

ZnO thin films with Cu, Ga and Ag dopants prepared by ZnS oxidation in different ambient

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Abstract. ZnO, ZnO: Cu, Ga, and ZnO: Cu, Ga, Ag thin films were obtained by oxidization of ZnS and ZnS: Cu, Ga films deposited onto glass substrates by electron-beam evaporation from ZnS and ZnS: Cu, Ga targets and from ZnS: Cu, Ga film additionally doped with Ag by the closed space sublimation technique at atmospheric pressure. The film thickness was about 1 μm . The oxidation was carried out at 600-650°C in air or in an atmosphere containing water vapor. Structural characteristics were investigated by X-ray diffraction (XRD) and atomic force microscopy (AFM). Photoluminescence (PL) spectra of the films were measured at 30-300 K using the excitation wavelengths of 337, 405 and 457.9 nm. As-deposited ZnS and ZnS: Cu, Ga films had cubic structure. The oxidation of the doped films in air or in water vapors led to complete ZnO phase transition. XRD and AFM studies showed that the grain sizes of oxidized films at wet annealing were larger than of the films after dry annealing. As-deposited doped and undoped ZnS thin films did not emit PL. Shape and intensity of the PL emission depended on doping and oxidation conditions. Emission intensity of the films annealed in water vapors was higher than of the films annealed in the air. PL of ZnO: Cu, Ga films excited by 337 nm wavelength exhibits UV (380 nm) and green emission (500 nm). PL spectra at 300 and 30 K excited by 457.9 and 405 nm wavelengths consisted of two bands – the green band at 500 nm and the red band at 650 nm. Location and intensities ratio depended on the preparation conditions.

Keywords: zinc oxide; zinc sulphide; oxidation; photoluminescence; x-ray diffraction

1. Introduction

Zinc oxide is an interesting optoelectronic material and has been widely used in different fields of industry, technique and medicine (Klingshirn *et al.* 2010). The great variety of important physical and chemical properties allows to consider this material as a unique one. A wide band gap with direct gap around 3.4 eV at room temperature and high exciton binding energy (about 60 eV) make this material very promising for the use in blue light-emitting devices, short-wave laser

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diodes and detectors in high-energy spectral region. Specific properties of ZnO such as high melting temperature, intensive sublimation, dissociation at sublimation, chemical activity to most materials at high temperatures, etc., result in the difficulties of homogeneous, high quality films and single crystals fabrication. Nevertheless, there are some methods of fabrication of polycrystalline ZnO films suitable for technical application. To produce thin films there are a variety of methods available. A relatively simple technique is to oxidize a thin Zn metallic film (Wang *et al.* 2003). Another possibility to obtain ZnO films is the oxidation of ZnS films in air, as has been described by Jayatissa (2003). It has been shown (Kryshtab *et al.* 2009) that the presence of the water vapor in an atmosphere noticeably accelerates the oxidation process and results in complete phase transition of ZnS thin film to ZnO one. Structural, optical, magnetic and electrical properties of ZnO films are shown to be governed by conditions of the films deposition, subsequent treatments and doping materials such as Mn, Al, Ag, Ga, Cu, etc. (Yang and Zhang 2013, Ding *et al.* 2009, Xue *et al.* 2008, Hsiao *et al.* 2015). It is known that gallium and silver are fast-diffusing impurities in semiconducting compounds and their presence affects structural and luminescent characteristics of the thin films.

In this paper, we present structural and luminescent properties of ZnO thin films prepared by the oxidation of ZnS films doped by Cu, Ga and Ag in atmospheres with and without water vapor, in order, to clarify the influence of a small amount of impurities on the process of the films fabrication.

