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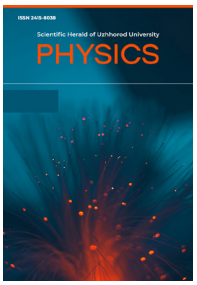

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The influence of implantation of Mg^+ ions and subsequent annealing on the composition, electronic structures, emission and optical properties of CdF_2

Akbarjon Abduvayitov
PhD in Physical and Mathematical Sciences
Tashkent State Technical University named after Islam Karimov
100095, 2 University Str., Tashkent, Uzbekistan
https://orcid.org/0000-0001-6453-6523

Gunel Imanova*
PhD in Physics, Associate Professor
Institute of Radiation Problems, Ministry of Science and Education Republic of Azerbaijan
AZ1143, 9 B. Vahabzadeh Str., Baku, Azerbaijan
UNEC Research Center for Sustainable Development and Creen Economy named after Nizami Ganjavi
AZ1007, 45A Abbas Sahhat Str., Baku, Azerbaijan
https://orcid.org/0000-0003-3275-300X

Dilnoza Tashmukhamedova
Doctor of Physical and Mathematical Sciences, Professor
Tashkent State Technical University named after Islam Karimov
100095, 2 University Str., Tashkent, Uzbekistan
https://orcid.org/0000-0001-5813-7518

Khurshid Boltaev
PhD in Physical and Mathematical Sciences
Tashkent State Technical University named after Islam Karimov
100095, 2 University Str., Tashkent, Uzbekistan
https://orcid.org/0000-0001-6453-6523

Boltakhodja Umirzakov
Doctor of Physical and Mathematical Sciences, Professor
Tashkent State Technical University named after Islam Karimov
100095, 2 University Str., Tashkent, Uzbekistan
https://orcid.org/0000-0002-9815-2111

Abstract

Relevance. In the case of bombardment with Mg metal ions, the changes are accompanied by the introduction of metal atoms and the formation of various types of compounds. Thus, CdF_2 is intensively decomposed into components in the near-surface layer in the process of ion implantation. A small part of these components

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*Corresponding author

can be sprayed from the surface. Due to the high chemical activity, almost all of the liberated fluorine atoms again enter into a chemical bond with both the atoms of the alloying element and the atoms of cadmium. Consequently, three-component compounds are formed in the near-surface layer. Therefore, it is necessary to define the electronic states, band energy, and optical parameters of CdF_2 and $Cd_0.6Mg_0.4F_2$ films.

Purpose. The composition, structure, and properties of CdF_2 implanted with Mg+ ions in combination with thermal and laser annealing for the first time were the research aims.

Methodology. The experimental studies were carried out at a vacuum of at least 10^{-7} Pa using the methods of Auger electron spectroscopy (AES) and ultraviolet photoelectron spectroscopy (UVES). The depth distribution profiles of atoms were determined by the AES method in combination with layer-by-layer etching of the surface with Ar^+ ions with $E_0 = 2-3$ keV.

Results. CdF_2 is intensively decomposed into components in the near-surface layer in the process of ion implantation. Consequently, three-component compounds are formed in the near-surface layer. Band-energy parameters and densities of the state of electrons in the valence band of this film are determined.

Conclusions. The effect of the implantation of Mg+ ions on the composition and electronic structure of single-crystal CdF_2/Si(III) films was studied for the first time. The densities of electronic states, band-energy and optical parameters of CdF_2 and $Cd_0.6Mg_0.4F_2$ films have been determined.

Keywords: atomic distribution profiles; ultrathin layers; band gap; heat treatment; surface layer

Introduction

Among the approaches available to solve problems of increasing the reliability and durability of machine and mechanism parts, cutting tools, and technological equipment, technological methods of surface hardening of structural materials play a key role. Photoelectrocatalytic water part offers a promising approach to change over daylight into economical hydrogen vitality. A careful understanding of the connections between the properties and capacities of photoelectrocatalytic materials plays a pivotal part in the plan and creation of productive photoelectrochemical frameworks for the water part. A study [1] presented the propels within the improvement of efficient photoelectrocatalytic materials. To begin with, the basics included within the photoelectrocatalytic water part are expounded. An important factor in the coating process is surface preparation, which includes, in addition to mechanical cleaning, the bombardment of the substrate surface with an intense stream of low-energy ions. According to studies [2; 3], these films are used for a controlled change in the E_g of dielectrics in certain cases, as well as for obtaining consistent layers at the interface of SIS (semiconductor-insulator-semiconductor) structures in three-dimensional integrated circuits. CdF_2/Si (111) hetero-structures with a CaF_2 buffer layer are of particular interest. The minimum thickness of the CaF_2 buffer layer is 0.9 nm. In this case, Z.A. Tursunmetova *et al.* proved that CaF_2 plays the role of a barrier layer for the chemical reaction between CdF_2 and Si substrates [4].

