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The temperature dependence of the reduced activation energy $w = \varepsilon/k_BT$ of the conductivity σ has been utilized for determining the impurity conduction mechanism in doped semiconductors in many studies. Herein, the formula for deconvoluting w when plural conduction mechanisms appear is used to confirm the analysis of the data of the Hall-effect measurements on Al-doped n-ZnSe samples. The analysis is performed on the basis of an impurity-Hubbard-band model which includes ε_2 conduction in the top Hubbard band as well as ε_3 and Efros-Shklovskii (ES) variable range hopping (VRH) conductions in the bottom Hubbard band. As the result of the analysis, transitions among the three hopping conduction mechanisms of ε_2, ε_3, and ES VRH are clearly shown in the temperature dependence of w as well as in that of the Hall mobility, which are hardly noticed in the temperature dependence of σ. In addition, the power-law exponent of the prefactor of ES VRH conductivity is determined through the fit to the temperature dependence of w to show that it decreases from ~1.5 to ~0 with increasing net donor concentration.

Keywords: Hopping conduction; Hall effect; ZnSe

1. Introduction

Impurity conduction in semiconductors is categorized into ε_2 and ε_3 conductions. In n-type semiconductors, ε_3 conduction occurs through nearest-neighbor hopping (NNH) of electrons from neutral donors D^0 to empty positive donors D^+ while ε_2 conduction occurs through NNH of electrons from neutral donors to neutral donors. In other words, ε_2 conduction corresponds to the transition of two neutral donors into negative- and positive-charged ions ($2D^0 \rightarrow D^- + D^+$). Since the overlap between the donor states becomes strong with the donor concentration, impurity bands appear as a consequence. The bands formed from the D^- and the D^0 states are called as the top and the bottom Hubbard band, respectively [1]. At sufficiently low temperatures, ε_3 conduction is altered to variable-

range hopping (VRH) conduction. VRH is further categorized into the Mott and the Efros-Shklovskii (ES) types. In general, hopping conductivity is described by the following expression:

$$\sigma = \sigma_0 (T_0/T)^s \exp\left[-(T_0/T)^p\right]. \quad (1)$$

In the three-dimensional system, $p = 1$ for NNH in both of the top and bottom Hubbard band while $p = 1/4$ and $1/2$ for Mott and ES type VRH, respectively.

Although impurity conduction in group-IV elemental and III-V compound semiconductors has been vigorously studied, that in II-VI compound semiconductors is not so extensively studied. In particular, studies on ε_2 conduction are restricted to several materials such as p-Ge [2], n-Ge [3, 4], n-Si [5, 6], p-Si [7], n-GaAs [8], and n-InP [9]. Thus, there are no studies on ε_2 conduction in II-VI compound semiconductors to date.

Furthermore, in general, the Hall effect for hopping conduction is not well understood yet. In the previous studies of the author, the complicated behaviour of the Hall coefficient $R_H(T)$ in group-IV elemental semiconductors of p-Ge [10], n-Ge [11], and n-Si [12] as well as that in III-V compound semiconductors of n-GaAs [8] and n-InP [9] has been well described using a Hubbard-band model.

In the present study, the Hubbard-band model is now applied to analyze the complicated behaviors of the temperature dependence of the conductivity and the Hall coefficient of *n*-ZnSe to show the existence of the narrow temperature region in which ε_2 conduction dominates.

For determining the dominant conduction mechanism, Zabrodskii [13, 14] proposed to use a graph of the temperature dependence of the reduced activation energy of conduction:

$$w = \frac{\varepsilon}{k_B T} = \frac{d(\ln\sigma)}{d(\ln T)} = -\frac{1}{T}\frac{d(\ln\sigma)}{d(1/T)} = -\frac{1}{\sigma T}\frac{d\sigma}{d(1/T)}. \quad (2)$$

The temperature dependence of $w(T)$ can be obtained by graphical differentiation [15-18] of the curve of ln σ vs ln T or numerical methods. As a numerical method, Shafarman et al. [19] used a formula of

$$w(T_2) = -\frac{1}{\sigma(T_2)T_2}\left[\frac{\sigma(T_3)-\sigma(T_1)}{(1/T_3)-(1/T_1)}\right], \tag{3}$$

where $T_1 < T_2 < T_3$.

When a conduction mechanism with the form of equation (1) dominates, equation (2) leads to

$$w = -s + p(T_0/T)^p . \tag{4}$$

If the second term in the right-hand side of equation (4) is much larger than the first, we have

$$\log w \approx \log p + p \log T_0 - p \log T , \tag{5}$$

so that the exponent p is given by the slope of log w against log T.

