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PLASMA-CHEMICAL DEPOSITION OF ANTI-REFLECTION AND PROTECTIVE COATING FOR INFRARED OPTICS

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The films of amorphous hydrogenated carbon doped with Si *and* O *were deposited onto the sample of crystalline silicon by method of plasma-chemical deposition in the mix of polyphenyl methylsiloxane vapors and argon. Physico-mechanical and optical properties of films were examined for their use as anti-reflection and protective coatings in infrared optics devices. Film transparency in the wavelength range of 2.5–8 μm was measured by method of infrared spectroscopy with a Fourier transform. The structure and composition of films were studied by methods of Raman and X-ray photoelectron spectroscopy. Hardness and other mechanical properties of films were determined by nanoindentation. It was shown that the double-sided deposition of a-*C:H:SiO_x *films onto* Si *plates allows increasing their integrated transmission in the wavelength region of 3–5 μm from 50 to 87%. The films possess excellent mechanical characteristics, thermal stability in the temperature range from room temperature to 500°C, and resistance to aqueous solutions of salt.*

Keywords: anti-reflection coatings, protective coatings, infrared optics, plasma-chemical synthesis.

INTRODUCTION

Films of amorphous hydrogenated carbon (a-C:H) are considered as promising protective anti-reflection coatings for the optics of medium (3–5 μm) infrared range [1]. Fluorides (BaF_2, ThF_4, PbF_2) and chalcogenides that are often used as multilayer coatings on optical infrared materials have low adhesion and mechanical strength [2]. Unlike them, a-C:H films have high resistance to salts, acids, alkali, and most organic solvents. High mechanical hardness and low friction coefficient render these films resilient to abrasion. Furthermore, a-C:H films have very good adhesion to Ge and Si, which makes it possible to use them on outer surfaces of silicon and germanium optics of thermographic cameras that are used in military equipment and/or operate under extreme climate conditions. Such films protect outer optical surfaces from the abrasive impact of dust particles in the air, from seawater and salt, high humidity etc. Amorphous hydrogenated carbon is characterized by moderate level of absorption and scattering in the entire infrared range of wavelengths, and its refraction index in the infrared range is close to 1.95.

Potential possibilities of using a-C:H films as anti-reflection and protective coatings were demonstrated in a number of publications. In [3] a-C:H films were deposited on both sides of a Si substrate by method of ion-beam sputtering of graphite in the mix of Ar and CH_4. It was shown that the films that have hardness of around 15–16 GPa allow increasing the average value of transmission coefficient of the Si substrate to 95.1% in the range of 3.5–5 μm. a-C:H films deposited on both sides of a Si substrate by method of radio frequency plasma-enhanced chemical vapor

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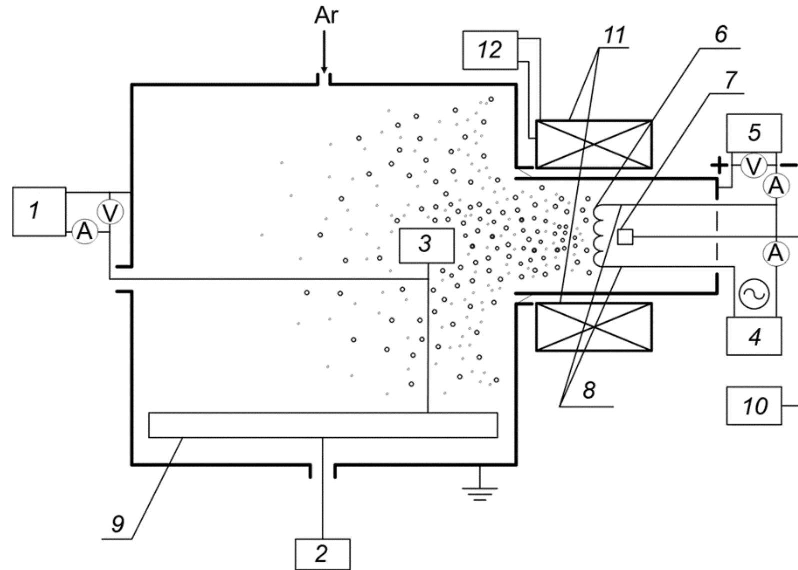