The study [5] confirmed that single-crystal cadmium fluoride is a solid dielectric that can be converted into a semiconductor by doping with donor impurities and subsequent heating in a reducing atmosphere. CdF_2 and CaF_2 share a common fluorite-type cubic crystal structure with similar lattice parameters, making them suitable for use in superlattices. However, their electronic and optical characteristics exhibit notable distinctions. Despite having a sizable band gap of approximately 8 eV, CdF_2, when appropriately doped and annealed, can exhibit n-type semiconductor properties. Additionally, research by R.C. Palomera *et al.* has shown that CdF_2 can exhibit efficient electroluminescence and, owing to its high density (6.38 g/cm^3) and relatively rapid luminescence decay time, can be employed as a scintillator [6].

In contrast, CaF_2 is an insulator with an exceptionally wide band gap, estimated to be between 11.8 and 12.1 eV, and it finds widespread use in various optical applications, such as resonant tunnelling diodes and quantum cascade lasers. R.B. Hughes-Currie *et al.* suggested that this behaviour can be attributed to the substantial (2.9 eV) discontinuity in the conduction band at the CdF_2-CaF_2 interface, as detected by X-ray photoelectron spectroscopy [7]. This study also delves into laser spectroscopy of Eu_2+ and Eu_3+ ions doped in CaF_2 within the CdF2-CaF_2 matrix and investigates the distribution of defect positions for dopant ions.

The electron beam method occupies a special place among the existing vacuum-plasma deposition methods. The studies [8; 9] noted that the essence of the method is in the kinetic energy of the electron beam being used to evaporate the substance and it converts into thermal energy in the treatment zone.

R. Shendrik & E. Radzhabov noted that it is also important to use these methods in modern micro- and nano-electronics to apply conductive and dielectric layers of different thicknesses [10].

The ion implantation method has been effectively used to obtain nanosized multicomponent structures and layers on the surface and subsurface region of semiconductors and dielectric films [11; 12]. The composition of CdF_2 implanted with Mg+ ions in combination with thermal and laser annealing for the first time was analysed in this study.

Materials and Methods

Well-polished and etched n-type CdF_2 (111) single crystals were used as research objects. The tests were introduced in an ultrahigh vacuum gadget – "EPOS-PVD-DESK-PRO" (Russia), which comprises two compartments. Strengthening, warm oxidation, and particle assault were carried out within the, to begin with compartment. The composition, thickness of state of valence electrons, band-energy parameters, outflow, and optical properties were considered within the moment one. The value of n determined by the ERES method already at small film thicknesses (d ~ 100 Å) differs sharply from n for Si and becomes characteristic of dielectrics. ERES method was applied to determine the inelastic mean free path (IMFP) of electrons, which is of crucial importance for quantitative electron spectroscopy. For this reason, it is highly desirable to verify the reliability of the ERES method for a variety of elements and different experimental geometries. The composition of CdF_2 implanted with Mg^+ ions in combination with thermal and laser annealing, was studied for the first time. Therefore, even at a film thickness of d ~ 600 Å, the refractive index of light almost does not differ from the value of n for a thick film. Based on this, it can be assumed that the penetration depth of photons with hν > 10 eV for CdF_2 lies in the range of 600-800 Å.

