Luminescence of ZnO heterolayers prepared by isovalent substitution on ZnTe substrates

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Abstract

The optical properties of undoped zinc oxide layers prepared by isovalent substitution technique are discussed. The singularities observed in the reflection and luminescence spectra occurring at 3.2 and 3.265 eV are related to the energy distances between the conduction band and the valence subbands, the basic one and that split due to spin-orbit interaction. The emission bands at the energies less than 3.2 eV are formed by transitions of charge carriers with the participation of local centres.

Introduction

Owing to a wide energy gap ($E_g = 3.3$ eV at 300 K) and a variety of point defects, zinc oxide manifests an extremely rich radiation spectrum [1]. In this respect, the most important technological task is preparation of the above material that ensures efficient luminescence in the desired spectral region, especially in the ultra-violet spectral range, which is poorly investigated. One of the possible lines of attack on this problem should be doping of the semiconductor with isovalent impurities [2]. In general, isovalent substitution technique that combines synthesis of a new compound and its simultaneous doping with an appropriate isovalent impurity may prove to be the most promising in this aspect [3]. Then the desired variations are implemented by using substrates of different chemical compositions. In turn, this brings to the forefront the studies of physical properties of the resulting heterolayers. The present work analyzes spectral characteristics of ZnO heterolayers, which are isovalently substituted and synthesized on the substrates based on single crystals of ZnTe.

Objects and methods of investigation

Original substrates of a standard size $4 \times 4 \times 1 \, \text{mm}^3$ were cut from the bulk crystals of zinc telluride of cubic modification (β-ZnTe). They were grown with the Bridgman-Stockbarger technique from the melt of stoichiometric composition. Especial care was

taken of undoping those substrates. The wafers were subject to step-by-step polishing, both mechanical and chemical, and the processing quality was checked using the criterion of appearance of the bulk photoluminescence effect. ZnO heterolayers were created by thermal annealing of the substrates in the air at $T_a \approx 700\ °C$ for 5–20 minutes. As a consequence, the surface changed its colour from red to white. In so doing, essential changes took place also in the reflection and luminescence spectra (see the detailed discussion presented below).

The optical spectra were measured on the installation comprising a diffraction monochromator MDR-23 and a standard synchro detection system. The photoluminescence was excited by means of a nitrogen laser with the wavelength of $\lambda_m = 0.337\ \mu m$. Its radiation power was varied by means of a calibrated set of light filters. Xenon lamp with a "smooth" spectrum in the range of photon energies under study was used for the reflection measurements. The spectra under test were recorded automatically and were corrected by nonlinearities of optical elements of the measuring setup, allowing the measurements of spectral characteristics in the two modes, the conventional and λ-modulation ones.

Results and discussion

Formation of a new chemical compound in the process of annealing of ZnTe substrates is proved by a number of principal changes in the reflection spectrum R'_ω and the luminescence spectrum N_ω (see Fig. 1). As follows from the data presented in Fig. 1, the negative peak of the curve R'_ω for the basic substrates is located at $\hbar\omega \approx 2.26$ eV, which agrees with the E_g value for the zinc telluride of cubic modification [4].

The maximum of the photoluminescence spectrum is shifted with regard to E_g towards the region of low energies, thus testifying participation of local centres in the recombination processes. The presence of photons with $\hbar\omega > E_g$ in the radiation points to the presence of a band-to-band component. Nevertheless, it is much less intensive if compare to the dominant impurity one.