Two years after the proposal by Zabrodskii, Rentzsch et al. [20] have already used this method for analyzing the impurity conduction mechanism in unintentionally doped n-ZnSe to find that p is in the range between 0.68 and 1.0, which suggests competition between ε_3 and ES VRH conductions. Timchenko and Nedeoglo [21] as well as Kasiyan et al. [22, 23] also used this method to investigate the impurity conduction mechanism in unintentionally doped and Al-doped n-ZnSe to show the existence of the temperature region in which ES-VRH conduction dominates.

Note that, when the first term in the right-hand side of equation (4) cannot be ignored in comparison with the second, one should plot log ($w + s$) against log T, as pointed out by Lisunov et al. [24] and Rodríguez et al. [25] Otherwise the curve of log w against log T shows a convex curvature for a positive value of s while shows a concave one for a negative value of s.

In the present study, we use the formula for w when plural conduction mechanisms appear in order to investigate the impurity conduction mechanisms in n-ZnSe. In particular, we focus on the effects of the ε_2 process in conductivity and the Hall effect in n-ZnSe.

In the following, we describe our analysis model in Sec. 2 and then describe in Sec. 3 the results of simultaneous fits to the experimental data of the conductivity σ, its reduced activation energy w, the Hall mobility μ_H, and the Hall coefficient R_H on the Al-doped n-ZnSe samples reported by Kasiyan et al. [23] The relations among the deduced parameters are discussed in Sec. 4. The summary is given in Sec. 5.

2. Analysis model

Analysis in the present study has been performed on the basis of the impurity-Hubbard band model developed in the previous study of the author [8]. In this model, the conductivity σ, the Hall coefficient R_H, and the Hall mobility μ_H are deconvoluted into

$$\sigma = \sigma_1 + \sigma_2 + \sigma_3 + \sigma_{VRH}, \tag{6}$$

$$R_H = \left(\frac{\sigma_1}{\sigma}\right)^2 R_{H1} + \left(\frac{\sigma_2}{\sigma}\right)^2 R_{H2} + \left(\frac{\sigma_3}{\sigma}\right)^2 R_{H3} + \left(\frac{\sigma_{VRH}}{\sigma}\right)^2 R_{HVRH}, \tag{7}$$

and

$$\mu_H = \frac{\sigma_1}{\sigma}\mu_{H1} + \frac{\sigma_2}{\sigma}\mu_{H2} + \frac{\sigma_3}{\sigma}\mu_{H3} + \frac{\sigma_{VRH}}{\sigma}\mu_{HVRH}, \tag{8}$$

respectively.

For n-type semiconductors, σ_1 denotes the free-electron conductivity in the conduction band; σ_2 and σ_3 denote the NNH conductivity in the top (D^-) and the bottom (D^0) impurity Hubbard band, respectively; σ_{VRH} denote the VRH conductivity in the bottom impurity Hubbard band. R_{Hi} and μ_{Hi} (i = 1, 2, 3, and VRH) are the Hall coefficients and the Hall mobilities due to the respective conduction mechanisms.

The respective conductivities are calculated as $\sigma_1 = en_1\mu_1$, $\sigma_2 = eN_t\mu_2$, $\sigma_3 = eN_b\mu_3$, and $\sigma_{VRH} = eN_b\mu_{VRH}$, where n_1 is the free-electron concentration in the conduction band while $N_t = N_D^- N_D^0 / N_D$ and $N_b = N_D^+ N_D^0 / N_D$ are the effective concentrations of electrons hopping in the top and the bottom Hubbard band, respectively, while μ_i's are the respective drift mobilities. The concentrations of the positively, negatively, and neutally charged state of donors are respectively calculated as $N_D^+ = N_D f_1$, $N_D^- = N_D f_{-1}$, and $N_D^0 = N_D f_0$, where N_D is the total donor concentration, using the charge-state distribution functions f_1, f_{-1}, and f_0 which are defined in the previous study [8]. In the calculation of the charge-state distribution functions, we assume that the energy gap between the bottom and the top Hubbard band is calculated as $U = E_b - E_t = 0.945E_b$ according to Poklonskiet al. [26], where E_b and E_t respectively denote the energy separations of the D^0 and the D^- states from the conduction-band bottom. Note that we assume here the widths of both the top and the bottom Hubbard band to be much narrower than the energy gap U and assume the density of states to be expressed by the Dirac δ function for both the impurity bands. This assumption can be justified for the samples treated in the present study since the net donor concentrations $N_{ND} = N_D - N_A$ ($\approx n_{300K}$) in these samples are much lower than the critical net donor concentration N_{NDcr} for the onset of the metal-insulator (MI) transition. **Figure 1** shows the band diagram of the impurity Hubbard bands in *n*-ZnSe. Note that this

figure corresponds to the dilute-impurity limit of Fig. 5 of Ref. [27], in which E_b and E_t are denoted as I and E, respectively, and the width 2Δ of the top Hubbard band is not zero but finite.