Fig. 1. Layout of the experimental unit for deposition of a-C:H:SiO$_x$ films: *1* – power source of the substrate voltage bias, *2* – table rotation motor, *3* – substrate holder, *4* – power source of the heating wire, *5* – power source of the discharge, *6* – heated tungsten cathode, *7* – source of PPMS vapors, *8* – copper holder electrodes, *9* – rotary table, *10* – pump for PPMS, *11* – electromagnetic coil, *12* – power source of the coil.

deposition (RF-PECVD) in the acetylene atmosphere demonstrated the increase in maximum transmission of Si to 89% in the wavelength range of 3–5 μm [4]. a-C:H films deposited by the same method on both sides of a Ge substrate allowed increasing maximum transparency of Ge to 91% in the wavelength range of 3–6 μm [5]. Transparency of Ge samples with a single-sided protective a-C:H coating with hardness of 20 GPa reached 65–67% in the wavelength range of 4.5– 6 μm, while transparency of the initial substrate was 51% [6].

Nevertheless, many sources report bad adhesion of a-C:H films due to strong internal stresses that emerge in them during deposition [7]. One can reduce internal stresses and increase thermal stability of a-C:H films to 500°C by doping them with silicon and oxygen [8, 9]. In terms of mechanical and tribological properties, a-C:H:SiO$_x$ films are on a par with diamond-like carbon films, their hardness is 10–20 GPa, wear rate does not exceed 10^{-5} mm^3/(N·m), and friction coefficient is in the range from 0.02 to 0.2. Doping of a-C:H films is easily done in the course of plasma-chemical synthesis by injecting the doping component into the plasma [10]. Various siloxanes, silazanes and silanes are used as such components.

Optical properties of a-C:H:SiO$_x$ films in the visible wavelength range are examined in publications [11, 12], the authors of which showed that they possess great potential for use as anti-reflection coatings for silicon-based solar panels. However, to our knowledge, there has never been any research on optical properties of a-C:H:SiO$_x$ films in the infrared wavelength range. That is why the goal of this paper was to study the anti-reflection and protective properties of a-C:H:SiO$_x$ films on Si substrates in the medium infrared range.

EXPERIMENTAL AND ANALYTICAL EQUIPMENT

Experiments on deposition of a-C:H:SiO$_x$ films were carried out using the vacuum unit, the layout of which is presented in Fig. 1. Substrates were plates of high-resistance optical silicon grown by method of float zone melting; their thickness was (350 ± 20) μm. The plates have *n*-type conductivity, double-sided surface polishing, crystal orientation (100), specific electrical resistance of (630±10) Ohm·cm. Before loading into the vacuum chamber, they

were treated in an ultrasonic bath for 5 min, the bath was first filled with isopropyl alcohol and then with chemically pure acetone and distilled water. Right before depositing the a-C:H:SiO_x film, the surface of substrates was cleaned in the argon plasma for 10 minutes. In this case the pressure of argon was 0.3 Pa, magnetic field in the substrate area was 3 G. Discharge voltage and current were (100 ± 5) V and (11 ± 0.5) A respectively. Bipolar pulse voltage bias was applied to the substrates, with a negative pulse amplitude of (1000 ± 50) V, pulse repetition rate of 100 kHz and filling factor of 60%.

Film deposition was done in the mix of argon and polyphenyl methylsiloxane vapors (PPMS, chemical formula – $((CH_3)_3SiO(CH_3C_6H_5SiO)_3Si(CH_3)_3)$). Working pressure of the mix was 0.1 Pa at PPMS consumption of ~100 μl/min. Distance between the plasma generator and the substrate was 100 mm, and magnetic field in the substrate area was 3 G. Heating current was at the level of (50 ± 2) A. Discharge voltage was (140 ± 5) V at discharge current of (5 ± 0.5) A. During the film deposition, the amplitude of the negative pulse of bipolar voltage bias was (500 ± 25) V.

