COPPER-RELATED DEFECTS IN ZnTe THIN FILMS GROWN BY THE CLOSE SPACE SUBLIMATION METHOD

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Abstract

Low-temperature photoluminescence (PL) is used to study defects evolution via immersion technique and annealing in vacuum of ZnTe thin films. In this paper we studied how copper doping from solutions of different molar concentrations affects PL of ZnTe thin films grown by close space sublimation (CSS) method. Undoped ZnTe thin films showed PL emission in the (520-680) nm wavelength region. The incorporation of copper in ZnTe produce a number of broad emission bands that correspond to an electron transition from the conduction band to spin-orbit states of the localized level of Cu^{2+} ions. All the studied samples had variable concentrations of oxygen and the possibility of the formation of auxiliary oxides is discussed.

Keywords: ZnTe thin films, ion-exchange doping, polymorph structure, Cu^{2+} defect level.

Rezumat

Fotoluminiscența (FL) la temperaturi joase este utilizată pentru a studia evoluția defectelor prin tehnica de imersie și tratare în vid a straturilor subțiri de ZnTe. În această lucrare am studiat modul în care doparea din soluții de diferite concentrații molare ale cuprului afectează FL straturilor subțiri de ZnTe crescute prin metoda sublimării în spațiu inchis (CSS). Staturile subțiri de ZnTe nedopate au prezentat emisie de FL în regiunea lungimilor de undă (520-680) nm. Încorporarea cuprului în ZnTe produce un număr de benzi largi de emisie care corespund unei tranziții de electroni de la banda de conducție la stările de spin-orbita a nivelului localizat al ionilor Cu2+. Toate probele studiate au avut concentrații variabile de oxigen și se discută posibilitatea formării de oxizi auxiliari.

Cuvinte cheie: straturi subțiri deZnTe, dopare cu schimb de ioni, structură polimorfă, nivel de defect Cu^{2+}.

1. Introduction

Zinc telluride (ZnTe) is a chemically stable and non-hygroscopic group II–VI metal chalcogenide semiconductor exhibiting many useful electrical and optical properties. It has a direct wide bandgap of 2.26 eV (300 K) and *p*-type conductivity [1, 2]. The main reason for the increased interest in the ZnTe semiconductor is its wide application in optoelectronic and microelectronic devices.

Zinc telluride thin films are used in tandem solar cell structures [3] and for synthesizing $Cd_xZn_{1-x}Te/ZnTe$ quantum-well structures [4]. Zinc telluride epitaxial layers are applied as a substrate for various heterojunctions and superlattices [5], γ-ray detectors [6], photodiodes [7], and light-emitting diodes [8]. To tune the optical and electrical properties of ZnTe thin films, some transition elements should be added as a dopant to ZnTe. Doping of ZnTe with transition metals has been studied to improve the *p*-type conductivity and the photoluminescence (PL) and optoelectronic properties. There are a number of reports that describe the synthesis of ZnTe thin films by different methods and their structural and optical properties [9–11]. According to [12–14], copper has the ability to form stable cations partly filled with an incompletely filled *d* orbital that can decrease the electrical resistance of ZnTe. However, all the above-mentioned reports are not sufficient to systematize the obtained physical parameters for industrial applications. Therefore, to determine the optimum doping conditions for ZnTe thin films, systematic studies of their structural, compositional, and PL properties are required. Here, we report PL of the ZnTe thin films doped with Cu taken in different concentrations via immersion into a $Cu(NO_3)_2$ solution.