The respective Hall coefficients are calculated as $R_{H1} = -A_{H1}/(en_1)$, $R_{H2} = -A_{H2}/(eN_t)$, $R_{H3} = -A_{H3}/(eN_b)$, and $R_{HVRH} = -A_{HVRH}/(eN_b)$, where A_{Hi}'s are the respective Hall factors. The respective Hall mobilities are calculated as $\mu_{Hi} = |R_{Hi}|\sigma_i = A_{Hi}\mu_i$.

For free electrons in the conduction band, the concentration n_1, the drift mobility μ_1, and the Hall factor A_{H1} are calculated within the relaxation-time approximation with taking into account scattering due to ionized impurities, neutral impurities, acoustic phonons, polar optical phonons, piezo-electrically active acoustic phonons. The relaxation times for these scattering mechanisms were calculated according to the study by Ruda [28].

The values of the effective mass m^* and the static dielectric constant ε_s were taken from the study by Ohyama et al. [29] Using these values, the effective Bohr radius a_B was calculated to be 32 Å. The value of the acoustic deformation potential E_{ac} was taken from the study by Emel'yanenko et al. [30] The valuesof the other material parameters for ZnSe were taken from the study by Ruda [28]. The material parameters are tabulated in **Table 1**.

It has been shown both experimentally and theoretically that the static dielectric constant at low temperature increases with the impurity concentration to diverge at the critical net donor concentration N_{NDcr} for the onset of the MI transition [31, 32]. Also for n-ZnSe, Kasiyan et al. [22, 33] as well as Nedeoglo et al. [34] suggested the increase of the dielectric constant with the net donor concentration near the MI transition. According to Poklonski et al. [32], we assume the form of

$$\varepsilon_{eff}(N_D^0) = (\varepsilon_s + 2N_D^0/N_{NDcr})(1 - N_D^0/N_{NDcr})^{-1}. \quad (9)$$

Regarding the critical concentration for the MI transition in n-ZnSe, we adopt the value of N_{NDcr} = 1.3×10^{17} cm^{-3} according to Kasiyan et al. [23], and calculated ε_{eff} according to equation (9).

As in the previous study [8], the hopping drift mobilities are assumed to be expressed as

$$\mu_i = \mu_{0i} (E_i / k_B T)^{s_i} \exp(-E_i / k_B T), \tag{10}$$

where i = 2, 3, and VRH for ε_2, ε_3, and ES-VRH conduction, respectively. μ_{0i}'s are temperature-independent constants. The activation energies E_2 and E_3 of drift mobilities for NNH in the top and the bottom Hubbard bands are treated as temperature-independent constants while E_{VRH} is treated as a temperature-dependent activation energy which is expressed as $E_{VRH} = k_B(T_{ES}T)^{1/2}$ with assuming ES VRH rather than Mott VRH as in the studies [21-23] on n-ZnSe. For the parameter s appearing in equation (4), we assume $s_2 = s_3 = 3/2$ for NNH according to the small-polaron theory [35-37] while $s_{VRH} = s_{ES}$ for ES VRH is treated as an adjustable parameter.

Note here that E_2 and E_3 are defined not as the activation energies of conductivities σ_2 and σ_3 but as those of drift mobilities μ_2 and μ_3. On the other hand, ε_2 and ε_3 usually denote the activation energies of conductivities σ_2 and σ_3, respectively. Since σ_2 and σ_3 are calculated as $\sigma_{2,3} = eN_{t,b}\mu_{2,3}$, ε_2 and ε_3 can be described as $\varepsilon_{2,3} = -k_B\, d(\ln\sigma_{2,3})/d(1/T) = E_{2,3} - (3/2)k_BT - k_B\, d(\ln N_{t,b})/d(1/T)$. Therefore, ε_2 and ε_3 are different from E_2 and E_3 by $-(3/2)k_BT$ plus the activation energies of N_t and N_b, respectively. At low temperatures, whereas N_b is approximated as $N_b \approx N_D^+ \approx N_A$ and thus can be regarded as independent of temperature, N_t is approximated as $N_t \approx N_D^- = N_D f_{-1}$. Since f_{-1} can be approximated as $f_{-1} \propto \exp(-U/k_BT)$ at low temperatures, the activation energy of N_D^- increases with decreasing temperature to be U at low temperatures [11].

