusters is reduced by the introduction of sp^2 -segments inside the stressed sp^3 -matrix. The distribution of the clusters and of the segments which bind them affects the energy gap of a-C:H in [38]. The reduction of the gap is most likely a consequence of the splitting of the smallest π -bonded clusters and of the introduction of local π -electron systems into a stressed-bonded rigid lattice in which mixed bonds predominate.

5.1. Relationship of the Tauc parameters to the absorption spectra of a-C:H films

The optical gap in the various modifications of a-C:H depends on the conditions, under which it was produced in glow discharge plasma. The gap is made smaller when the energy delivered to the condensate is increased by raising the temperature of the carrier gas in [39] or substrate in [4, 20], by raising the power of the RF discharge [26], and by raising the voltage in [21, 40–42]. The conductivity of the a-C:H films increased when the optical gap decreased in [40].

For studying absorption spectra of a-C:H in the visible region, thin films were deposited from pure acetylene (C_2H_2) or a mixture of it with argon (Ar) at the ambient temperature. **Table 2** shows the conditions of preparation of the samples of the films. Samples *a* and *b* were prepared from pure acetylene with $P = 0.1$ Pa and $U = 600$ and 1200 V, respectively. Samples *c* and *d* were obtained with $P = 0.01$ Pa and $U = 900$ V from mixtures of acetylene with 50% and 70% argon.

Samples	P , Pa	Precursor	U , V	I_{600}/I_{800}	E_{max} , eV	E_T , eV	$B \times 10^4$ eV ⁻¹ cm ⁻¹
<i>a</i>	0.1	C_2H_2	600	2.7	2.07	2.09	2.3
<i>b</i>	0.1	C_2H_2	1200	0.33	1.65	1.65	5.0
<i>c</i>	0.01	$C_2H_2/50\%Ar$	900	0.4	1.65	1.09	7.9
<i>d</i>	0.01	$C_2H_2/70\%Ar$	900	4.5	2.07	1.14	5.6

Table 2. The deposition conditions and parameters of the absorption spectra E_{max} and I_{600}/I_{800} , along with the Tauc parameters E_T and B for a-C:H films.

The spectral variations in the absorption α (λ) at wavelengths in the range 400–2400 nm were obtained from the reflection spectra of films with thicknesses of 0.3–0.5 μm deposited on polished copper substrates. These spectra can be resolved into a series of Gaussian-type bands. In the wavelength interval from 400 to 1000 nm, two absorption bands were identified with peaks at 600 ± 5 and 800 ± 40 nm in [43]. The ratio of the integrated intensities of these absorption bands (I_{600}/I_{800}) and the energies E_{max} of the peaks in the spectra are listed in **Table 2**.

The absorption edge of this a-C:H films, like that of other amorphous semiconductors, was adequately fit by the Tauc equation in [44]. The Tauc optical gap E_T was determined by extrapolating a plot of $(\alpha E)^{1/2}$ as a function of energy E as described in [42]. The reflection and transmission spectra of the films were recorded from 200 to 1000 nm on a Hitachi spectrophotometer. In these measurements, the a-C:H films with a thickness of 0.2 μm are deposited on quartz substrates. The natural absorption coefficient α of the films was calculated using the Lambert–Beer law. The resulting values of E_T and the slope B of the straight line drawn as a function of E for the a-C:H films are listed in **Table 2**. The a-C:H film obtained from pure acetylene with a minimal voltage of $U = 600$ V and a relatively high pressure ~ 0.1 Pa had the narrow band in the spectra with a peak at 600 nm and the ratio of $I_{600}/I_{800} = 2.7$ (sample *a* in **Table 2**). It is characterized by a wide optical gap of about 2.09 eV. Increasing the voltage glow discharge doubled ($U = 1200$ V) led to a change in the absorption spectra and the appearance of additional isolated peaks. The maximum was at 750 nm, and the ratio $I_{600}/I_{800} = 0.33$ (sample *b* in **Table 2**). Raising the discharge voltage also changes the Tauc parameters of the a-C:H

films. E_T fell to 1.65 eV, while B increased. This indicates a rise in the density of states at the edge of the absorption band of the film. Dilution of the C_2H_2 with argon Ar leads to a significant change in the spectra of the a-C:H films.

