PHYSICAL REVIEW B VOLUME 58, NUMBER 16 15 OCTOBER 1998-II

Compensating levels in *p*-type ZnSe:N studied by optical deep-level transient spectroscopy

S. Q. Wang, F. Lu, Z. Q. Zhu, and T. Sekiguchi
Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai, Japan

H. Okushi
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba-shi, Ibaraki, Japan

K. Kimura
Joint Research Center for Atom Technology, Angstron Technology Partnership, 1-1-4 Higashi, Tsukuba, Japan

T. Yao
Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai, Japan
and Joint Research Center for Atom Technology, National Institute for Advanced Interdisciplinary Research,
1-1-14 Higashi, Tsukuba, Japan

(Received 30 March 1998)

Compensating levels in *p*-type ZnSe:N were studied by optical deep-level transient spectroscopy (ODLTS). A donor level was detected electrically. The activation energy of the donor level was determined to be 56 ±5 meV from the thermal emission process of trapped electrons. The energy position of the donor level was also detected by a photoexcitation process of electrons from the valence band to the donor level. The concentration of the donor level was estimated from the height of the ODLTS peak to be about 21% of the total incorporated N atoms. This is much greater than the concentration of a hole trap detected in the same sample. The donor level is concluded to be the most important factor in the compensation process in ZnSe:N. [S0163-1829(98)06839-8]

I. INTRODUCTION

Although N produced in a plasma source is by far the best dopant in the production of *p*-type ZnSe,[1] the net acceptor concentration is limited to $N_A^- - N_D^+ = 1\times10^{18}$ cm^{-3} due to compensation despite the fact that more than 10^{19} cm^{-3} N atoms can be incorporated into the material.[2] There were a number of reports on optical studies on the compensation process in ZnSe:N. Hauksson *et al.*[3] and Simpson *et al.*[4] observed two sets of donor-acceptor-pair (DAP) transitions with zero phonon lines at 2.696 and 2.678 eV using photoluminescence (PL) and suggested the existence of shallow donors with a binding energy of 26 meV, which is close to that of hydrogenic donors and N-related deep donors with a binding energy of 44 meV. Typically, the shallow donors appear when $N_A^- - N_D^+ < 1\times10^{17}$ cm^{-3} and even in undoped ZnSe, while the deep donors appear when $N_A^- - N_D^+ > 1\times10^{17}$ cm^{-3}. These facts suggest that the shallow donors are attributed to unintentionally doped impurities, while the deep ones to N-associated donors. Murdin *et al.*[5] observed optically detected magnetic resonance from the deep donors and they claimed that the anisotropic resonance was consistent with the defect-related deep donor that they proposed to consist of a Se vacancy and a N substituting at a Se site. Zhu *et al.*[6] determined the deep donor levels to be 55±5 meV by measuring the temperature dependence of the PL spectra. Since most of these studies were carried out by optical methods based on the transition between the N-related donor level and the N-related acceptor level or the valence band, it is difficult to characterize the compensating centers in detail other than the energy position.

An energy level in the band gap can influence the conductivity of the semiconductor by affecting carrier concentrations in the conduction or valence bands and can also influence the capacitance of the Schottky contact or *p*-*n* junction by affecting the space charge density in the depletion layers. Electrical methods that measure conductivity, admittance, capacitance, etc., are capable of detecting these effects and thus are necessary to obtain more information such as the concentration, capture cross section, and energy position. There have been a number of studies on deep levels in *p*-type ZnSe:N based on electrical methods, however, mostly for deep hole traps.[7–12] Only a few have reported deep electron traps. Tanaka, Zhu, and Yao[13] have found a deep electron trap associated with N doping with an activation energy of 0.36 eV below the conduction band of *n*-type ZnSe co-doped with Cl and N. Lu *et al.*[14] have detected an electron trap with an activation energy of 50 meV in highly compensated ZnSe:N by using photoinduced admittance spectroscopy. However, no information about the concentration of the level has been reported.

The energy levels detected so far are shown in Table I. Although a number of electron traps (donor levels) have been reported, their concentrations still remain unclear. On the other hand, although the concentrations of the hole traps were evaluated, none of them seem to dominate the compensation process due to the low $N_T/(N_A - N_D)$ in heavily doped ZnSe:N. Thus the compensation process has been discussed only on a qualitative level and the dominant compensating levels have not been clarified on the basis of their concentrations. In order to study the compensation process on a quantitative level, the concentration of every level lo-

TABLE I. Reported energy levels and their concentrations in ZnSe:N. The energy position E_T denotes the activation energy of the carrier emission process in the case of deep levels. N_T denotes the concentration of the levels. [N] denotes the concentration of incorporated N atoms.

E_T (eV)	[N] (cm^{-3})	N_T (cm^{-3})	$N_A - N_D$ (cm^{-3})	$N_T/(N_A - N_D)$	$N_T/[\mathrm{N}]$	Reference
$E_C - 0.026$			1×10^{17}			3
$E_C - 0.044$			1.5×10^{17}			3
$E_C - 0.050$						14
$E_C - 0.055$			2×10^{17}			6
$E_C - 0.056$	2.4×10^{18}	9×10^{17}	6×10^{17}	1.5	3.7×10^{-1}	present study
$E_C - 0.36$	10^{17}		$8\times10^{18\mathrm{a}}$			13
$E_V + 0.22$		$(0.2-3.0)\times10^{14}$	1×10^{17}	$(0.2-3.0)\times10^{-3}$		8
$E_V + 0.46$		7×10^{13}	5.1×10^{15}	1.4×10^{-2}		10
$E_V + 0.51$		$(2-8)\times10^{14}$	1×10^{17}	$(2-8)\times10^{-3}$		8
$E_V + 0.63$		$(2-8)\times10^{14}$	1×10^{17}	$(2-8)\times10^{-3}$		8
$E_V + 0.64$		4.9×10^{15}	5×10^{17}	9.8×10^{-3}		12
$E_V + 0.67$		1×10^{15}	5.1×10^{15}	1.9×10^{-1}		10
$E_V + 0.67$	3×10^{18}	1×10^{15}	1.2×10^{18}	8×10^{-4}	3.3×10^{-4}	9
$E_V + 0.72$		$(1-2)\times10^{14}$	8×10^{15}	$(1.2-2.5)\times10^{-2}$		7
$E_V + 0.79$		4.6×10^{15}	4×10^{17}	1.1×10^{-2}		11
$E_V + 0.85$			5×10^{16}			13

