Vol. 92 (1997) ACTA PHYSICA POLONICA A No. 5

Proceedings of the XXVI International School of Semiconducting Compounds, Jaszowiec 1997

EFFICIENT TWO-CENTER AUGER MECHANISM OF ELECTRON TRAPPING BY Fe^{3+} IONS IN ZnSe:Fe,Cr

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A detailed analysis of decay kinetics of light induced electron spin resonance signals of Cr^{1+} and Fe^{3+} ions in ZnSe:Fe,Cr is given. We observe that the Cr^{1+} electron spin resonance signal decays once free electrons are thermally ionized from shallow donors of ZnSe. Such unusual behavior of the Cr^{1+} electron spin resonance signal is explained by efficient two-center Auger recombination: the Cr^{1+} center is ionized due to the Auger-type energy transfer from the electron being trapped by the Fe^{3+} ion. Such process is shown to be consistent with the temperature dependence of the decay times of electron spin resonance signals. Its quantum efficiency is estimated to be as large as 18% for Cr and Fe concentrations which were studied.

PACS numbers: 71.55.Gs, 76.30.He, 78.55.Et

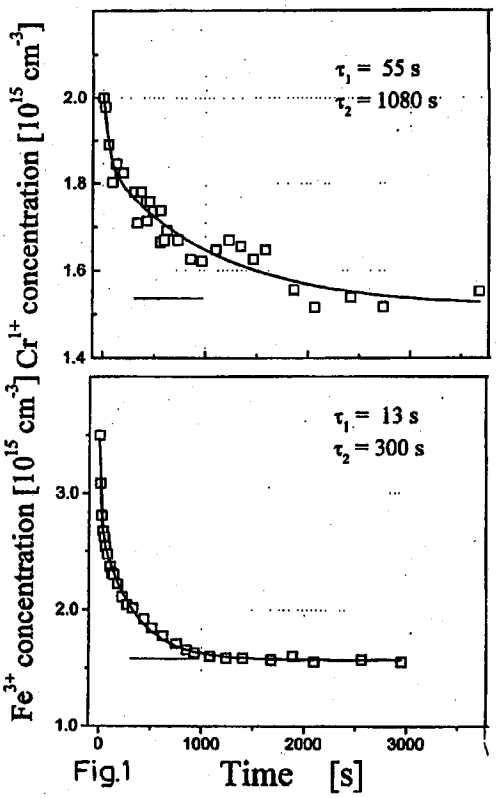
1. Introduction

Transition metal (TM) impurities such as chromium and iron are known to be efficient trap centers in wide band gap ZnS and ZnSe semiconductors [1, 2]. We have shown [2] that for both these materials the bypassing process is responsible for high efficiency of photoluminescence (PL) deactivation by TM ions. By the bypassing process we mean here a subsequent trapping of electron–hole pairs by TM ions, due to relatively large electron and hole capture cross-sections of Fe and Cr ions in ZnS and ZnSe [2]. As a consequence, both these TM ions play a very important role in nonradiative processes of energy relaxation and decrease intensity of visible PL in ZnS and ZnSe [1, 2]. The three-center Auger recombination process (energy of recombining donor–acceptor pair is transferred to TM ion) was also shown to be efficient in some cases [2, 3].

2. Experimental results

We performed electron spin resonance (ESR) and PL investigations of ZnSe crystals intentionally doped with iron to the concentration varying from 10^{17} cm^{-3} to 4×10^{18} cm^{-3}. In addition to iron, ZnSe crystals contained copper, manganese

and chromium impurities. In the ESR study we observed in dark a known ESR signal of Mn^{2+} ions. Under illumination with photon energy of about 2.3 eV ESR signals of Cr^{1+} and Fe^{3+} were photo-generated. Both these ESR signals were observed only at low temperature and decayed slowly when the light was turned off. The spectral dependences of the excitation and quenching of the ESR signals were measured, but will not be discussed here. Instead, we concentrate here on the discussion of the decay kinetics of photo-generated ESR signals after turning off the light (Fig. 1). The observed decay kinetics could be described by a two-exponential function, due to a presence of a slow and a fast component of the decay. A slow component of the decay of photo-excited ESR signals was observed by us in several cases and was explained by Cr^{1+}-acceptor tunneling, which was a rather inefficient process [4].



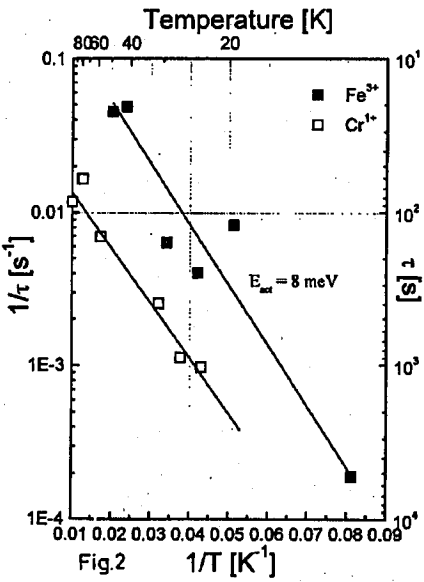


Fig. 1. Fe^{3+} and Cr^{1+} decay kinetics after turning off exciting light (2.3 eV) in 40 K. Dotted lines are due to the two-exponential kinetics: $A\exp((t-t_0)/\tau_1) + B\exp((t-t_0)/\tau_2)$, fitted to the experimental data.

Fig. 2. The fast component of the Fe^{3+} and Cr^{1+} decay kinetics vs. temperature. The activation character is clearly visible.

