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THE OPTICAL AND STRUCTURAL PROPERTIES OF QUANTUM WELLS $Mg_{0.27}Zn_{0.73}O/ZnO$ PRODUCED BY PULSED LASER DEPOSITION

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The multiple quantum wells (MQW) $Mg_{0.27}Zn_{0.73}O/ZnO$ have been grown by pulsed laser deposition method with different well width L_w. The optical and structural characteristics of MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ have been investigated. The quantum confinement effect showing up in the blue shift of exciton peak in low temperature (8 K) photoluminescence spectra at well width reduction has been studied. It is established that intensity exciton peak I_{ex} and Einstein's characteristic temperature Θ_E increase at reduction of well width L_w. It is revealed that the discontinuity ratio of conduction and a valence bands in heterostructure $Mg_{0.27}Zn_{0.73}O/ZnO$ is 0.65/0.35 that corresponds to the literature.

1. INTRODUCTION

The semiconductor two-dimensional structures, such as quantum wells and the superlattices, serve for more than a decade as a basis for a wide spectrum of optoelectronic devices. Recently the great attention is given to $A^{II}B^{VI}$ (or $A^{III}B^{V}$) wide gap semiconductors because the optoelectronic devices based on them are capable of working in ultra-violet and visible ranges of wavelengths [1-5]. Of particular interest in this range of semiconductors is zinc oxide, thanks to wide band gap E_g=3.37 eV and high exciton binding energy (60 meV) that provides effective exciton emission at higher temperatures on comparison with III-V optical semiconductors [6]. High heat conductivity, effective luminescence, as well as mechanical and chemical stability allow the ZnO based devices to work under most extreme conditions [7]. The excitons in the quantum wells (QW) based on ZnO have higher stability on comparison with III-V QW because of exciton binding energy increase and exciton-fonon interaction reduction, caused by quantum confinement. Thanks to these effects, the excitons should play the important role in such processes as stimulated radiation in the multiple quantum wells (MQW) based on zinc oxide even at a room temperature [6].

In the present work the series $Mg_{0.27}Zn_{0.73}O/ZnO$ MQW with different well widths has been grown. The quantum confinement effect showing up in the blue shift of exciton peak in photoluminescence spectra (PL) is investigated at well width reduction. It is established that the intensity of exciton peak and Einstein's characteristic temperature increase at well width L_w reduction. The values of conductivity and valence bands discontinuity in heterostructure $Mg_{0.27}Zn_{0.73}O/ZnO$ have been defined. The research of structural properties of $Mg_{0.27}Zn_{0.73}O/ZnO$ has been conducted.

2. EXPERIMENTAL TECHNIQUE

The series of multiple quantum wells $Mg_{0.27}Zn_{0.73}O/ZnO$ with a well width range from 1.04 nm to 20 nm was grown on sapphire substrates (00.1) by pulsed laser deposition method. The growth of MQW was carried out in a high vacuum chamber with initial vacuum not worse than 10^{-7} Torr. The ablation of ceramic targets was made by excimer laser LC-7020 at pulse repetition frequency of 10 Hz (λ =248 nm, τ =15 ns), the energy density of laser radiation on the target being 3 J/cm^2. The detail of experimental setup we already reported in [8].

As the mismatch of *a*-parameter of ZnO lattices and the sapphire (00.1) substrate is ~18 % the buffer layer $Mg_{0.27}Zn_{0.73}O$ of thickness ~50 nm was preliminarily grown on the substrate. The thickness *b* of individual barrier layers $Mg_{0.27}Zn_{0.73}O$ and the total thickness $m*L_w$ of ZnO layers was constant for all the MQW (*b*=6 nm and $m*L_w$=40 nm, *m* – the number of periods). The substrate temperature during growth was maintained in the range $(450\pm5)^0$C. The substrates were mounted within 7 cm from the targets. For achievement of an atomic-smooth surface, the substrates with the grown on them buffer layer $Mg_{0.27}Zn_{0.73}O$ were annealed for 2 hours in oxygen atmosphere at the temperature 1000^0C. The oxygen (O_2) was used as buffer gas; its pressure in the chamber was 5 mTorr.