Also according to the small-polaron theory [35-37], the Hall factors for ε_2 and ε_3 conductions are assumed to be expressed as

$$A_{Hi} = (k_B T / I_{Hi}) \exp(K_H E_i / k_B T), \tag{11}$$

where $K_H = 2/3$ and I_{Hi} are temperature-independent constants. On the other hand, as in the previous study [8], the Hall factor $A_{H\mathrm{ES}}$ for ES-VRH conduction is assumed to be expressed as

$$A_{HES} = A_{0HES} (T_{ES}/T)^{1-s_{ES}} \exp\left[(1-\nu_{ES})(T_{ES}/T)^{1/2}\right] \tag{12}$$

with A_{0HES} and ν_{ES}being temperature-independent constants.

According to the model described in the above, simultaneous fits to experimental data of σ, R_H, and μ_H reported by Kasiyan et al. [23] were performed using equation (6), (7), and (8), respectively. However, the fitting results in the next section reveal that the fits can be well performed with neglecting the third term in each of the right-hand side of equation (7) and (8), i.e., the contribution from ε_3 conduction, for all the samples investigated. This indicates that the Hall effect is absent for NNH in the bottom Hubbard band.

When conductivity is described by the sum of several terms by $\sigma = \sum_i \sigma_i$, as in equation (6), the reduced activation energy can be expressed by [38]

$$w = -\frac{1}{\sigma T}\frac{d}{d(1/T)}\sum_i \sigma_i = \sum_i \frac{\sigma_i}{\sigma} w_i , \tag{13}$$

where

$$w_i = -\frac{1}{\sigma_i T}\frac{d\sigma_i}{d(1/T)} . \tag{14}$$

Thus, the total reduced activation energy w can becalculated as the weighted mean of all the respective reduced activation energies w_i just like the total Hall mobility. Therefore, the total reduced activation energy as well as the total Hall mobility can be deconvoluted into the contribution from the respective conduction mechanisms. We calculated $w(T)$ and $w_i(T)$ from the calculated results of $\sigma(T)$ and $\sigma_i(T)$ using equation (3).

3. Fitting results

Kasiyan et al. [23] reported the results of the temperature-dependent Hall-effect measurements on more than twenty samples of Al-doped n-ZnSe with different shallow donor concentrations N_D in the temperature range between 1.6 and 300 K. Besides the data of the conductivity and the Hall-effect measurements, they showed the temperature dependence of w which was obtained through the graphical differentiation of $\sigma(T)$. Among the samples, those with N_D higher than 1×10^{17} cm^{-3} exhibited metallic conduction while those with lower concentrations exhibited activated conduction at low temperatures. Among the samples which exhibited activated conduction, we analyze here the experimental data of $\sigma(T)$, $w(T)$, and $R_H(T)$ on eight samples.

Dotted lines in **Figure 2**(a) and (b) show the $w(T)$ curves obtained by Kasiyan et al. [23] for the seven samples out of eight. From the $w(T)$ curves, Kasiyan et al. identified the ε_1 region as well as the ε_3 region which is replaced by VRH in the lower temperature region. From the slope of the lowest-temperature linear portion of the log w versus log T dependence, they determined the power exponent p to be 0.5. They also deduced the activation energies ε_1 and ε_3 but did not deduced the characteristic temperature T_{ES} for ES VRH. Although they did not refer to the possibility of ε_2 conduction, the existence of the temperature region in which ε_2 conduction dominates will be proved

later in the present study through the deconvolution of the $w(T)$ curves as well as by that of $R_H(T)$ and $\sigma(T)$.

Fitting to the experimental data was performed in the way described in the previous study [9], in which the values of fitting parameters are determined almost one by one. Therefore, the best-fit values of the fitting parameters can be determined almost uniquely, in spite of the large number of the fitting parameters. The best-fit values of the fitting parameters are shown in **Table 2** for the eight samples. For Sample 642, since the fits were well performed without assuming ε_2 conduction, the parameters related to the top Hubbard band have not been extracted. On the other hand, for three samples of 614, 626, and 630, since the fits were well performed without assuming ε_3 conduction, the parameters related to ε_3 conduction have not been extracted. For samples of 642, since the data of the Hall-effect measurements are not reported, the parameters related to the Hall effect are not extracted. For samples of 626, 630, and 635, since the low temperature ends of the Hall-effect measurements were not sufficiently low for the effect of ES VRH on R_H to be observed, the parameters A_{0HES} and ν_{ES} related to the Hall effect for ES VRH cannot be extracted.