Hardness *H* and elasticity modulus *E* of the produced samples were measured by the Oliver–Pharr method [13] using the Nanotest 600 nanoindenter at the load of 20 mN. Ten hardness measurements were performed with this load, and then the average value was calculated. In order to measure the transmission of samples in the infrared wavelength region, the Nicolet 5700 infrared Fourier spectrometer was used. It registers spectra in the range of 2.5–25 μm. Raman spectra were measured using the Centaur U HR complex (at the laser excitation wavelength of 532 nm) in the range of 800–1800 cm^{-1} with spectral resolution of 1.5 cm^{-1}. Surface morphology of the produced samples was examined using the Solver P47 atomic force microscope (AFM) in the semi-contact mode. Elemental composition of the produced a-C:H:SiO_x films was examined by method of X-ray photoelectron spectroscopy (XPS) on the spectrometer manufactured by SPECS Surface Nano Analysis GmbH. Monochromated radiation AlK_α ($h\nu$ = 1486.74 eV) was used to record the spectra. Micro-Scratch Tester MST-S-AX-0000 was used to measure the adhesive strength of the film. This method relies on identifying the critical load on the indenter at the moment of film destruction/exfoliation in the course of controlled scratching using a diamond indenter with a curvature radius of 100 μm. Optical images of the sample surfaces were captured using the μVizo-MET-221 optical microscope. Ellipse 1891 SAG spectral ellipsometry complex operating in the wavelength range of 350–1000 nm with resolution of 2 nm was used to examine the optical parameters, such as refraction index and extinction coefficient.

RESULTS AND DISCUSSION

Thin films of a certain thickness and with a known refraction index are used to increase the transmission coefficient of optical elements in the visible or infrared wavelength region. The thickness of anti-reflection coatings and the wavelength are linked by the following ratio:

$$d = \lambda/4 \cdot n, \tag{1}$$

where *d* is the thickness of anti-reflection layer, λ is the wavelength to which the minimum of reflectivity must correspond, and *n* is the refraction index of anti-reflection layer.

Values of refraction index *n* and extinction coefficient (*k*) measured using the ellipsometry method in the wavelength range from 350 to 1050 nm are shown in Fig. 2.

In the visible region of the spectrum, refraction index is in the range from 2 to 2.27. In the near infrared region it goes down to 1.75 at the wavelength of 1050 nm. These values conform well with the results of [14], where refraction index of a-C:H:SiO_x films, depending on the value of high-frequency voltage of substrate bias, was in the range of 1.6–2.1 at the wavelength of 1050 nm. Extinction coefficient of the a-C:H:SiO_x film in the near infrared region is low, as in the case of a-C:H films [3], which is of great practical importance for the production of infrared coatings.

In order to increase the transmission in the medium infrared wavelength range, the minimum of reflectivity must correspond to the wavelength ~4 μm, i.e. when refraction index of the anti-reflection layer is ~1.75, its thickness must be 570 nm. Thereafter, films with thickness of (500±50) nm were deposited onto the Si plates.

Fig. 3 presents the transmission spectra in the infrared region of wavelengths (2.5–8 μm) of the initial silicon plate, as well as the plate with single-sided and double-sided deposition of the anti-reflection a-C:H:SiO_x film. Single-

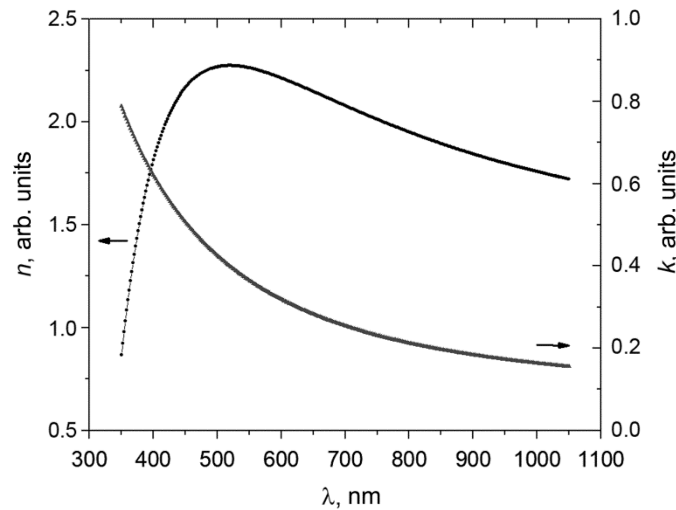

Fig. 2. Spectral dependence of refraction index and extinction coefficient of the a-C:H:SiO_x film.

