Plasma treatment of $Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) single crystals

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The antireflection effect of a diamond-like carbon (DLC) film in the a-C:H:N/CdZnTe optical system in the 2–16 μm range was determined from the optical transmission spectra. An investigation of the plasma treatment effect on the surface of $Cd_{1-x}Zn_xTe$ ($x \sim$ 0.04) substrate prior to DLC films fabrication was carried out. The irradiation of semiconductor substrate with argon plasma was found to be optimal for improving its optical transmittance. Analysis of the absorption spectra of DLC films obtained by FTIR-spectrometry technique into the interval 1000–3000 cm^{-1} has been done. Peaks corresponded to deformation and stretching vibrations of C-H bonds as well as C–C and C=O bonds were observed.

Изучена роль ионно-плазменной обработки монокристаллов $Cd_{1-x}Zn_xTe$ ($x \sim 0{,}04$) при нанесении просветляющего покрытия — алмазоподобной углеродной пленки a-C:H:N. Обработка проводилась плазмой аргона, азота и водорода в едином вакуумном процессе перед нанесением покрытия. Контроль оптических свойств системы a-C:H:N/Cd$_{1-x}$Zn$_x$Te показал, что наиболее эффективной в плане повышения просветления является обработка плазмой аргона. Проведен анализ спектров поглощения системы a-C:H:N/Cd$_{1-x}$Zn$_x$Te, позволивший установить присутствие полос, соответствующих валентным и деформационным колебаниям C–H связей, а также C–C и C=O связям, наличие которых необходимо учитывать при конструировании и синтезе изучаемых оптических покрытий.

1. Introduction

Single crystals of $Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) are widely used as a substrate material in infrared (IR) photoelectronics, in particular, in cooled back-side illuminated optical detectors for the (3–5) μm and (8–12) μm spectral range based on $Cd_xHg_{1-x}Te$ epilayers [1]. Cadmium-zinc-tellurium immersion lenses have been also successfully used to improve the parameters of uncooled IR photodetectors [2]. In all cases, the performance of a detector is determined by the optical properties of the entire multilayer semiconductor structure.

As is known, the reflection losses of incident radiation can be reduced using antireflection coatings [3]. For semiconductor photodetectors, the optimum coating must combine the antireflection properties with the ability to passivate the detector surface so as to increase the stability, decrease the recombination losses and leak currents, etc. We believe that a promising technical solution is offered by diamond-like carbon (DLC) films. Such films have been successfully applied as passivating, protecting, and antireflection coatings in solar cells based on single- and polycrystalline silicon, being competitive in this respect with the traditional antireflection coatings [4]. The expediency of using DLC films as antireflection coatings in IR photodetectors is determined primarily by the advantageous features of their deposition (low substrate temperature, simplicity and low cost of the PE-CVD (Plasma Enhanced Chemical Vapor Deposition) technology), as well as by the possibil-
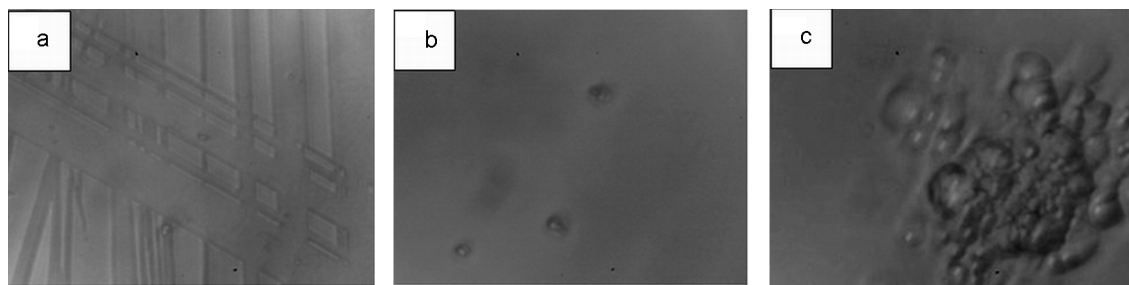
Fig. 1. Optical micrographs of the surface of $Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) substrates exposed to the plasma using various gases: H_2 (a), N_2 (b), Ar (c). Optical field (240×200) μm.

ity to control the optical and mechanical properties of the films by varying the deposition conditions.

Before, we have studied the antireflection properties of a-C:H:N films obtained by plasma-chemical deposition on $Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) single crystals [5]. It was found that the plasma-stimulated deposition of the dielectric coating on the semiconductor substrate provides the formation of a complex optical system with two transition layers and the optical transmittance amounting 80 %. It is necessary to point out that the preparation of the CdZnTe substrate surface to deposition of the antireflection coating consists of a sequence of operations including preliminary plasma treatment which is used for surface cleaning. At the same time, this operation may result in violation of the stoichiometry and degradation of the properties of a near-surface layer of the substrate [6−10]. Physical damage is primarily induced by high-energy ion bombardment during etching. Indeed, a change in the regime (power, duration) of CdZnTe treatment in an oxygen plasma may result in the surface degradation (rather than to its passivation) and to a change in the resistance of a near-surface layer [6].

