Simplified approach for modeling ZnO luminescence dependence on excitation level with and without surface plasmon resonance

A P Tarasov\textsuperscript{1,2}, Ch M Briskina\textsuperscript{1}, M V Ryzhkov\textsuperscript{1}, S I Rumyantsev\textsuperscript{1}, V M Markushev\textsuperscript{1}

\textsuperscript{1}Kotel’nikov Institute of Radio Engineering and Electronics of Russian Academy of Sciences, Moscow 125009, Russian Federation
\textsuperscript{2}Moscow Institute of Physics and Technology (State University), Dolgoprudny, Moscow Region 141700, Russian Federation

E-mail: tarasov.ap@phystech.edu

Abstract. The research of excitation level dependence of ZnO UV and visible luminescence was carried out. To describe the behavior of radiation intensity there was proposed the model based on the set of rate equations. The simultaneous equations include the set of parameters which characterizes processes participating in luminescence. The values of parameters were estimated using experimental dependence of luminescence intensity on excitation level. Proposed model can give the way for optimization of samples structure to maximize the effect of surface plasmon resonance influence on luminescence intensity.

1. Introduction
Research of the SPR influence on the recombination luminescence intensity of ZnO films covered by Ag island films was carried out. Different excitation sources were used. In the case of He-Cd laser luminescence enhancement (compared to the same ZnO sample without Ag cover) was observed. However, while using the Nd:YAG laser for the excitation of the same samples the luminescence quenching was observed, and enhancement could be achieved only with significant decreasing of excitation level. It was shown that the dependence of luminescence intensity on pumping level in presence of Ag cover is significantly nonlinear, while the dependence without Ag cover is, as a rule, linear (see for example [1]). This nonlinearity leads to the following effect: while the excitation increases, the luminescence enhancement decreases and finally turns into quenching.

It is suggested simplified approach for description of ZnO luminescence and the SPR influence on it. This approach bases on the set of rate equations (SRE), which describes processes taking part in the luminescence. As is known, luminescence of ZnO consists of near-UV part caused by exciton recombination and visible part caused by defects which form energy levels in the band-gap. Proposed approach gives an opportunity for modeling the dependence of radiation intensity on excitation level and to estimate the values of parameters in SRE.

The analyze of luminescence of various ZnO films with Ag cover using SRE allows to estimate variation of different characteristics, for example, losses, closeness of luminescence maximum wavelength to SPR and others. In order to use suggested SRE it is necessary to consider that all processes participants have corpuscular nature.

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Using SRE we describe time dependence of concentrations for: electrons in conduction band \((n_1)\), holes in valence band \((n_3)\), excitons \((n_4)\), photons caused by exciton recombination and forming plasmons \((n_5)\), photons which simplistically describe field produced by plasmons in nanoscale region between Ag cover and ZnO \((n_0)\) and phonons caused by heating \((n_6)\).

It should be noted that a part of this investigation has already been reported by authors in [2]. But in that article phonons caused by heating of the ZnO/Ag system were not taken into account. In course of investigation it was discovered that maximum of spectra shifts to long wavelength region with the increase of pumping energy. Most likely, that the shift is caused by band-gap narrowing with temperature growth. The value of the shift equals approximately 4-5 nm (~40 meV). Taking into account that band-gap decreases by ~0.35 meV with 1 K heating [3] in the case of \(T > 200 \text{ K}\) it is possible to estimate that ZnO/Ag system temperature rises up to ~380 K. This results in necessity of addition of the equation for phonons in SRE.

2. UV radiation

The set of rate equations for recombination (UV) radiation is following:

\[
\frac{d n_1}{d t} = P e^{-\frac{(t-10)^2}{26.4}} - (M + B) n_1 n_3
\]

\[
\frac{d n_2}{d t} = H n_4 + A(1 - L_A n_6) n_5 n_4 - C n_2 - S n_2
\]

\[
\frac{d n_3}{d t} = P e^{-\frac{(t-10)^2}{26.4}} - (M + B) n_1 n_3
\]

\[
\frac{d n_4}{d t} = M n_1 n_3 - R n_4 - A(1 - L_A n_6) n_5 n_4
\]

\[
\frac{d n_5}{d t} = N_0 (1 - L_N n_6) S n_2 - N_0 (1 - L_N n_6) S n_2 W(1 + L_W n_6) n_2 - T n_5
\]

\[
\frac{d n_6}{d t} = \alpha P e^{-\frac{(t-10)^2}{26.4}} + V n_2 + S n_2 W(1 + L_W n_6) n_2 - E n_6
\]

Here \(t\) refers to time in nanoseconds, \(n_i\) refers to concentration in \(10^{18} \text{ cm}^3\), \(P\) refers to excitation level, multiplier by \(P\) is time dependence of excitation pulse that corresponds to experiment. Rough estimation shows that to the energy density of excitation pulse 1 mJ/cm\(^2\) corresponds to \(P = 3.3\).

