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Influence of Surface Plasmon Resonance on ZnO Films Photoluminescence. Role of Excitation Level

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RESEARCH ARTICLE

In the course of luminescence enhancement investigation of ZnO films coated with Ag the authors discovered that enhancement by surface plasmon resonance takes place only under low enough pumping level while under a high pumping level only quenching is observed. For interpretation of this effect simplified mathematical model describing influence of surface plasmon resonance on near band edge luminescence in ZnO is proposed. Proposed model is presented by set of rate equations considering particularly increasing of exciton recombination probability and losses depended on pumping level. These losses most likely should be of Joule's type. Experimental dependences of excitonic luminescence intensity of ZnO films coated with Ag on pumping level appear to be close to simplified theoretical ones based on this model.

Keywords: Surface Plasmon Resonance, Zinc Oxide, Role of Excitation Level, Rate Equations.

1. INTRODUCTION

At present surface plasmon resonance (SPR) and its various manifestations are being studied intensively. Much attention was paid to the investigation of the enhancement of photoluminescence under the influence of SPR, particularly on ZnO films (see for example Refs. [1–3]). However, these investigations do not consider role of excitation level, i.e., pumping level in this process.

Current ideas about the mechanism of interaction between emitting centers, for example excitons, and localized surface plasmons (LSP) are following:[4] recombination of excitons, primarily excited by external pumping source, transmits photons to form surface plasmons that generate a strong electromagnetic field nearby the metal nanoparticle. This field stipulated by plasmons enhances the rate of exciton radiative recombination but at the same time plasmons - vibrating electrons - provide losses. From this description it is obvious that pumping level is significant in this mechanism.

2. EXPERIMENT AND SAMPLES

Up to now the vast majority of investigations in the field of SPR in ZnO/Ag have been carried out using He–Cd laser pump (continuous wave of 325 nm, power∼20 mW), i.e., at a low excitation level. These investigations carried out by the authors on some samples of ZnO films with Ag coating demonstrated luminescence enhancement in case of using He–Cd laser pumping and luminescence quenching in case of Nd:YAG laser pumping (third harmonic, 355 nm, pulse duration∼10 ns, pulse energy∼mJ). However, the decrease of Nd:YAG laser pumping intensity to the level of microjoules allows to achieve the enhancement of ZnO films luminescence due to Ag coating (SPR effect). This is illustrated in Figures 1 and 2.

Generally speaking, it is likely that different results between pumping by He–Cd and Nd:YAG lasers are determined not only by the intensity of pumping but also by its wavelength and its temporary characteristics. However, based on our results the strong dependence of luminescence enhancement under the influence of SPR on pumping intensity does not give rise to doubt.

As far as we know dependence of photoluminescence enhancement under the influence of SPR on pumping level was observed only in Ref. [8] but in this paper no theoretical interpretation of this dependence was given. It should be noted that dependence of electroluminescence enhancement under the influence of SPR on electrical current density is shown in Figure 3 in paper[9] but there is no detailed interpretation either.

Experiments were performed with ZnO sample prepared by thermal deposition (Fig. 3(a)). The sample surface was

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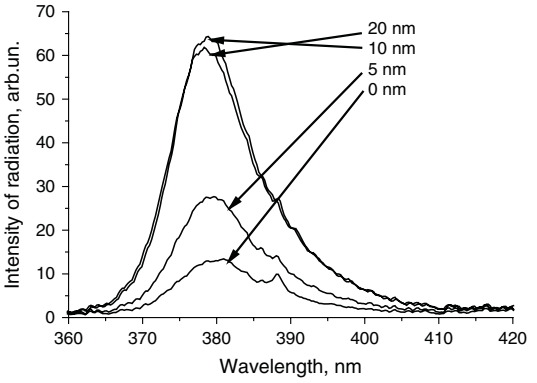

Fig. 1. Spectra of the sample with Ag coating of different thickness, registered with pumping by He–Cd laser (CW, 325 nm, 20 mW).