To study the optical properties of MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ the low temperature (8 K) spectra of a photoluminescence were measured in the short-wave area. The PL excitation was carried out by a continuous He-Cd laser (λ =325 nm, W=23 mW) and a pulsed-periodical KrF excimer laser, the PL spectra were registered by Ocean Optics HR4000 spectrometer. The research of structural characteristics, diffusion processes and interface quality of multiple quantum wells $Mg_{0.27}Zn_{0.73}O/ZnO$ was performed by the multi-purpose X-ray diffractometer D8 Discover (Bruker-AXS). The surface morphology was investigated by an atomic force microscope (AFM) DME DualScope 2401.

3. RESULTS AND DISCUSSION

The research of surface morphology of the buffer layer $Mg_{0.27}Zn_{0.73}O$ by the atomic force microscopy method has shown that the surface roughness after the deposition is 5-12 nm. To reduce the surface roughness the substrates with buffer layers were subjected to thermal annealing at various temperatures in oxygen atmosphere. From Fig.1 it is seen that the minimum roughness of the surface not exceeding 1 nanometer is reached at annealing temperature 1000^0C.

The band gap of the buffer and barrier layers $Mg_{0.27}Zn_{0.73}O$ was 3.57 eV, and for the active layer ZnO it was 3.36 eV. The X-ray analysis of ZnO and $Mg_{0.27}Zn_{0.73}O$ films has indicated that their lattice mismatch does not exceed 0.66 %. A study has been made of the low temperature photoluminescence spectra (at 8K) of multiple quantum wells $Mg_{0.27}Zn_{0.73}O/ZnO$.

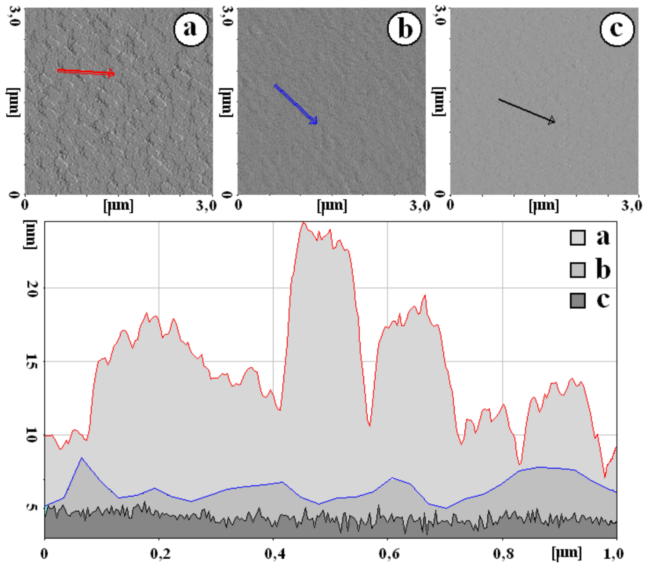

Fig.1. The surface morphology of buffer layer $Mg_{0.27}Zn_{0.73}O$ on a sapphire substrate (00.1): (a) – before annealing, (b) – annealed at 800^0C, (c) - annealed at 1000^0C, and cross-section profiles of corresponding surfaces (below).

On Fig.2 the photoluminescence spectra of the $Mg_{0.27}Zn_{0.73}O$/ZnO MQW series with the well width L_w varying from 1.04 nm to 20 nm are presented. The PL spectrum of 70 nm ZnO film is presented in this figure for comparison. The monotonous nonlinear blue shift of the UV peak position with the quantum well width reduction characterizes the quantum confinement effect in the two-dimensional structures $Mg_{0.27}Zn_{0.73}O$/ZnO [6,9-11].

