Hopping conduction in Mn-doped ZnO

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The dc and ac conductivities of Mn-doped ZnO were investigated at temperatures from 10 to 100 K. The temperature dependence of the dc conductivity from 10 to 100 K shows an abrupt change at ~18 K, manifesting a much lower activation energy for conduction below 18 K. From 10 to 18 K, the ac conductivity, $\sigma_{ac}(\omega)$, varies as $\sigma_{ac}(\omega)=A\omega^s$ in the frequency range from 10^2 to 10^6 Hz with s in the range of 0.6–1. The dc and ac conductivity observations suggest that the dominant conduction mechanism at temperatures between 10 to 18 K in these samples is a hopping conduction. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1535262]

Hopping conduction occurs in a wide range of materials,[1–5] such as doped semiconductors, amorphous semiconductors, high temperature superconductors, glasses, polymers, and many low-dimensional materials. Therefore, it has become an increasing important topic in materials physics. For a doped semiconductor (considering an n-type semiconductor for convenience), at sufficiently low temperatures, most of the free electrons are recaptured by the donors. As a result, the free-electron band conduction becomes less important, and electron hopping directly between donors in the impurity band will make the main contribution to the conductivity. An obvious phenomenon is that the conductivity exhibits a remarkable decrease from band conduction to hopping conduction. The hopping conduction is associated with electron jumping from occupied donors to empty ones, and therefore the presence of empty donors is necessary. This condition can be fulfilled only by donor-acceptor compensation at low temperatures. Hopping conductivity is governed by the hopping probability between impurity sites. At relatively high temperatures, the hopping probability is dominated by the random spatial distribution of the impurities. Consequently, the hopping conductivity is determined primarily by nearest-neighbor hops. This is so-called nearest-neighbor hopping (NNH) mechanism. At lower temperatures, typical resistances between nearest-neighbor impurities become larger than those between impurities whose energy levels are within a few kilotesla of the Fermi level. Therefore, electron hops between these impurities dominate the conductivity. Due to the fact that the impurities with levels close to the Fermi level are not necessarily correlation in the spatial positions, the hopping length could vary for each hop. This is so-called variable-range hopping (VRH) mechanism.

Hopping conduction was extensively studied on numerous semiconductors,[1–4] such as Ge, Si, GaAs, GaSb, InSb, InP, CdS, and diamond. However, except one earlier work on hopping conduction in In-doped ZnO,[5] few investigations on hopping conduction in ZnO were reported. In the present work, hopping conduction in Mn-doped ZnO were verified and studied by analyzing the dc and ac conductivity data.

Reagent grade ZnO powders (Aldrich, 99.9% purity) were used. Mn doping was incorporated using alcohol solutions of $Mn(NO_3)_2\cdot 4H_2O$. Powder compacts of ZnO doped with 0.1, 0.3, and 0.6 mol % Mn, respectively, were prepared by conventional ceramic process (see Ref. 6 for the detailed procedure). The compacts were quickly inserted in the center of the furnace which has already been raised to 1200 °C. After being sintered at 1200 °C for 2 h, the samples were quenched to room temperature in air. No second phase was observed in these sintered samples from x-ray diffraction, scanning electron microscopy with energy dispersive x-ray spectroscopy (EDS), and transmission electron microscopy with EDS analyses. All the samples show uniform equiaxed grains. The average grain sizes are between 5 and 10 μm, and their relative densities range between 95% and 97%.

Sintered samples were polished on both sides, and then vacuum deposited with gold electrodes or covered with In–Ga electrodes. Using a computer aided system, the ac conductances of these samples were measured in a cryogenic system by an impedance analyzer (Solartron 1260, England). Temperature control and measurement were performed with a calibrated silicon diode and a microprocessor cryogenic temperature controller. The low temperature dc conductance was measured in the same cryogenic system by an electrometer.

Figure 1 shows the temperature dependence of the dc

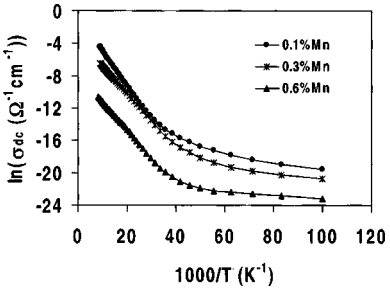

FIG. 1. Temperature dependence of the dc conductivity of ZnO samples doped with 0.1, 0.3, and 0.6 mol % Mn, respectively.