Figure 3(a) and 3(b) show the comparison between the experimental and fitted results of the temperature dependence of conductivity σ for Sample 614and 637, respectively. In each figure, the experimental results of σ are plotted as a function of $T^{-1/2}$ by closed or open circles while the simulated results are shown by a violet solid line. Also shown by green, red, yellow, and blue curves are the calculated results of σ_1, σ_2, σ_3, and σ_{VRH}, respectively. Closed triangles and dotted curves in (a) represents the experimental and the calculated results of $\sigma T^{3/2}$. Note that the logarithmic plot of σ against $T^{-1/2}$ shown in Figure 2(a) for Sample 614 is not perfectly straight but shows a slightly convex

curvature in the ES-VRH dominant temperature region while that of $\sigma T^{3/2}$ is perfectly straight. This is due to the positive value of $s_{ES} = 3/2$.

The comparison between the experimental and fitted results of the temperature dependence of the reduced activation energy w is shown in Figure 2, where (a) shows the results for two samples of 614 and 630 while (b) shows those for five samples of 633, 635, 637, 639, and 642. The calculated results of the contribution from ε_1, ε_2, ε_3 and VRH conductions are shown by green, red, yellow, and blue curves, respectively.

Kasiyan et al. [23] identified the conduction mechanism in the temperature range of 7-14 K as ε_3 conduction on the basis of the slope of $w(T)$ in this temperature region for all the samples. In the present study, however, both curves of $\sigma(T)$ and $w(T)$ for three samples of 614, 626, and 630 can be fitted well without ε_3 conduction, as shown in Figure 2(a) and 3(a) for Sample 614. In the present study, the slight convex curvatures of the $w(T)$ curves shown in Figure 2(a) for these samples, as well as that of the logarithmic plot of $\sigma(T)$ against $T^{-1/2}$ shown in Figure 3(a) for Sample 614, in the ES-VRH dominant temperature region are attributed to the positive values of s_{ES}.

Figure 4 shows comparison between log-log plots of w and $w + 1.5$ versus T for Sample 626. As can be seen in the figure, whereas the log-log plot of w is not straight but exhibits a convex curvature, the log-log plot of $w + 1.5$ is on a straight line with a slope of -1/2. A fine straight solid line represents $w + 1.5 = (1/2)(T_{ES}/T)^{1/2}$ with $T_{ES} = 625$ K. Thus, the conduction mechanism in the temperature range of 7-14 K for three samples of 614, 626, and 630 has been assigned to be ES VRH with $s_{ES} = 1.5$. Also for the other five samples, the values of s_{ES} were obtained through the fits to the $w(T)$ curves rather than the $\sigma(T)$ curves.

For the five samples of 633, 635, 637, 639, and 642, contribution from ε_3 conduction cannot be so clearly noticed in the $\sigma(T)$ curves, as shown in Figure 3(b) for Sample 637. However, contribution from ε_3 conduction is clearly noticed as the appearance of the peak in the $w(T)$ curves for the four samples of 635, 637, 639, and 642, as shown in Figure 2(b). For Sample 633, a faint swell around 8 K in the $w(T)$ curve can be attributed to ε_3 conduction.

For the three samples of 614, 626, and 630, although contribution from ε_2 conduction cannot be clearly noticed in the $\sigma(T)$ curves, as shown in Figure 3(a) for Sample 614, the sharp rise of the $w(T)$ curve at about 20 K before the onset of ε_1 conduction can be attributed to the onset of ε_2 conduction, as shown in Figure 2(a). Being different from the three samples of 614, 626, and 630, the other five samples exhibit no clear signatures of ε_2 conduction in their $w(T)$ curves. As can be seen Figure 2(b), the effect of ε_2 conduction appears only as a broad tail of the peak due to ε_1 conduction in each $w(T)$ curve.

The contribution from ε_2 conduction can also be seen in both of the $\mu_H(T)$ and the $R_H(T)$ curves while that from ε_3 conduction can hardly be seen in both the curves. **Figure 5** and **6** show comparison between the experimental and fitted results of the temperature dependence of the Hall mobility μ_H and that of the Hall coefficient $-R_H(T)$, respectively. In each figure, closed and open circles represent the experimental results for Sample 614and 637, respectively. The calculated results of the contribution from ε_1, ε_2, and VRH conductions are shown by green, red, and blue curves, respectively. The temperature region in which the contribution from ε_2 conduction dominates appears in the $\mu_H(T)$ curve as well as in the $R_H(T)$ curve even for Sample 637 for which the temperature region in which $\sigma_2/\sigma_1 > 1$ is absent. This is partly owing to the large value of A_{H2} (about 10 at 30 K) due to the small values of I_{H2}. On the other hand, ε_3 conduction hardly contributes to the

Hall mobility and the Hall coefficient. This can be attributed to the small value of A_{H3}. The reason for the small value of A_{H3} will be discussed in Sec. 4.2.