Thus, in this study, the effect of the plasma treatment of $Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) single crystals prior to plasma-chemical deposition of antireflection coating is investigated. In addition, the identification of transition layers is discussed.

2. Samples and measurement technique

During the unified technological process, the $Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) single crystals were treated by Ar, H_2 and N_2 plasma and then DLC films were deposited onto semiconductor substrate. The effectiveness of the antireflection effect of a DLC film in the a-C:H:N/CdZnTe optical system was determined with IR spectroscopy method from the optical transmission spectra in the 2−16 μm range. Optical parameters of the a-C:H:N/CdZnTe was studied by ellipsometry using a laser ($\lambda = 632.8$ nm) photoelectric compensation zero ellipsometer (LEF 3M-1, Russia).

Prior to DLC deposition, the $Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) substrates of 1.5 mm thickness were cut into (10 mm × 10 mm) squares and were treated for 5 min in high-frequency (13.56 MHz) discharge Ar, H_2 and N_2 plasma at a pressure of 25 Pa and at a discharge power of $W = 175$ W. Then, the DLC (a-C:H:N) films were deposited for 40 min at a discharge power of $W = 250$ W. The discharge was initiated in an Ar:CH_4:H_2:N_2 (1:3:5:9) gas mixture at a total pressure of 100 Pa. The control Si plate was treated simultaneously.

3. Results

In Fig. 1, the optical micrographs of the $Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) samples surface exposed to the plasma action using various gases are shown. The Ar plasma clearly induced a maximal surface modification as well as caused around 200 nm thick damaged layers in comparison to those of a damaged-area thickness of around 10 nm or less by N_2 and H_2 plasmas (see Table). Furthermore, a critical effect of plasma-induced damage is the change in the optical

Table. Optical characteristics of the $Cd_{1-x}Zn_xTe$ substrate exposed to the plasma action using various gases: k is an extinction coefficient, n is a refractive index and d is a damaged-area thickness

	k	n	d, nm
Initial surface	0.2	2.55	−
Processed by N_2	0.29	3.02	8.63
Processed by Ar	0.04	3.2	210
Processed by H_2	0.08	3.2	10

characteristics of semiconductor substrate. The disturbed layer formed due to nitrogen plasma treatment has optical parameters that are most close to the parameters of cadmium telluride ($n = 2.98$, $k = 0.35$ for $\lambda = 632.8$ nm [11]). At the same time, treatment with argon or hydrogen substantially, by an order of magnitude, decreases the extinction coefficient (from 0.2 to 0.04) in the disturbed layer of samples under study and increases the refractive index (from 2.55 to 3.2). It is also worth noting that these coefficients, as to their value, are close to the optical coefficients of one of the layer ($n = 3.56-3.87$; $k = 0.02$ for $\lambda = 632.8$ nm [5]), which is formed in the course of application of a-C:H:N dielectric coating onto $Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) semiconductor substrate. Thus, we may assume that the nature of formation of this layer is connected exactly with ion-plasma treatment prior to application of the DLC coating onto semiconductor substrate.

The antireflection effect of a DLC film in the a-C:H:N/$Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) optical system pretreated by Ar, N_2 and H_2 plasma was determined from the optical transmission spectra as illustrated in Fig. 2. It was obtained a complex optical system with two transition layers. The transmittance of an uncoated CdZnTe crystal is on the average about $T \sim 55$ %. The application of an a-C:H:N film with a thickness of $d \sim 0.9$ µm increases the transmittance on the average up to about $T \sim 70$ %. The spectral interval of maximum clarification corresponds to a near-IR range (3–6 µm) that coincides with the transparency window of the atmosphere. The transmittance reaches $T \sim 80$ % and oscillations in the transmission spectra is observed for the a-C:H:N/$Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) optical system pretreated with Ar plasma. It should be noted that, after the treatment of substrate with argon plasma, the oscillations of transmission are observed in the region of maximal antireflection of a-C:H:N/CdZnTe system (see inset of the Fig. 2).