2. Experimental details

Doped ZnS:Cu, Ga and undoped ZnS thin films were deposited onto glass substrates by electron-beam evaporation (EBE) method from two ZnS:Cu, Ga and ZnS powder targets, respectively. The concentrations of Cu and Ga in the target were the same and equal to 0.2 at %. The substrate temperature was 120°C. The film thickness was about 1 μm . ZnO:Cu, Ga films were prepared by thermal oxidization of ZnS:Cu, Ga films at 600-650°C during 5 hours in a dry atmosphere containing only the air (“dry annealing”) or in a wet atmosphere containing the water vapor (“wet annealing”) with the water quantity of 0.08 g/m³. Some of as-deposited ZnS:Cu, Ga films were additionally doped with Ag. The doping process was carried out by the closed space sublimation technique (Kryshtab *et al.* 2007) from Ag plate at 570°C in O₂-rich atmosphere that was created by decomposition of oxygen-containing compound. The Ag concentration in the film was not measured, but it can be qualitatively estimated as a small one (≤ 1 at %) because the X-ray diffraction (XRD) patterns of the film did not reveal the reflection of Ag or its compounds. Such film was annealed in a “dry atmosphere” at 600°C. Structural characteristics of the obtained films were studied by X-ray diffraction (XRD) using D8 Advance Bruker X-ray diffractometer with Cu K_{α} radiation. Atomic force microscopy (AFM) operated in tapping mode (Park Scientific) was used for the evaluation of the film’s surface morphology. Photoluminescent (PL) spectra of the films were measured with a spectrometer at 300, 77 and 30 K. The wavelengths of the exciting light were 337, 405 and 457 nm.

3. Results and discussion

The analysis of XRD patterns demonstrated that ZnS and ZnS:Cu, Ga powders in targets before EBE had hexagonal structure and after evaporation process remained part in a target had only

cubic structure. The XRD pattern of as-deposited ZnS and ZnS:Cu, Ga thin films revealed only one strong peak that coincides with the position for 111 diffraction peak for cubic crystal structure or 002 diffraction peak for hexagonal crystal structure (Fig. 1(a)). The presence of one peak indicates strong preferred grains orientation (texture) in corresponding directions. Since, the positions of such peaks almost coincide and films were strongly preferred orientated, the crystal structure of the films were investigated by X-ray texture goniometer with Eulerian cradle for measuring the XRD patterns from films at different orientations by inclination and rotation of the samples. The peaks for hexagonal crystal structure were not observed. So, it is possible to conclude that only cubic crystal structure is formed with a strong texture in the $\langle 111 \rangle$ direction.

The “dry annealing” of undoped ZnS films resulted only in the appearance of a small amount of ZnO phase, meanwhile the same annealing of ZnS:Cu, Ga film leads to complete phase transition from ZnS cubic structure to ZnO hexagonal structure with feebly marked texture in 100 direction (Fig. 1(b)). The presence of water vapor in the oxidation process of ZnS film resulted in almost complete phase transition from ZnS phase to ZnO phase with strong texture in 002 direction. The influence of water vapor on the oxidation process of ZnS:Cu, Ga film results only in redistribution of the peak intensities with the increase of the texture in 002 direction (Fig. 1(c)). The oxidation of ZnS:Cu, Ga, Ag films at “dry annealing” results in the formation of ZnO:Cu, Ga, Ag film with strong texture in 002 direction. The Ag concentration in the film was not measured, but it can be qualitatively estimated as a small one (≤ 1 at %) because the X-ray diffraction (XRD) pattern of the film did not reveal the reflection of Ag or its compounds.