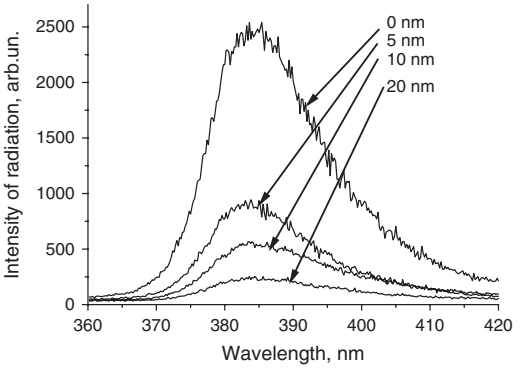

Fig. 2. Spectra of the sample with Ag coating of different thickness, registered with pumping by Nd:YAG laser (pulsed, 6 ns, 355 nm, ~100 μJ).

divided into four parts and coated with different layers of Ag by magnetron sputtering. As in many other investigations (for example Refs. [1–3, 5, 6]), Ag was selected for coating because it has a wide extinction maximum in the wavelength range of ZnO exciton recombination radiation. Indicated Ag layer thicknesses (5 nm, 10 nm, 20 nm) are conditional values calculated based on the assumption that Ag used for treatment of ZnO samples forms continuous and uniform layers.

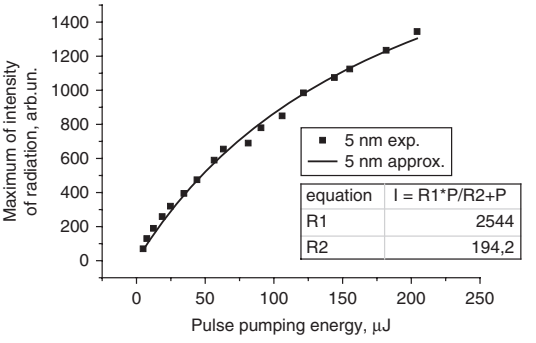

Fig. 4. Dependence of luminescence intensity on pumping level for the part of the ZnO sample coated with 5 nm of Ag (pumping spot diameter on the sample is ≈1 mm).

From Figure 3(b) it can be seen that Ag coating does not result in continuous layer but forms stand alone almost spherical Ag nanoparticles embedded in ZnO polycrystalline film elements. Spectra of ZnO exciton emission under different pumping levels of the third harmonics of pulsed Nd:YAG laser (355 nm, repetition rate–15 Hz) were registered using monochromator MDR-23 and photomultiplier PET-79. Measurements of luminescence intensity were performed by integration of spectral curve in the range from 360 nm up to 420 nm. Dependences of luminescence intensity on pumping level for ZnO sample parts coated and non-coated with Ag were registered and analyzed.

It was revealed that photoluminescence intensity of non-coated part of ZnO film depends linearly on pumping level. This fact correspond with results from by Figure 3 of paper,[10] for example. In the case of Ag-coated parts of ZnO sample this dependences are considerably nonlinear. An example of such dependence is demonstrated in Figure 4. (In this figure there is also an approximation of the curve that will be described below).

So it is experimentally proven that enhancement of excitonic luminescence due to SPR exists only under low enough pumping level and luminescence intensity dependence on pumping level has the shape like the one demonstrated in Figure 4.

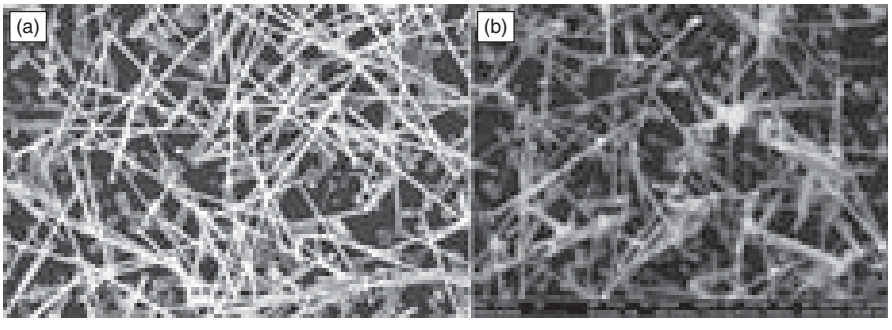

Fig. 3. SEM images of the ZnO sample investigated that was prepared by thermal deposition: (a) non-coated part; (b) coated part (10 nm of Ag).

3. THEORETICAL MODEL

The first natural assumption about the origin of this effect is its connection with losses in ZnO/Ag system due to plasmons that convert a part of exciton recombination energy into losses. These losses most likely should be of Joule's type. The correctness of this assumption can be checked by analyzing the dependence of photoluminescence intensity on pumping level by comparing experimental results with the results of simplified theoretical consideration.