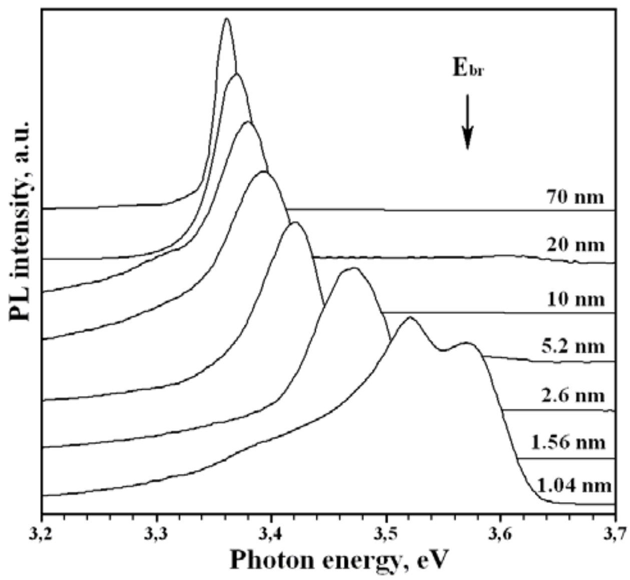

Fig.2. The low temperature photoluminescence spectra of MQW $Mg_{0.27}Zn_{0.73}O$/ZnO with various well width L_w.

The important parameter in designing heterostructures is the value of energy band discontinuity in the conduction and valence bands. The solution of the Schrödinger equation for a finite square potential well under the condition of symmetry and continuity of the wave function in the conduction and valence bands is possible to obtain as follows [12]:

$$\tan\left[\sqrt{\frac{2m^*_{1(e,h)}E_n^{(e,h)}(L_w)}{\hbar^2}}L_w\right] = \sqrt{\frac{m^*_{2(e,h)}(\Delta E_{(C,V)} - E_n^{(e,h)}(L_w))}{m^*_{1(e,h)}E_n^{(e,h)}(L_w)}}, \quad (1)$$

where $\hbar$ - Planck's constant, E_n^e and E_n^h - the proper values of energy in the potential wells for an electron and a hole respectively, n=1,2,3 … - an integer number, ΔE_C and ΔE_V - the discontinuities in the conduction and valence bands. The values of electron and hole effective masses have been chosen as m_{1e}*=0.28m_0 and m_{1h}*=1.8m_0 for the active layer ZnO [13] and m_{2e}*=0.4m_0 and m_{2h}*= 2m_0 for the barrier layers $Mg_{0.27}Zn_{0.73}O$ [14]. Within the limits of the given model the light holes were not considered.

The resulting exciton energy in a quantum well at n=1 will be defined by the expression:

$$E(L_w) = E_g(ZnO) + E_1^e(L_w) + E_1^h(L_w) \quad (2)$$

Fig.3 illustrates the dependence of energy position of photoluminescence MQW exciton peak on the well width L_w is presented. The relation between the discontinuities of the conduction band ΔE_C and valence band ΔE_V was used as a fitting parameter. The best coincidence of the numerical and experimental data has been obtained at the ratio $\Delta E_C/\Delta E_V$=0.65/0.35 that is in a good agreement with the results of the work [15].

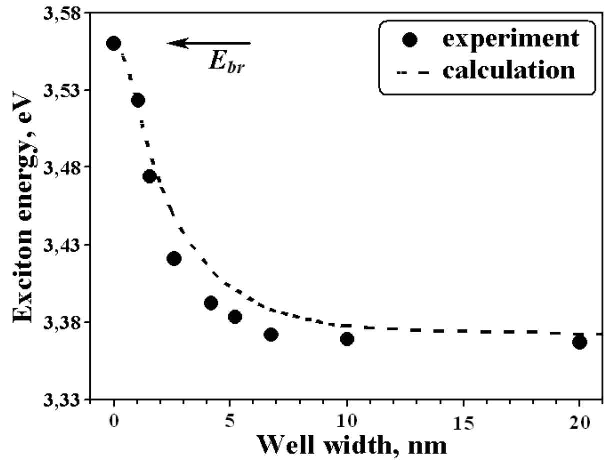

Fig.3. The dependence of position of MQW $Mg_{0.27}Zn_{0.73}O$/ZnO photoluminescence exciton peak on quantum well width L_w.