Most things were carried out in a vacuum of at the slightest 10-7 Dad utilizing the strategies of Wood screw electron spectroscopy (AES) and bright photoelectron spectroscopy (UVES). The profundity dissemination profiles of particles are decided by the AES strategy in combination with layer-by-layer carving of the surface with Ar^+ particles with E_0 = 2-3 keV. Before ion implantation, CdF_2 is degassed by heating to T = 900 K for 3 hours in combination with soft etching of the surface with Ar^+ ions at a vacuum of 10^{-7} Pa. Implantation of Mg+ ions are carried out with E_0 = 1 keV doses D = $8 \cdot 10^{16}$ cm^{-2}. For comparison with the beginning of implantation, the conduction of Ar^+ ions with different energies at D = Dn. The optical method, SERE method and the Auger electron spectroscopy method were used to determine the values of n for Si with a CdF_2 surface film of different thicknesses.

Results and Discussion

The crystal lattice of CdF_2 has a cubic fluorite-type structure and a lattice constant close to that of silicon. H.M. Mahmudov *et al.* noted it has been established that the MBE growth of the CdF_2/Si (111) film at the initial stage proceeds according to the Stranski-Krastanov mechanism, and then the growth occurs according to the Frank-Van der Merve mechanism [13]. The (1×1) CdF_2(111) surface is formed after high-temperature (T = 1120 K) heating of films with d ≥ 150 ÷ 200 Å [14].

As follows from Table 1, in the case of thin CdF_2 films, n is strongly affected by the silicon substrate. The role of the substrate is especially noticeable in the visible and infrared regions of light, i.e., in the region where the energy of electromagnetic radiation (ħν < 2 eV) is much less than the band gap of the CdF_2 film (E_g ~ 7.5-8 eV). In the indicated energy range of radiation, the dielectric film turns out to be almost transparent. Therefore, light, penetrating deep into the sample, mainly interacts with silicon atoms. Some decrease in n in the case of thick films is apparently due to the presence of impurity atoms in the bulk of the CdF_2 film. In the region of ultraviolet radiation, especially at hν > 10.2 eV (<1200 Å), a strong absorption of light by the film occurs. Therefore, even at a film thickness of d ~ 600 Å, the refractive index of light almost does not differ from the value of n for a thick film. Based on this, it can be assumed that the penetration depth of photons with hν > 10 eV for CdF_2 lies in the range of 600-800 Å.

Table 1. The values of the refractive index n for CdF_2 films

Method	Film thickness d, Å							
	0 (Si)	100	200	400	600	800	1200	2000
Optic: =1050 Å (UF)	3.5	3.0	2.2	1.8	1.6	1.6	1.55	1.55
=6700 Å (R)	3.4	3.2	3.2	-	3.2	3.0	3.0	3.0
=10640 Å (IR)	3.1	3.1	3.0	-	-	-	3.0	2.9
SERE	3.35	1.7	1.48	1.52	-	1.43	-	1.45

Source: compiled by the authors

A slight difference between n of a film with a thickness of d ~ 100 Å and n for a thick film is probably caused not only by the contribution of the matrix to the excitation of interband transitions and plasma oscillations but also by the imperfection of the stoichiometric composition and crystal structure of

the film due to the influence of the substrate. In the case of thick films, the values of n obtained by the elastically reflected electron spectroscopy (ERES) method and by the optical method in the ultraviolet region are close.

During the bombardment of CdF_2 with ions of inert gases Ar+, CdF_2 is decomposed into components, the surface layers are disordered, the diffusion of atoms, the evaporation of atoms from the surface, etc. In the case of bombardment with Mg metal ions, these changes are accompanied by the introduction of metal atoms and the formation of various types of compounds. To clarify this, the dependence of I_F – (fluorine intensity) on the depth h of a CdF_2 film bombarded with Ar^+ ions with different energies at $D = D_s$ (Fig. 1), where D_s is the ion saturation dose, was analysed. Figure 1 shows that at $E_0 = 0.5$ keV, the intensity of the IF peak sharply (by a factor of ~ 4) decreases and it practically does not change up to a depth of h = 20-25 Å, which corresponds to the projected range of Ar^+ ions. It is also confirmed by the data presented in the work [15].