In the most simplified variant of consideration it is not difficult to show that intensity of luminescence

$$I(P) = \frac{R_1 P}{R_2 + P} \tag{1}$$

Where P is total pumping level, R_1 and R_2 are parameters.

To obtain (1) it is necessary to make following simplifications:

(1) Exciton concentration temporal dependence can be described using rate equation.
(2) Process is steady-state
(3) Due to SPR the rate of exciton recombination increases by the value proportional to intensity I.
(4) Losses are proportional to the pumping level P.

In Figure 4 it is shown that experimental dependences of luminescence intensity on pumping level for the part of ZnO sample coated with Ag can be approximated by expression (1) rather well.

So, the proposed simplified approach to the analysis of the influence of SPR on luminescence allows to estimate the dependence $I(P)$ using two parameters. However this approach does not give any information about the process of interaction between SPR and excitons. Different approaches to the analysis of the influence of SPR on luminescence are interesting both for better understanding of its nature and for the practical use.

Simplified but more detailed and improved modeling of the influence of SPR on luminescence by solving the set of rate equations and comparison it's solutions with experimental results is provided below. Comparison of experimental dependences with calculated ones provides an opportunity to make some conclusions about characteristics of effect investigated.

Proposed model is presented by set of rate equations for concentration of electrons in conduction band (CB) is n_1, concentration of holes in valence band (VB) is n_3, concentration of excitons is n_4, concentration of photons that appear due to exciton recombination is n_2, concentrations of Photons Caused by Plasmon Vibration (PCPV) is n_5. It should be noted that examination of the rate equation for such photons instead of electric field caused by plasmons is a considerable simplification of the model. However it will be shown below that results obtained using this model for dependence of luminescence intensity on pumping level appear to be close to experimental ones for ZnO microfilms.

Set of rate equations is following:

$$\begin{cases} \dfrac{dn_1}{dt} = P \cdot e^{-(t-10)^2/26,4} - (M+B) \cdot n_1 \cdot n_3 \\ \dfrac{dn_2}{dt} = H \cdot n_4 + A \cdot n_5 \cdot n_4 - C \cdot n_2 - S \cdot n_2 \\ \dfrac{dn_3}{dt} = P \cdot e^{-(t-10)^2/26,4} - (M+B) \cdot n_1 \cdot n_3 \\ \dfrac{dn_4}{dt} = M \cdot n_1 \cdot n_3 - R \cdot n_4 - A \cdot n_5 \cdot n_4 \\ \dfrac{dn_5}{dt} = N_0 \cdot S \cdot n_2 \cdot (1 - n_2 \cdot CA) - A \cdot n_5 \cdot n_4 - T \cdot n_5 \end{cases}$$

In these equations t is time in nanosecond unit of measure, n_i are concentrations in unit of measure $10^{18} \cdot \mathrm{cm}^{-3}$, parameters which determine rate:

H, C, S, R, T are in unit of measure ns^{-1},
M, B, A are in unit of measure $10^{-18} \cdot \mathrm{cm}^3 \cdot \mathrm{ns}^{-1}$,
CA is in unit of measure $10^{-18} \cdot \mathrm{cm}^3$.

Here $P \cdot e^{-(t-10)^2/26,4}$ is pulse of photoexcitation (exponent show time behavior close to experimental one). Estimation shows that pulse with energy density 1 μJ/cm^2 corresponds to $P \approx 3.3 \cdot 10^{18}\ \mathrm{cm}^{-3} \cdot \mathrm{ns}^{-1}$. Set of rate equations has been solved using Mathcad by Runge-Kutta method. Result of calculation is $\sum_t n_2'$—sum of photon concentration by time–the value proportional to integrated intensity of exciton luminescence.

Parameters which determine process kinetics in set of rate equations in film area without Ag covering are following: B determine interband recombination, M determine rate of exciton formation, R determine rate of spontaneous exciton recombination, H determine rate of photon formation due to spontaneous exciton recombination ($H < R$), C determine rate of photons escape from the system.