[a] $N_D - N_A$.

cated in the band gap has to be measured. This is especially important for the N-related deep donor in ZnSe:N, which has been discussed but with the concentration still not clear. In this paper the concentrations of the donor level and a hole trap were estimated using optical deep-level transient spectroscopy (ODLTS) and deep-level transient spectroscopy (DLTS), respectively. The energy position of the donor level was confirmed by photocapacitance transient spectroscopy (PCTS) and photocurrent measurements. A quantitative discussion of the compensation process in ZnSe:N is also presented.

II. PRINCIPLE OF MEASUREMENTS

In ODLTS measurements, light pulses are used for excitation and capacitance transient is recorded after the excitation. In the excitation procedure, carrier transition happens between possible states. The occupation of carriers on a level is a combined effect of emission and capture of carriers. The electron occupancy of an energy level in a depletion layer during the light pulse can be expressed by[15]

$$f=\frac{e_p^o+\Delta n\sigma_n v_{\mathrm{th},n}+e_p^t}{e_n^o+e_p^o+\Delta n\sigma_n v_{\mathrm{th},n}+\Delta p\sigma_p v_{\mathrm{th},p}+e_n^t+e_p^t}, \tag{1}$$

where e_p^o (e_n^o) is the optical emission rate of holes (electrons), e_p^t (e_n^t) the thermal emission rate of holes (electrons), Δp (Δn) the concentration of free holes (electrons) in the depletion layer including photogenerated carriers, σ_p (σ_n) the capture cross section of holes (electrons), and $v_{\mathrm{th},p}$ ($v_{\mathrm{th},n}$) the thermal velocity of holes (electrons).

At low temperature, thermal emission is much smaller than the optical emission, i.e., $e_p^t \ll e_p^o$ and $e_n^t \ll e_n^o$, thus e_p^t and e_n^t are negligible. In order to determine the concentration of the donor level in p-type ZnSe, it is necessary to saturate the level with electrons in the excitation procedure. For this purpose, a 325-nm HeCd laser was used as a light source. When this above-gap light is directed into a ZnSe layer, fundamental absorption takes place and electrons are excited from the valence band to the conduction band. The fundamental absorption is much stronger than the absorption between energy levels and the bands, thus the capture of photogenerated carriers is much stronger than the excitation of carriers between the level and the bands, i.e., $\Delta n\sigma_n v_{\mathrm{th},n} \gg e_p^o$ and $\Delta p\sigma_p v_{\mathrm{th},p} \gg e_n^o$,[16] and thus e_p^o and e_n^o are negligible. As a result, Eq. (1) reduces to

$$f=\frac{\Delta n\sigma_n v_{\mathrm{th},n}}{\Delta n\sigma_n v_{\mathrm{th},n}+\Delta p\sigma_p v_{\mathrm{th},p}}. \tag{2}$$

The occupation is mainly dependent on the free-carrier concentration. Because the sample is highly doped, the depletion layer of the Schottky barrier is very thin, which is estimated to be about 410 Å when $N_A^- - N_D^+ = 6\times10^{17}\ \mathrm{cm}^{-3}$. The absorption coefficient is calculated from $\alpha \approx 2.0\times10^4(h\nu - E_g)^{1/2}$ to be about $2.1\times10^4\ \mathrm{cm}^{-1}$.[17] The strength of the laser light is strong enough to enter ZnSe to about $1/\alpha = 4600$ Å, thus the laser light can enter the bulk ZnSe through the depletion layer and electron-hole pairs are also generated in the bulk. The electron-hole pairs generated within a diffusion length adjacent to the depletion layer diffuse towards the depletion layer. The electrons drift through the depletion layer, while the holes are repelled by the potential barrier. Thus the total electron concentration drifting into the depletion layer is much higher than that of the holes, i.e., $\Delta n \gg \Delta p$, and f approximates 1.[18] This means that both donors and acceptors in the depletion layer tends to capture electrons, i.e., donors capture electrons to be neutralized, while acceptors remain ionized. If most of the donor levels are occupied by electrons, it is possible to estimate the concentration of the donor level from the peak height of the ODLTS spectrum.[19]

The concentration of an energy level is determined by the height of the ODLTS peak. If the concentration is small compared to the free-carrier concentration, the small-signal approximation is valid and the ODLTS signal is normally defined as the difference of the capacitance within a rate window. However, because the concentration of the donor level in the *p*-type ZnSe:N is rather large, the small-signal approximation of conventional ODLTS is invalid. Instead of using the difference of the capacitance, the concentration should be determined using the difference of the square of the capacitance as[20]

$$N_D^+ = \frac{[C^2(t_1) - C^2(t_2)](N_A^- - N_D^+)}{C^2(\infty)\left[\exp\left(-\frac{t_1}{\tau}\right) - \exp\left(-\frac{t_2}{\tau}\right)\right]}, \tag{3}$$

where $C^2(t_1) - C^2(t_2)$ is the height of the ODLTS peak defined by the difference of the square of the capacitance $\tau = (t_1 - t_2)/\ln(t_1/t_2)$, i.e., the reciprocal value of the rate window, $N_A^- - N_D^+$ the net acceptor concentration that can be determined by C-V measurements, and $C^2(\infty)$ the steady-state dark capacitance.