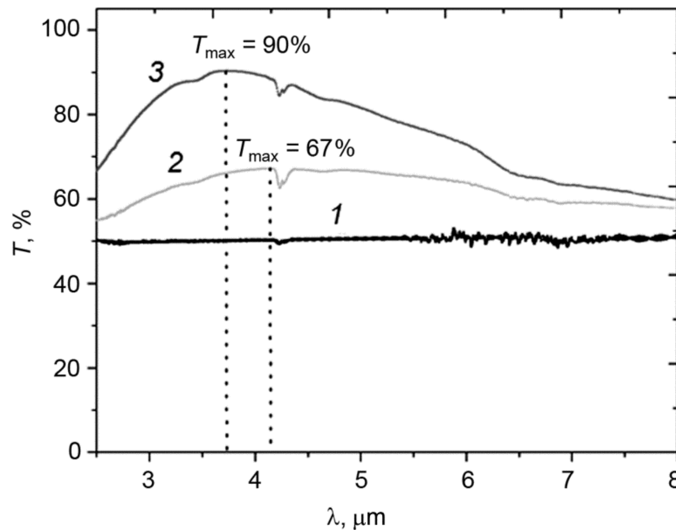

Fig. 3. Transmission spectra in the infrared region of wavelengths of the initial Si substrate (curve *1*), substrate with single-sided deposition of the a-C:H:SiO_x film (curve *2*), and substrate with double-sided deposition of the a-C:H:SiO_x film (curve *3*).

sided deposition of the a-C:H:SiO_x film ensures the increase in integrated transmission in the wavelength region of 3–5 μm from 50 to 65.5% with transmission maximum at the wavelength of 4.1 μm. Double-sided film deposition increases the integrated transmission to 87% with transmission maximum at the wavelength of 3.8 μm. Therefore, a-C:H:SiO_x films are on a par with a-C:H films in terms of their optical characteristics in the medium infrared range of wavelengths.

Samples with double-sided deposition of the a-C:H:SiO_x film were tested for thermal stability. For that, they were annealed in the air for 2 hours at 250 and 500°C. Fig. 4 presents the change in transmission spectra of the produced samples in the wavelength region of 2.5–8 μm after annealing in the air. When the temperature increases, there is a small shift in transmission maximum to the region of smaller wavelengths. This means that the optical

TABLE 1. Mechanical and Elastoplastic Characteristics of the Silicon-Based a-C:H:SiO_x Film

H, GPa	E, GPa	H/E	H^3/E^2, MPa	W_e,%
18±2	140±10	0.13±0.01	325±25	78

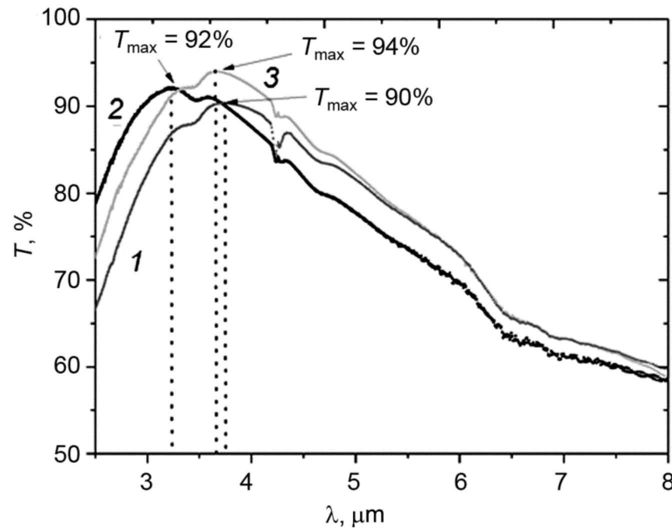

Fig. 4. Transmission spectra in the infrared wavelength region of Si samples with double-sided deposition of the a-C:H:SiO_x film: curve *1* – without annealing, curve *2* – after annealing at 250°C, curve *3* – after annealing at 500°C.

