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DEEP CENTERS IN S^+ IMPLANTED ZnSe

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Measurements of thermal emission rates show that S^+ implantation into ZnSe eliminated the two main deep centers, A ($E_c - 0.30$ eV) and B ($E_c - 0.33$ eV) usually observed in as-grown crystals and created a new center E5. The electron capture behavior of the center E5 obviously differs from that of center B. The results support the assignment that the centers A and B can be attributed to $V_{Se}-V_{Se}$ and a V_{Se}-related complex, respectively, and the center E5 is a S_{Zn}-related center.

1. Introduction

ZnSe is one of the most promising candidates for making blue light emitting diodes (LED). The main problem on the material is the self-compensation effect. Many efforts have been made to reveal the origin of the self-compensated center. Several possibilities have been tested: native defects, background impurities or some complexes involving either or both. Deep level transient spectroscopy (DLTS) measurements of Besomi and Wessels [1] observed two centers, located at 0.30 and 0.33 eV below the conduction band in Au–ZnSe Schottky barriers, and labeled them as A and B center, respectively. Based on the fact that the concentrations of the two centers, N_T, are proportional to the 1st and 2nd power of the ratio of the vapor pressure of Zn and Se, p_{Zn}/p_{Se}, the authors attributed the centers to the divacancy $V_{Se}-V_{Se}$ and V_{Se}-related, respectively. Results of several groups [2–5] supported this assignment from different aspects, for example, intentional doping with shallow donor or acceptor impurities, varying the composition of the alloy ZnS_xSe_{1-x}, electron irradiation, etc. But it is desirable to get direct proof. In order to check the assignment, Se^+ implantating into ZnSe had been carried out in our Lab [6]. The result is positive. In order to confirm this, S^+ was chosen to be implanted into ZnSe. The results coincide with that of the Se^+ implantation experiment, giving more direct evidence for Besomi's assignment. The experiment and results will be described in section 2, and in section 3 relevant discussions will be presented. A summary will be given in section 4.

2. Experiments and results

2.1. Samples

The original materials were unintentionally doped n-type ZnSe crystals grown by sublimation followed by Zn-treatment at 850 °C in The Changchun Physics Institute. Implantation conditions were chosen as follows: Energy: 150 keV, dose: 2×10^{13}–2×10^{14} cm^{-2}, target temperature: 77 K. For a group of implanted samples, a Si_3N_4 layer of 2500 Å was deposited on the implanted surface, then annealed at 350 °C in nitrogen atmosphere for 20 min. For comparison, another group of implanted samples was kept to be not annealed, another sample 3-3a was unimplanted and unannealed, but the sample 4-2b was annealed under the same conditions as above but without implan-

Table 1
Sample conditions

Sample	Dose (cm^{-2})	Annealing	n (10^{15} cm^{-3})
3-3a	–	No	1.4
4-2b	–	Yes	1.9
2-2a	2×10^{14}	No	13
3-2	2×10^{14}	Yes	5.1
4-2a	2×10^{13}	No	2.7
3-3b	2×10^{13}	Yes	3.8

tation. The details on the samples used in the experiments are listed in table 1.

The Au Schottky barriers used for capacitance measurements were made on the implanted layers after annealing or on the top face of the unimplanted ones. An In ohmic contact was made on the back face for each sample. Then the samples were fixed on a TO-5 holder. The net free carrier concentrations determined from C–V measurement are also presented in table 1.

2.2. Thermal emission rate (e_n^t)

DLTS measurement [7] was carried out using an Innovance DLTS system. Three typical spectra, for the samples 3-3a (unimplanted), 2-2a (implanted without annealing) and 3-2 (implanted and annealed) are shown in fig. 1. Three peaks appear for every spectrum but with some observable differences between different spectra. Therefore, different labels are used for different peaks on the spectra. An Arrhenius plot is presented in fig. 2 for some of them only, for explicity. The thermal excitation energies E_T and concentrations N_T of the deep centers may be determined from the measured data. The results are compiled in table 2. In the table, the label of the peak corresponding to the center is written under the value of N_T.

It can be seen from fig. 1 that the peaks c_2 and f_1 are superposed on each other, therefore the E_T value for the center c_2 is difficult to determine accurately. Influence of the superposition on peak c_2 is likely to shift the peak temperature to higher values, then the E_T value gets larger. We shall

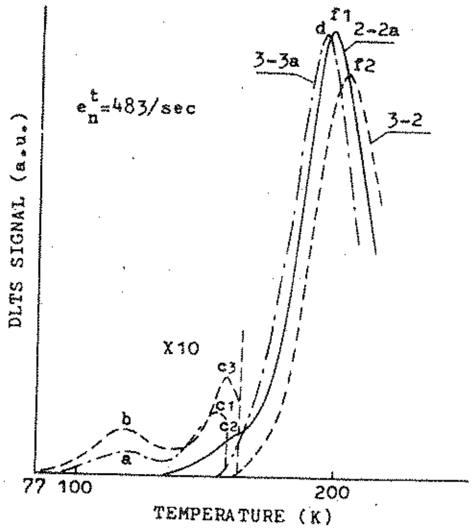

Fig. 1. DLTS spectra of the samples 3-3a, 2-2a and 3-2.