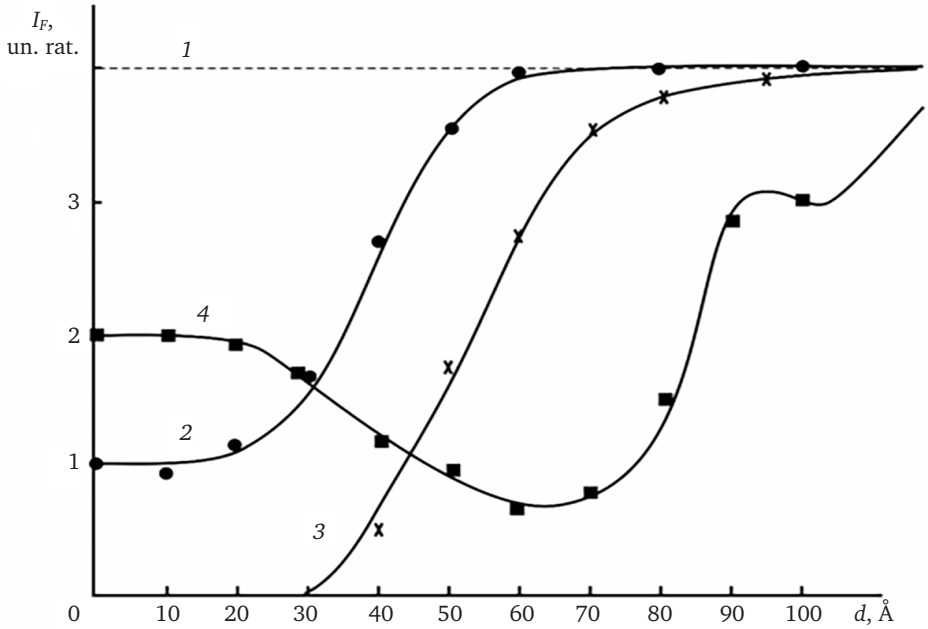

Figure 1. Depth distribution profiles of F atoms of CdF_2 bombarded with Ar^+ ions at $D = D_H$ with different energies E_0, keV
Note: 1 – undoped CdF_2, 2 – 0.5; 3 – 1; 4 – 5, D_H - saturation dose
Source: compiled by the authors

All F atoms in the form of F_2 molecules evaporate from these layers. In the range d ≈ 25 – 50 Å, the IF concentration increases and, starting from h ≈ 50 Å, the stoichiometric composition of CdF_2 is completely established. However, further studies showed that these CdF_2 layers down to a depth of h ≈ 130 – 150 Å were strongly disordered. In the case of $E_0 = 1$ keV, the surface layers of CdF_2 up to a depth of h = 30 – 40 Å are completely decomposed into components and almost all F atoms evaporate from these layers; an amorphous Cd film with a thickness of d = 30 – 40 Å is formed on the surface (curve 3, Fig. 1). When CdF_2 is bombarded with $E_0 = 5$ keV, the highest rate of decomposition occurs at the depth of the projected range of Ar^+ ions (h ≈ 60 – 70 Å). Most of the fluorine atoms escape into the vacuum, while the other part diffuses deep into the target; therefore, the concentration of F at a depth h = 80 – 100 Å increases significantly. A different picture is observed during the implantation of Mg^+ ions in CdF_2.

Figure 2 shows the Auger spectra of a well-cleaned CdF_2 surface before and after implantation of Mg^+ ions with $E_0 = 1$ keV at $D = D_n = 8 \cdot 10^{16}$ cm^{-2}. It can be seen that after implantation of ions, the intensity of Cd and F ions decreases up to 2-3 times and peaks characteristic of Mg appear. With this ion-doped layer, compounds of the Mg-F and Mg-Cd-F types are predominantly formed. Most of the Mg atoms do not enter into a chemical bond and accumulate on the surface. Auger analysis shows that the surface concentration of Mg atoms is ~ 40-45 at.%. Cd-35 40 at.%, and F – 15-20 at.%.