Thus, the deposition of a a-C:H:N dielectric film onto a $Cd_{1-x}Zn_xTe$ semiconductor substrate ($x \sim 0.04$) results in the formation of a multilayer system with the optical properties different from those of the initial substrate. At that, the layer nearest to the substrate is formed as a consequence of the plasma treatment of the semiconductor surface. As to antireflection, treatment with argon plasma is the most efficient.
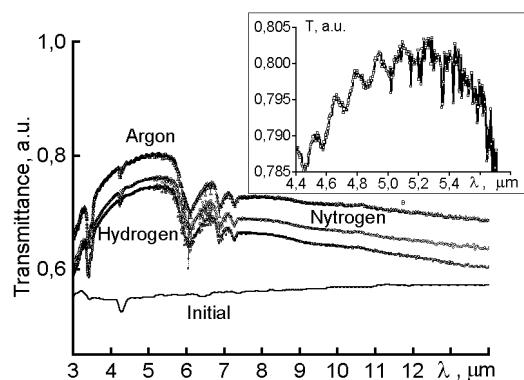

Fig. 2. Optical transmission spectra of a-C:H:N/$Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) structures pretreated by Ar, N_2 and H_2 plasma. Insert: The oscillations of transmission observed for the a-C:H:N/$Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) optical system pretreated by Ar plasma.

However, it is worth noting that, in the case of application of a-C:H:N dielectric films as antireflection coatings for the infrared region, one should take into account the presence of absorption bands characteristic of their vibration spectra. As is seen in Fig. 2, the transmission spectra of a-C:H:N/CdZnTe structure contain regions of absorption, characterized by deformation and stretching vibrations of C–H bonds. A detailed analysis of the infrared absorption spectrum of the synthesized structure has shown also the presence of C–C, C=O and OH bonds.

Spectra of infrared absorption of a-C:H:N/CdZnTe structure were recalculated from the transmission spectra of the sample with regard for the thickness of coating being obtained, the reflection and the antireflection effect. The fraction of incident light reflected from the CdZnTe/air interface was determined using the formula [4]:

$$R = \left(\frac{n_1 - n_0}{n_1 + n_0} \right)^2, \qquad (1)$$

which yielded $R \approx 21-27$ % for the (3–16) µm spectral range. Here $n_1 = 2.7-3.15$ is the refractive index of substrate material, $n_0 = 1$ is the refractive index of air. For the CdZnTe/a-C:H:N/air system, the reflection coefficient can be calculated as follows [4]:

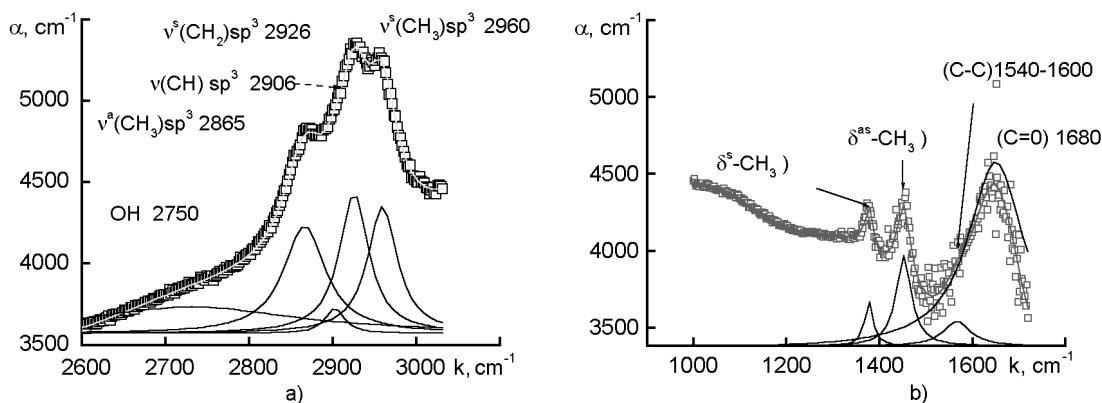$$R = \left(\frac{n_1 n_0 - n_2^2}{n_1 n_0 + n_2^2} \right)^2. \qquad (2)$$

Fig. 3. Spectra of infrared absorption of a-C:H:N/Cd$_{1-x}$Zn$_x$Te ($x \sim 0.04$) structure.

The R value given by this formula is less than 1 % for $n_2 = 1.55{-}1.8$ and increases to 3 % for $n_2 = 1.95$.

In Fig. 3a, the absorption peaks in the range of 2700–3100 cm^{-1} for C–H stretching vibrations are shown. Fig. 3b displays the absorption peaks in the range of 1300–1700 cm^{-1} for C–H deformation vibrations. The broad absorption peak at 2750 cm^{-1} (Fig. 3a) was O–H vibrational mode. The peak positions were obtained from the corresponding Lorentz curves fitted to the experimental ones [12].