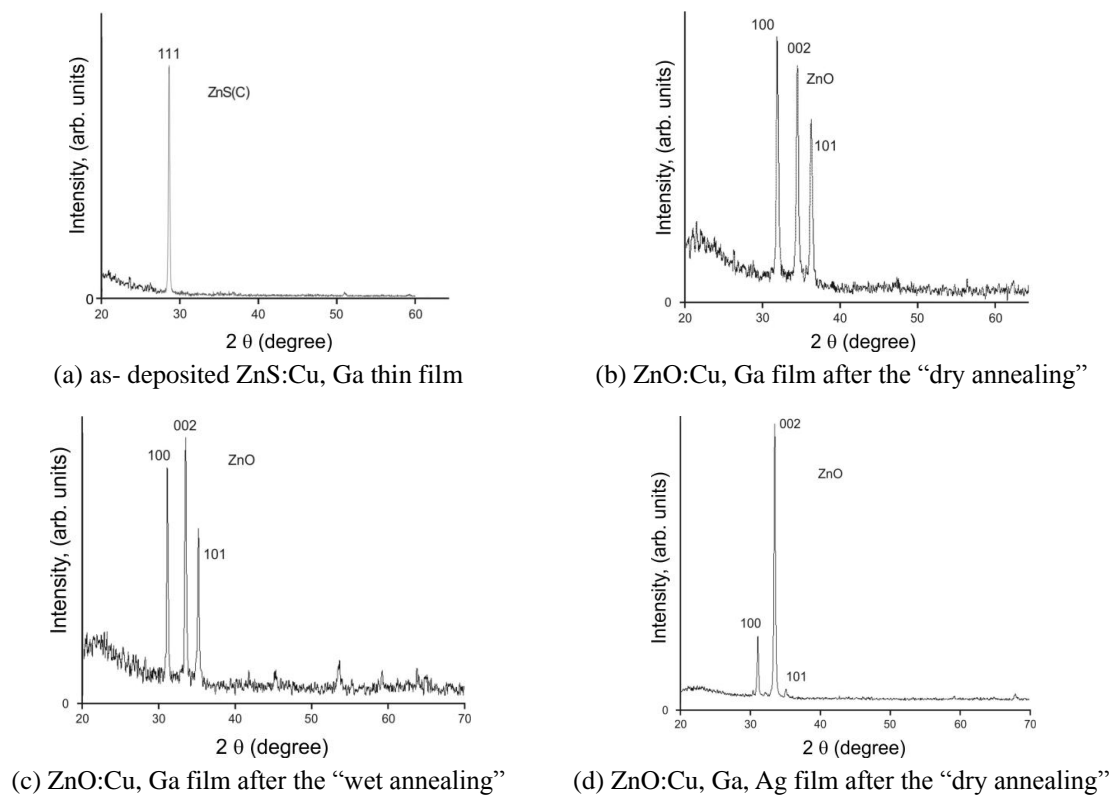


Fig. 1 XRD patterns of doped ZnS – ZnO thin films

The average grain size was estimated from the full-width at a half-maximum (FWHM) of 111 diffraction peak for ZnS phase and 002 diffraction peak for ZnO phase using the Scherrer equation as has been described by Warren (1990). The as-deposited ZnS:Cu, Ga film had the calculated average grain sizes of 27 nm. The calculated average grain sizes for ZnO:Cu, Ga films in 002 direction after the “dry annealing” and the “wet annealing” were 31 and 38 nm, respectively. The average grain size for ZnO:Cu, Ga, Ag film obtained after the “dry annealing” was 44 nm. The presence of Cu and Ga dopants at the thermal oxidation resulted not only in a phase transition in the whole volume of the thin film, but also induced a grain growth process. An additional Ag doping intensified this process even more.

AFM investigation of as-deposited ZnS:Cu, Ga thin films showed that the island growth mechanism is realized during the EBE deposition (Fig. 2(a)) and the film consisted of small grains with the size of 80-100 nm. The average grain size for ZnS thin film calculated from XRD data was the smallest.

The grains of ZnO:Cu, Ga films obtained after the “dry annealing” (Fig. 2(b)) and the “wet annealing” (Fig. 2(c)) enlarged and the average grain sizes were about 140 and 170 nm, respectively. After the “dry annealing” of ZnS:Cu, Ga, Ag film the grains enlarged more (size was about 210 nm), and became clearly separated. The observed hexagonal shape of the grains also confirms the phase transition from cubic to hexagonal crystal structure (Fig. 2(d)). The grain sizes estimated from AFM images were larger than those calculated from XRD data. As it is known, XRD investigations give the size of perfect crystallites (coherent domains) and AFM shows the grains as clusters of crystallites, which can have sizes in 5-6 times larger (Wang *et al.* 1999).

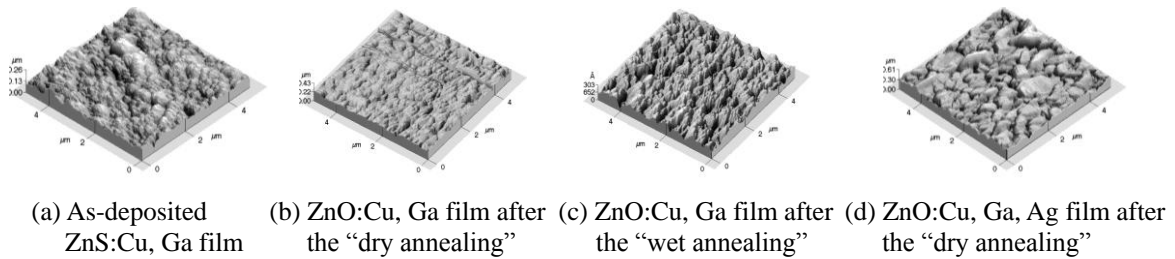


Fig. 2 AFM images of thin films as-deposited and after oxidation in different atmospheres