III. EXPERIMENTAL DETAILS

A. Sample preparation

Samples used for this study were prepared by molecular-beam epitaxy on (100)-oriented p^+-GaAs substrates. N doping of ZnSe epitaxial layers was performed using a high-power radio-frequency plasma source.[21] The thickness of the ZnSe layer was about 2 μm. A Au semitransparent electrode with a diameter of 1 mm and a thickness of 200 Å was prepared by thermal evaporation on top of the ZnSe surface. The In at the back side of the GaAs substrates that glued the substrates onto a substrate holder during the growth process acted as an Ohmic contact to p^+-GaAs substrates.

B. Experimental procedures

The basic technique used in the experiment was capacitance spectroscopy. In order to determine the net acceptor concentration $N_A^- - N_D^+$ in ZnSe:N, C-V measurements were carried out at frequencies from 10 kHz to 1 MHz using a Hewlett-Packard (HP) 4275 capacitance meter. The capacitance transients in the ODLTS, optical isothermal capacitance transient spectroscopy (OICTS), PCTS, and DLTS measurements were recorded using a HP 4280 C-t meter. The thermal activation energy and the concentration of the donor level were estimated by ODLTS and OICTS. These two measurements were carried out using a HeCd laser light through a mechanical shutter that produced light pulses with a pulse width of 30 s. The energy location $E_C - E_D$ of the donor level was also determined by the comparison of the photocurrent spectrum, which gives the band-gap energy E_g and PCTS, which gives the energy gap between the valence band and the donor level $E_D - E_V$. The light source used in the photocurrent and PCTS measurements was a 125-W halogen lamp through a monochromator. The photocurrent was measured at steady state using a HP 4140B pA meter. The PCTS measurements were carried out using monochromatic light through the mechanical shutter to produce pulses with a pulse width of 5 s. DLTS measurements were carried out under dark condition to determine the concentration of hole traps. The width of the voltage pulse was 30 s and the height was −1 V. The bias was 1 V.

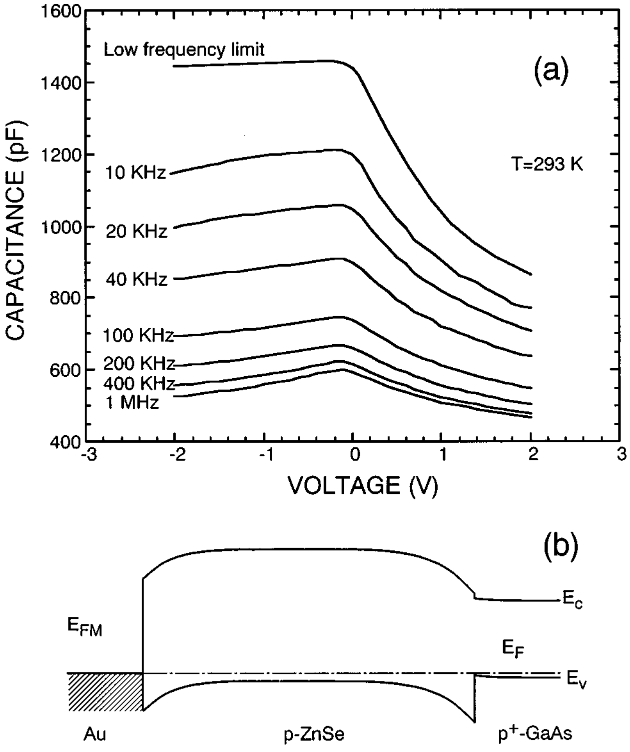

FIG. 1. (a) Frequency correlated C-V curves of the Au/p-ZnSe/p^+-GaAs sample at room temperature. The curve labeled as the low-frequency limit is the fitted result from the equivalent circuit in Fig. 2. The positive voltage denotes the reverse bias of the Au/p-ZnSe Schottky barrier and the forward bias of the p-ZnSe/p^+-GaAs heterojunction. (b) Energy-band diagram for the sample at zero bias.

IV. RESULTS AND DISCUSSION

A. C-V characteristics

The C-V curves recorded at 293 K are shown in Fig. 1(a). The capacitance was measured between the Au electrode and the In Ohmic contact. The band diagram of the sample is shown in Fig. 1(b). There are two depletion layers in the sample: One is that of the Au/ZnSe:N Schottky barrier at the surface and the other one is that of a p-ZnSe/p^+-GaAs heterojunction at the interface of the ZnSe epilayer and the GaAs substrate. The measured capacitance is the total capacitance of the Au/ZnSe:N Schottky barrier and the p-ZnSe/p^+-GaAs heterojunction.

The C-V curves consists of two regions: One is the region at positive voltages and the other is the region at negative voltages. At the positive voltage region, the Au/p-ZnSe Schottky barrier is reverse biased and its capacitance decreases with the increase of the positive voltage. The $N_A^- - N_D^+$ can be evaluated from the slope of the $1/C^2$-V curve.