It is seen in Figure 6 that the contribution from ε_2 conduction plays the dominant role in $-R_H$ around its peak. The dominance of the contribution from the ε_2 conduction in the Hall coefficient around its peak has also been revealed for a p-Ge sample [10] as well as for the n-GaAs and n-InP samples [8, 9] in our previous studies. On the other hand, the contribution from ε_3 conduction can be ignored in the $\mu_H(T)$ curve as well as in the $R_H(T)$ curve even for Sample 637 in spite of the appearance of the peak due to ε_3 conduction in the $w(T)$ curve for this sample.

4. Discussion

4.1: Ionization energy E_b

In the present study, the simultaneous fits to the experimental data of $\sigma(T)$ and $R_H(T)$ in the ε_1 conduction dominant temperature region have enabled us to deduce the values of E_b for the eight samples of Table 2. For unintentionally doped n-ZnSe, Nedeoglo [39] plotted his own data of E_b together with the data of Aven et al. [40] as a function of the total impurity ion concentration $2N_A + n$ to find the relation of $E_b = E_{b0} - \alpha_0(2N_A + n)^{1/3}$, where $E_{b0} = 33$ meV and $\alpha_0 = 4.9 \times 10^{-5}$ meV cm. In the previous study of the author, on the other hand, it was shown that the relation of $E_b = E_{b0} - \alpha_0 N_A^{1/3}$ proposed by Pődör [41] shows better fits to the experimental results not only for n-InP but also for n-GaAs [9]. The linear dependence of E_b on the cube root of the compensating impurity concentration rather than that of the major impurity concentration has been also show for p-InP [42].

In **Figure 7**, the values of E_b for the eight samples of n-ZnSe of Kasiyan et al. [23] listed in Table 2 deduced in the present study are plotted by closed circles (●) as a function of $N_A^{1/3}$. Also

plotted are the E_b data for Al-doped (◆) and unintentionally doped (◇) n-ZnSe samples of Vaziri et al. [43], Ga-doped n-ZnSe samples of Vaziri et al. [44] (○), and unintentionally doped n-ZnSe samples of Aven [40] (×), Nedeoglo [39] (□), Emel'yanenko et al. [30] (◇), and van Houten et al. [45] (+). A solid straight line indicates the relation of $E_b = E_{b0} - \alpha_0 N_A^{1/3}$, where E_{b0} = 33 meV and α_0 = 7.0 ×10^{-5} meV cm. It can be seen in Figure 7 that, excepting a few, almost of the values of E_b deduced for the above samples including the eight samples in the present study are coincident with this relation.

For the hydrogenic impurities, the ionization energy E_{b0} at the limit of the dilute impurity concentration can be estimated as $E_{b0} = (m_p/m_0)(\varepsilon_0/\varepsilon_s)^2 E_h$, where E_h is the binding energy of the hydrogen atom and m_p is the polaron mass which is calculated as $m_p = m^*(1 + \alpha_F/6)$ with the Fröhlich coupling constant α_F [29]. When $m^* = 0.135\ m_0$ and $\alpha_F = 0.575$ [29] is adopted for ZnSe, the value of $\varepsilon_s = 7.8\ \varepsilon_0$ is needed for yielding E_{b0} = 33 meV. This value of ε_s is slightly smaller than the value used for the calculation of σ_1.

4.2: ε_3 conduction

As can be seen in Table 2, the values of E_3 obtained in the present analysis are rather larger than those of ε_3 obtained by Kasiyan et al. [23] This is mainly owing to the difference between the present analysis and the previous one in the assumed temperature dependence of the pre-exponential factor of ε_3 conduction. Namely, we have assumed the $T^{-3/2}$ dependence for the pre-exponential factor in the present analysis while the temperature-independent pre-exponential factor had been assumed by Kasiyan et al. [23]. When assuming the form of equation (10) with $s_3 = 3/2$ for μ_3, the slope of the Arrhenius plot of σ_3 can be written as $d(\ln\sigma_3)/d(1/k_BT) \approx -E_3 + (3/2)k_BT$. Therefore, when the value

of ε_3 is deduced from the slope of the Arrhenius plot of σ around $T = 14$ K, it will be smaller than the present value of E_3 by (3/2) $k_B T \approx 1.8$ meV. This value almost explains the difference between the values of E_3 obtained in the present study and those of ε_3 obtained byKasiyan et al. [23].