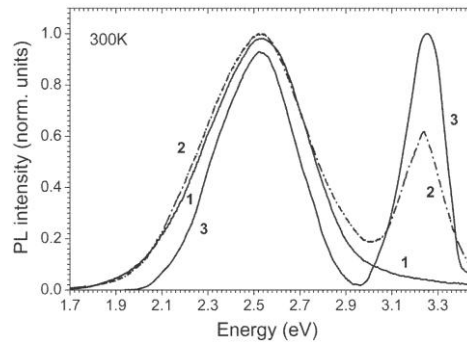


Fig. 3 PL spectra of undoped ZnO (1); doped ZnO:Cu, Ga (2); and ZnO:Cu, Ga, Ag (3) thin films after “wet annealing” ($T_{\text{meas}} = 300 \text{ K}$, $\lambda_{\text{excit}} = 337 \text{ nm}$)

It is well-known that for effective luminescent center formation in $A^{II}B^{VI}$ compounds there are used elements of group IB (Cu, Ag, Au) as an activator and group IIIA (Al, Ga, In) as co-activator for compensation of noncompensated charge of monovalent cation at its substitution of Zn divalent cation. The condition of charge compensation for doping impurity results in specific emission bands. As-deposited doped and undoped ZnS thin films did not luminesce under sufficiently intensive excitation (3.67 eV) neither at room (300 K) nor at low (77 K) temperatures. Luminescence appeared only after the thermal treatment that resulted in zinc oxide formation. An intensive green luminescence, which is typical for ZnO thin films (Karak *et al.* 2013), was observed uniformly in the whole area of the sample ($2 \times 2 \text{ cm}^2$) at 300 K. At the temperature to 77 K the intensity increased noticeably.

Room-temperature PL emission spectra of undoped ZnO, doped ZnO:Cu, Ga and ZnO:Cu, Ga Ag films after “wet annealing” are shown in Fig. 3. The excitation was realized in the intrinsic absorbing region ($\lambda = 337 \text{ nm}$).

In emission spectra of undoped ZnO films we observed only a visible radiation at 2.5 eV, meanwhile in PL of doped films two bands were present: a visible “green” band at 2.5 eV and ultra-violet (UV) band at 3.2 eV. Position of the emission band maxima did not change at the changing of excitation intensity. The intensity of UV band was about 0.6 of the intensity of visible band in PL spectrum of the film doped with Cu and Ga (Fig. 3, curve 2) and its FWHM was 220 meV, meanwhile the additional doping by Ag results in the considerable increase of the intensity of UV band (Fig. 3, curve 3) with the FWHM decreasing to 200 meV. At the temperature of 77 K the maximum position of “green” band did not change, but the UV band position shifted to the high-energy. The annealing atmosphere determined the maxima position of ultra-violet band. After the “dry annealing” the maximum position of UV band corresponded to 3.34 eV, but for the films after the “wet annealing” the maximum position of UV band shifted up to 3.35 eV. FWHM for the ultra-violet band at 3.35 eV was 60 meV. At the temperature of 77 K the intensity of ultra-violet band sharply decreased. The obtained results indicate that the visible radiation must be attributed to local center and ultra-violet radiation to the host lattice.

To exclude the influence of ultra-violet component in the spectrum and for more detailed investigation of the visible emission band, PL spectra of doped ZnO films were investigated in dependence on composition of doping impurities and oxidation conditions at low-energy excitation of 3.06 eV ($\lambda = 405 \text{ nm}$). The emission spectra of ZnO:Cu, Ga films prepared in “dry” (curve 1)

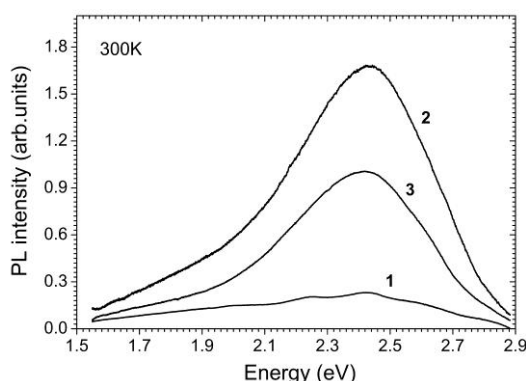


Fig. 4 PL spectra of thin films: ZnO:Cu, Ga - after “dry annealing” (1); and after “wet annealing” (2); and ZnO:Cu, Ga, Ag - after “dry annealing” (3) ($T_{\text{meas}} = 300\text{K}$, $\lambda_{\text{excit}} = 405 \text{ nm}$)