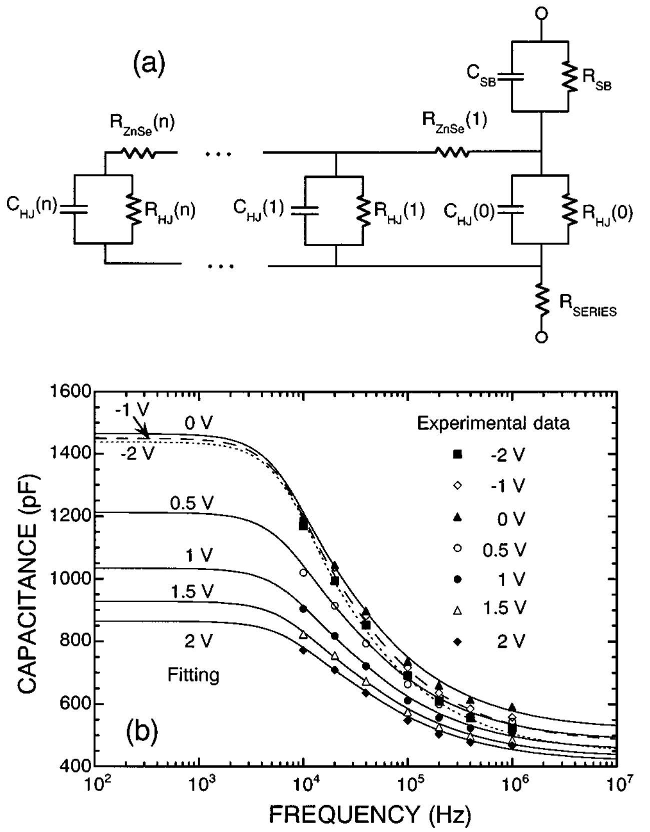

FIG. 2. (a) Equivalent circuit of the Au/p-ZnSe/p^+-GaAs sample. (b) Fitting of the capacitance-frequency curve of the present sample together with experimental data at various voltages using the equivalent circuit.

Since the substrate is highly conductive, the depletion layer of the heterojunction mainly extends to the ZnSe layer. Thus, at the negative voltage region, the capacitance of the heterojunction decreases when the negative voltage increases and results in the decrease of the measured capacitance.

The measured capacitance at low frequency is larger than that at the same voltage at high frequency. One possible reason is that the effective area of the heterojunction varies with the frequency. We have fitted the frequency correlation of the capacitance with an equivalent circuit as shown in Fig. 2(a).[22] The calculated capacitance-frequency curves at various voltages are shown in Fig. 2(b). In the calculation, the diameter of the Schottky barrier was set to 1 mm, equal to the diameter of the Au electrode of the sample. The area of the heterojunction was assumed to be infinite and was separated to numerous unit areas. The resistance $R_{\mathrm{ZnSe}}(i)$ $(i=1,2,...,n)$ is due to the resistivity of the ZnSe:N layer connected with each branch of the circuit. The resistivity was derived to be about 2 Ω cm from the fitting. It was found that the devotion of $C_{\mathrm{HJ}}(i)$ $(i=1,2,...,n)$ in Fig. 2(a), which represents the capacitance of the heterojunction not located directly beneath the Au electrode, to the total capacitance decreases as the frequency increases. This indicates that the effective area of the heterojunction decreases with the increase of the frequency. Thus the total capacitance decreases with the increase of the frequency. On the other hand, when the frequency is lower than about 1 kHz, the measured capacitance approaches that of the Schottky barrier.

The accuracy of the $N_A^- - N_D^+$ determined by the C-V curve depends on the frequency. At low frequency, a more accurate $N_A^- - N_D^+$ is expected because the measured capacitance approaches the capacitance of the Schottky barrier. However, the experiment was limited by the C-V meter to 10 kHz. In order to extrapolate the C-V curve to the low-frequency limit, the capacitance-frequency fitting was carried out at various voltages and the capacitance at the low-frequency limit was determined for each voltage. Thus the C-V curve at the low-frequency limit was obtained and was plotted with the experimental results in Fig. 1(a) for comparison. The $N_A^- - N_D^+$ value was determined from this curve to be about 6×10^{17} cm^{-3}. On the other hand, $N_A^- - N_D^+$ estimated from the 1-MHz curve was about 3×10^{17} cm^{-3} and that from the 10-kHz curve was about 5.6×10^{17} cm^{-3}. It can be seen that there is considerable error when $N_A^- - N_D^+$ is simply estimated from high-frequency C-V curves.

Another possible reason for the frequency correlation of the capacitance is that the deep levels exist in the depletion layer of the heterojunction and/or Schottky barrier, which act as trap centers for free carriers.[23] This should be considered with care when majority carrier traps exist. In general, the concentration of trapped carriers measured at high frequency becomes higher than that measured at low frequency because the thermal release time of carriers from the trap levels becomes longer than that of cycle of the applied ac voltage and the apparent concentration of trapped carriers increases at high frequency. The high concentration of trapped carriers reduces the space-charge density of the depletion layer and then the capacitance. This effect depends on the concentration of the deep levels and will be investigated by the estimation of the concentration of the deep levels with DLTS.

B. ODLTS measurements

The ODLTS spectra are shown in Fig. 3. A positive peak around 100 K is clearly observed. The ODLTS signal here is the difference of the square of the capacitance $C^2(t_1) - C^2(t_2)$ at two fixed sampling times t_1 and t_2 $(t_1<t_2)$. The positive signal indicates a decrease in capacitance after turning off the light, suggesting the decrease of the space-charge density. Since the sample is p type and the space charge is negative, the decrease of the negative space charge is due to the thermal emission of electrons in the depletion layer. Thus the most possible origin of the peak is an electron trap in the depletion layer.

The ODLTS measurements were carried out under various voltages. The same peak was detected under all of the voltages, but different behaviors were observed. Under positive voltage, the position shifts to lower temperature and the height of the peak becomes larger, while under negative voltage the position shifts to higher temperature and the height becomes smaller. The position shift of the peak is most likely due to the electric-field enhancement of the thermal emission process known as the Poole-Frenkel effect.[24] Under the positive voltage the Schottky barrier is reverse biased and the electric field in the depletion region is stronger. The thermal emission of the trapped electrons is accelerated by the electric field, thus the peak of the ODLTS spectrum shifts to low temperature. On the other hand, under the negative voltage the Schottky barrier is forward biased and the electric field

