OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 1, No. 10, October 2007, p. 528 - 530

Simulation of the effects of rare earth elements presence in the growth of III-V compound layers

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Rare earth elements (RE) present in the growth melt have purifying effect on the III-V compounds layers because they form insoluble aggregates with chemical species responsible for shallow donors. Theory of this gettering phenomenon, based on particle conservation laws and mass action equation, is given and explicit form of the carrier concentration *n* versus RE content [RE] dependence is found. Also modeled is the case when the RE addition itself can contribute carriers so that the *n* - versus - [RE] curves exhibit a minimum. Computed results reproduce plausibly the observed data and provide new insights into some aspects of the gettering process.

(Received August 24, 2007; accepted August 31, 2007)

Keywords: Crystal growth, Rare earth elements, Gettering effects, III-V compounds

1. Introduction

Achieving true doping effects of rare earth elements (RE) has proven difficult in most III-V compounds: their atoms, owing to large atomic radii, are not readily incorporated into the host lattice. There are exceptions to this rule, e.g. ytterbium in InP and other indium-containing III-V compounds as well as erbium in GaAs were reported, quite early, to evince spectral features ascribable to transitions involving 4f levels [1-3]. Nitrides (e.g. GaN), too, due to elevated lattice constant values, can accommodate bulky RE atoms with relative ease [4].

On the other hand, RE atoms possess enhanced chemical affinity towards most species of the shallow donors in III-V compounds (e.g. S or Si), forming insoluble microscopic aggregates in the melt and thus purifying the material without requiring extended bake-out of the growth solutions. Carrier densities as low as on the order of 10^{14} cm^{-3} have been obtained in crystals grown by LPE process with RE admixtures present in the melt. Removal of deleterious impurities is of vital importance in applications such as gamma-ray and nuclear particle detector structures [5] or PIN photodiodes [6] where high electron and hole drift velocities are appreciated.

While there is now a considerable number of experimental studies on this topic, the theoretical side of the problem has not been, to our knowledge, adequately addressed so far. In Section 2 we present a model of gettering phenomenon based on the mass action law and conservation equations for the particle species involved. Explicit form of the carrier concentration *n* versus RE content [RE] dependence is found. In Section 3, this model is extended to cover situations, sometimes observed, where there is a minimum in the *n* versus [RE] plots. Results of numerical evaluations for realistic parameter values are also presented in these two sections. Section 4 contains discussion and conclusions.

2. The model and computed results

Denoting [RE ^{f}] and [D ^{f}] the concentrations of free RE and donor atoms, respectively, [D] the total donor atoms concentration, and [RED] the concentration of donors chemically bound to RE atoms, we can write the particle conservation equations

$$[\mathrm{D}] = [\mathrm{D}^f] + [\mathrm{RED}] \tag{1}$$

$$[\mathrm{RE}] = [\mathrm{RE}^f] + [\mathrm{RED}]. \tag{2}$$

Equilibrium of the chemical reaction

$$\mathrm{RE}^f + \mathrm{D}^f \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{RED} \tag{3}$$

is expressed by the mass action law

$$[\mathrm{RE}^f]\,[\mathrm{D}^f] / [\mathrm{RED}] = k_2 / k_1 \equiv \mathrm{K}(T)\,, \tag{4}$$

where k_1 and k_2 are rate constants for formation and decomposition of the RED compound; K is the chemical equilibrium constant for reaction (3).

Physically admissible solution of Eqs (1), (2), and (4) is

$$[D^f] = \frac{[D]-K-[RE]}{2} + \sqrt{\left(\frac{[D]+K+[RE]}{2}\right)^2 - [D][RE]}\ . \tag{5}$$

At room temperature virtually all shallow donors are ionized so that one can assume with good accuracy

$$n \approx [\mathrm{D}^f] + n_i\ , \tag{6}$$

where n_i, the intrinsic thermally excited electron concentration, can at room temperature be neglected in most III-V compounds, barring narrow gap materials like InSb.

The computed *n* – versus – [RE] dependences are shown in Fig. 1. To demonstrate the general trends, two shallow donor concentrations [D] = 1×10^{16} cm^{-3} and 3×10^{16} cm^{-3} were chosen in this particular example, as well as two values of the equilibrium constant K = 1×10^{15} cm^{-3} (solid lines) and 1×10^{13} cm^{-3} (dotted lines).

