Van der Pauw Hall Measurement on Intended Doped ZnO Films for p-Type Conductivity *

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A Van der Pauw Hall measurement is performed on the intended doped ZnO films (Na doped ZnO) grown by using the molecular beam epitaxial method. All as-grown samples show n-type conductivity, whereas the annealed samples (annealing temperature 900°C) show ambiguous carrier conductivity type (n- and p-type) in the automatic Van der Pauw Hall measurement. A similar result has been observed in Li doped ZnO and in as-doped ZnO films by other groups before. However, by tracing the Hall voltage in the Van der Pauw Hall measurement, it is found that this alternative appearance of both n- and p-type conductivity is not intrinsic behavior of the intended doped ZnO films, but is due to the persistent photoconductivity effect in ZnO. The persistent photoconductivity effect would strongly affect the accurate determination of the carrier conductivity type of a highly resistive intended doped ZnO sample.

II-VI semiconductor ZnO has attracted much attention for short wavelength optoelectronic devices due to its wide bandgap (3.37 eV) and high exciton binding energy (60 meV) at room temperature. Novel devices such as transparent field effect transistors and UV photodetectors have been developed based on homo- and hetero-epitaxial ZnO.[1−5] However, similar to most wide bandgap semiconductors, ZnO experiences a serious doping asymmetry problem, i.e. it can be doped easily as n-type, but not p-type, because ZnO has a low valence band maximum with respect to the vacuum.[6−8] The difficulty of fabricating p-type ZnO, which is a key step for p-n junction based optoelectronic devices, has so far greatly hindered its practical application. Recently, several different I-group (Li and Na) and V group dopants (N, As, P and Sb) have been reported for the realization of p-ZnO,[9−15] but most of these intended doped p-ZnO films have showed high resistivity and instability for p-type conductivity. These problems are attributed to either spontaneous formation of compensating defects with the coexistence of equivalent acceptor and donor defects in p-ZnO films or the impact of laboratory environmental variables such as light exposure and gas ambient.[10,16] Moreover, from the perspective of experiments, these problems will make accurate characterization of the electrical property of these intended doped p-ZnO samples very difficult.

In this Letter, we report a Van der Pauw Hall measurement performed on the intended doped ZnO films

(Na doped ZnO) grown by using the molecular beam epitaxial method (MBE). It is observed that an alternative carrier conductivity-type carrier (both n- and p-type) appears in the annealed ZnO samples by the Van der Pauw measurement. We demonstrate that this behavior is not an intrinsic behavior of the samples, but is due to the persistent photoconductivity (PPC) effect. The PPC effect would strongly affect the accurate determination of the carrier conductivity type of highly resistive intended doped ZnO samples.
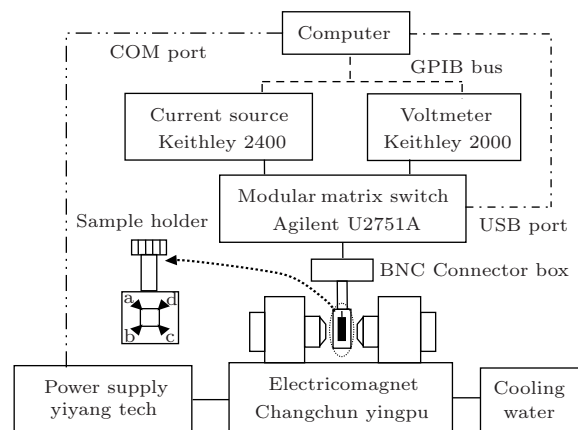

Fig. 1. Schematic diagram of the automatic four-probe Hall measurement setup with a Van der Pauw configuration.

