Synthesis of amorphous hydrogenated carbon (a-C:H) films on Germanium by the use of the linear anode layer source

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Abstract. A method for the synthesis of amorphous hydrogenated carbon (a-C:H) films with high adhesion is proposed, based on the implantation of carbon ions into a monocrystalline germanium substrate. The flow of ionized carbon was created by an anode layer ions source in crossed electric and magnetic fields. Propane gas was introduced into the area with an increased electron concentration. The gas flow rate varied from 4.5 to 10 sccm. Ionized fragments of propane, including carbon ions, were accelerated by the electric field and deposited on the substrate. At the same time, ionized carbon penetrated into the surface layer of germanium, creating an interlayer that provides film’s adhesion. The substrate was argon sputtered for several minutes before the deposition. The synthesis of the coating includes two-stage process. At the first stage, the films were deposited by an ion beam with a mean energy of about 1.6 keV for 0.5 to 1 hour to obtain an adhesive interlayer. Then the mean energy of the beam was reduced to 0.3 keV and the deposition continued for 3.5 hours to maintain the hardness of the coatings. The deposition rate was changed from 0.3 to 1.3 Å/sec. Adhesion, the bond between the coating and the substrate is high. There is no detachment of the film while scratching by diamond Berkovich nanoindent with a load of up to 50 mN. The maximum film hardness is 20 GPa. Spectroscopic studies have shown the maximum transmission of germanium with a single side a-C:H coating is 67% at a wavelength of 5 µm, while bare substrate transmission is 51%. The results of the work can be applied in the creation of protective antireflective coatings of optical systems, the creation of medical implants and mechanical devices.

1. Introduction

The use of a-C:H films is actual in various fields from the food industry and medicine to engineering and energy. Of particular interest is the use of a-C:H films as antireflective and protective coatings for IR optical systems [1, 2] and solar cells [3, 4]. Such protective anti-reflective coatings, for example, on germanium, must satisfy the specified properties as high adhesion, spectral transparency, required for optical coatings hardness, corrosion resistance and thermal stability. The combination of such controlled properties is not an easy task. The various synthesis technologies used are generally critical to the actual conditions of film coating production, including thermal conditions of film growth on substrates. As a result, the repeatability and reproducibility of the required characteristics is a constant difficulty of the created technologies.
High adhesion of the coating is the first important characteristic while maintaining other necessary properties. With the growth of carbon films become stronger internal mechanical stresses. With a weak adhesion of the films to the substrate the films detach. The peculiarity lies in the fact that the destruction may occur much later after deposition of the coating. This case is especially dangerous because it is hidden. At the same time, environmental conditions can easily provoke the process of destruction. Among the developing methods the ion beam synthesis of a-C:H films seems to be promising in connection with control of the growth process of the coating as the energy of the ion beam, the flux density and other important process conditions.

There are works in which the synthesis of carbon films from ion beams is carried out at different energies in the range from 40 to 5000 eV [5-8]. As a rule, the formation of an interlayer between the substrate and the film occurs as a result of the interaction of atoms of the surface layer of the substrate and the deposited atoms or molecules. A thin interlayer formed binds the atoms of the substrate and the atoms of the coating. However, internal stresses resulting from, for example, different thermal expansion coefficients and structural features often exceed the forces that bind the coating to the substrate by this thin layer. The result is a detachment of the coating. A possible solution is to increase the bond between the substrate and the deposited material by increasing the interlayer thickness. The way is to implant the deposited atoms, carbon ions, with increased deposition energy into the surface layer of the substrate. In this case, the thickness of the interlayer increases significantly and the adhesion between the substrate atoms and coating atoms increases [2, 9]. The disadvantage of this method is the formation of defects, which is critical for the elements of micro and nanoelectronics. For the formation of protective coatings for optical systems this approach is acceptable.

We propose to use a gridless anode layer ion source, which does not introduce impurities into the coating as a result of spraying the material of grids or cathode nodes. The ion source used makes it possible to vary the energy of the beam ions in a wide range with a mean energy of 0.3 to 1.6 keV. High-energy ions provide adhesive interlayer and low-energy ions are favorable conditions for the growth of the coating.