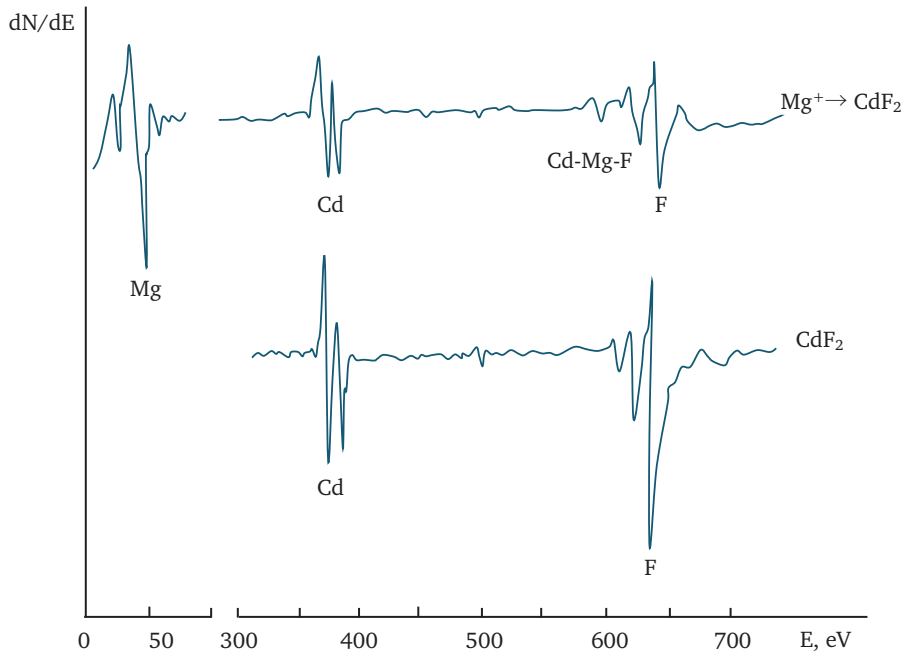

Figure 2. Auger spectra
Note: 1 – well-cleaned CdF_2 surface; 2 – CdF_2 implanted with Mg^+ ions with $E_0 = 1$ keV at $D = 8 \cdot 10^{16}$ cm^{-2}
Source: compiled by the authors

In this way, CdF_2 is goal decayed into components within the near-surface layer within the particle implantation. The study [16] noted that a small portion of these components can be splashed from the surface. Due to the prolonged chemical reaction, nearly all of the freed fluorine iotas join both the molecules of the alloying component and the atoms of cadmium. Subsequently, three-component compounds are shaped within the near-surface layer. As follows from the experimental data, at $E_0 \leq 3$ keV, along with the formation of various compounds, "excess" atoms of the alloying element appear, the concentration of which increases with increasing dose (Fig. 3a). At high ion energies ($E_0 \geq 3$ keV) a noticeable desorption of fluorine from the surface occurs, which leads to the accumulation of Cd atoms near the surface (Fig. 3b). The highest concentration of the latter is 40-45 at.%. The stoichiometric composition characteristic of CdF at E = 3 keV is restored only at d = 120 Å.

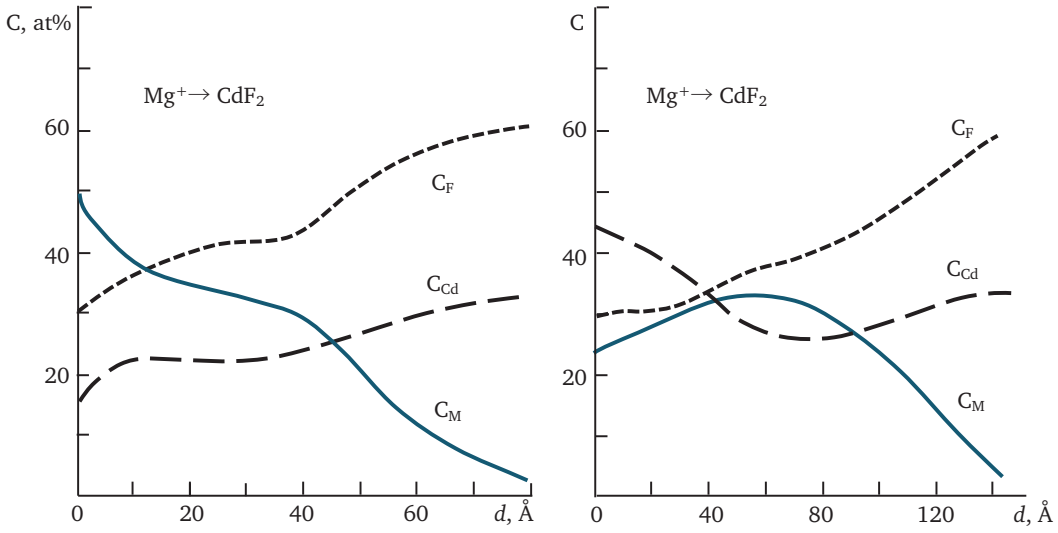

Figure 3. Dependences of C_{Mg}, C_{Ca}, C_F on d for CdF_2, doped ionic Mg^+ with $E_0 = 0.5$ keV and 3 keV. $D = 8 \cdot 10^{16}$ cm^{-2}