Additional parameters, which determine process kinetics in part of film with Ag covering, are following: A determine rate of radiative recombination of excitons under the influence of PCPV, S determine rate of conversion photons to PCPV by means of plasmon vibrations, T determine rate of decreasing PCPV concentration due to attenuation of plasmon vibrations, N_0 is maximum amount of PCPV created by single photon. As is well-known radiation intensity I is proportional to E^2 where E is amplitude of the field and in the same time I is proportional to the photon concentration n. Since for example close to spherical particle[11] $E_{\mathrm{pl}} = F(\omega) E_{\mathrm{ph}}$ where E_{pl} and E_{ph} are amplitudes of fields created by plasmons and photons correspondingly, $F(\omega)$—resonance factor that in the condition of resonance is significantly greater than unit, the value of N_0 is greater than unit also.

As additional simplification it is supposed that parameter CA determines losses so that the value CAn_2 is the contribution of lost PCPV. Really n_2 is proportional to E_{ph}^2 which determines square of current and correspondingly Joule's losses. So in the equation for concentration of PCPV n_5 term $N_0 \cdot S \cdot n_2 \cdot (1 - n_2 \cdot CA)$ appears.

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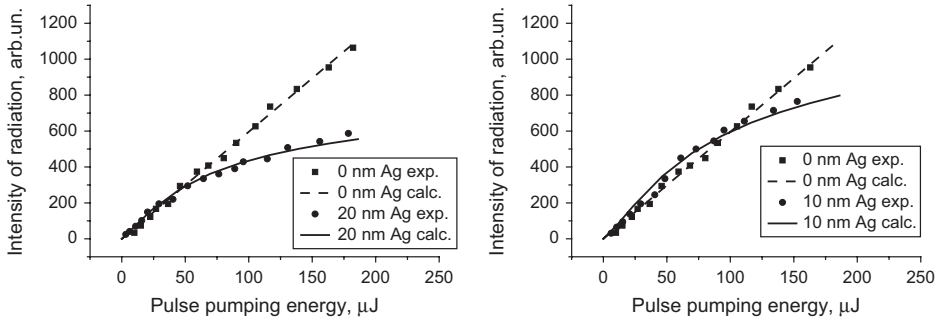

Fig. 5. Dependences of integrated luminescence intensity on excitation pulse energy. Dots show experimental values, lines—calculated ones.

Parameters in calculation for uncovered part of the film are close to experimental values (exciton luminescence lifetime ≈100 ps, efficiency—ratio of energy radiated by spontaneous exciton recombination as photons to the whole energy released during recombination process ≈5%). It gives $R = C = 10$, $H = 0.5$ We also stated $B = M = 20$.

4. COMPARISON OF EXPERIMENTAL RESULTS WITH CALCULATIONS

As it was mentioned above experiment has been performed on ZnO film prepared by thermal evaporation. Sample surface have been divided into 4 parts that have been covered with Ag films of different thickness (0, 5, 10, 20 nm) by magnetron sputtering. Values of the thicknesses are based on assumption that Ag forms uniform layer on sample surface.

To compare experimental dependences of luminescence intensity on pumping level $I(P)$ with calculated ones they must be plotted in the same scale. To make the same scale on X axis we should take into account that as was mentioned above pulse energy density of 1 μJ/cm^2 corresponds to $P = 3.3$. In order to have the same scale on Y axis we need to make additional simplification: we should assume that calculated linear dependence $I(P)$ obtained with parameters values specified for non-covered part of sample coincides with experimental ones.

Comparison of experimental and calculated dependences of luminescence intensity on photoexcitation pulse energy $I(P)$ for ZnO film with 10 nm and 20 nm Ag layers is shown on Figure 5.

Calculated curves for 10 nm and 20 nm Ag layers differ only by parameter which determines losses (CA) and probability of conversion of photons into plasmon vibrations—PCPV (S).

Transition from 10 nm layer to 20 nm layer entails the increase of CA parameter from 0.03 to 0.06, whereas S parameter decreases from 0.4 to 0.3. It should be noted that no changes of other parameters (A, N_0, T) ensure such a transition, i.e., to approximate experimental dependence of luminescence on excitation level in case of 20 nm Ag layer without changing the rest of the parameters valid for 10 nm layer.

Thus, results of the proposed approach for the analysis of the impact of SPR on luminescence allow us to obtain information about properties of investigated phenomenon, namely, in case of Ag covering by magnetron sputtering the increase of conditional thickness of Ag layers entails the growth of losses and decrease of efficiency of plasmon excitation.

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