2. Experimental Details

Zinc telluride thin films were grown on glass substrates by the close spaced sublimation (CSS) method. The substrates were pre-treated in a solution of a mixture of chromium (7 g of $K_2Cr_2O_7$ + 10 mL of H_2O + 100 mL of H_2SO_4) at room temperature for 2–3 h; after that, they were thoroughly washed in distilled water and finally dried in a furnace with a hydrogen atmosphere at a temperature of 200 °C. The growing and doping conditions were described in paper [15]. We only mention here the molar concentrations of copper nitrate $Cu(NO_3)_2$ in solution. In 50 mL of methanol was dissolved $Cu(NO_3)_2$ with molar concentrations from $4{,}2\cdot10^{-3}$ mol/l to $10{,}5\cdot10^{-3}$ mol/l. Subsequently, the annealing of ZnTe thin films at 300 °C for 20 min was performed.

Photoluminescence (PL) spectra were measured at 80 K using a setup based on an MDR-2 high optical power monochromator (with a 600 mm^{-1} diffraction grating and a resolution of ~1 meV) and a multi-alkaline photomultiplier [$(Na_2K)Sb$-Cs]. Photoluminescence was excited using a MDL-III-405 CNI laser (λ = 405 nm) at an average emission power of 100 mW.

The structural parameters recorded with a Rigaku X-ray diffractometer using CuK_α radiation (λ = 1.54056 Å) and the elemental composition of the surface region studied by X-ray photoelectron spectroscopy (XPS) results presented in previous paper [15] will be used for interpretation of the PL data.

3. Results and Discussion

X-ray diffraction patterns (XRD) of undoped ZnTe thin films obtained by CSS at technological conditions mentioned above exhibits polycrystalline polymorph structure with

strong [111] preferred orientation of the crystallites along (111) plane belonging to cubic phase and weak hexagonal phase [15]. The lattice parameter of cubic phase equals to 6.17 Å agrees well with the bulk value of ZnTe (6.085 Å) [16]. For the hexagonal phase of 7.8% Cu-doped ZnTe thin films, the lattice parameters values yield a=3.99 Å and c = 9.43 Å. These values indicate that the hexagonal structure in Cu-doped ZnTe films is distorted in comparison with ideal hexagonal lattice structure. The internal stress induced by the excess volume at grain boundaries is suggested to be the main reason for the lattice distortion. An increase of Cu concentration causes a slightly shift towards lower diffraction angles, a decrease in the full width at half maximum (FWHM) of the peak and an increase in the lattice internal strain.

In Fig.1 are presented XPS spectra of undoped ZnTe (left) thin film and doped with 4.6 at. % Cu (right).

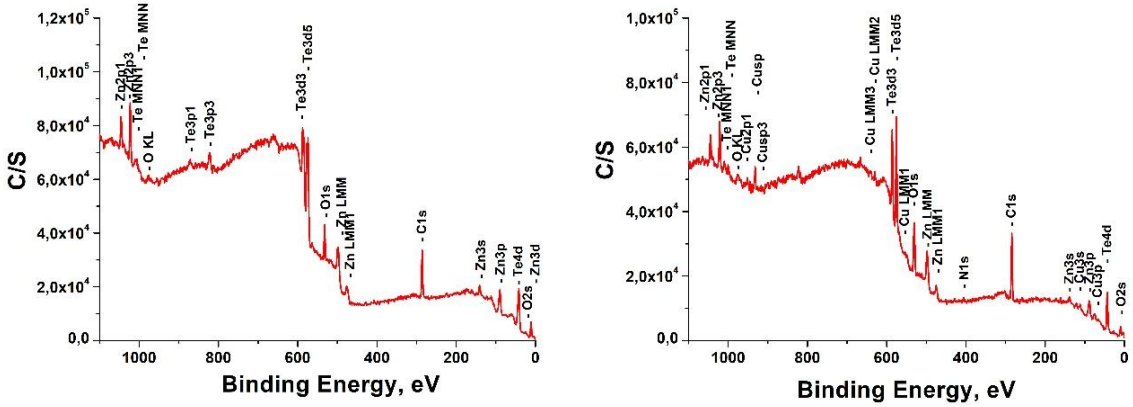


Fig. 1 XPS spectra of undoped ZnTe (left) thin film and doped with 4.6 at. % Cu (right).