Considering the spectrum, one can obtain that the DLC film was mostly composed of sp^3 hybridized bonding and has high bonded hydrogen content. The band of the C–H stretching vibrations includes sp^3 CH$_3$ symmetrical absorption at 2865 cm^{-1}, sp^3 CH absorption at 2902 cm^{-1}, the asymmetrical sp^3 CH$_2$ absorption at 2926 cm^{-1} as well as the asymmetrical sp^3 CH$_3$ absorption at 2960 cm^{-1}. A great occurrence of the CH$_3$ radical in deposited film is evidence of the methyl mechanism of the formation of the one. Methyl radicals included in the film formation are produced as a consequence of dissociation of methane molecules by electron impact. The presence of CH$_2$ and CH groups in the film is produced by the removal of the bonded hydrogen from the film surface: CH$_4 \leftrightarrow$ CH$_3$ + H; CH$_3 \leftrightarrow$ CH$_3^*$; CH$_3^*$ + H$\leftrightarrow$CH$_2^*$ + H$_2$; CH$_2^*$ + H$\leftrightarrow$ CH* + H$_2$ (* — radicals incorporated in the film).

It is established that the optical characteristics of the a-C:H:N films are stable with respect to thermal cycling and ultrasonic treatment [5]. According to [13], the cavitation charging in cryogenic liquid was used for testing the mechanical properties of diamond-like carbon film. It was obtained that at least the first 10–15 min of the cavitation charging, DLC film exhibited negligible surface damage. After about 30 min of treatment, diamond film show significant surface swelling and breaking of the coating continuity. Fig. 4a, b, c show the optical micrographs of the samples irradiated during varying time. It is necessary to point out the local variation of the film color in the interaction region, which can point out changes in its thickness.

4. Conclusion

Thus, the deposition of a dielectric film a-C:H:N onto a semiconductor substrate Cd$_{1-x}$Zn$_x$Te ($x \sim 0.04$) causes the formation of a multilayer system with the layer near-
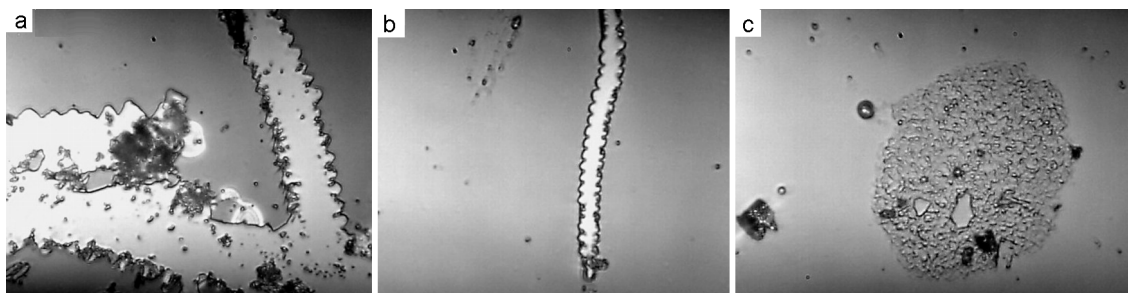

Fig. 4. Optical micrographs of a-C:H:N sample exposed to the acoustic cavitation in liquid nitrogen during: (a) and (b) — 30 min, (c) — 45 min. Optical field (150×180) μm.

est to the substrate is formed due to the plasma treatment of the semiconductor surface. At that, the Ar plasma clearly induced a maximal surface modification and a maximal antireflection effect for the a-C:H:N/Cd$_{1-x}$Zn$_x$Te ($x \sim 0.04$) optical system pretreated by Ar plasma is attained in comparison with those with N$_2$ and H$_2$ plasmas. The spectral interval of maximum clarification (where the transmittance reaches $T \sim 80$ %) corresponds to a near-IR range (3÷6 μm) that coincides with the transparency window of the atmosphere.

Considering the a-C:H:N absorption spectra, one can obtain that the DLC film was mostly composed of sp^3 hybridized bonding of the carbon. We have shown that, due to the presence of absorption bands in the vibration spectra of a-C:H:N, there arise losses, which have to be taken into account in designing and synthesizing optical coatings for detectors of the infrared region of the spectrum.

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Іонно-плазмова обробка монокристалів Cd$_{1-x}$Zn$_x$Te ($x \sim 0.04$)

О.Б.Смірнов

Вивчено роль іонно-плазмової обробки монокристалів Cd$_{1-x}$Zn$_x$Te ($x \sim 0.04$) при нанесенні просвітлюючого покриття — алмазоподібної вуглецевої плівки a-C:H:N. Обробка проводилася у плазмі аргону, азоту та водню в єдиному вакуумному процесі перед нанесенням покриття. Контроль оптичних властивостей системи a-C:H:N/Cd$_{1-x}$Zn$_x$Te показав, що найбільш ефективною для збільшення пропускання є обробка плазмою аргону. Проведений аналіз спектрів поглинання системи a-C:H:N/Cd$_{1-x}$Zn$_x$Te дозволив встановити присутність смуг, що відповідають валентним і деформаційним коливанням C–H зв'язків, а також C–C та C=O зв'язкам, наявність яких необхідно враховувати при конструюванні та синтезі оптичних покриттів, що досліджувалися.