Let us fix on the system parameters in more detail. In equations for \(n_1\) and \(n_3\) parameter \(B\) refers to interband recombination probability, parameter \(M\) refers to exciton formation probability. Those two equations coincide and difference of results are caused only by different initial conditions.

In the equation for excitons \((n_4)\) parameter \(R\) is probability of exciton spontaneous recombination, parameter \(A\) refers to probability of exciton recombination under the influence of resonance field formed by plasmons, parameter \(L_A\) refers to the influence of system heating on parameter \(A\).

In the equation for photons produced by exciton recombination \((n_5)\) parameter \(H\) is radiation exciton recombination probability \((H < R)\), parameters \(C\) and \(S\) are probabilities of photons escape from the system and interaction of photons with Ag cover with plasmons formation respectively.

In the equation for photons produced by plasmon field \((n_6)\) parameter \(N0\) is a coefficient that refers to plasmons field increasing against the field of photons that form plasmons, parameter \(L_N\) refers to the influence of system heating on \(N0\), parameter \(T\) is the characteristics of plasmons radiation decay, parameter \(W\) is the characteristics of Joule's losses in Ag cover that are determined by Ag electrical resistivity, parameter \(L_W\) refers to temperature dependence of Ag electrical resistivity.

In the equation for phonons \((n_6)\) parameter \(\alpha\) refers to relation of the part of photoexcitation converted into heat to the part of photoexcitation that was used to ZnO excitation, parameter \(V\) is the probability of phonon attenuation, parameter \(E\) is the probability of direct conversion of photon into phonon.
Consider the term of equation that determines Joule’s losses in more details. Photons caused by exciton recombination get inside $Ag$ cover. The rate of their input equals $\gamma = Sn_0^0$ (per unit time). They produce electron vibrations (plasmons). Those vibrations actually appear to be an electrical current. The second power of electrical current is determined by the concentration of input photons $- FR \sim n_2$. Losses with power of $FR \sim n_2$ arise in $Ag$ cover. Dividing this value by the energy of photon $h\nu$ it is possible to estimate photon lifetime before its conversion into heat: $1/\tau = F/R/h\nu \sim n_2$. To estimate the amount of photons which will be converted into heat after they form plasmons let us assume $d(Sn_2)/dt = - (Sn_2)/\tau$. From this relation it follows: $Sn_2 = Sn_2^0 \exp(-t/\tau) \approx Sn_2^0(1 - t/\tau)\ \mathrm{if} \ t/\tau << 1$. As is known, electric field strength in the interface is much higher than field strength inside the metal [4] in the equation for $n_2$ term which describes plasmon input rate should be multiplied by $N0 > 1$. As expression $-Sn_2Wn_2$ describes heat losses it appears in the equation for phonons $(n_p)$ with positive sign.

The set of rate equations was solved using MathCAD by Runge-Kutta numerical method. The result of calculation is the sum of photon concentrations $I_x = \Sigma n_x^0$ at all (50000) points of time, in which the calculation was performed. This value is proportional to the integrated luminescence intensity. Calculation time was defined by the duration of photo excitation laser pulse.

For the uncovered part of the film, parameters which correspond to exciton luminescence lifetime $\sim 100$ ps and efficiency $\sim 5\%$ were taken. Those values are rather close to experimental ones. The values equal: $R = C = 10$, $H = 0.5$. We also set $B$ and $M$ to 20.

Consider estimations of parameters that are taking into account the influence of heating (phonons) on the process in consideration. As was mentioned in the Introduction the heating the system $ZnO/Ag$ in the experiment was $\sim 100$ degrees. By virtue of the fact that the temperature dependence of the resistance is $R = R_0[1+\beta(T-T_0)]$, where for $Ag \beta = 0.0037$ the change of resistance must be around 40\%. That is why the value of $L_y$ equals 0.3. Parameters $L_x$ and $L_y$ should take into account widening of the $Ag$ extinction spectrum and, as a result, resonance degradation. Because the width of this spectrum is big even at low temperature, heating does not play significant role in this process. Solutions of the set of rate equations using values of $L_x$ and $L_y$ equal 0.3 and 1 correspondingly gave the same result for $I_x$ so for those parameters the value 0.3 was taken. For parameters $\alpha$, $E$ and $V$ more or less arbitrary values were taken ($\alpha = 10$, $E = 1000$, $V = 1$). Preliminary calculations have shown that the variation of those parameters values (staying in constant order of magnitude) does not affect the result significantly.

For the comparison of experimental dependencies of luminescence intensity on excitation level $I(P)$ with the calculated ones those dependences should be plotted in the same scales. To get the same scale on $X$ axis we should take into account that, as it was mentioned above, energy density of excitation pulse of 1 mJ/cm$^2$ corresponds to $P = 3.3$. To make the same scale along $Y$ axis we should add one more simplification: we should assume that calculated linear dependence $I(P)$ obtained using parameters for uncovered part of the film coincides with experimental dependence.