Source: compiled by the authors

The influence of post-implantation thermal and laser annealing on the composition, structure, and properties of the ionic implanted CdF_2 film was also studied. The experimental results showed that the optimal heating temperature for CdF_2 implanted with Mg^+ ions is 900 K. In this case, the near-surface layers are completely crystallized and films of the $Cd_{0,7}Mg_{0,3}F_2$ type with a thickness of ~ 25-30 Å are formed on the CdF_2 surface [17; 18]. In the case of laser annealing at an energy density of ~ 1.7 J·cm^{-2}, a $Cd_{0,6}Mg_{0,4}F_2$ film with good stoichiometric composition is formed with a thickness of ~ 40 – 45 Å (Fig. 4).

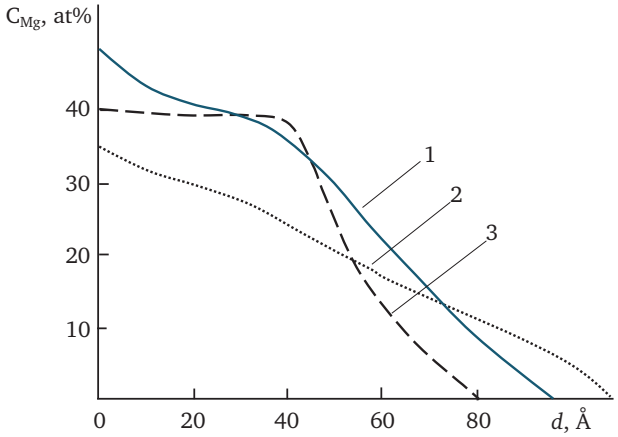

Figure 4. Dependences C_{Mg} (h) for CdF_2 implanted with Mg^+ ions with E_0 = 1 keV at D = 8 · 10^{16} cm^{-2} after heating at T = 900 K (curve 1), after laser annealing with W = 1.7 J·cm^{-2} (curve 2) and spectrum in the initial case (curve 3)
Source: compiled by the authors

Figure 4 shows the UVE spectra of the CdF_2 and $Cd_{0,6}Mg_{0,4}F_2$ films. It can be seen that the density of states of the electrons in the valence band differs significantly from the current density for CdF_2 [19; 20]. Possible mechanisms for the formation of maxima are given in the CED of photoelectrons. The parameters of energy bands $Cd_{0,6}Mg_{0,4}F_2$ are estimated in Figure 5 based on Table 2.

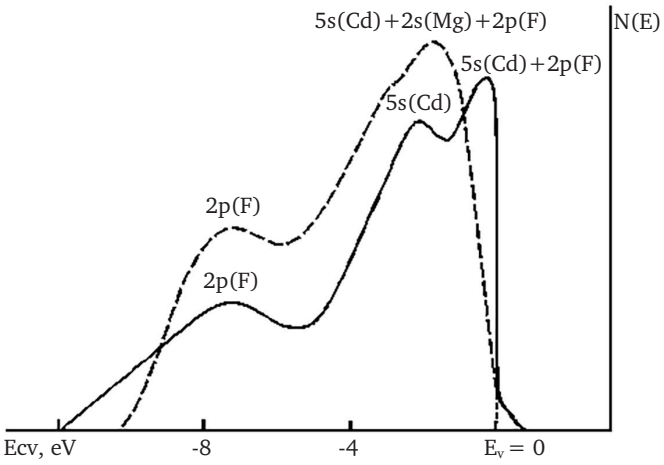

Figure 5. Ultraviolet photoelectron spectra of CdF_2 and $Cd_{0,6}Mg_{0,4}F_2$ films
Source: compiled by the authors

Table 2. Parameters of energy bands CdF_2 and $Cd_{1-x}Mg_xF_2$

Parameters, eV	CdF_2	$Cd_{0,6}Mg_{0,4}F_2$
E_V	9.8	10.6
E_F	2.3	-
E_g	7.6	8.5
χ	2.2	2.1

Source: compiled by the authors

Table 3 lists the optical parameters (n and r) measured at a light wavelength of 1050 Å (UVE) for CdF_2 and $Cd_{0.6}Mg_{0.4}F_2$.