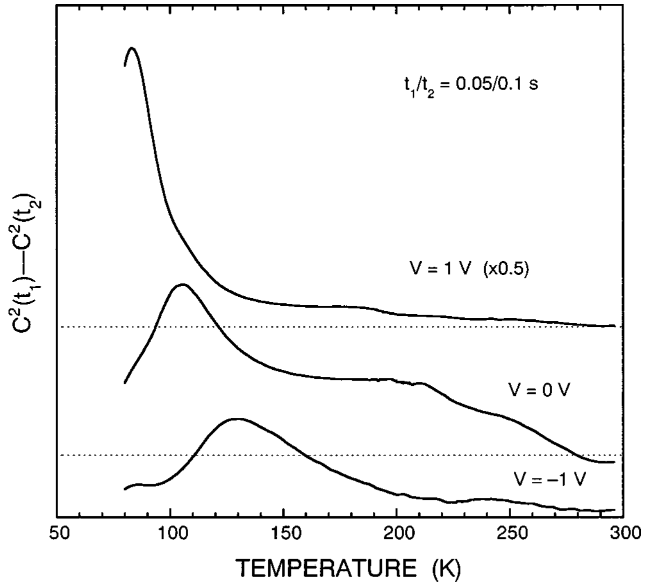

FIG. 3. ODLTS spectra of the Au/p-ZnSe/p^+-GaAs sample measured under various voltages. The light source was a 10-mW HeCd laser light. The light pulse width was 5 s. The rate window was 13.86 s^{-1}.

becomes weaker; the thermal emission is less accelerated by the electric field and thus the peak is located at higher temperature. The thermal activation energy of the level should be derived under the condition that is less influenced by the electric field. Under the positive voltage, the capacitance of the heterojunction becomes larger and thus the measured capacitance mainly depend on the capacitance of the Schottky barrier and the height of the ODLTS peak becomes larger. The concentration of the donor level was estimated at 1 V since the ODLTS peak presents a maximum height at 1 V.

Accordingly, with the experimental results obtained so far, it can be concluded that the positive peak in the ODLTS spectra originates from the thermal emissions of electrons from the donor level in the ZnSe:N of the Schottky barrier. The thermal activation energy of the donor level was determined by an Arrhenius plot to be around 56 ± 5 meV under the condition that the Schottky barrier is forward biased and the thermal emission is less influenced by the electric field. We have systematically studied the temperature dependence of PL, photocurrent, and PCTS, which suggest that the observed 56-meV level is well correlated with the N-related donor level responsible for DAP emission.

The concentration of the donor level was estimated from the ODLTS spectrum measured at 1 V. The concentration was calculated to be 2.2×10^{17} cm^{-3} directly from the height of the ODLTS peak using Eq. (3). However, since the C-t meter used in the ODLTS measurements works at a fixed frequency of 1 MHz, as discovered by multifrequency C-V measurements, the measured capacitance at high frequency is smaller than the capacitance of the Schottky barrier. Figure 2(b) shows that the capacitance measured at 1 V using 1 MHz is about 50% of the capacitance at low-frequency limit. Thus the height of the ODLTS peak $C^2(t_1)-C^2(t_2)$ measured at 1 MHz can be assumed to be about 25% of the value if the measurements were carried out at the low-frequency limit. However, this does not affect the determined N_D^+ because the value of $C^2(\infty)$ in Eq. (3) measured at 1 MHz is also assumed to be 25% of the value at low-frequency limit.

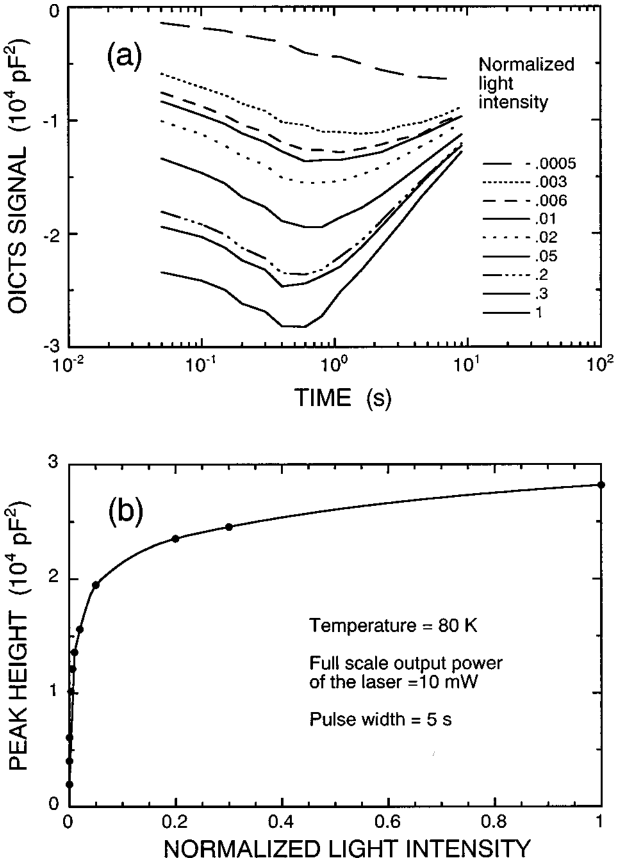

FIG. 4. (a) OICTS spectra of the present sample measured at various intensities of the laser light. (b) OICTS peak height vs normalized intensity of the laser light showing the saturation of electrons on the donor levels under the excitation of the laser light with high intensity.

C. OICTS measurements

Since the concentration of the donor levels estimated by ODLTS measurements is the concentration of the electrons trapped on the donor levels in the excitation procedure, the accuracy of this result depends on whether the donor levels are saturated with electrons in this procedure. In order to investigate this factor, OICTS measurements were carried out with various light intensity. The pulse light is the same as that in ODLTS measurements. The temperature was selected at 80 K, where the OICTS peak correlating with the ODLTS peak is well observed. The normalized light intensity changed from 5×10^{-4} to 1. The OICTS spectra are shown in Fig. 4(a) and the height of the OICTS peaks plotted against the normalized light intensity is shown in Fig. 4(b). As shown, the peak height increases quickly with the increase of the light intensity when the intensity is smaller than about 0.1, but increases slowly when the intensity is larger than about 0.2. This indicates that most of the donor levels were filled with electrons when the light intensity was selected to 1. Since the ODLTS measurements were carried out at this condition, the concentration of the donor levels estimated by ODLTS spectra approximates the actual value.