and in “wet” (curve 2) atmosphere and of ZnO:Cu, Ga, Ag film prepared in “dry atmosphere” (curve 3) are shown in Fig. 4. After the annealing in different atmospheres the position of band maximum almost did not change, but the intensity of the spectra for the films obtained at “wet annealing” increased by an order of magnitude. The additional doping of ZnO:Cu, Ga films by Ag resulted in a similar effect.

The excitation of PL by low-energy radiation led to changing of emission band shape and maximum position to 2.45 eV. Green band had symmetric shape at the excitation with 3.67 eV (Fig. 3), but at the excitation with 3.06 eV a band asymmetry appeared (Fig. 4). At the cost of the decrease of green band intensity appeared longer wave bands.

PL spectra of ZnO:Cu, Ga films prepared in “dry” and in “wet” atmospheres measured at 300 and 30 K are shown in Fig. 5. The emission intensity of the films prepared in “wet atmosphere” is noticeably higher than of the films prepared in “dry atmosphere”. All emission bands are asymmetrical. The largest contribution of “red” emission centers is observed at 30 K for the films obtained in “dry” atmosphere (Fig. 5, curve 2).

The excitation by even lower energy radiation ($\lambda = 457.9$ nm) led to even more suppression of green band emission and appearance of two bands (green and red) instead of one band at 30 K, since this wavelength corresponds to the excitation band edge. The same two emission bands were observed after oxidation of undoped ZnS thin films with “wet annealing” (see Fig. 6). The same two emission bands were observed after oxidation of undoped ZnS thin films using “wet annealing”

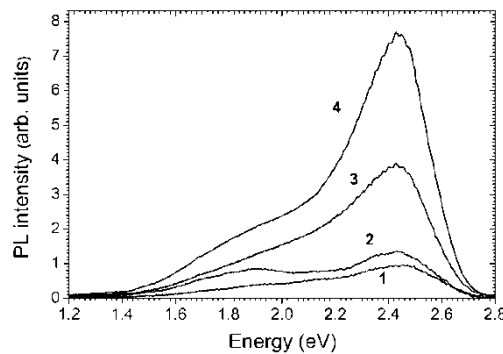


Fig. 5 PL spectra of ZnO:Cu, Ga thin films obtained after “dry annealing” - (curves 1 and 2); and “wet annealing” - (curves 3 and 4) ($T_{\text{meas}} = 300$ K – curves 1 and 3; $T_{\text{meas}} = 30$ K – curves 2 and 4; $\lambda_{\text{excit}} = 405$ nm)

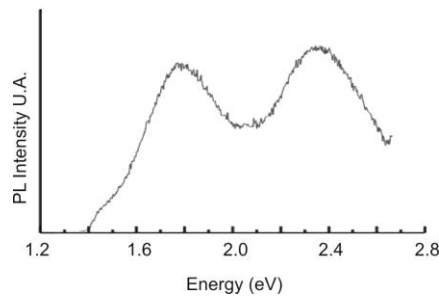


Fig. 6 PL spectra of ZnS:Cu, Ga thin film obtained after “wet annealing” ($T_{\text{meas}} = 30$ K, $\lambda_{\text{excit}} = 457.9$ nm)

Table 1 Resolution of the PL spectra of ZnO: Cu, Ga thin films obtained after “dry annealing” and “wet annealing”, measured at 300 and 30 K

Peak N°	“dry annealing”				“wet annealing”			
	300 K		30 K		300 K		30 K	
	Peak position (eV)	Rel. Int. (%)	Peak position (eV)	Rel. Int. (%)	Peak position (eV)	Rel. Int. (%)	Peak position (eV)	Rel. Int. (%)
1	2.45	100	2.45	100	2.45	100	2.45	100
2	2.18	62	2.22	66	2.26	52	2.28	63
3	1.92	36	1.93	54	1.96	25	1.94	33
4	1.74	20	1.74	36	1.77	20	1.77	13
5	1.55	7	1.58	15				

with “the largest water vapor quantity” of 0.08 g/m^3 (Kryshtab *et al.* 2009).