The impact of the ions of the inert gas on the growing film (sample *c*) is equivalent to increasing a voltage of a glow discharge in the case sample *b* in **Table 2**. However, the magnitude of E_T decreased and the numerical value B increased compared with sample *b* of **Table 2**. The ratio of intensities of the absorption bands in the spectrum increased in favor of the band at 600 nm considerably as the result of diluting C_2H_2 with argon and decreasing the rate of the a-C:H film deposition up to 1 Å/s (a sample *d* in **Table 2**) in [43]. The width of the Tauc gap in the studied a-C:H films changes from ~2 to 1 eV. The constant B increases from 2.3×10^4 to 9.2×10^4 eV⁻¹ cm⁻¹ (**Table 2**), which indicates a rise in the density of states at the absorption edge of a-C:H with decreasing E_T . The nature of the π - π^* transitions, which determine the optical gap width, is not clear from the plot of $(\alpha E)^{1/2}$ as a function of E . A comparison of the magnitudes of E_{max} , which corresponds to the energy of the most probable π - π^* transition, and E_T showed that the a-C:H films with several peaks in their spectra have $E_{max} \approx E_T$ (**Table 2**, *a* and *b*), while the a-C:H films with a broad absorption spectrum have $E_{max} > E_T$ (samples *c* and *d* of **Table 2**). Varying the optical gap correlated with changing in a resistivity (ρ) films. **Figure 8** shows the experimental data of ρ and E_T versus the deposition rate of the a-C:H films. The values of ρ and r are plotted in a logarithmic scale. Representative Tauc gap data changed from ~0.8 up to ~1.7 eV, and an exponential rise of ρ of five orders of magnitude from $\sim 10^8$ to $\sim 10^{13}$ Ω cm was observed at the same time in [45] (**Figure 10**).

Figure 10. The electrical resistivity ρ and Tauc gap E_T vs. the deposition rate of the a-C:H films.

The atomic structure of the diamond-like can be described as a stressed-bond rigid lattice, in which mixed bonds predominate with local electronic systems of π -bond atoms imbedded in it. The presence of CH-groups in the sp^3 -state in the a-C:H structure reduces the extent of the π -bond clusters in [38], favors localization of their π -electrons, and raises the tunnel barrier between them in [32]. The distribution of the π -bond clusters in the sp^3 -bound matrix is governed the Tauc parameters of the a-C:H films. The schemes of the density of states as a function of energy E generalizing the obtained data are shown in **Figure 11**. The structure of the optical gap of the a-C:H modification with $E_T > 1.5$ eV and a resistivity exceeding $10^{10} \Omega \text{ cm}$ can be illustrated by scheme *a* (**Figure 11**).

Figure 11. Schematic diagrams of the electronic structure of the optical absorption edge and optical gap of (a) insulating and transparent in the visible region and (b) absorbing and conductive a-C:H films.

The optical gap of the a-C:H films is determined by the energy of the most probable electronic π - π^* transition. It should be noted a transition of a valence π -electron localized either on isolated linear chains or on complicated π -bound structural elements to a corresponding free π^* -level in the conduction band. The spectra of these films contain weak discrete absorption bands, which lie below the energy $E_{\max}$ with peaks at ~ 1 , ~ 0.7 , and ~ 0.6 eV in [43]. They correspond to localized states within a pseudo gap whose distribution can also be described by a Gaussian curve. Scheme (b) of **Figure 9** describes the structure of the optical gap for a-C:H films with $E_{\max} > E_T$ (samples *c* and *d* in **Table 2**). The discrete energy levels lying at the optical absorption edge below the level corresponding to the energy $E_{\max}$ form a dense quasi-continuous electron spectrum, which can be described by a Gaussian curve. There are essentially no states within the pseudo gap for $E_T \ll 1.0 \pm 0.1$ eV. In this case, E_T corresponds to the minimum transition energy of a valence π -electron to the corresponding empty π^* -level in the conduction band. This kind of electronic structure is typical of a-C:H films, which absorb in the visible region and have a resistivity of $< 10^9 \Omega \text{ cm}$. A low content of sp^3 -bound states in the films ensures raising the conductivity. In the proposed schemes of **Figure 11**, the edge of the conduction band lies near the vacuum level

E_{vac} (scheme a) or below it (scheme b), consistent with current ideas regarding the electronic structure of a-C:H in [34]. The changes in the intensities of the absorption bands of the a-C:H were compared with changes in the resonance Raman scattering spectra to understand their electronic structure, the nature of the visible absorption, and their conductivity in [43].

5.2. Studying the a-C:H nanostructure using resonant Raman scattering spectroscopy

The Raman scattering spectra of amorphous carbon in its different modifications consisted of a broad band and can easily be resolved into two Gaussian-type bands. The first has a peak in the interval 1530–1580 cm^{-1} and was initially attributed to an active 1585 cm^{-1} line of single-crystal graphite, while the second band near 1300–1400 cm^{-1} , with a line at 1355 cm^{-1} , corresponds to a disordered mode in [46]. However, a high-frequency shifts of the principal maximum observed in the Raman scattering spectra of various modifications of a-C:H when the excitation energy is raised that has cast doubt on this interpretation in [47, 48]. It is the result of scattering from π -bond elements of the a-C:H structure, which is enhanced resonantly at photon energies approaching the π - π^* resonance. The bands near 1400 and 1530 cm^{-1} may be associated with scattering on large- and small-sized π -bond clusters, respectively, in [48].