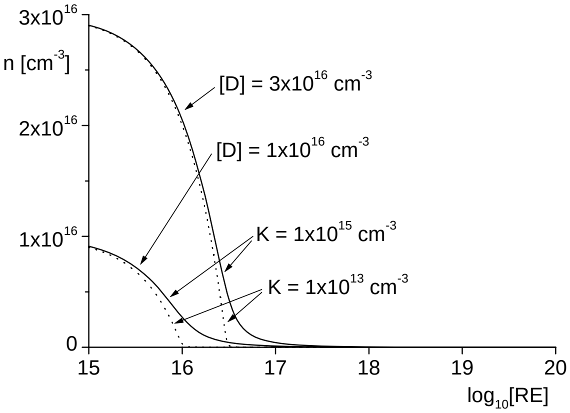

Fig. 1. Dependences of the free carrier concentration n ≈ [D ^{f}] on [RE] for two values of the donor concentration [D] and two values of the equilibrium constant K.

3. The case of non-monotonous *n* – versus – [RE] dependence

Gao, Krier and Sherstnev [7] reported existence of a minimum in the dependence of carrier concentration on RE content in InAs layers prepared by LPE with gadolinium in the growth melt. Similar behaviour was observed by our group for InP layers and erbium admixture [8]. The authors did not speculate on the underlying physical mechanisms.

One can surmise that this phenomenon is caused, paradoxically, by the introduction of additional donor species by the same agent that serves to purify the material, namely the RE addition in the melt. There may be individual differences, but the purity of the RE preparations available on the market is generally lower than that of, e.g., indium or phosphorus. Presumably number of these inadvertently brought in chemically unbound donors represents only a tiny fraction, $k_3 \ll 1$, of [RE], otherwise there would be no purifying effect observable. (One can call k_3 the contamination constant.) These notions are represented by replacing Eq. (6) with

$$n \approx [\mathrm{D}^{\mathrm{f}}] + n_{\mathrm{i}} + \mathrm{k}_3\,[\mathrm{RE}] \ . \qquad (7)$$

The last term on the right hand side of the latter equation, k_3 [RE], is a linearization of a more general dependence, say *g*([RE]). Higher order terms in the Taylor expansion of *g* would be required to take account of the formation of clusters of impurity atoms.

The *n* versus [RE] dependences computed on the basis of this modified model are shown in Figs. 2, 3, and 4. Fig. 2 demonstrates the impact of growing doping efficiency (expressed by increasing values of k_3) of the RE admixture, Fig. 3 highlights the role of thermodynamic stability of RED compound in this situation and Fig. 4 presents a fit to the experimental data published in [7].

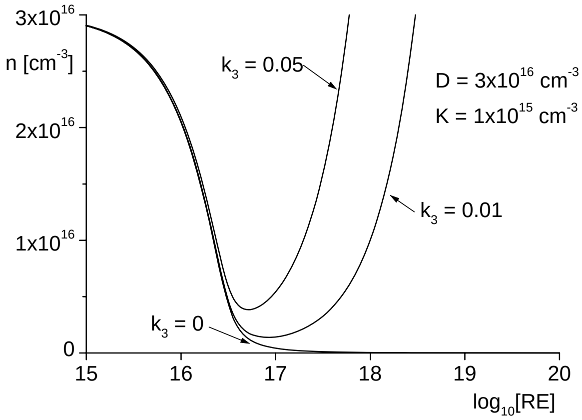

Fig. 2. Numerical simulation of the situation in which addition of RE to the melt beyond certain limit leads to an increase of the carrier concentration. Three values of constant k_3 (0, 0.01, and 0.05) correspond to increasing doping efficiency of RE admixture in the melt.