thickness of the film goes down. Nevertheless, integrated transmission in the range of 3–5 μm does not go down and equals 86.8% (without annealing), 86.3% (after annealing at 250°C) and 89.4% (after annealing at 500°C).

The authors of [15] studied thermal stability of a-C:H:SiO_x films annealed in the air at the temperature from 200 to 600°C. The impact of thermal treatment was assessed on the basis of change in the Raman spectra, hardness and wear rate of the films. It was shown that the indicated changes in a-C:H:SiO_x films begin at 400°C, which is 100°C higher than for the amorphous carbon films. Yang and co-authors explain this by the presence of Si–O bonds in the film [16].

One can notice the absorption peaks at the wavelength of 3400 and 4300 nm on the spectra (Fig. 3 and 4). The first peak belongs to sp^3 C–H_n bonds [17]. The second peak is caused by valence vibrations of CO_2 molecules formed as a result of carbon atom oxidation by atmospheric oxygen [18].

A protective coating must have higher hardness than the substrate (optical element). When silicon is used as an optical material, hardness of the protective film must be more than 5–11 GPa. In order to increase resistance to elastic deformation of destruction and reduce plastic deformation, the material of protective coating ought to possess high hardness combined with low elastic modulus. High hardness of the film guarantees resistance to scratching and abrasive wear, and low elastic modulus ensures high resistance to plastic deformation. The hardness-to-elastic modulus ratio H/E, also referred to as plasticity index, is used for the comparative quantitative assessment of resistance of the film material to elastic deformation of destruction. Parameter H^3/E^2 is used to assess the resistance to plastic deformation. Parameter of elastic recovery W_e is used as a parameter characterizing the strength of the surface layer associated with elastic recovery of properties during nanoindentation. Research demonstrated that, in addition to the bleaching effect, a-C:H:SiO_x films also have good protective properties, i.e. high hardness (H = 18 GPa), high values of plasticity index (H/E = 0.13) and resistance to plastic deformation (H^3/E^2 = 325 MPa) (Table 1). Value W_e equals 78%, which corresponds to adhesive and hard a-C:H coatings [1].

TABLE 2. Results of the Raman Spectrum Analysis for the Silicon-Based a-C:H:SiO_x Film

ω_D, cm^{-1}	Γ_D, cm^{-1}	ω_G, cm^{-1}	Γ_G, cm^{-1}	I_D / I_G
1379	316	1527	156	2.2

Note. Here ω_D is the location of the *D* peak maximum, ω_G is the location of the *G* peak maximum, Γ_D is the full width at the level of half-amplitude of the *D* peak, Γ_G is the full width at the level of half-amplitude of the *G* peak, I_D / I_G is the ratio of *D* and *G* peak surfaces.

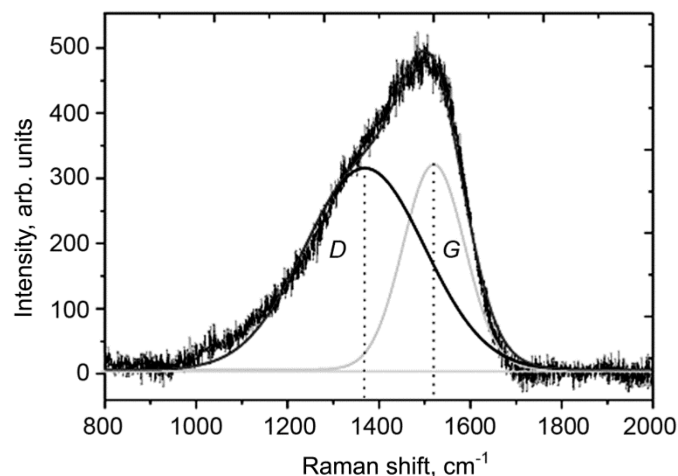

Fig. 5. Raman spectrum of the a-C:H:SiO_x film on the silicon substrate.