The theoretical expression for the conductivity activation energy ε_3 has been obtained by Ginzburg [46] as well as by Abboudy [47]. Ginzburg [46] obtained the expression on the basis of his molecular-pair theory as

$$\varepsilon_3 = \varepsilon_{03} - 2\frac{e^2}{4\pi\varepsilon_0\varepsilon_s}\left(\frac{2}{3}\rho - \frac{1}{\rho}\right)\exp(-\rho), \tag{15}$$

where

$$\varepsilon_{03} = 0.99\frac{e^2}{4\pi\varepsilon_0\varepsilon_s}N_D{}^{1/3}\left(1 - 0.29K^{1/4}\right) \tag{16}$$

and

$$\rho = \frac{R_m}{a_B} = \frac{\eta}{2}\alpha N_D{}^{-1/3}. \tag{17}$$

Here, R_m is the maximum distance between the centers in a percolation chain, $\alpha = 1/a_B$ is the reciprocal Bohr radius of the N_D^0 state, and η is the numerical factor. Shklovskii [48] theoretically deduced the value of $\eta \approx 1.78$ for an isotropic conduction minimum. On the other hand, Abboudy [47] obtaineda similar but slightly different analytical exression:

$$\varepsilon_3 = \varepsilon_{03} - 1.73\frac{e^2}{4\pi\varepsilon_0\varepsilon_s}\frac{2}{3}\rho'\exp(-\rho'), \tag{18}$$

where

$$\rho' = \alpha\left(\frac{4\pi}{3}N_D\right)^{-1/3} = 0.62\alpha N_D{}^{-1/3}. \quad (19)$$

Since the hopping conductivity is described by $\sigma_3 = eN_b\mu_3$, the activation energy ε_3 of σ_3 includes not only the activation energy E_3 of μ_3 but also the activation energy of N_b. At sufficiently low temperatures, however, since $N_b = N_D^+ N_D^0 / N_D$ can be approximated by the temperature independent value of $N_b \approx N_A(N_D - N_A)/N_D$, the activation energy of N_b can be neglected. Therefore, we can equate ε_3 with E_3.

The value of $\varepsilon_3$was calculated according to equation (15) or (18) for $K = 0.5$ while that of $\varepsilon_{03}$was calculated according to equation (16). In **Figure 8**, solid lines of blue, red, and yellow show the calculated results according to equation (16), (15), and (18), respectively, with $\varepsilon_s = 7.8\ \varepsilon_0$ while broken lines show those calculated with $\varepsilon_s = 9.2\ \varepsilon_0$.

From the comparison of the calculated results in Figure 8 with the values of ε_3 in the brackets in Table 2 which were obtained by Kasiyan et al. [23], it is noticed that the latter are too low in comparison with the former. On the other hand, almost good agreement can be seen in Figure 8 between the deduced values of E_3 in the present study and the calculated values of ε_3 according to equation (18) when adopting the value of $\varepsilon_s = 7.8\ \varepsilon_0$. However, when adopting the value of $\varepsilon_s = 9.2\ \varepsilon_0$, the calculated values according to equation (15) seem to be closer to the the deduced values of E_3. The reported values of ε_s are ranging from 7.1 ε_0 to 9.6 ε_0 [49]. Owing to this ambiguity in ε_s, it is difficult to judge which of equation (15) or (18) is better.

As already mentioned in the above, contribution from ε_3 conduction can be substantially neglected on fitting $R_H(T)$ and $\mu_H(T)$ results of Sample 633, 635, 637, and 639 in spite of the appearance of the peak due to ε_3 conduction in their $w(T)$ curves. This indicates that the Hall factor

A_{H3} for ε_3 conduction is substantially zero. Malwah and Bene [50] theoretically showed that A_{H3} vanishes when the bottom Hubbard band is half-filled. Kogutyuk et al. [51] confirmed this result. Note, however, that both of these studies are regarding the a.c. Hall effect in the high-frequency limit. On the other hand, Movaghar et al. [52] showed that A_{H3} decreases with decreasing frequency ω as ω^s to be constant at low frequencies, where s decreases with increasing density of hopping sites. Therefore, the Hall effect in the $\omega = 0$ limit, i.e., the d.c. Hall effect, for ε_3 conduction will be more hardly observed than the a.c. Hall effect for samples in the vicinity of the half-filled band condition. The compensation ratios of Sample 633, 635, 637, and 639 are in the range between 0.4 and 0.5. Thus, the condition for vanishing A_{H3} seems to be almost fulfilled for these samples since $N_D^0 = N_D f_0 \approx N_D(1-K)$ stands at low temperatures.