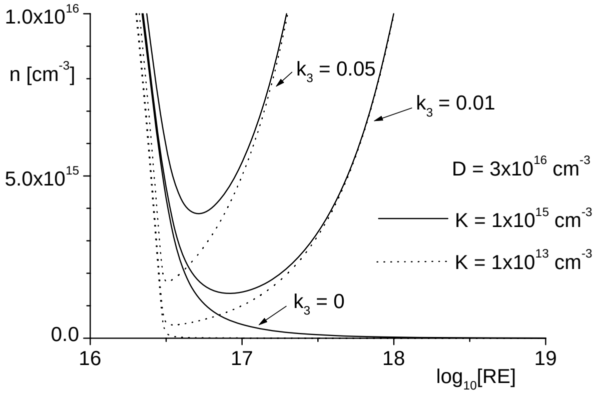

Fig. 3. n – versus – [RE] dependences for the model encompassing introduction of additional donors by the RE addition computed for two values of the equilibrium constant K. (To make picture less cluttered and more readable, variable ranges were restricted compared with Fig. 2).

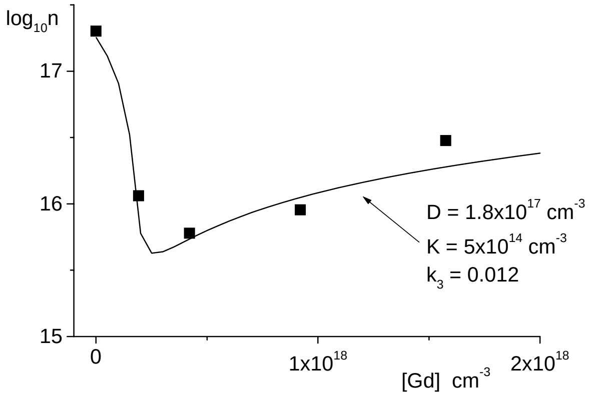

Fig. 4. Experimental data of Gao, Krier, and Sherstnev [7] (filled squares) and the least-squares fit (solid line) computed on the basis of Eqns (1), (2), (4), and (7).

4. Discussion and conclusions

The course of the curves in Fig. 1 is in agreement with the expected attributes of the gettering effect: the shallow donor concentration diminishes with increasing [RE], down to total depletion at [RE] ≈ [D]. The free electron concentration is reduced to n_i. The latter is particularly true for lower values of the equilibrium constant K (K = 1×10^{13} cm^{-3}, dotted lines); the gettering process terminates quite abruptly as [RE] reaches the [D] level. This case corresponds to thermodynamically more stable RED compounds, as follows from K = k_2 / k_1. By contrast, higher values of K (K = 1×10^{15} cm^{-3}, solid lines) mean that RED compounds are less stable; the gettering effect is then marked by lingering presence of unbound donors. An excess of about one order of magnitude of [RE] above [D] is required to remove the donors thoroughly.

Fig. 2 suggests that – providing k_3 values remain reasonably low – the gettering process remains virtually undisturbed by the unwanted side-effect of doping by RE admixture. The increase in carrier concentration occurs when RE content in the melt exceeds the amount necessary for shallow donors removal. Nonetheless, the minimum achievable carrier concentration may be, especially at relatively elevated k_3 values, higher compared with the case of ideal RE purity (k_3 = 0). Detail shown in Fig. 3 shows that thermodynamic stability of the RED compound, characterized by the value of K, plays an important part here: stable RED (low K) guarantees markedly lower carrier concentrations when the level of RE admixture is chosen judiciously near the value [RE] = [D].

Fig. 4 demonstrates that a plausible fit to experimental data can be achieved by simulations based on the present model. (Given the limited achievable accuracy of carrier concentration measurements, attempts to get closer agreement of experimental and computed data would be misleading). On the basis of the fitting parameter values, one can qualify the InAs material measured in [7] as containing moderate number of shallow donors (D = 1.8×10^{17} cm^{-3}), the thermodynamic stability of compounds these donors form with gadolinium as being quite low (K = 5×10^{14} cm^{-3}); value of the contamination constant seems to be suitably low (k_3 = 0.012), affording effective gettering when RE percentage in the melt is near optimum. One should bear in mind that several shallow donor species are probably present, so that the ascertained parameter values should be regarded as some kinds of averages.

In conclusion, the two generic types of the dependence of carrier density on the RE content in the growth melt, namely the monotonous decrease to the negligible thermal equilibrium value and the course with a minimum, can be qualitatively explained and quantitatively reproduced using a model based on the particle conservation and chemical equilibrium laws. Some new insights into details of the gettering phenomena have been gained.

Acknowledgment

Financial support of the Grant Agency of the Czech Republic (project number 102/06/0153) is gratefully acknowledged.

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