The full width at half maximum (FWHM) of the exciton peak in MQW also increased with reduction of the quantum well width L_w that can be explained by random fluctuation of the width $L_w \pm \delta L_w$ of quantum wells, which leads to non-uniform broadening of the photoluminescence spectrum. The smaller is the width of a well L_w, the higher is the influence of this fluctuation δL_w on half width of an UV peak in the photoluminescence spectra of MQW [6,16].

The nonlinear growth of exciton peak intensity I_{ex} was observed in PL spectra of MQW $Mg_{0.27}Zn_{0.73}O$/ZnO at the quantum well width L_w reducing (Fig.4). The maximum PL intensity value I_{ex} was evidenced in MQW with the well width L_w=2.6 nm, at further reduction of L_w the PL intensity was sharply decreased.

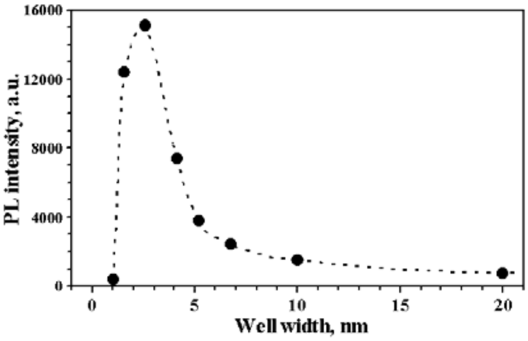

Fig.4. The dependence of MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ photoluminescence intensity on quantum well width L_w.

According to Boze-Einstein model the exciton energy in a quantum is expected to vary with temperature under the following law [10]:

$$E(T) = E(0) - \frac{2\alpha_E}{\exp(\frac{\Theta_E}{T}) - 1}, \qquad (3)$$

where α_E – a constant corresponding to exciton-phonon interaction, $\Theta_E=hf/k$ - Einstein's characteristic temperature, and $E=k\Theta_E$ – the averaged phonon energy, h – Planck's constant, k – Boltzmann constant, f – the frequency of phonon fluctuations.

To define the character of Einstein temperature Θ_E dependence on quantum well width we studied the temperature dependence of the photoluminescence spectra of MQW $Mg_{0.27}Zn_{0.73}O/ZnO$. The PL spectra of MQW (L_w=2.6 nm) in a range of temperatures 8÷325 K are presented on Fig.5, and the insert of Fig.5 depicts the temperature dependence of exciton energy, obtained from these spectra. The theoretical dependence (3) derived from the adjustment of α_E and Θ_E parameters is also presented.

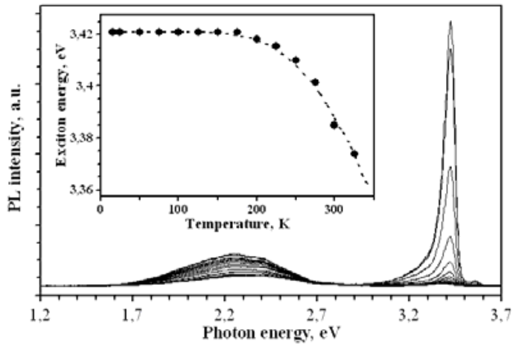

Fig.5. The PL dynamics of MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ (6 nm/2.6 nm) on temperature in the range 8÷325 K. An insert illustrates the temperature dependence of exciton energy in MQW.