In order to obtain more detailed information about the changes of PL emission spectra of ZnO:Cu, Ga thin films in dependence on the presence of water vapors in the process of the film oxidation we resolved the emission spectra into several Gaussian components. The results of this resolving are presented in Table 1.

The obtained results indicate that “wet annealing” leads not only to PL intensity increase, but also in changing of maximum positions for all the bands except the “green” one (2.45 eV). The position of this band remains invariable both at the change of the annealing atmosphere and at the decrease of the measurement temperature up to 30 K. In fact, at the temperature decrease only “yellow-green” band shifted to the high-energy spectral region.

It is obvious, that the part of “red” centers has the largest total contribution for the films obtained without the water vapors. In PL spectrum of the film obtained in “dry atmosphere” an infrared (1.55 eV) band appeared.

The changes observed in the process of doped ZnS films transformation, allow concluding that the presence of Cu^+ , Ag^+ and Ga^{3+} ions accelerates chemisorption of oxygen in the film that leads to the change of structure, surface morphology and PL spectra composition. The similar acceleration of the oxidation process by the presence of trivalent Al^{3+} ion has been described by Behera and Acharaya (2008). The almost random grains distribution in ZnO film after ZnS film oxidation in the presence of Cu and Ga is observed. The use of additional Ag dopant leads to ZnO film formation with the strong grains preferred orientation in 002 direction.

Analysis of the obtained results shows that there are two excitation channels – high-energy and low-energy. The first one located in the region of $\geq 3.3 \text{ eV}$ and corresponds to transmission of the energy obtained at electron transition from valence band to conducting band. The second channel appears as the result of energy impurity absorption at ionization or excitation of impurity or intrinsic defects.

The green emission exists in ZnO and it is centered between 2.4 and 2.5 eV, and the origin of this emission is still an open question. Both native defects and impurities can be the sources of this emission. In the obtained ZnO films the dominant 2.45 eV band can be attributed to the radiative transition between the band and the local center of luminescence (for example Cu_{Zn}) or to the donor- acceptor pair. Also, the Zn vacancy as acceptor-type defect is a likely candidate as has been shown by Janotti and Van de Walle (2009), but Studenikin *et al.* (1998) suggested that oxygen vacancies are responsible for green luminescence. Most probably that both types of mentioned

centers are present in our case.

The excitation mechanism of “yellow” centers (2.2 eV) is the same as for “green” one. But the influence of water vapors on the centers composition is different. “Wet annealing” results in considerable maximum position shift of these centers on 0.08 eV in high-energy region. At temperature decrease the largest shift is observed for “yellow” band. This allows to conclude that the radiative transition responsible for this band is realized between the band and the level in band gap, whereas the rest of transitions correspond to donor-acceptor pairs.

The possible origin of the observed red emission can be attributed to defect complexes that include Ga atoms as has been proposed by Buyanova *et al.* (2009) for Ga doping ZnO films grown by MBE. Besides, the Ga doping on ZnO films can enhance the green emission intensity (Kim *et al.* 2008).

4. Conclusions

The polycrystalline doped ZnO thin films are obtained by oxidation of doped ZnS thin films. The presence of small amount of Cu and Ga impurities (about 0.2 at %) in the ZnS thin films, deposited by electron beam evaporation method, results in complete transition from ZnS to ZnO structure at the oxidation process both in “dry” and “wet” atmospheres. The use of additional Ag doping leads to a strong grain orientation in 002 direction of the obtained ZnO film.

The presence of water vapors in the atmosphere at the ZnS thin film oxidation significantly increases the PL intensity in the whole visible spectral range. In PL spectra of doped ZnO films excited at 337 nm wavelength two bands are observed, as visible 2.5 eV band and UV 3.2 eV band. The intensity of UV band increases at additional Ag doping. The annealing atmosphere determines the maximum position of UV band.

The impurity type does not influence on the shape of visible band. Resolution of the visible PL spectra, excited at 405 nm, into several Gaussian components shows that the “wet annealing” results not only in PL intensity increase, but also in changes of maxima positions for all the resolved bands except the “green” one (2.45 eV). The position of this band remains invariable both at the change of the annealing atmosphere and at the decrease of measurement temperature down to 30 K. The corresponding luminescent centers have different composition that follows from the temperature dependence of the emitting spectra.

Acknowledgments

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