Table 3. Optical parameters of CdF_2 film and CdF_2 film $Cd_{0.6}Mg_{0.4}F_2$ measured at $\lambda = 1050$ Å

Optical parameters	CdF_2 d = 800 Å	$Cd_{0.6}Mg_{0.4}F_2$ d = 40-45 Å
n	1.6	1.5
r, %	9	11

Source: compiled by the authors

The E_g value of the three-component film is noticeably larger in comparison to the E_g of the CdF_2 film. Based on the data, the change in the Mg concentration correlates with the change in the band gap of the dielectric CdF_2 film [21; 22]. However, the x value could be varied in the range from 0.2 to 0.5 by implantation of Mg^+ ions followed by annealing. It can be seen from Table 3 that $Cd_{0.6}Mg_{0.4}F_2$ nanofilms do not significantly change the values of n and r for light with a wavelength of 1050 Å.

Similar studies have been conducted by other researchers. The paper [6] presents a systematic study on Cd1−xMgxTe thin film development via co-evaporation of CdTe and Mg. Deposition rates were adjusted to create films with varying stoichiometry and a wide range of band gaps (1.47 to 2.41 eV). Structural parameters varied systematically with Mg content, but XRD reflections remained similar to pure CdTe at lower Mg concentrations. XPS analysis shed light on Mg incorporation, supporting band gap variations seen in UVE–Vis spectroscopy. Mg consideration affected film photoresponse. A.M. Bothwell *et al.* [1] analysed photoluminescence, carrier lifetime, and quantum effectiveness, which showed enhancements when a shorter preheat time was utilized. Auxiliary particle mass spectrometry profiles showed that $CdCl_2$ passivation was protected when CdMgTe was briefly preheated. Moreover, extra gadgets were subjected to an HCl corrosive carve treatment and a CdTe cap layer, autonomously, after applying the CdMgTe layer. This was done to play down magnesium oxidation [23]. The CdTe cap gadget illustrated a beginning guarantee, accomplishing a gadget proficiency of 13.1%. The study conclusions [2] are comparative to those achieved in this research. There was a survey of the exploratory comes about on the consideration of the Si, GaAs, and CaF_2 surface layers that are made utilizing the low-energy particle implantation displayed. Optical and electron spectroscopy and microscopy are utilized within the tests.

Conclusions

The effect of the implantation of Mg^+ ions on the composition and electronic structure of single-crystal CdF_2/Si (III) films was studied for the first time. After heating at T = 900 K CdF_2 implanted with Mg^+ ions at $D = 8 \cdot 10\text{-}16$ cm^{-2}, a $Cd_{0.6}Mg_{0.4}F_2$ film with a thickness of 40-45 Å is formed. For this film, the value of E_g was ~ 8.5 eV. During the bombardment of CdF_2 with ions of inert gases Ar^+, CdF_2 is decomposed into components, the surface layers are disordered, the diffusion of atoms, the evaporation of atoms from the surface, etc. In the case of bombardment with Mg metal ions, these changes are accompanied by the introduction of metal atoms and the formation of various types of compounds. Most of the fluorine atoms escape into the vacuum, while the other part diffuses deep into the target; therefore, the concentration of F at a depth h = 80 – 100 Å increases significantly. A different picture is observed during the implantation of Mg^+ ions in CdF_2. Thus, CdF_2 is intensively decomposed into components in the near-surface layer in the process of ion implantation. A small portion of these components can be showered from the surface. Due to the prolonged chemical action, nearly all of the freed fluorine particles once more enter into a chemical bond with both the molecules of the alloying component and the molecules of cadmium. Thus, three-component compounds are shaped within the near-surface layer. The densities of electronic states, band energy, and optical parameters of CdF_2 and $Cd_{0.6}Mg_{0.4}F_2$ films have been determined. This effect can be interesting for application in optical memory cells. Further research may involve delving deeper into the mechanisms driving these changes, investigating the stability of the modified material under different conditions, and potentially optimizing the process for specific applications. Additionally, exploring the potential applications of the modified CdF_2 material in fields such as optoelectronics, photonics, or materials science could be a valuable avenue for future research. Photonics and optoelectronics have emerged as key disciplines in the advancement of technology, with vast potential for various applications. In recent years, there has been a growing interest in exploring the unique properties of two-dimensional materials and their integration into photonic and optoelectronic devices. This field holds great promise for revolutionizing several industries, including telecommunications, energy, sensing, and computing.