XPS study show that undoped films are slightly Te rich and have shown the oxygen in composition. According to XPS measurements the Cu concentration in the ZnTe films was found to change from 1.4 at. % to 7.8 at. %. XPS also proved excessive of Zn atoms on the surfaces of samples after doping with Cu. After doping with copper, there may exist Cu_xTe, that is consistent with references [17,18].

All the studied samples had variable concentrations of O and therefore the possibility of the formation of auxiliary oxides exists.

The PL spectrum of undoped ZnTe thin films measured at 80 K is shown in Fig. 2.

The spectrum exhibit three bands and a shoulder: the more distinct green luminescence band at 535 nm, which becomes predominant in intensity in all studied Cu-doped ZnTe thin films. The broader less intensive band is situated at 580 nm and one another less intensive is located at 645 nm. The PL spectrum of ZnTe doped with $C_M = 4.2 \cdot 10^{-3}$ mol/L of $(CuNO_3)_2$ keep the most intensive peak at 535 nm, as in the case of undoped ZnTe (Fig. 3).

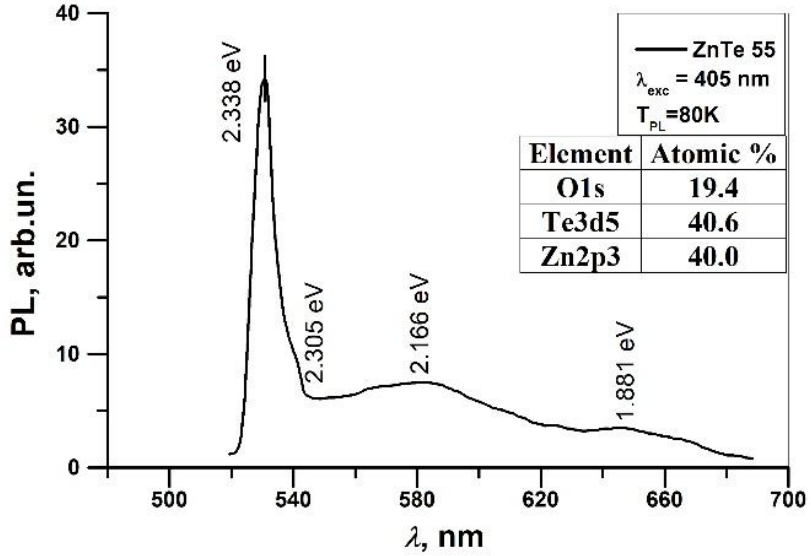


Fig. 2. Photoluminescence spectrum and XPS concentration of elements of undoped ZnTe thin film.

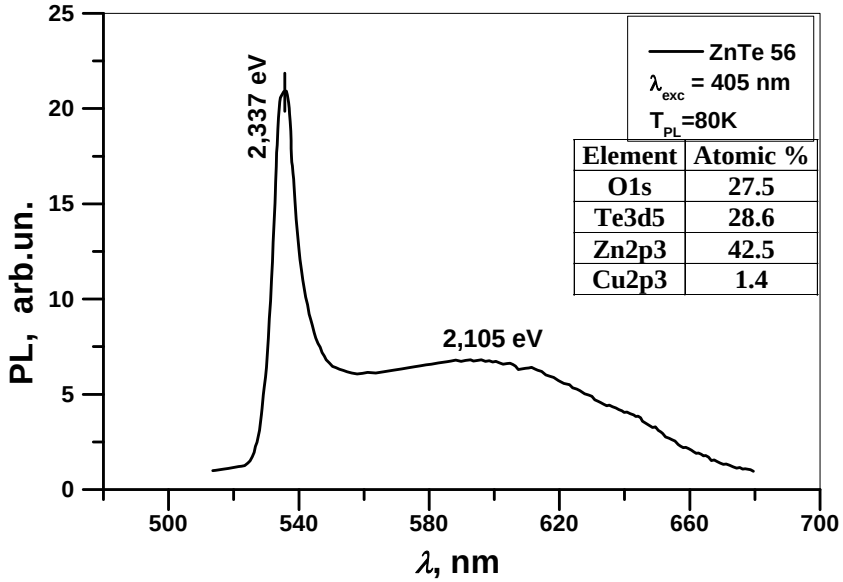


Fig. 3. Photoluminescence spectrum and XPS concentration of elements of 1.4 at% Cu-doped ZnTe thin film.