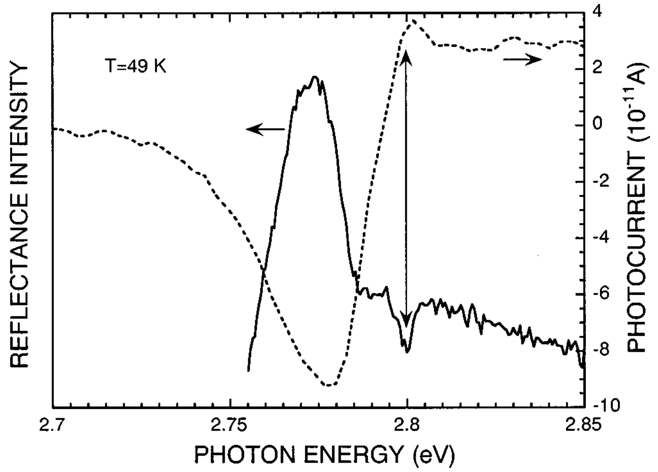

FIG. 5. Reflectance and photocurrent spectra at 49 K. The reflectance shows a free-exciton absorption at 2.8 eV. The step of photocurrent at 2.8 eV correlates with free-exciton absorption.

D. Photocurrent and PCTS measurements

The activation energy determined by ODLTS is through the thermal emission process of the trapped electrons. For comparison, the energy location of the donor level was also determined through the photoexcitation process, i.e., subtracting the energy gap between the valence band and the donor level from the band gap E_g.

The band-gap energy E_g can be determined from the reflectance spectrum as shown in Fig. 5. The dip corresponding to the absorption of free exciton was clearly observed at 2.8 eV, thus E_g can be determined by adding the binding energy of 21 meV to the peak position.[25] However, the free-exciton absorption peak was detected only below a temperature of 70 K. On the other hand, the photocurrent spectrum measured at zero bias shows a clear step at the same energy of the free-exciton absorption. When the photon energy is larger than this value, the current due to fundamental absorption in the Schottky barrier flows towards the substrate. Thus the band-gap energy can be determined by adding 21 meV to the energy where the step of the photocurrent occurs. The similar photocurrent spectrum was obtained until room temperature and gave band-gap energies at various temperatures.

The energy gap between the valence band and the donor level can be determined by the threshold energy of photocapacitance.[26] When the photon energy is larger than the threshold energy, the transition of electrons from the valence band to the donor level is possible and the capacitance increases due to the trapping of electrons on the donor levels. We have tried photocapacitance measurements, but the spectra were not well resolved. Therefore, PCTS measurements were carried out in order to find the threshold photon energy for the transition of electrons from the valence band to the donor level. Different from photocapacitance, the capacitance transient was measured after a pulse light is turned off instead of measuring the steady-state capacitance during illumination. A set of capacitance transients correlating with photon energy were obtained as shown in Fig. 6(a), in which the capacitance transients at various sampling times after the light pulse are plotted against photon energy.

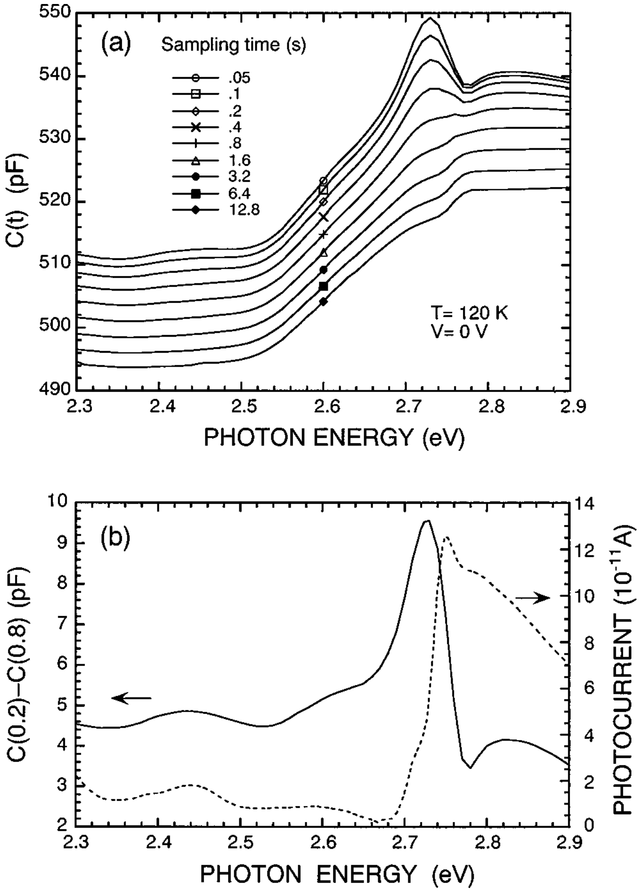

FIG. 6. PCTS and photocurrent results at 120 K. (a) Capacitance transient plotted against photon energy at sampling times from 0.05 to 12.8 s after the photoexcitation with a monochromatic light pulse. (b) Plot of the differential capacitance of 0.2 and 0.8 s showing a well-resolved peak that helps to determine the exact photon energy that incurs the transition of electrons from the valence band to the donor level. The photocurrent gives a band-gap energy E_g.

If one analyzes the capacitance transients correlating to photon energy, one can see that the capacitance transient at the photon energy around 2.71–2.74 eV decreases faster than those at other photon energies. When the photon energy matches with the threshold energy to cause the transition of electrons from the valence band to the donor level, the filling of electrons to the donor level dominates the photoexcitation process and thus the thermal emission of electrons from the donor level dominates the capacitance transient after the light pulse. The time constant of the capacitance transient at the photon energy around 2.71–2.74 eV is about 0.4 s, while the time constant at the photon energy below and above this region is larger than 3 s. The differential capacitance at two sampling times 0.2 and 0.8 s is plotted against photon energy as shown in Fig. 6(b). The differential capacitance at 2.71–2.74 eV is much larger than that at low photon energies, indicating that the thermal emission of electrons from the donor level dominates the capacitance transient at 2.71–2.74 eV. Thus it is possible to determine E_D-E_V to be about 2.725 eV.