Suggested approach was applied to 2 types of $ZnO$ films with different manufacturing methods. The first film was prepared by thermal evaporation; the second film was prepared by magnetron sputtering. On the first film there were 3 regions: uncovered $ZnO$ and $ZnO$ covered with 10 nm and 20 nm $Ag$ film (effective thickness was determined using the suggestion of uniform $Ag$ distribution on semi-sphere). On the second film there were two regions: uncovered $ZnO$ and $ZnO$ covered with $\sim 10$ nm $Ag$ film.

The comparison between experimental and calculated dependences $I(P)$ for the first $ZnO$ film is shown on Fig.1. Calculated curves for 10 nm and 20 nm $Ag$ approximate experimental data rather well. Those calculated curves differs one from the other only by the value of parameter $W$ (determines losses in $Ag$ cover) and $S$ (probability of interaction of photons with $Ag$ cover with plasmon formation). All other parameters coincide for both curves. It turns out that with the increase of $Ag$ film...
thickness losses and probability of interaction of photons with Ag cover with plasmon formation become higher.

![Fig. 1. Comparison of experimental and calculated dependences of luminescence intensity on excitation level for the first ZnO/Ag sample (thermal deposition): (a) Ag thickness is 10 nm; (b) Ag thickness is 20 nm](image)

On Fig.2 the dependence $I(P)$ for the second film is shown. It can be seen that in this case significantly greater enhancement of luminescence intensity is possible. In comparison with the first film here noticeable greater value of parameter $A$ that characterize probability of exciton recombination under the influence of resonance field of plasmons and lower value of losses ($W$) was obtained.

So, such approach to analysis of dependence of luminescence intensity on excitation level gives a possibility to optimize samples structure for the highest possible luminescence intensity enhancement due to SPR.

![Fig. 2. Comparison of experimental and calculated dependences of luminescence intensity on excitation level for the second ZnO/Ag sample (magnetron sputtering)](image)

3. Visible ZnO radiation

The suggested approach can be used for zinc oxide visible radiation consideration along with UV radiation. For this purpose the set of rate equation is supplemented with the rate equations for the population of energy levels in band-gap, caused by defects, for photons of visible radiation, caused by transitions between levels mentioned above and/or valence band, and (in the presence of SPR) for photons of visible radiation which we use for description of field produced by plasmons in nanoscale region between Ag cover and ZnO. As a result, in the case of single defect level in ZnO band-gap, SRE consists of 9 equations. In the case of existence of donor-acceptor pairs (DAP) in ZnO, in other words in case of two energy levels in ZnO band gap SRE consists of 10 equations.
In [1] it was experimentally demonstrated that for radiation of ZnO the dependence of visible radiation intensity on excitation level with high accuracy could be approximated by following relation: 

\[ I(P) \sim P^{1/3}. \]

Mathematical modelling of the dependence of visible radiation intensity on excitation level using suggested SRE revealed that the dependence like \( I(P) \sim P^{1/3} \) can be obtained only for the case of DAP existence i.e. two energy levels existence in band-gap (Fig. 3b). If in band gap only one defect level exists the dependence \( I(P) \) looks like \( I(P) \sim P^k \), where \( 1/3 < k < 1 \) (Fig. 3a).

![Fig. 3. Calculated dependences of luminescence intensity on excitation level for: (a) one donor energy level in band-gap; (b) two energy levels in band-gap (DAP)](image)

So, utilization of suggested simplified approach to mathematical modeling in combination with experimental dependences \( I(P) \) can give additional information about the origin of ZnO visible radiation.

4. Conclusion

For the analysis of the influence of SPR on recombination radiation intensity of ZnO films and origin of visible luminescence of such films simplified approach was suggested. This approach is based on the system of rate equations (SRE) which gives the possibility to calculate the dependence of radiation intensity on excitation level. SRE includes the set of parameters that describe processes determining luminescence.

Comparison of experimental and calculated dependences of UV radiation intensity on excitation level allows estimating parameters that characterize ZnO films with or without Ag cover. Those parameters could give a possibility to optimize sample characteristics, for example, for higher intensity and enhancement. In particular, it was shown that while thickness of Ag cover increases (from 10 to 20 nm), losses also increase.

It was found out that it is possible to make a conclusion about visible radiation origin on the base of the analysis of the dependence of radiation intensity on excitation level. Namely, if visible radiation is caused by existence of DAP in ZnO the dependence will look like \( I(P) \sim P^{1/3} \); in other cases index of power will be bigger than 1/3 (but less than 1). In conclusion, it is worth noting that the proposed approach can be applied not only to ZnO but to other materials also.

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