The minimum of the reflection spectrum for the synthesized heterolayer is located at $\hbar\omega \approx 3.2$ eV, which is close to the value E_g peculiar of the hexagonal zinc oxide ($E_g \approx 3.3$ eV for α-ZnO at 300 K [1]). The difference in the E_g values is due to the fact that the isovalently substituted heterolayer has a different crystalline structure, cubic in our case (i.e., β-ZnO). This assumption is proved by a variety of experimental facts. First of all, the crystalline structure of heterolayers prepared with the isovalent substitution technique conforms the structure of the basic substrates [3]. Second, the energy gap of ZnO layers synthesized on β-ZnSe and β-ZnS substrates is also equal to 3.2 eV at 300 K [5]. And, finally, the position of the positive peak in the reflection spectrum corresponds to "bend" on the curve N_ω (see curves 2′ and 2 in Fig. 1). The above features are caused by transitions with participation of the valence subband split due to spin-orbit interaction. The absence in the optical spectra of other peculiarities related to the crystalline field
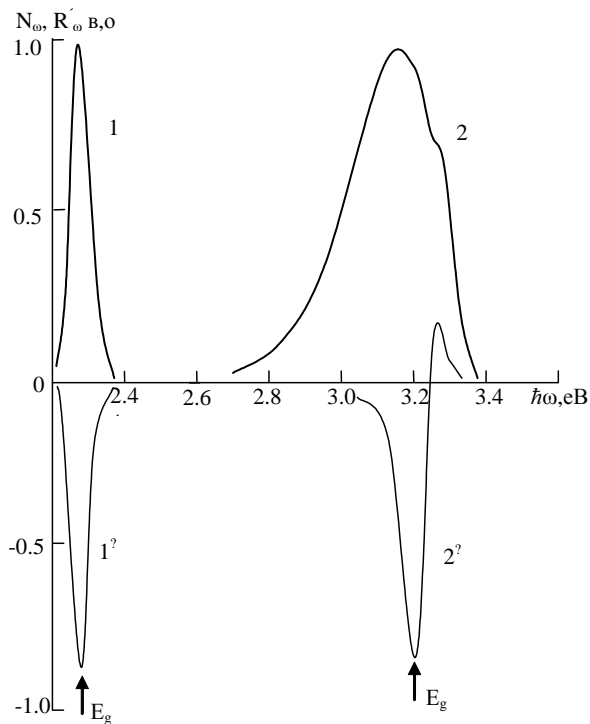
Fig. 1. Radiation (curves 1 and 2) and reflection (curves 1′ and 2′) spectra for the ZnTe substrates (1, 1′) and ZnO heterolayers (2, 2′) at 300K.

typical of hexagonal modifications bears additional witness to the formation of just β-ZnO.

In all the heterolayers we observe an intense luminescence in the UV region, with the efficiency equal approximately to 15 % at 300 K. An abnormally broad radiation spectrum of the heterolayers (see curve 2 in Fig. 1) indicates that we deal with a superposition of several elementary bands. Some of them can be revealed experimentally, using a lower excitation level (Fig. 2), while the rest can be calculated analytically.

Let us dwell on these issues in a more detail, with regard to the peculiar power points previously obtained from the reflection spectra. Using the known expression for the band-to-band radiative transitions [6],

$$N_\omega \sim (\hbar\omega)^2 \sqrt{\hbar\omega - E_g} \cdot \exp\left(-\frac{\hbar\omega - E_g}{kT}\right), \tag{1}$$

and the value $E_g = 3.2$ eV, we obtain the curve denoted in Fig. 2 by the symbol A. The discrepancy between the calculated and experimental values of N_ω in the high-energy region is caused, as mentioned earlier, by the electron transitions to the split valence band. This A_Δ band can also be calculated from Eq. (1) with the E_g replaced by another parameter $E'_g = E_g + \Delta_{SO} = 3.2 + 0.065$ eV which, after summing with the A band, describes well the high-energy "wing" of the edge radiation (Fig. 2). We mark that the resulting value of Δ_{SO} correlates with a similar parameter found from the reflection spectrum (see curve 2 in Fig. 1). At the same time, the value of Δ_{SO} does not correspond to the energy of spin-orbit splitting for α-ZnO [1], which represents a complementary
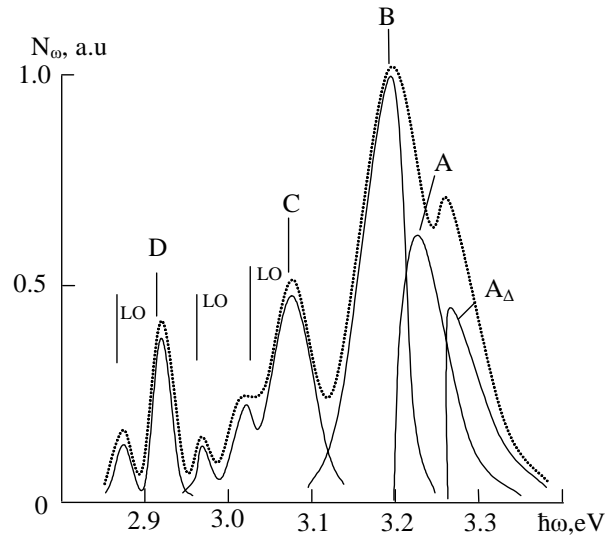
Fig. 2. Photoluminescence spectra recorded at 300 K: the experimental values are marked with dots and the calculated ones with solid lines.

evidence in favour of the cubic structure of the resulting ZnO heterolayers.