The aim of the work is to investigate the effect of the adhesive interlayer deposited by the high-energy ion beam on the structure, mechanical and optical properties of a-C:H films on germanium.

2. Experimental technique

2.1. Film deposition
Films were deposited using the anode layer ion source of the ring type. The mean diameter of the ring ion beam is 90 mm. The voltage of the anode did not exceed 5 kV, the maximum mean energy of ions in the beam was about 1.6 keV. The vacuum chamber was pumped to a residual pressure of \(10^{-3}\) Pa. To pump out the condensing components a cryogenic pump with liquid nitrogen with a pumping speed of at least \(10^4\) L/sec was used. After the supply of the precursor gas during the deposition, the pressure in the vacuum volume was about \(5\cdot10^{-3}\) Pa. In the ionization area propane gas (C\(_3\)H\(_8\)) was applied, a flow rate was varied from 1.4 to 4.2 sccm. To clean from adsorbed atoms and molecules the substrate was sputtered by argon ions with a mean energy of 0.3 keV from 5 to 10 min. This treatment contributes to the excitation of surface states of the substrate. This allows improving the chemical bond between the growing film and the substrate, at a starting temperature of 25°C. On the basis of preliminary experiments, the synthesis of coatings was carried out under three modes, which differed primarily in the energy of the deposited ions.

Mode A. The films were deposited from ion beams with a mean energy of 0.3 keV for 2 to 3 hours. The anode voltage was 1 kV and anode current was 20 mA. This method of deposition by a low-energy ion beam does not involve the formation of an interlayer for strong adhesion of the coating.

Mode B. The adhesion interlayer was formed by propene fragment ions with a mean energy of 1.6 keV for 30 min to 1 hour. The anode voltage was 5 kV and anode current was 50–60 mA. This mode of deposition is aimed at the formation of an adhesive interlayer by implantation of high-energy
ions. After that, the average beam energy was reduced to 0.3 keV and the deposition continued for 3.5-4 hours. The anode voltage was 1 kV and anode current was 20 mA. Low-energy stage is aimed at the growth of hard coating. A tungsten electron emitter was used to compensate the space charge of the ion beam.

Mode C. The films were deposited from ion beams with a mean energy of 1.6 keV for two hours. The anode voltage was 5 kV and anode current was 50–60 mA. A tungsten electron emitter was used to compensate the space charge of the ion beam.

2.2. Film characterization
The film thickness was measured by the laser ellipsometer LEF-752 (Russia) at a wavelength of 632 nm in the mode of multi-angle measurements [10]. To calculate the thickness, the model "homogeneous film – substrate" was used, in which the optical substrate constants are known [10, 11].

The coating hardness was determined by nanoindentation technique on the scanning nanoindentor "NanoScan-3D" (Russia). To exclude the influence of the substrate on the result of hardness measurements, the model proposed in [12] was used. The adhesive strength of the films was estimated by the critical load of the film detachment while scratching with a changing load, followed by scanning the surface topography in the atomic force probe mode. As a result of the test, the surface relief before and after scratching and the curve of dependence of the loading force and indenter depth are obtained. The analysis of the obtained information allows to estimate the threshold load of the transition from plastic deformation to crack formation and to measure the thickness of the coating at the point of detachment.

Raman spectra were obtained on the T64000 spectrometer (Horiba Jobin Yvon) with an excitation wavelength of 514.5 nm. The aim was to study the structural features of a-C:H films. The IR spectra were obtained on the IR Fourier spectrometer FT-801 (Russia) in the wavelength range from 2.5 to 16.7 µm for studying the antireflective properties of coatings.

3. Results and discussion

3.1. Adhesion and hardness
Protective films should have a hardness value higher than the hardness of the substrate (optical element). When using germanium as optical material, the hardness of the protective film should be more than 10 GPa. Good adhesion is necessary to extend the life of the protective coating. In order to improve adhesion and preserve the quality of the coating, we used mode B. We assume that at the first stage the ions penetrate the surface layer to a depth of several nanometers due to implantation process [9, 13, 14]. Some of the implanted ions can form a chemical compound of germanium carbide. In the second stage lowered energy of the ions supply efficient synthesis of a-C:H coating. This ion energy is sufficient to form C-C bond the deposited material to the adhesive interlayer.