The absence of graphite clusters in the structure of fresh and thermally worked at a temperature of 400 °C in vacuum a-C:H films has been confirmed by comparing resonant Raman scattering spectra of a-C:H and graphite in [49]. The observed features of the a-C:H Raman scattering spectra lead to the conclusion that their structure includes a set of scattering centers characterized by different excitation energies of π - π^* electronic transitions and vibration energies. The different sizes of the π -bond elements of the structure lead to different values of the coupling parameter. The strong disordered interaction among them causes the large spread in their electronic and vibration spectra. Resonant excitation of the Raman spectra produces a selective enhancement in the scattering at the frequencies of those centers for which these conditions are optimal. The width and shape of the Raman scattering bands are determined by the dependencies of the vibration frequency and location of an absorption band on the length of the coupling chain and on the size distribution of the elements. In this case, the procedure of expanding the complicated Raman scattering band and absorption bands in the electronic spectra into Gaussian profiles is arbitrary.

The way the relative intensity of the Raman scattering bands of fresh and thermally processed a-C:H depended on the excitation wavelength has been shown that these bands correspond to different types of structural elements, which are polyene chains of various lengths and polycyclic aromatic groups with different numbers of rings. The former predominates in the intensity of the band at ~1540 cm^{-1} and the latter, to that of the band at ~1340 cm^{-1} , is extremely probable, since in the Raman scattering spectra of the corresponding molecular structures, the most intense bands lie in the corresponding range of vibration frequencies in [49].

The existence of olefin chains in the structure is confirmed by studies of a-C:H films by elastic neutron scattering in [50] and by nuclear magnetic resonance and neutron diffraction in [51, 52]. Theoretical calculations of resonant Raman scattering spectra of amorphous carbon have shown that the band shapes are determined by a complex of sp^2 -clusters with six or fewer rings. Polyene chains can contribute to the formation of the 1540 cm^{-1} band when the Raman

scattering spectra are excited by visible light, while a lattice sp^3 -structure has no direct effect on the resonant Raman scattering spectra in [53].

5.3. Comparison of Raman scattering and absorption spectra in the visible region

Resonant Raman scattering spectroscopy is an extremely informative and highly sensitive method for investigating the characteristics of middle-range π -bond elements in a-C:H structures. Increasing the energy of the ions involved in the condensation of a-C:H in RF in [54, 55], and DC glow discharge plasmas in [30] leads to a rise in the intensity ratio of the main bands at 1340 and 1540 cm^{-1} (I_{1340}/I_{1540}) in the Raman scattering spectrum. These changes can be explained by an increased amount of polycyclic aromatic groups compared to polyene chains in the a-C:H structure. Decreasing the amount of CH-groups in sp^3 -states and the optical gap were observed in [42] concurrent with the rise in I_{1340}/I_{1540} . Since the Raman scattering spectra are caused by resonant scattering on π -bond elements of the structure, changes in these elements should correlate with changes in the electronic absorption spectra of a-C:H films. **Figure 12** shows plots of the band intensity ratio I_{600}/I_{800} in the absorption spectra and of the ratio I_{1340}/I_{1540} of the principal bands in Raman scattering spectra of a-C:H films obtained in [30, 49] vs. the voltage.

Figure 12. The variation in the ratio I_{600}/I_{800} of the integrated intensities of the principal bands in the absorption coefficient $\alpha(\lambda)$ and in the ratio I_{1340}/I_{1540} of the fundamental bands in the Raman spectra of a-C:H films vs. the voltage (U).

It can be seen that as the ratio I_{600}/I_{800} in the absorption spectrum decreases, the ratio I_{1340}/I_{1540} in the Raman scattering spectrum increases. It is known that the limiting wavelength in the absorption spectra of the polyene is 610 nm. Therefore, the peak near 600 nm in the absorption spectra correlates with the distribution of isolated polyene-type linear chains in the a-C:H structure. The Gaussian-like band at 800 ± 40 nm reflects the distribution of combined π -bond elements in the structure a-C:H. They can include polyene chains of various lengths, as well as polycyclic groups with a different number of aromatic rings. The many kinds of combina-

tions of this π -bond structural elements with a single system for coupling of the multiple bonds, along with isolated polycyclic groups and polyene chains, are the most likely chromophores responsible for visible absorption in a-C:H films. Taking this circumstance into account, we may assume that the absorption spectra of a-C:H films are formed by the superposition of absorption spectra corresponding to electronic π - π^* transitions in isolated π -bond elements of the structure and they are quasi-continuous. The composition of the π -bond elements, their spatial distribution in the film structures, and the interaction probability of their π -electron systems determine the position of the peak, the intensity of the Gaussian-like bands which stand out in the spectrum, and the structure of the edge of the absorption band.