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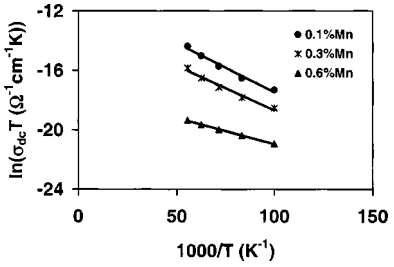

FIG. 2. Plots of $\ln(\sigma_{dc}T)$ vs $1000/T$, for ZnO samples doped with 0.1, 0.3, and 0.6 mol % Mn, respectively.

conductivity for ZnO doped with different Mn contents. It can be observed that two regimes with different conductivity-temperature dependence can be easily distinguished. One is from about 18 to 100 K with an activation energy of about 0.04 eV, and the other is from 10 to 18 K with a much lower activation energy of 10^{-3} eV. On the other hand, we found that the measured dc and ac conductances in the present work are independent of the type of the electrodes (Au or In–Ga) and are also inversely proportional to the thickness of the samples, and that all the samples showed linear dc current–voltage behavior at room temperature.[6] Hence, the measured conductivities should reflect the bulk properties of the materials. The activation energy determined in the temperature range from 18 to 100 K is close to the ionization energy of the main shallow donor in these samples,[7,8] which indicates that this temperature range corresponds to the freezing of the free electrons. Therefore, in Fig. 1, the abrupt change in the temperature dependence of conductivity at ~18 K and the much lower activation energy for conduction below 18 K indicate a transition from band to hopping conduction,[1–3] i.e., hopping conduction becomes the dominant conduction mechanism below 18 K.

For a NNH mechanism, the dc conductivity, σ_{dc}, is described by[4]

$$\sigma_{dc} = CT^{-1}\exp(-\varepsilon_3/\mathrm{kT}), \tag{1}$$

where C is a constant independent of temperature T, and ε_3 is the activation energy for hops. According to Eq. (1), the plots of $\ln(\sigma_{dc}T)$ vs $1/T$ from 10 to 18 K are shown in Fig. 2, which exhibit well linearity. The activation energies (ε_3) and the pre-exponential coefficients (C) determined from these plots are presented in Table I.

The defect chemistry calculation[8] showed that in the present samples, Mn dissolved into ZnO forming a deep donor with an energy level of ~2.0 eV below the conduction band bottom at room temperature, and the main shallow donor and acceptor are zinc interstitial and zinc vacancy, respectively. The existence of Mn deep donors depresses the concentration of the main shallow donor, Therefore, the more the Mn concentration, the less the shallow donor concentration and the conductivity (Fig. 1). The main donor (N_D) and acceptor (N_A) concentrations obtained from the defect chemistry calculation[8] are given in Table I. In Table I, the effective Bohr radius of the shallow donor in ZnO (a) was calculated from $a = 2\varepsilon_r\varepsilon_0 h/(m^* e^2)$ with $\varepsilon_r = 8$ and $m^* = 0.28 m_0$ (m_0 is free electron mass),[2] the theoretical value of ε_3 was obtained by $\varepsilon_3 = 0.99 e^2 N_D^{1/3}/(4\pi\varepsilon_r\varepsilon_0)$ for very weak compensation ($N_A/N_D \ll 1$),[2,4] the critical temperature for transition

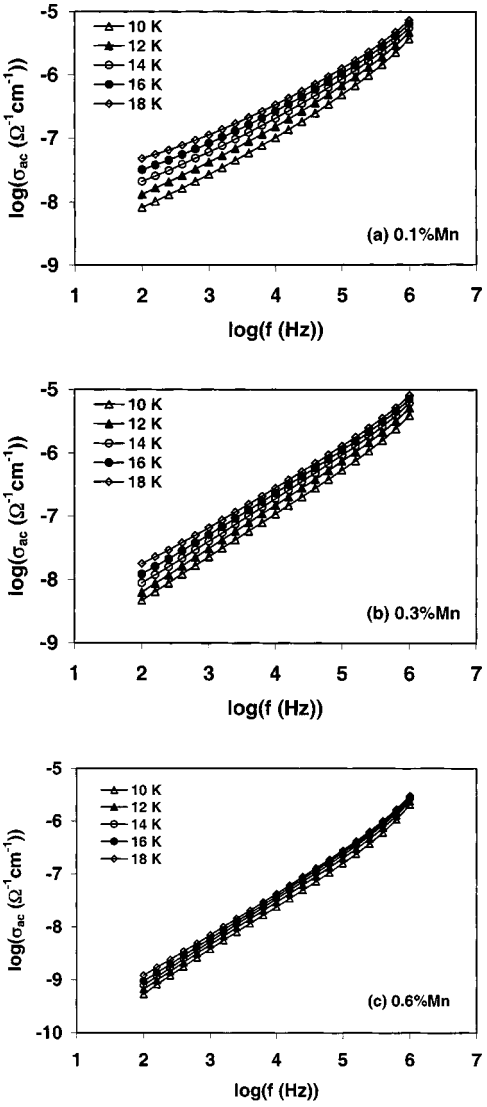

FIG. 3. Plots of $\log\sigma_{ac}$ vs $\log f$ at several temperatures, for ZnO samples doped with (a) 0.1, (b) 0.3, and (c) 0.6 mol % Mn, respectively.

TABLE I. Parameters for Mn-doped ZnO samples, where N_D and N_A are the main shallow donor and acceptor concentrations, N_A/N_D is the compensation ratio, a is the effective Bohr radius of the shallow donor in ZnO (~1.51 nm), C and ε_3 (exp.) are the experimental determined pre-exponential coefficient and activation energy in Eq. (1), ε_3 (theory) is the theoretical calculated activation energy, T_C' and T_C'' are the temperatures for transition from NNH to VRH determined by Shklovskii and Efros's model and Pollak's model, respectively.