The photocurrent measurements were carried out at the same temperatures as PCTS. The results are shown in Fig. 6(b). The photocurrent shows a step at a threshold photon energy of 2.745 eV, which indicates the absorption of free excitons. The band gap E_g can be estimated to be 2.745

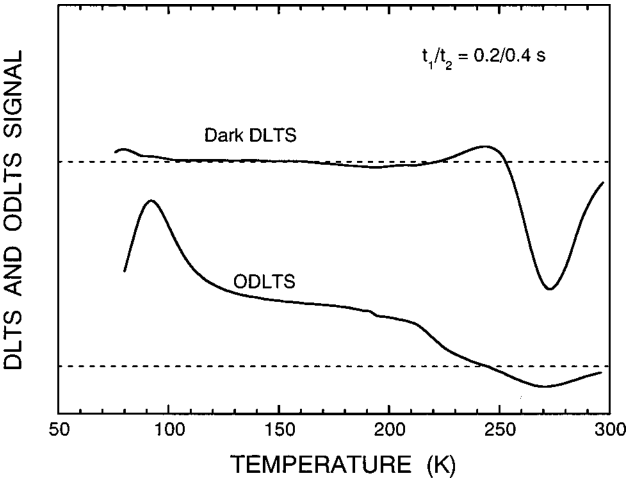

FIG. 7. DLTS spectrum of the present sample measured in the same range of temperature together with the ODLTS spectrum as a comparison. The height of the electrical filling pulse in the DLTS measurements was -1 V and the pulse width was 30 s. The ODLTS spectrum was taken from the same measurement of the spectrum under 0-V voltage in Fig. 3. The rate window was selected to 3.47 s^{-1} in order to show the peak of the hole trap completely.

$+0.021 \approx 2.766$ eV. The energy location of the donor level can be derived by the comparison of the photocurrent and PCTS results to be $E_C - E_D \approx 2.766 - 2.725 \approx 0.041$ eV, which agrees with the results of ODLTS fairly well.

E. DLTS measurements

In the ODLTS spectra, a negative peak, which denotes a hole trap, was observed within a temperature range 240–290 K. The activation energy of thermal emission process was evaluated by an Arrhenius plot to be 0.54 ± 0.03 eV. In order to determine the concentration of this hole trap, DLTS measurements were carried out on the same sample. The spectrum is shown in Fig. 7 together with the ODLTS spectrum. The peak of the same hole trap was observed. The same value of activation energy was obtained by an Arrhenius plot. Using an electrical filling pulse, the hole trap levels located above the Fermi level are entirely filled with holes, thus the concentration of the trap can be obtained from the height of the peak. The concentration of the hole trap was estimated by Eq. (3) to be 2×10^{16} cm^{-3}. Thus the ratio of $N_T/(N_A^- - N_D^+)$ can be determined to be 3×10^{-2}.

The capture process of the hole trap was studied by isothermal capacitance transient spectroscopy measurements where the hole filling pulse width varies from 0.01 to 30 s. Within a temperature range from 242 to 272 K, the capture cross section varies from 9.8×10^{-27} to 2.2×10^{-25} cm^2. The capture cross section can be expressed by an Arrhenius expression $\sigma = 1 \times 10^{-17} \exp(-0.39\ \mathrm{eV}/kT)$. The capture cross section can be evaluated to be $\sigma_\infty = 1 \times 10^{-17}$ cm^2. The presence of a potential barrier of about 0.39 eV for the carrier capture process indicates that large lattice relaxation is induced in the hole capture emission processes.

This hole trap was also detected in *p*-type ZnSe:N by DLTS in our previous work.[27] Hu *et al.* have reported a similar level with an activation energy of 0.51 eV, as shown in Table I,[8] and have correlated this level with N doping in ZnSe. Although the concentration evaluated in the present study is higher than that in Ref. 8, noticing that the $N_A^- - N_D^+$ of the sample used in this study is also higher, the $N_T/(N_A^- - N_D^+)$ is just slightly larger than that in Ref. 8. This is consistent with the suggestion that this level is related with N doping. On the other hand, since the concentration of this hole trap is much smaller than $N_A^- - N_D^+$, it is not likely the dominant reason for the frequency correlation of the *C*-*V* curves in Fig. 1(a).

F. Compensation by the 56-meV donor level

As demonstrated above, the 56-meV level was detected by observing the thermal emissions of the trapped electrons from this level into the conduction band with ODLTS measurements. The increase of negative charge in the depletion layer by the trapping of electrons was confirmed by the polarity of the ODLTS signal. This result indicates that the level correlates with the conduction band and that the level is a donor level. It is suggested that this donor level is closely related to that responsible for DAP emission.

The energy position of this level was also determined by PCTS measurements. The activation energy determined by ODLTS measurements includes the potential barriers for carrier capture process. However, the PCTS measurements estimate the energy position of the level by observing the photoexcitation of electrons from the valence band to the level without the influence of the barrier. Thus, from the difference of the results of the two kinds of measurements, the potential barrier height can be estimated. The fact that the two results are very close indicates that the potential barrier is negligible.