The adhesion of a-C:H films on germanium is high. The films with the adhesive interlayer did not detach up to maximum scratching load of 50 mN. Moreover, the destruction of the film wasn’t observed for more than two years while films stored in room conditions. The described method gave good values of hardness up to 20 GPa when the deposition of the adhesive interlayer took 35 min and up to 15 GPa when the interlayer was deposited during 60 min.

The deposition from high-energy ion beam (a mean value is 1.6 keV) at mode C provides good adhesion and high synthesis rate up to 1.1-1.3 Å/sec. However, the hardness of the coating in this case does not exceed the hardness of germanium 10 GPa.

When ions are deposited on germanium with an energy of 0.3 keV without an adhesive interlayer (mode A), the coating hardness lies in the range from 13.5 to 16 GPa. Adhesion of such films is worse, the detachment occurs at the scratching load of 10 mN. Coating growth rate was 0.3 Å/sec.
3.2. Optical properties
Figure 1a presents IR transmission spectra of a-C:H films in germanium. Maximum value of interference is about 65-67% observed in the wavelength range of 4.5–6 µm. In this case film thickness lies in the range from 600 to 750 nm (specimens B1 and A1).

![Figure 1](image1.png)

**Figure 1.** (a) IR transmission spectra of germanium with single-side antireflective protective a-C:H coatings. The thickness of the films is 600 nm (B1), 750 nm (A1) and 950 nm (C1). (b) IR absorption spectra of a-C: H films on germanium.

![Figure 2](image2.png)

**Figure 2.** Deconvolution of Raman spectra of films obtained in the modes (a) A, (b) B and (C) to D and G peaks; (d) comparison of the spectra of samples A, B and C.
For comparison, in figure 1a a transmittance spectrum of bare germanium is shown. IR absorption spectra (figure 1b) show weak absorption bands for the stretching vibrations of CH- groups in the region 3100-2700 cm$^{-1}$. This confirms the presence of hydrogen in the films due to the use of propane as precursor.

3.3. Raman spectroscopy

To analyze the dependence of the film structure on the energy of the deposited ions in the modes A, B and C Raman spectroscopy was chosen. Spectra were deconvoluted into two Gaussian peaks (figure 2a-c), corresponding to D and G vibration modes [15, 16]. For the purpose of comparison in figure 2d all spectra are shown. Comparison of Raman spectra of films (figure 2) obtained by the use of the modes A, B and C shows that the positions of D and G peaks are shifted to the high wavenumber region, the intensity and HWHM of D peak increases and of G peak it decreases. The ratio of the integral intensities of the peaks $I_D/I_G$ increases with the rise of energy of the deposited particles. This may be due to an increase in the fraction of sp$^2$ hybridized carbon atoms and, as a consequence, with the graphitization of films. This explains the decrease in the hardness of the films with increasing energy of the ion beam. The temperature increase of the growth surface of the film during the synthesis process leads to the increase of the concentration of sp$^2$ carbon hybridization and its ordering [17]. The reduction of the sp$^3$ hybridized carbon atoms concentration in the film (C-C bond) caused by local overheating of the growth surface leads to a decrease in the hardness of the coating.

4. Conclusions

Amorphous hydrogenated carbon films with high adhesion are obtained on single crystal germanium. It was found that the formation of the adhesion interlayer and film occurs due to the implantation and deposition of pure carbon ions and propene hydrocarbon ionized fragments formed in the ion source plasma with a mean energy of 1.6 keV. It provides to the increase of the coating adhesive strength. The best coating hardness 20 GPa was achieved in two-stage deposition process. The adhesion interlayer was synthesized by an ion beam with a mean energy of 1.6 keV. Then the deposition continued with a mean energy of 0.3 eV. Transmission of germanium with a single-side protective antireflective a–C:H coating reaches 65–67% in the wavelength range of 4.5–6 µm. The results are applicable in the creation of optical devices and IR systems.

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