The films produced were examined using Raman spectroscopy. It is one of the easiest methods to study the structure of carbon-based films, because it allows qualitatively assessing the ratio of sp^3- and sp^2-hybridized carbon atoms in terms of intensity, position and ratio of *D* and *G* peak surfaces. For diamond-like carbon films, including those that contain silicon and oxygen, one can identify a wide band on the Raman spectra in the region of 1000–1700 cm^{-1} [14]. Splitting the band into Gaussians, one can identify two main peaks – *D* and *G* (Fig. 5). Table 2 presents the results of the Raman spectra analysis for the a-C:H:SiO_x films. The *D* peak maximum is located on the wave number 1379 cm^{-1}, the *G* peak maximum – on the wave number 1527 cm^{-1}, and the ratio of integrated intensities of *D* and *G* peaks I_D / I_G equals 2.2.

The value of I_D / I_G ratio is often used to estimate the number and size of sp^2 clusters in the diamond-like carbon films [19]. For a film entirely consisting of carbon in the state of sp^3 hybridization, I_D / I_G tends toward zero. Results of the Raman spectrum analysis of the a-C:H:SiO_x film (Table 2) presented in this publication turned out to be close to analogous parameters of a-C:H:SiO_x films deposited by method of plasma-assisted chemical vapor deposition [20]. The latter had the I_D / I_G ratio in the range of 1.55–1.9.

Fig. 6 presents the AFM image of surface morphology of the a-C:H:SiO_x film on the silicon substrate. The film surface is rather uniform and smooth. The root-mean-square roughness of the surface R_q on the 5×5 μm area is only 0.35 nm.

Table 3 presents the elemental composition of the a-C:H:SiO_x film produced by method of X-ray photoelectron spectroscopy. According to the data, the films contain 55 at.% C, 13 at.% Si, 24 at.% O, and the ratio C/Si = 4.2. Unfortunately, this method does not allow identifying the hydrogen content in the film. The presence of nitrogen, sodium and tungsten traces in the film can be explained by the impact of residual atmosphere in the course of film deposition, surface contamination during sample transportation and evaporation of incandescent cathode respectively. a-C:H:SiO_x films deposited using an ion source with a closed electron drift had similar composition [21]. When using hexamethyldisiloxane ($(CH_3)_3SiOSi(CH_3)_3$) as a precursor, the films contained 59 at.% C, 13.4 at.% Si, 27.6 at.% O, and the ratio C/Si equaled 4.5.

TABLE 3. Elemental composition of the a-C:H:SiO_x film produced by X-ray photoelectron spectroscopy

C, at.%	Si, at.%	O, at.%	N, at.%	Na, at.%	W, at.%	O/Si	C/Si
55	13	24	4	1	3	1.84	4.2

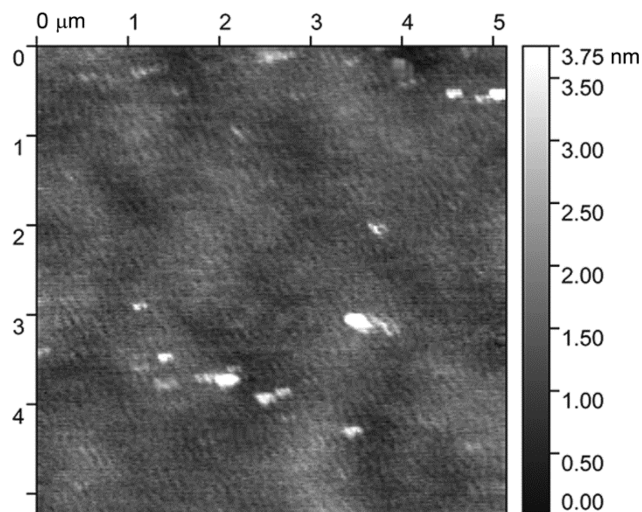

Fig. 6. AFM image of surface morphology of the a-C:H:SiO_x film on the silicon substrate.