Sample (%)	N_D (cm^{-3})	N_A (cm^{-3})	N_A/N_D (%)	$aN_D^{1/3}$	C ($\Omega^{-1}\,\mathrm{cm}^{-1}\,\mathrm{K}$)	ε_3 (exp.) (meV)	ε_3 (theory) (meV)	T_C' (K)	T_C'' (K)
0.1	1.79×10^{15}	2.03×10^{13}	1.13	1.84×10^{-2}	1.79×10^{-5}	5.63	2.16	0.16	2.42
0.3	6.43×10^{14}	3.67×10^{13}	5.71	1.30×10^{-2}	2.91×10^{-6}	5.11	1.54	0.08	1.22
0.6	3.44×10^{14}	5.37×10^{13}	15.6	1.06×10^{-2}	2.64×10^{-8}	3.02	1.25	0.05	0.81

TABLE II. Experimentally determined values of s and $\log A$ from the frequency dependence of the ac conductivity at 10, 14, and 18 K, for Mn-doped ZnO samples.

	10 K		14 K		18 K	
Sample	s	$\log A$	s	$\log A$	s	$\log A$
0.1% Mn	0.65	−10.02	0.59	−9.45	0.53	−8.95
0.3% Mn	0.71	−10.34	0.70	−10.05	0.66	−9.67
0.6% Mn	0.85	−11.67	0.85	−11.51	0.82	−11.27

from NNH to VRH proposed by Shklovskii and Efros[2] (T_C') is determined by $T_C'=0.34e^2aN_D^{2/3}/(4\pi\varepsilon_r\varepsilon_0 k)$, and this critical temperature proposed by Pollak[9] (T_C'') is determined by $T_C''=5.2e^2aN_D^{2/3}/(4\pi\varepsilon_r\varepsilon_0 k)$. As shown in Table I, the value of $aN_D^{1/3}$ is much less than Mott's critical value of 0.26 for a metal–insulator transition[1] so that the condition for theory of hopping in lightly doped semiconductors is fulfilled. The sample temperatures in the present work ($\geqslant 10$ K) are much higher than the critical temperature for transition from NNH to VRH proposed either by Shklovskii and Efros or by Pollak. In fact, VRH in crystalline semiconductors was often reported to occur at temperatures below 10 K.[1–4] Therefore, we believe that NNH other than VRH is the dominant conduction mechanism at temperatures from 10 to 18 K in the present samples. On the other hand, the activation energies obtained from experiments are in the same order of magnitude with the theoretical ones. With increasing Mn content, the activation energy and the pre-exponential coefficient decrease. Defect concentration calculation[8] showed that the shallow donor concentration decreases with the increase of the Mn content in these samples. Therefore, the dependence of the activation energy and the pre-exponential coefficient on the donor concentration is qualitatively consistent with the theoretical prediction for the hopping conduction.[1–3] Further experimental support for the occurrence of the hopping conduction in the temperature range from 10 and 18 K arises from the ac conductivity data.

It is well known that the ac conductivity for hopping conduction, $\sigma_{ac}(\omega)$, in the intermediate frequency regime (usually kilohertz range) can be expressed as[10,11]

$$\sigma_{ac}(\omega)=A\omega^s, \tag{2}$$

where ω is the angular frequency of the ac signal ($\omega=2\pi f$), and the power s is normally in the range of 0.6–1, which slightly increases with frequency. Figure 3 shows the plots of $\log\sigma_{ac}$ vs $\log f$ at several temperatures for ZnO doped with 0.1, 0.3, and 0.6 mol % Mn, respectively. Clearly, for each sample in the temperature range of 10–18 K, σ_{ac} in the frequency range of 10^2-10^6 Hz follows an apparent power law [Eq. (2)] in which the power weakly increases with frequency. The determined average values of s and $\log A$ from the plots at 10, 14, and 18 K for each sample are summarized in Table II. As shown in this table, the values of s are in the range of 0.6–1, except two slightly smaller values. With increasing temperature, s slightly decreases and A increases for each sample. When the Mn content is increased, which results in decreasing the shallow donor concentration, s increases and A decreases. In addition, Fig. 3 shows that the temperature dependence of σ_{ac} becomes weaker with increasing frequency. All of these results are consistent with the theoretically predicted features of the ac conductivity for hopping conduction,[10,11] and therefore further support the conclusion that hopping conduction becomes the dominant conduction mechanism at temperatures from 10 to 18 K.

In conclusion, the data of the dc and ac conductivities of Mn-doped ZnO samples suggest that hopping conduction becomes the dominant conduction mechanism in the low temperature range between 10 and 18 K. With increasing Mn content, the activation energy and pre-exponential coefficient for the dc hopping conductivity decrease, and the power for ac conductivity increases. This is due to the fact that the shallow donor concentration decreases with the increase of the Mn content in these samples.

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