Acknowledgements

None.

Conflict of Interest

None.

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Вплив імплантації іонів Mg^+ та подальшого відпалу на склад, електронну структуру, емісійні та оптичні властивості CdF_2

Акбаржон Абдумаджидович Абдувайтов

Кандидат фізико-математичних наук
Ташкентський державний технічний університет імені Іслама Карімова
100095, вул. Університетська, 2, м. Ташкент, Узбекистан
https://orcid.org/0000-0001-6453-6523

Гунель Іманова

Кандидат фізичних наук, доцент
Інститут радіаційних проблем Міністерства науки і освіти Азербайджанської Республіки
AZ1143, вул. Б. Вагабзаде, 9, м. Баку, Азербайджан
Дослідницький центр сталого розвитку та зеленої економіки UNEC імені Нізамі Гянджеві
AZ1007, вул. Аббаса Саххата, 45A, м. Баку, Азербайджан
https://orcid.org/0000-0003-3275-300X

Дільноза Артикбаевна Ташмухамедова

Доктор фізико-математичних наук, професор
Ташкентський державний технічний університет імені Іслама Карімова
100095, вул. Університетська, 2, м. Ташкент, Узбекистан
https://orcid.org/0000-0001-5813-7518

Хуршид Хамідович Болтаєв

Кандидат фізико-математичних наук
Ташкентський державний технічний університет імені Іслама Карімова
100095, вул. Університетська, 2, м. Ташкент, Узбекистан
https://orcid.org/0000-0001-6453-6523

Болтаходжа Ерматович Умірзаков

Доктор фізико-математичних наук, професор
Ташкентський державний технічний університет імені Іслама Карімова
100095, вул. Університетська, 2, м. Ташкент, Узбекистан
https://orcid.org/0000-0002-9815-2111

Анотація

Актуальність. При бомбардування іонами металу Mg зміни супроводжуються впровадженням атомів металу та утворенням різного типу сполук. Таким чином, CdF_2 інтенсивно розкладається на компоненти в приповерхневому шарі в процесі іонної імплантації. Невелику частину цих компонентів можна розпорошувати з поверхні. Завдяки високій хімічній активності майже всі звільнені атоми фтору знову вступають у хімічний зв'язок як з атомами легуючого елемента, так і з атомами кадмію. Внаслідок цього в приповерхневому шарі утворюються трикомпонентні сполуки. Тому необхідно визначити електронні стани, визначено зонно-енергетичні та оптичні параметри плівок CdF_2 та Cd_0, $6Mg_0$, $4F_2$.

Мета. У цій роботі вперше досліджено склад, структуру та властивості CdF_2, імплантованого іонами Mg^+, у поєднанні з термічним та лазерним відпалом.

Методологія. Експериментальні дослідження проводили в умовах вакууму не менше 10-7 Па методами електронної спектроскопії (AES) та ультрафіолетової фотоелектронної спектроскопії (UVES). Профілі розподілу атомів по глибині визначали методом AES у поєднанні з пошаровим травленням поверхні іонами Ar+ з E_0 = 2-3 кеВ.

Результати. CdF_2 інтенсивно розкладається на компоненти в приповерхневому шарі в процесі іонної імплантації. Внаслідок цього в приповерхневому шарі утворюються трикомпонентні сполуки. Визначено зонно-енергетичні параметри та густини станів електронів у валентній зоні цієї плівки.

Висновки. Вперше досліджено вплив імплантації іонів Mg^+ на склад та електронну структуру монокристалічних плівок CdF_2/Si(III). Визначено густини електронних станів, зонно-енергетичні та оптичні параметри плівок CdF_2 та Cd_0, $6Mg_0$, $4F_2$.

Ключові слова: профілі розподілу атомів; надтонкі шари; заборонена зона; термообробка; поверхневий шар