Figure 2 shows a temperature dependence of the fast component of decay time of the ESR signals measured for the heavily iron doped sample (4×10^{18} cm^{-3}). The same deactivation energy of about 8 meV was found from the temperature dependences of the decay of ESR signals of Cr^{1+} and Fe^{3+}. A decay of ESR signals is described by a similar temperature dependence as the decay of donor–acceptor pair emissions observed in the PL study. The latter process is explained by thermal ionization of shallow donors active in radiative recombination transitions. The observed process of the decay of ESR signals (fast component) is, thus, either directly or indirectly related to thermal ionization of shallow donors.

3. Discussion

In ZnS and ZnSe crystals intentionally doped with Cr the Cr^{1+} ESR signal first rises after turning off the exciting light once shallow donors are thermally ionized [4, 5], since electrons thermally activated to the conduction band are efficiently captured by Cr^{2+} ions. However, in the ZnSe samples doped with iron we surprisingly observe only a decay of the Cr^{1+} population once shallow donors are thermally ionized. To describe this unusual behavior of the ESR signal we considered three processes which may affect the Cr^{1+} population after turning of the light:

1. The process of capture of free electrons activated from shallow donors by Cr^{2+} ions. This process is temperature activated and leads to a rise of the Cr^{1+} population.
2. The tunneling transitions between Cr ions and donors or acceptors, which may lead to either a rise or a decay of Cr^{1+} population. This process is rather inefficient and is temperature independent [4].
3. The three-center Auger recombination of donor–acceptor pairs and Cr^{1+} ions [3]. This process was shown to be rather inefficient in ZnSe lattice [6, 7].

Neither of these processes can describe the observed fast component of decay kinetics of the Cr^{1+} population and its temperature dependence. To understand the kinetics of Cr^{1+} population we propose another mechanism — a two-center Auger recombination. In the process Cr^{1+} ions are ionized by energy transfer from free electrons being captured by Fe^{3+} ions. This process leads to a simultaneous decay of both Cr^{1+} and Fe^{3+} populations in agreement with the experimental results shown in Fig. 1.

The initial population of Cr^{1+} level (n_{Cr}), as calculated from the amplitude of the ESR Cr^{1+} signal, was of about 2×10^{15} cm^{-3}, whereas the initial Fe^{3+} population (n_{Fe}) was of about 3.5×10^{15} cm^{-3}. Therefore, from the crystal neutrality equation ($n + n_D + n_{Cr} = p + n_{Fe} + p_A$) and assuming negligible concentrations (n, p) of free carriers we estimate that the initial concentration of populated donors (n_D) was of about 1.5×10^{15} cm^{-3} and was larger than the initial concentration of populated acceptors (p_A). After approximately 1000 s (at 4 K) of the decay of the ESR signals the population of Fe^{3+} level is saturated at about 1.5×10^{15} cm^{-3} but the population of Cr^{1+} still slowly decreases. Since the decay of the Fe^{3+} ESR signal directly relates to electron trapping by Fe ions, the saturation of the signal at some metastable concentration means that after about 1000 s the concentration

of populated shallow donors equals zero. We assume here that after such long delay time after turning off the light the contribution of donor–acceptor pair recombination transitions is negligible. Therefore, changes of acceptor concentration at long delay times after turning off the light are due to the tunneling process.

Combining the experimental results with the neutrality condition we could estimate the initial concentration of populated donors (n_D). The total change of the Fe^{3+} concentration is equal to 2×10^{15} cm^{-3}, which is larger than the estimated n_D concentration being of about 3.6×10^{14} cm^{-3}. So the major part of electrons captured by Fe^{3+} must come from other electron trap centers — the Cr^{1+} level in the present case, which is ionized due to the Auger-type energy transfer transitions. The estimation of the initial n_D concentration confirms thus our proposition of a correlation between Cr^{1+} ionization and electron trapping by Fe^{3+} ions.

Taking into account a recapture of electrons excited from Cr^{1+} ions by Fe^{3+} ions we calculated the quantum efficiency of the postulated two-center Auger transfer process. The estimated quantum efficiency of the Auger process is of about 18% in ZnSe doped with iron to the concentration of about 4×10^{18} cm^{-3}. This is a very efficient process.

4. Conclusions

The two-center Auger energy transfer between iron and chromium ions is proposed to describe decay kinetics of the Cr^{1+} and Fe^{3+} ESR signals after turning off the light. It is shown that for heavily (4×10^{18} cm^{-3}) iron doped ZnSe samples the quantum efficiency of this process is as large as 18%, which may account for the high efficiency of the bypassing process for this TM ion.

This work was partly supported by the Committee for Scientific Research grant No. 2 P03B 018 13.

References

[1] M. Tabei, S. Shionoya, H. Ohmatsu, *Jpn. J. Appl. Phys.* **14**, 240 (1976).

[2] M. Godlewski, A. Zakrzewski, in: *II–VI Semiconductor Compounds*, Ed. M. Jain, World Scientific, Singapore 1993, p. 205.

[3] A. Zakrzewski, M. Godlewski, *Phys. Rev. B* **34**, 8993 (1986).

[4] A. Zakrzewski, M. Godlewski, unpublished results.

[5] M. Godlewski, *Phys. Status Solidi A* **90**, 800 (1985).

[6] M. Surma, M. Godlewski, T.P. Surkova, *Phys. Rev. B* **50**, 8319 (1994).

[7] M. Surma, A.J. Zakrzewski, M. Godlewski, *Phys. Rev. B* **52**, 11879 (1995).