Deconvolution of a broad band show a maximum at 589 nm and the disappearance of the emission band observed in undoped ZnTe at 645 nm.

With an increase in the molar concentration of Cu(II) nitrate the PL spectrum of Cu-doped ZnTe (Fig. 4) exhibits the same most intensive band as that in the case of the undoped sample

slightly shifted to 528.5 nm.

Deconvolution fitted with a Gaussian distribution in the same intensive slightly shifted narrow band show a shoulder in the shorter wavelengths with maximum at 558 nm. With further increasing in the molar concentration of the Cu(II) nitrate solution C_M =8.4·10^{-3} mol/L, the PL spectrum shown in Fig. 5 exhibits a single broad emission band with a maximum at 539.8 nm. Deconvolution fitted with a Gaussian distribution resulted in three bands: the most intensive bands at 534.1 nm, a less intensive band at 577 nm, and a weak band at 510.8 nm.

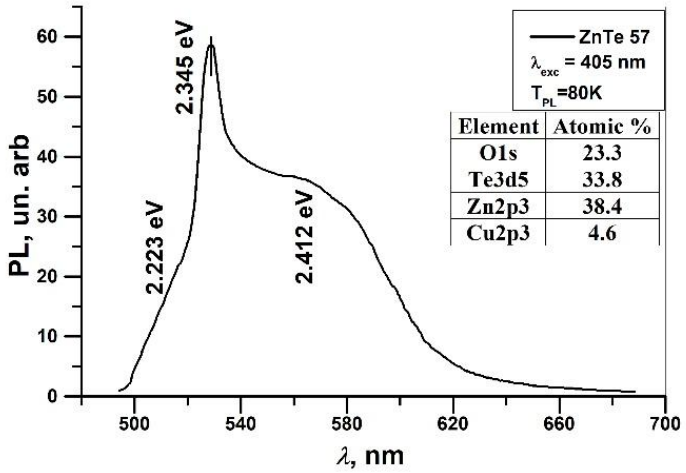


Fig. 4. Photoluminescence spectrum and XPS concentration of elements of 4.6 at% Cu-doped ZnTe thin films.

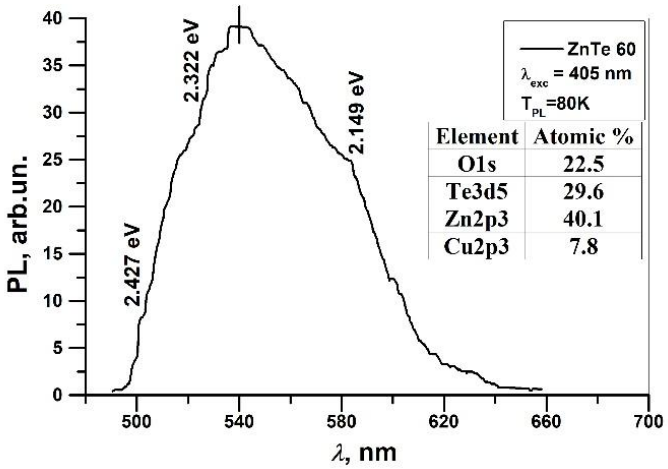


Fig. 5. Photoluminescence spectrum and XPS concentration of elements of 7.8 at% Cu-doped ZnTe thin films.