The concentration of the donor level N_D^+ was estimated from the ODLTS spectra to be about 2.2×10^{17} cm^{-3}. The net acceptor concentration $N_A^- - N_D^+$ was determined by *C*-*V* measurements to be 6×10^{17} cm^{-3}. The acceptor concentration N_A^- can be determined to be 8.2×10^{17} cm^{-3}. The concentration of a hole trap was estimated from dark DLTS spectra to be 2×10^{16} cm^{-3}. Thus the detected donor level occupies about $2.2 \times 10^{17}/(2.2 \times 10^{17} + 8.2 \times 10^{17} + 2 \times 10^{16}) \approx 37\%$ of the detected levels related with doped N atoms. Secondary ion mass spectroscopy measurements showed that the incorporated N atomic concentration was 1×10^{18} cm^{-3}, consistent with the sum of the concentrations of the donor level, the acceptor level, and the hole trap. This suggests that the incorporated N mainly forms the three kinds of levels and the 56 meV donor level is the dominant compensating level.

V. SUMMARY

A donor level with a thermal activation energy of 56 ± 5 meV in the band gap of *p*-type ZnSe:N was studied using ODLTS and OICTS. The concentration of this level was estimated to be about 2.2×10^{17} cm^{-3} in the sample with $N_A^- - N_D^+ = 6 \times 10^{17}$ cm^{-3}, indicating that at about 21% of the doped N atoms are involved in the formation of this donor level. A hole trap with the thermal activation energy of 0.54 ± 0.03 eV was also detected with a concentration of about 2×10^{16} cm^{-3} estimated by dark DLTS, which is much smaller than the concentration of the donor level. The donor level has been considered to play the main role in the compensation process in N-doped ZnSe due to the high concentration.

ACKNOWLEDGMENTS

The author S. Q. Wang would like to express his thanks to Professor N. Kuroda for many valuable discussions and providing optical measuring equipment. This study was partly supported by New Energy and Industrial Technology Development Organization.

---

[1] T. Yao and Z. Zhu, Phys. Status Solidi B **187**, 387 (1995).

[2] J. Qiu, J. M. Depuydt, H. Cheng, and M. A. Haase, Appl. Phys. Lett. **59**, 2992 (1991).

[3] I. S. Hauksson, J. Simpson, S. Y. Wang, K. A. Prior, and B. C. Cavenett, Appl. Phys. Lett. **61**, 2208 (1992).

[4] J. Simpson, I. Hauksson, S. Y. Wang, H. Stewart, K. A. Prior, and B. C. Cavenett, Physica B **185**, 164 (1993).

[5] B. N. Murdin, B. C. Cavenett, C. R. Pidgeon, J. Simpson, I. Hauksson, and K. A. Prior, Appl. Phys. Lett. **63**, 2411 (1993).

[6] Z. Q. Zhu, K. Takebayashi, K. Tanaka, T. Ebisutani, J. Kawamata, and T. Yao, Appl. Phys. Lett. **64**, 91 (1994).

[7] K. Ando, Y. Kawaguchi, T. Ohno, A. Ohki, and S. Zembutsu, Appl. Phys. Lett. **63**, 191 (1993).

[8] B. Hu, G. Karczewski, H. Luo, N. Samarth, and J. K. Furdyna, Appl. Phys. Lett. **63**, 358 (1993).

[9] Y. Kawakami, T. Ohnakado, M. Tsuka, S. Tokudera, Y. Ito, Sz. Fujita, and Sg. Fujita, J. Vac. Sci. Technol. B **11**, 2057 (1993).

[10] H. Goto, T. Tanoi, M. Takemura, and T. Ido, Jpn. J. Appl. Phys., Part 2 **34**, L827 (1995).

[11] T. Matsumoto, K. Egashira, T. Kato, J. Cryst. Growth **159**, 280 (1996).

[12] K. Hellig, G. Prösch, M. Behringer, M. Fehrer, R. Beyer, H. Burghardt, D. Hommel, and D. R. T. Zahn, Appl. Phys. Lett. **71**, 2187 (1997).

[13] K. Tanaka, Z. Q. Zhu, and T. Yao, Appl. Phys. Lett. **66**, 3349 (1995).

[14] F. Lu, S. Q. Wang, H. D. Jung, Z. Q. Zhu, and T. Yao, J. Appl. Phys. **81**, 2425 (1997).

[15] H. G. Grimmeiss and C. Ovrén, J. Phys. E **14**, 1032 (1981).

[16] C. T. Sah, L. Forbes, L. L. Rosier, and A. F. Tasch, Solid-State Electron. **13**, 759 (1970).

[17] J. I. Pankove, *Optical Processes in Semiconductors* (Prentice-Hall, Englewood Cliffs, NJ, 1971).

[18] B. Hamilton, A. R. Peaker, and D. R. Wight, J. Appl. Phys. **50**, 6373 (1979).

[19] R. Brunwin, B. Hamilton, P. Jordan, and A. R. Peaker, Electron. Lett. **15**, 349 (1979).

[20] H. Okushi and Y. Tokumaru, Jpn. J. Appl. Phys. **20**, L45 (1981).

[21] K. Kimura, S. Miwa, H. Kajiyama, T. Yasuda, L. H. Kuo, C. G. Jin, K. Tanaka, and T. Yao, Appl. Phys. Lett. **71**, 485 (1997).

[22] T. Marshall, S. Colak, and D. Cammack, J. Appl. Phys. **66**, 1753 (1989).

[23] D. V. Lang, J. D. Cohen, and J. P. Harbison, Phys. Rev. B **25**, 5285 (1982).

[24] G. Karczewski, B. Hu, A. Yin, H. Luo, and J. K. Furdyna, J. Appl. Phys. **75**, 7382 (1994).

[25] Z. Q. Zhu, K. Takebayashi, T. Yao, and Y. Okada, J. Cryst. Growth **150**, 797 (1995).

[26] A. Ito, T. Sukegawa, and J. Nishizawa, IEE Technical Report No. TR-32 1967 (unpublished).

[27] S. Q. Wang, F. Lu, H. D. Jung, C. D. Song, Z. Q. Zhu, H. Okushi, B. C. Cavenett, and T. Yao, J. Appl. Phys. **82**, 3402 (1997).