Einstein's characteristic temperature Θ_E was defined for all the samples MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ by similar approximation of equation (3). Fig.6 presents the dependence of Einstein's characteristic temperature Θ_E on quantum well width L_w. It is seen that Θ_E increases as the quantum well width reduces up to L_w=2.6 nm, and then sharply decreases. The dependences shown on Fig.4 and Fig.6 very well correlate among themselves and have, on our opinion, the common nature. The exciton peak intensity I_{ex} and Einstein's characteristic temperature Θ_E growth with reduction of quantum well width L_w can be explained by an increase in characteristic exciton binding energy in a quantum well that has been demonstrated in works [15,17].

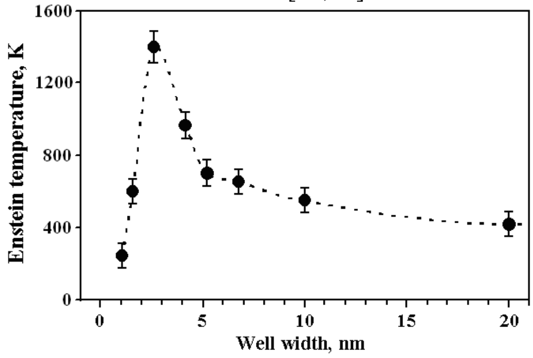

Fig.6. The dependence of Einstein's characteristic temperature Θ_E of MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ on quantum well width L_w.

The abrupt decrease of I_{ex} and Θ_E for L_w<2.6 nm can follow from the quantum well width L_w getting comparable with the value of interface roughness which is ~1 nm and excitons undergo scattering on these irregularities, which leads to quenching of photoluminescence.

As noted above, the excitons are expected to play an important role in stimulated radiation [6]. For studying a possibility of stimulated radiation in MQW the photoluminescence spectra have been investigated in relation to power density of exciting radiation under pumping with excimer KrF laser. Fig.7(a) presents on a logarithmic scale the photoluminescence spectra of MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ with well width L_w=5.2 nm, measured at a room temperature on pumping with the excimer KrF laser with intensity from 50 to 850 kW/cm^2. For comparison, the PL spectrum of the same structure excited by a continuous He-Cd laser is shown.

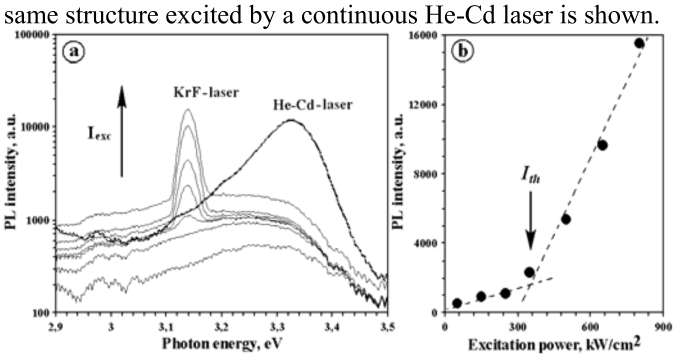

Fig.7. The PL spectra of a line 3.14 eV of MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ with a well width L_w=5.2 nm: (a) excitation by the He-Cd laser and the excimer KrF laser with pump power variation from 50 to 850 kW/cm^2; (b) dependence of PL amplitude of a line 3.14 eV of MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ on excimer KrF laser pump power.

At optical pump power densities ~350 kW/cm^2, the PL spectra produced a wide FWHM peak of 112.4 meV corresponding to the exciton line inside the quantum well of 3.34 eV. Further increase of pulsed pump power resulted in predomination of a narrow line with FWHM equal to 31.3 meV, shifted to the red region by 0.2 eV, its intensity rising sharply. As this took place, a characteristic bend corresponding to the threshold of stimulated radiation excitation was observed on the plot of PL line intensity dependence at 3.14 eV on KrF laser pump power. The intensity of this line, unlike the exciton peak of 3.34 eV in the quantum well, was practically not varied. The similar result was observed in works [6,17].

Fig.8 shows the cross-section image of 20 quantum wells $Mg_{0.27}Zn_{0.73}O/ZnO$ produced by a scan electron microscope.