The investigations have demonstrated that the photoluminescence spectrum in the region of energies $\hbar\omega < E_g$ is represented by three bands (B, C and D) formed with participation of local centres. In this case, according to the theory [6], the shape of the band with the maximum at $\hbar\omega_m$ can be described by the relation

$$N_\omega = \sum_{n=0}^{\infty} N_{\omega_n} \exp\left[-\frac{(\hbar\omega - \hbar\omega_m \pm n\hbar\omega_0)^2}{\sigma^2} \right],$$ (2)

where $\hbar\omega_0$ is the phonon energy and the signs "+" and "–" correspond to the processes of phonon absorption and emission, respectively. The amplitude $N_{\omega n}$ of the n-phonon band is determined as

$$N_{\omega_n} = N_{\omega_0} \overline{M}/n!,$$ (3)

where $\overline{M}$ denotes the degree of electron-phonon interaction found experimentally from the relationship $N_{\omega 0}/N_{\omega 1}$. The parameter σ is related to the half-width $\hbar\omega_{1/2}$ of the phonon-free band via the relation

$$\sigma = h\omega_{1/2}/8\ln 2 .$$ (4)

In the first approximation, the half-width can be assumed with a sufficient degree of accuracy to be equal to $1.5kT$. The experimentally found energy of the LO-phonon is ≈ 50 meV, which is considerably less than the corresponding parameter known for α-ZnO ($\hbar\omega_0 \approx 74$ meV [1]). This is further proof of obtaining the zinc oxide layers with a different crystalline structure.

Using the experimental values of the parameters $\hbar\omega_m$, $\hbar\omega_0$ and $\overline{M}$, one can calculate the shape of the B, C and D bands from Eqs. (2)–(4). As follows from Fig. 2, the calculated curves describe fairly well the radiation bands observed in the appropriate spectral range. At the same time, the final answer to the question regarding the nature of the recombination centres, as well as the crystalline structure of heterolayers synthesized by us need further investigations exceeding the scope of this paper.

Conclusions

Thus, the results obtained by us testify a possibility for obtaining isovalently substituted layers of zinc oxide with a high enough radiation efficiency (~ 15% at 300 K) in the UV range. The luminescence spectrum consists of a series of bands caused by the band-to-band transitions and the recombination of carriers with participation of local centres. The energies of the longitudinal optical phonons and the spin-orbit splitting have been determined.

References

1. Özgür Ü, Alivov YaI, C. Liu, A. Teke, M. A. Reshchikov, Doan S., Avrutin V., Cho S-J, and Morkoç H, 2005. A comprehensive review of ZnO materials and devices. J. Appl. Phys. 98: 041301

2. Fistul VI, Atoms of doping impurities in semiconductors. Moscow: Fizmatlit Publ. (2004).

3. Makhniy VP, Baranjuk VE, Demich N V, Melnyk VV, Malimon IV, Slyotov Mikhail M, Sobistchanskiy BM, and Stets E V, 2001. Isovalent substitution: a perspective method of producing heterojunction optoelectronical devices. Proceedings SPIE. **4425**: 272–276.

4. Georgobiani AN, 1974 Wide-gap A^2B^6 semiconductors and prospects of their application. Uspekhi Fiz. Nauk. **113**: 129–155.

5. Makhniy VP, Slyotov MM and Khusnutdinov SV, 2007. Preparation of ZnO heterolayers on substrates of zinc chalcogenides. Inorgan. Mater. **43**: 1–3.

6. Gribkovskiy V.P. Theory of light absorption and emission in semiconductors. Minsk: Nauka i Tekhnika (1975).