4.3: VRH conduction

Figure 9, **10**, and **11** respectively shows the plots of s_{ES}, T_{ES}, and μ_{0ES} as a function of $N_D - N_A$. As shown in Figure 9, while s_{ES} remains constant at 1.5 for $N_D - N_A < 3.2 \times 10^{16}$ cm^{-3}, it decreases with $N_D - N_A$ for larger values than 3.2×10^{16} cm^{-3} to be ~0 but slightly negative. Similarly, while T_{ES} does not decrease so quickly for $N_D - N_A < 3.2 \times 10^{16}$ cm^{-3}, it drastically decreases with $N_D - N_A$ for larger values than 3.2×10^{16} cm^{-3}. The dependence of μ_{0ES} upon $N_D - N_A$ also seems to show marked difference between the two regions in which $N_D - N_A$ is smaller and larger than 3.2×10^{16} cm^{-3}. Note that, in the three samples with $N_D - N_A < 3.2 \times 10^{16}$ cm^{-3}, the ε_3 conduction region hardly observed between VRH conduction region and the ε_2 conduction region.

Rodríguez et al. [53] theoretically showed that, when the impurity overlap wave function has the form of $\psi(r) \propto r^{-j} \exp(-r/\xi)$, where ξ is the localization length, s_{ES} can be represented as $s_{ES} \approx$

– (4j – 1)/2. The wave function of the ns state in the Coulomb potential has the asymptotic form with $j = 1 - n$ while that in the short-range potential has the form with $j = 1$. This leads to the positive value of $s_{ES} \approx (4n - 3)/2$ for the ns state in the Coulomb potential while leads to the negative value of $s_{ES} \approx -3/2$ for the short-range potential. The values of $s_{ES} \approx 3/2$ for $N_D - N_A < 3.2 \times 10^{16}$ cm^{-3} lie between the values for the 1s and 2s state in the Coulomb potential. On the other hand, $s_{ES} \approx 0$ for $N_D - N_A > 3.2 \times 10^{16}$ cm^{-3} suggests that the effective potential which determines the impurity overlap wave function changes its character from Coulomb-like long-rang potential to short-range one for $N_D - N_A > 3.2 \times 10^{16}$ cm^{-3}.

The decrease of T_{ES} with increasing impurity concentration has often been observed for various semiconductors such as p-Ge [10], n-Si [12], and n-GaAs [8].

4.4: ε_2 conduction

Figure 12 shows $\varepsilon_2 = E_2 + 0.945E_b$ as a function of αd_{ND}, where $d_{ND} = (4\pi/3)^{-1/3}N_{ND}^{-1/3}$ is the averaged distance between neutral donors at low temperatures. A straight line in Figure 12 shows the relation of $\varepsilon_2 = \varepsilon_{02}\alpha\left(d_{ND} - d'_{NDcr}\right)$ with ε_{02} = 20.6 meV and d'_{NDcr} = 17 nm for n-ZnSe. This value of d'_{NDcr} corresponds to $N_{ND} = N_D - N_A = 4.8 \times 10^{16}$ cm^{-3}. This value of N_{ND} is much smaller than the assumed value of $N_{NDcr} = 1.3 \times 10^{17}$ cm^{-3} for the MI transition in n-ZnSe. This situation is different from the cases of n-Ge [54] and n-InP [9], in which the values of N_{ND} corresponding to d'_{NDcr} are almost coincident with N_{NDcr}.

Figure 13 shows I_{H2} as a function of ε_2. It can be seen there that I_{H2}increases exponentially with ε_2.The similar dependence of I_{H2} upon ε_2 has also been observed for p-Ge [10], n-Si [12], and n-GaAs [8].

5. Summary

The experimental data of σ, w, and R_H for Al-doped n-ZnSe reported by Kasiyan et al. [23] have been analyzed on the basis of the impurity-Hubbard-band model developed in the previous study [8]. Furthermore, newly developed method utilizing the temperature dependence of w was used to confirm the validity of the analyzed results. It has been shown that the contribution from the top Hubbard band at the intermediate temperatures is more clearly seen in the temperature dependence of w and μ_H rather than that of σ. The Hall effect for NNH in the bottom Hubbard band has been shown to be substantially absent even for the samples for which the peak due to ε_3 conduction appears in the $w(T)$ curve. In addition, the pre-exponetial factor of ES VRH conductivity was determined through the fit to the temperature dependence of w to show that it decreases from ~1.5 to ~0 with increasing net donor concentration.

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