So, the PL spectra of undoped and doped ZnTe thin films with different molar concentration of Cu (1.4 at.%, 4.6 at.%, 7.8 at.%) are dominated by the narrow green luminescence band. Deconvolution of the most intensive band of undoped ZnTe thin film yielded

an intensive narrow band at 2.338 eV, which is attributed to the radiative recombination of bound excitons trapped at imperfections in ZnTe and a shoulder at 2.305 eV, which indicates a radiative recombination of donor–acceptor pairs. According to the XPS of Te3d and Zn2p3 regions in undoped sample presented in [15] publication, we suppose that PL spectrum consists of essentially bands due to the Zn-Te and Te-O bonds in ZnTe and TeO_2, respectively. A possible interpretation of the donor and the acceptor that contribute to this emission band is that the acceptor is a Zn-vacancy and the donor is a crystal imperfection, such as Te-vacancy or impurities. The emission in the PL spectrum at 2.166 eV is related to the recombination of excitons bound to some extended structural defects. The emission band revealed at 1.881 eV is associated with O_{Te} centers due to the contamination of the ZnTe thin films with oxygen. We agree with the authors of [19] that this most noticeable feature—emission around at 1.881 eV—is attributed to exciton emission bound to isoelectronic oxygen substituting Te atoms (O_{Te}).

The deconvolution of 1.4 at.% Cu-doped ZnTe revealed more intensive broad band with maximum at 589 nm and the disappearance of the emission band observed in undoped ZnTe at 1.881 eV. XPS analysis provides evidence that Cu acting as acceptor center in substitutional site for zinc as believed in [9] publication. According to the high-resolution of Cu2p region for Cu-doped ZnTe films presented in [15] binding energies situated at 931.5 ± 0.3 eV and 951.4 ± 0.3 eV correspond to Cu^+ and Cu^{2+} oxidation states. The binding energy of 951.4 eV is characteristics for Cu-O binding. Thus, coexistence of Cu^+ and Cu^{2+} ions in Cu-doped ZnTe can be concluded and the emission in the PL spectrum at 2.105 eV can be attributed to the presence of copper in ZnTe.

With increase in the molar concentration of Cu(II) nitrate, the interplanar distance (*d*) of the ZnTe phase decreases from 3.5183 Å for $C_M = 4.2 \cdot 10^{-3}$ mol/L to 3.5167 Å for $C_M = 6.3$ mol/L. This fact indicates that the Cu^{2+} ions replace the Zn^{2+} ions according to the reactions:

$$Zn \rightarrow Zn^{2+} + 2e, Cu^{2+} + 2e \rightarrow Cu.$$

The presented XPS of $Te3d_{5/2}$ and Te $3d_{3/2}$ region in [15] at a binding energy of 573.2 and 583.6 eV proves the Zn–Te bonding, while the other two peaks located at 575.3 and 587.2 eV show the co-existence of Te oxide forms in ZnTe that correspond to TeO_2. Ii is of interest that the intensity of the oxide phase of Te is more pronounced than that of the transition peaks of Te representing Zn–Te bonding.

The fact that the Cu-doped ZnTe samples contain excess Zn and the evidences obtained from XPS measurements [15] and in [13, 14] suggest involvement of Cu^{2+} ions in all doped samples. The PL spectrum of 7.8 at% Cu-doped ZnTe (Fig. 5) exhibits the same most intensive peak as that in the case of the undoped sample; it is slightly shifted to 528.5 nm. Deconvolution fitted with a Gaussian distribution resulted in the same intensive slightly shifted narrow band at 2.345 eV attributed to the radiative recombination of bound excitons trapped at the imperfections in ZnTe and a shoulder at 2.223 eV. It can be assumed that this band is attributed to the thermal dissociation of the bound exciton, which liberates the electrons. The intensive broad emission band at 2.412 eV could be assigned to ZnO:Cu.