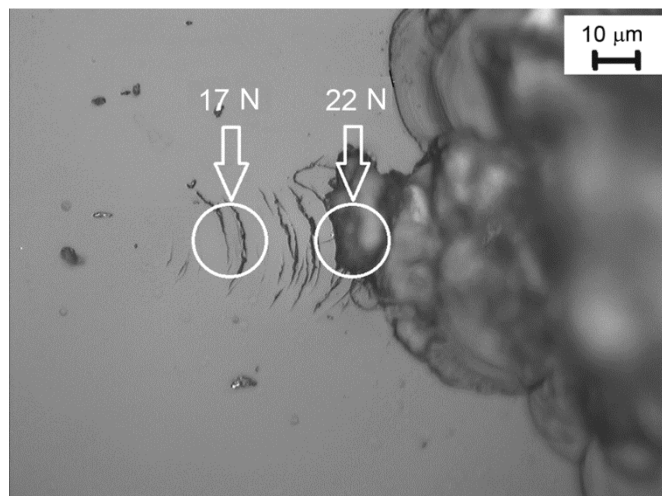

Fig. 7. Image of a scratch on the surface of the a-C:H:SiO_x film captured using the optical microscope.

Adhesive strength of a-C:H:SiO_x films was studied using the scratch test method. Fig. 7 presents an image of a scratch on the a-C:H:SiO_x film surface that was captured using an optical microscope. One can see that microfractures on the surface start forming at the load on indenter of 17 N, and the critical load at which one observes film exfoliation is 22 N. Increase of the load on indenter to 17 N does not lead to the surface destruction, which indicates good adhesive strength of the film with the substrate.

Operation of optical elements with anti-reflection layers in aggressive environments can lead to the destruction and degradation of the film surface. For instance, in the humid sea air the salt settles onto the surface destroying it. The produced coating was tested for compliance with the U.S military specification MIL-C-48497A "Coating, Single or Multilayer, Interference: Durability Requirements for" (08 September 1980). According to par. 4.5.5.2 of this specification, films must not disintegrate when immersed into the sea salt solution (170 g of salt per 4.5 l of water at room temperature) for 24 hours. After being immersed in the sea salt solution, the samples are washed in distilled water and dried, and their surface is examined for defects (exfoliations, cracks etc.). The samples with the a-C:H:SiO_x film were immersed into the sea salt solution for 5 24-hour periods (120 hours). No damage to the film occurred after immersion of the samples into the sea salt solution.

CONCLUSIONS

This paper demonstrates that films of amorphous hydrogenated carbon doped with silicon and oxygen (a-C:H:SiO_x) can be used as protective anti-reflection coatings for silicon-based optical elements in the medium (3–5 μm) infrared wavelength range. The films were deposited by method of plasma-chemical deposition without using any intermediary buffer layers that are necessary for adhesion. It was shown that in the case of double-sided deposition of the 500 nm thick a-C:H:SiO_x film onto the silicon plate, integrated transmission in the wavelength region of 3–5 μm increases from 50 to 87%. The film has good mechanical characteristics (hardness is (18±2) GPa, plasticity index H/E = 0.13, plastic resistance H^3/E^2 = 325 MPa, elastic recovery parameter W_e = 78%) and good adhesion. The scratch test method was used to show that the critical load at which film exfoliation occurs is 22 N. According to the results of atomic force microscopy, the film has low root-mean-square roughness of the surface R_q = 0.35 nm. In addition to good optical and mechanical characteristics, the film has great thermal stability in the air (up to 500°C) and chemical resistance to the sea salt solution. In terms of their combined characteristics, a-C:H:SiO_x films surpass protective anti-reflection coatings on the basis of amorphous hydrogenated carbon and can be used as single-layer broadband anti-reflection coatings in the infrared range.

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