The Van der Pauw Hall measurement was performed in a homemade automatic four-probe Hall

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measurement system (EMO 600, IPCAS) with a Van der Pauw configuration as shown in Fig. 1. For the four-probe Hall measurement, the constant current I is supplied by a programmable dc current source (Keithley 2400) and the corresponding voltage drop V between contacts is measured using a high-impedance high-resolution voltmeter (Keithley 2000). They are controlled by a computer through a GPIB bus with the IEEE 488 protocol. The contacts are appropriately exchanged using a computer-controlled (USB port) modular matrix switch (Agilent U2751A) which supports 4×8 arrays. The magnetic field is generated by employing an electromagnet (Changchun YingPu) with a computer-controlled (COM port) current source (Yilang Tech 4102). The sample holder is an own-designed printed circuit board with four metal electrode spring-clips to contact four corners of a sample, marked as a, b, c and d. In the Van der Pauw Hall measurement, the conductivity of a sample is given by[17,18]

$$\sigma = \left[\frac{\pi t}{\ln 2} \frac{R_{ab,dc} + R_{ad,bc}}{2} f\left(\frac{R_{ab,dc}}{R_{ad,bc}}\right)\right]^{-1}, \quad (1)$$

where t is the sample thickness and the resistance of $R_{ab,dc}$ is defined as $R_{ab,dc} = V_{dc}/I_{ab}$. V_{dc} is the voltage drop between contacts d and c when the current is I_{ab} passing between contacts a and b. The resistance $R_{ab,dc}$ and $R_{ab,dc}$ are defined correspondingly. The function $f(x)$ in equation (1) is defined by the equation

$$\cosh\left(\left[\frac{x-1}{x+1}\right]\frac{\ln 2}{f}\right) = \frac{1}{2}\exp\left(\frac{\ln 2}{f}\right). \quad (2)$$

With a magnetic field B the Hall coefficient R_H is calculated by

$$R_H = \frac{d}{2B}\left[R_{ac,bd}(+B) - R_{ac,bd}(-B)\right], \quad (3)$$

where $R_{ac,bd}(+B)$ and $R_{ac,bd}(-B)$ are the resistances of $R_{ac,bd}$ measured at positive and negative magnetic field B, respectively. For a p-type (n-type) semiconductor, the condition $R_H > 0$ (< 0) is satisfied, and carrier concentration and mobility are calculated by

$$n = \frac{1}{eR_H}, \quad \mu = \sigma R_H. \quad (4)$$

The samples for p-type doping are Na doped ZnO films which were prepared on sapphire (0001) substrates in an rf plasma assisted MBE system with a base pressure about 1×10^{-10} Torr, for which the growth condition is well-established for undoped ZnO.[19] Active oxygen was produced by an rf-plasma system (SVTA). The flow rate of oxygen gas was controlled by a mass flow controller (ROD-4, Aera). The typical thickness of samples is about 300 nm. The Na impurity density in ZnO was measured by a secondary ion mass spectrometer (SIMS). Van der Pauw Hall measurement was conducted on $5\,\text{mm} \times 5\,\text{mm}$ samples with a dc current $I = 100\,\text{nA}$ and a magnetic field $B = 1\,\text{T}$. Electrical contacts were made using soldered In dots. All the measurements were performed in darkness.

The result of the automatic Van der Pauw Hall measurement is given in Table 1. Four samples are measured in our experiment, where sample A is an undoped ZnO film and both samples B and D are Na doped ZnO films with a varied Na impurity density. All of the as-grown samples show n-type conductivity, and the electron concentration decreases from $1.1 \times 10^{17}\,\text{cm}^{-3}$ (undoped) to $2.5 \times 10^{15}\,\text{cm}^{-3}$ (Na: $7.9 \times 10^{18}\,\text{cm}^{-3}$) as the Na impurity density increases in ZnO. However, for the annealed samples (annealing temperature: 900°C) the Van der Pauw Hall measurement yields an ambiguous carrier type (n- or p-type) in the same sample, and both carrier concentration and mobility become smaller. Similar results have been observed in Li doped ZnO and P doped ZnO films by other groups before.[10,11] This is attributed to the strong compensation effect with an equivalent concentration of electrons and holes in their samples. However, it is found that this alternative appearance of two kinds of conductivity type in these samples can be reproduced in our experiment, and it depends on the Van der Pauw measurement configuration. Concretely, when the cross current supplied is rotated by 90°, e.g. I_{ac} to I_{bd}, the sign of the calculated Hall coefficient R_H is changed, so the conductivity type is also changed. Therefore, to further determine the reason for this appearance of the ambiguous carrier type in these samples, the Van der Pauw Hall measurement is traced in detail.