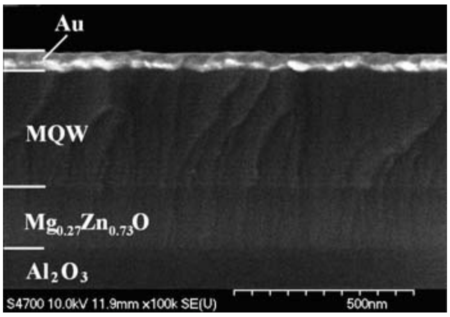

Fig.8. A SEM-image of cross-section of 20 quantum wells $Mg_{0.27}Zn_{0.73}O/ZnO$ grown on a sapphire substrate (00.1) with a buffer layer $Mg_{0.27}Zn_{0.73}O$. For contrast the structure was covered by a gold film.

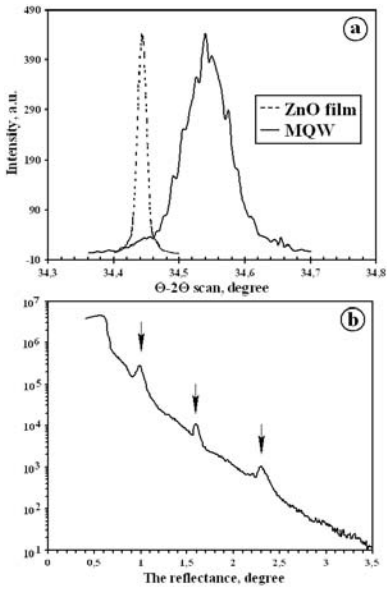

Fig.9. Θ-2Θ scans of a ZnO film and MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ with the well width L_w=2.6 nm (a). A curve of mirror reflection of MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ with the well width L_w=5.2 nm.

The structural properties of MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ were examined by X-ray reflectometry method. The width of the X-ray beam was 0.2 mm, the collect slot in front of the detector also had the size of 0.2 mm. On Fig.9(a) are shown Θ-2Θ the scans of a ZnO film and MQW $Mg_{0.27}Zn_{0.73}O/ZnO$. The characteristic period of signal modulation and a special software package LEPTOS were used to define the width L_w=2.6 nm of a single well that agrees nicely with the expected thicknesses set by the growth speed [18].

To evaluate the quality of interfaces, the chart of reciprocal space has been measured in the vicinity of point 000 of the reciprocal lattices (a curve of mirror reflection). Fig.9(b) presents the curve of mirror reflection of MQW $Mg_{0.27}Zn_{0.73}O/ZnO$ presented in Fig.8, which has been obtained by subtraction of diffusion scattering distribution from the experimental Θ-2Θ curve. The presence of the resonant diffusion scattering effect indicates to correlation in interface morphology in the whole structure, i.e. roughnesses of the top layers are inherited from the bottom ones and do not exceed 1 nm.

4. CONCLUSION

The multiple quantum wells $Mg_{0.27}Zn_{0.73}O/ZnO$ grown by the pulsed laser deposition method have shown high structural quality and sharp interfaces. We observed the quantum confinement effect in multiple quantum wells $Mg_{0.27}Zn_{0.73}O/ZnO$ showing up in a blue shift of exciton energy at the well width reduction. This reduction caused a nonlinear rise of PL exciton peak intensity I_{ex} and Einstein's characteristic temperature Θ_E which also characterizes the quantum confinement effect in two-dimensional structures. It was found that the ratio of energy zone discontinuity values in the conduction and valence bands is 0.65/0.35. The effect of stimulated exciton radiation in MQW was revealed with the excitation threshold of ~350 kW/cm^2. The effects mentioned above have a fundamental character, but can be applied in designing light emitting diodes and lasers with the tunable wavelength and high temperature stability based on heterostructures $Mg_xZn_{1-x}O/ZnO$.

5. ACKNOWLEDGMENTS

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