6. Application of optical properties of the films

The a-C:H films with $n \approx 2$ are ideal antireflection coatings for germanium with $n = 4$ in [22–24, 56, 57]. These films differ from well-known multilayer antireflection coatings in their high chemical durability and mechanical strength. The spectra in **Figure 13** illustrate the effect of the absorption in a-C:H films with $n = 2$ on the transmission of germanium. Single-layer coatings based on a-C:H films with the optical thickness $l/4$ equal to 0.5 and 1.25 μm for $\lambda = 4$ and 10 μm , respectively, were deposited from acetylene by the above-described method onto both sides of a Ge substrate. Due to the absence of absorption in a-C:H in the range 3.5–5 μm , an increase of up to 100% in the transmission of Ge was obtained in this spectral region (**Figure 13**). For wavelengths above 5 μm , the effect of the absorption of IR radiation in the a-C:H films becomes more pronounced.

Figure 13. Transmission spectra (T) of germanium coated with quarter-wave a-C:H layers for wavelengths of (1) 4 and (2) 10 μm .

The transmission of a Ge sample that has both sides coated with a-C:H films does not exceed 90% at a wavelength of 10 μm due to the absorption loss in the a-C:H coatings in [27]. Due to their combination of chemical and mechanical durability, radiation resistance, and transpar-

ency in the IR region, diamond-like a-C:H films can be used as protective coatings for IR optics, in particular, for copper mirrors. Higher breakdown thresholds were observed on a-C:H coatings obtained with deposition rates $< 2 \text{ \AA/s}$. Such coatings have the depths of trap levels not exceeding $\sim 1.5 \text{ eV}$ and by resistivity of $10^7\text{--}10^8 \text{ }\Omega \text{ cm}$ in [58]. The a-C:H layer with the absorption coefficient about $4 \times 10^4 \text{ cm}^{-1}$, and having resistivity in the interval from 10^{10} to $10^{11} \text{ }\Omega \text{ cm}$, and E_T in the interval from 1.25 up to 1.5 eV ensure effective optical isolation of the a-Si:C:H photoconductor in [44]. The intensity of reading out radiation has no influence on photo-addressing of the a-Si:C:H. The a-C:H films absorbing in the visible region were employed as a light-blocking layer in the optically addressed spatial light modulators operating in the reflective mode with a-Si:C:H photosensor. It is allowed to decide the problem of optical decoupling of the write and read light signals in [59–61]. The a-C:H films that are transparent in the visible spectral range, with $n < 1.7$ and high resistivity ($\sim 10^{13} \text{ }\Omega \text{ cm}$), can arbitrarily be referred to as polymer-like, which were used as orienting layers for liquid crystals. The orienting layers were obtained from liquid and gaseous hydrocarbons at low temperatures in [62].

7. Conclusion

Results of studies on the preparation of the a-C:H films by plasma-activated CVD in various hydrocarbon precursors and their structure and optical properties are reviewed. The dependences of the deposition rate of the films obtained by CVD process in a DC glow discharge with the magnetron plasma localized near the anode on the voltage, relative content of an inert gas in the mixture with a hydrocarbon, were discussed. Knowing them, one can control the process of condensation. One can vary the refractive index of a-C:H films in the interval 2.35–1.55 and modify their structure and properties from diamond-like carbon to polymer by increasing the deposition rate and the choice of the appropriate hydrocarbon precursor. Identifying the a-C:H film as a diamond-like or polymer-like film can use their vibration spectra, since they have specific features. A characteristic feature of the IR spectra of the diamond-like films is the presence of a band at $\sim 1250 \text{ cm}^{-1}$ due to the stretching vibrations of the C–C bonds in four-functional branching points of the structure. The spectra of polymer-like films show strong absorption bands due to the stretching and bending vibrations of CH groups, as well as of carbonyl and hydroxyl groups. The integrated intensity of the band of CH vibrations peaked at $\sim 2900 \text{ cm}^{-1}$ decrease exponentially by an order of magnitude with an increase in refractive indices from 1.55 to 2.4. Nanostructure of the a-C:H films can characterize using the absorption spectra in the visible region and the Raman scattering. Absorption in the range 400–600 nm is caused by $\pi\text{--}\pi^*$ transitions in polyene chains, while the absorption in the range 600–800 nm is related to similar transitions in more complex π -bond combinations, including polycyclic aromatic groups. A conductivity a-CH films increase with decreasing a width of the optical gap. Diamond-like films can be used as an optical antireflection coating for infrared optical elements, and light-blocking layers in the visible spectral region. Transparent in the visible region polymer-like films can be used as alignment layer in LC devices due to their surface properties. A

wide range of optical properties of the film holds great promise for application in different optical devices.

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