According to the deconvolution of the O1*s* XPS region of Cu-doped ZnTe thin films presented in [15], its exhibits three peaks: the binding energy located at 531.3 eV corresponds to lattice oxygen (O^{2-}) bonded to the metal, the binding energy of the peak at 530.8 eV corresponds to ZnO, while the peaks at 532 and 532.3 eV are attributed to OH contamination on the surface, which can be due to chemisorption or dissociated oxygen [12].

Therefore, an increase in the PL intensity of the broad emission band at 2.412 eV is mostly attributed to the incorporation of Cu into the ZnO phase. To understand the mechanism, we can suggest that Zn ions are replaced by Cu atoms; the Cu atoms donate two electrons during the

formation of the band and will be in a neutral state with respect to the Cu^{2+} state. This copper related impurity rapidly increases the luminescence intensity.

With a further increase in the molar concentration of the Cu(II) nitrate, the interplanar distance (*d*) of the ZnTe phase decreases from 3.5183 Å for $C_M = 4.2 \cdot 10^{-3}$ mol/L to 3.5159 Å for $C_M = 8.4 \cdot 10^{-3}$ mol/L. The PL spectrum shown in Fig. 5 exhibits a single broad emission band with a maximum at 539.8 nm. The most intensive band at 2.322 eV (534.1 nm) is attributed to the radiative recombination of bound excitons trapped at imperfections in ZnTe; however, the less intensive band at 2.149 eV is attributed to the presence of copper in ZnTe. The PL weak band at 2.427 eV (510.8 nm) is associated with the incorporation of Cu in the ZnO phase. According to XPS analysis, a further increase in the molar concentration of the Cu(II) nitrate to $C_M = 10.5 \cdot 10^{-3}$ mol/L leads to a decrease in the atomic concentration of Cu and gives a Cu content of 1.4 at %. The percentage of the hexagonal phase in ZnTe thin films varies as a function of the $Cu(NO_3)_2$ solution concentration. The hexagonal phase appears only upon a decrease in the excess tellurium level. The PL spectrum of ZnTe with a molar concentration of the Cu(II) nitrate of $C_M = 10.5 \cdot 10^{-3}$ mol/L has the same form as that in the case of the sample with the molar concentration of Cu of $C_M = 4.2 \cdot 10^{-3}$ mol/L.

So, the incorporation of copper in ZnTe has been found to produce a number of broad emission bands that correspond to an electron transition from the conduction band to spin-orbit states of the localized level of Cu^{2+} ions.

4. Conclusions

Zinc telluride thin films have been grown by the CSS method. Copper-doped ZnTe thin films have been synthesized using a Cu(II) nitrate solution as the dopant via simple immersion and subsequently annealing in vacuum. The XRD published results in [15] show that the ZnTe phase in the films has a zinc blende and wurtzite structures. The XRD analysis of the Cu–doped ZnTe films has revealed an increase in the intensity with an increase in the Cu concentration. XPS studies [15] confirmed the presence of the Cu^{2+} oxidation state, and perhaps the Cu_2Te phase also exists but it's difficult to detect, because its three main peaks are located at the same diffraction angles as in ZnTe. The PL spectra are observed in a range of 520–580 nm. The PL spectrum of the undoped and all Cu-doped ZnTe films exhibits an intensive narrow band at 2.338 eV, which can be attributed to the radiative recombination of bound excitons trapped at imperfections in ZnTe. A shoulder at 2.305 eV can be assigned to radiative recombination of the donor–acceptor pairs. The emission in the PL spectrum at 2.166 eV may be associated with the recombination of excitons bound to some extended structural defects. The emission band revealed at 1.881 eV is attributed to O_{Te} centers due to the contamination of the ZnTe thin films with oxygen. All bands presented in PL spectra of Cu-doped ZnTe doped with different molar concentrations (1.4%, 4.6%, and 7.8 at %), outside the narrow band, are related to Cu^{2+} oxidation states.

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