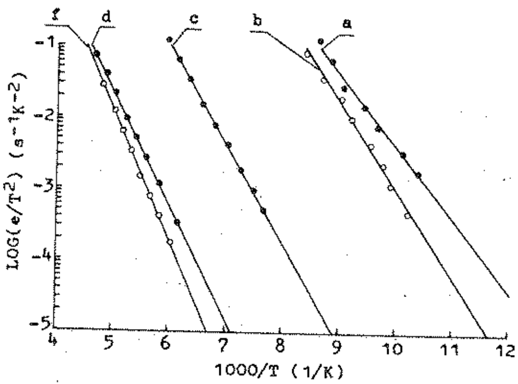

Fig. 2. Arrhenius plot.

Table 2
Results of e_n^t measurement

Center	E_T (eV)	N_T (10^{11} cm^{-3}) for sample condition: Unimplanted	Implanted without annealing	Implanted and annealed
E1	0.20	22 (a)		
E2	0.24			0.6 (b)
E3 (A)	0.30	49 (c_1)		1.5 (c_3)
	0.32		13 (c_2)	
E3 (B)	0.33	140 (d)		
E5	0.34		430 (f_1)	
	0.35			81 (f_2)

neglect the difference of the E_T values of c_1, c_3 (0.30 eV) and c_2 (0.32 eV).

For both purposes of checking temperature determined in DLTS measurement and extending the temperature range for e_n^t measurement, a single shot dark capacitance transient technique was used. Combining it with the DLTS technique, a group of e_n^t data across 5 orders of magnitude for the center A was obtained. Then its E_T value, 0.30 eV, is a more accurate one.

Inspecting table 2, some points may be noticed:
(1) After S^+ implantation, the center E1 (E_c- 0.20 eV) disappeared and a new one, E_2 ($E_c - 0.24$ eV), was created after annealing.
(2) Concentration of the center E3 (same as Besomi's A) decreased to one third of its original value after S^+ implantation and decreased again

Table 3
Results of electron capture cross section

Sample condition	Center	E_T (eV)	σ_n^t (cm^2)	E_b (eV)
Unimplanted	E3	0.30	1.75×10^{-12}	0.17
	E4	0.33	8.2×10^{-15}	0.18
Implanted without annealing	E5	0.34	1.7×10^{-13}	0.23
Implanted and annealed	E5	0.35	3.4×10^{-14}	0.23

Let

$$S'(T) = S_{max}(T) - \left[Ax \ln(t_p) + B\right]; \quad (2)$$

then the plot of $\ln\{[S'(T) - S_\infty(T)]/S_\infty(T)\}$ versus t_p should be a straight line with a slope of

This is just the fact observed in our experiment (see table 1).

(2) Center E4: Several authors in their works published previously reported a deep center located at 0.33 eV below the conduction band in as-grown ZnSe crystals and assigned it as V_{Se}–Y complex, where Y is an unidentified impurity. The center E4 observed in our experiment has the same E_T value. After S^+ implantation, this center disappeared completely. It is reasonable to conclude that this center is V_{Se}-related. A question left here is why the concentration of the center E4 decreased much faster than the center E3 did after S^+ implantation. There are two possible explanations for this. A possibility more easy to be considered is that formation energy of E4 (V_{Se}–Y) is larger than that of E3 (V_{Se}–V_{Se}), but, as well known, V_{Se}–V_{Se} is more stable than V_{Se}. Then V_{Se}–Y should have even larger formation energy. Another possibility is that the impurity Y involved in the center E4 transferred into a more stable structure than Y itself, after S^+ implantation. For example, if Y is one of the group I elements, e.g. Li or Na, then a large amount of vacant Zn sites, formed after S^+ implantation, are suitable for Y to occupy. From the results obtained in our experiment, it is difficult to clarify the problem further.

(3) Center E5: The center E5 is a new one created after S^+ implantation. There are two candidates for assignment of this center: interstitial S, S_i, and antisite S_{Zn}. Considering the formation enthalpy of the interstitial in ZnS, $\Delta H(S_i)_{ZnS} = 21$ eV [9], which is nearly equal to that of the Se_i in ZnSe, but the formation enthalpy of the antisite is only several eV, much smaller than that of antisites. Therefore, it is more likely that the E5 center is the antisite S_{Zn} or S_{Zn}-related complex.

4. Summary

(1) S^+ implantation into ZnSe eliminated the centers E3 ($E_c - 0.30$ eV) and E4 ($E_c - 0.33$ eV), and created a new center E5 ($E_c - 0.34$ eV). Even though the thermally activated energies of the centers E4 and E5 are close to each other, they have quite different electron capture behavior, and therefore they should be different centers. The results give more direct evidence for the assignment that the centers E3 and E4 stem from V_{Se}–V_{Se} and V_{Se}–Y complexes, respectively.

(2) Combining DLTS and single shot techniques, a more accurate E_T value, 0.33 eV, has been determined.

(3) Ion implantation has some advantages on identification of some kinds of native defects in semiconductors.

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