Table 1. Data of the Van der Pauw Hall measurement.

Sample	Na impurity density (cm^{-3})	As grown sample			Annealed sample (900°C)		
		Carrriers concentration (cm^{-3})	Mobility (cm^2/Vs)	Type	Carrriers concentration (cm^{-3})	Mobility (cm^2/Vs)	Type
A	undoped	1.1×10^{17}	32.1	n	1.2×10^{17}	57.2	n
B	2.6×10^{18}	7.9×10^{16}	26.4	n	1.5×10^{15}	4.5	p/n
C	4.4×10^{18}	5.6×10^{16}	30.5	n	2.6×10^{16}	2.1	p/n
D	7.9×10^{18}	2.5×10^{15}	7.1	n	Semi-insulating		

Figure 2 shows the tracing curves of sample C with the x-axis being time, which is marked by the period of consecutive sample points and with the y-axis being Hall voltage V_{hall}. In the Van der Pauw measurement configuration, the current passes through contacts a and b, simultaneously the Hall voltage between contacts d and c is measured. The magnetic field is manually controlled to turn on or turn off. Obviously, there is a linear background in the tracing curve of Fig. 2, which originates from the PPC effect in ZnO.[20,21] When a positive 1 T magnetic field is applied in a direction perpendicular to the sample, the Hall voltage V_{hall} will decrease but will increase under a negative 1 T magnetic field in the linear background. After subtracting this linear background as shown in the inset of Fig. 2 it is clear that the Hall coefficient R_H is negative, and sample C exhibits n-type conductivity. The negative offset of V_{hall} at $B = 0$ is just due to the geometrical mismatch in voltage contacts b and d.
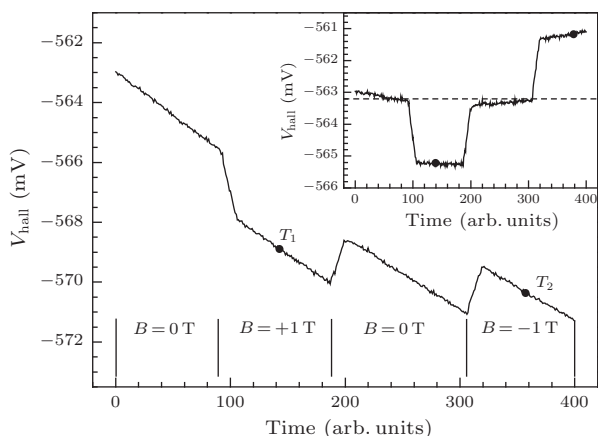

Fig. 2. A tracing curve of the Van der Pauw Hall measurement for sample C.

In the automatic Van der Pauw Hall measurement, this linear background is kept in the calculation. For example, $V_{hall}(+B)$ and $V_{hall}(-B)$ are recorded at T_1 and T_2 points, respectively. $V_{hall}(+B)$ is larger than $V_{hall}(-B)$, resulting in a positive Hall coefficient R_H. Thereby, sample C shows p-type conductivity. On the other hand, correspondingly, when the Van der Pauw measurement configuration is changed, i.e., where the current is passed between contacts b and d, and the Hall voltage is measured between contacts c and a, both the slopes of the linear background and the offset of V_{hall} become positive due to the geometrical mismatch of contacts, thus the Hall coefficient R_H becomes negative, and sample C shows n-type conductivity. Thus the alternative appearance of two kinds of carrier conductivity type observed in the automatic Van der Pauw Hall measurement is not intrinsic behavior of these intended doped ZnO films, but due to the persistent photoconductivity effect.

Actually, the PPC effect is quite general for ZnO,

and it originates from deep-energy impurity states in ZnO, e.g. oxygen vacancy.[22] For the n-type ZnO sample, the influence of the PPC effect on the Van der Pauw Hall measurement is negligible due to its lower resistivity. However, this effect will strongly affect the accurate determination of carrier conductivity type in highly resistive intended doped ZnO samples for p-type conductivity. From the perspective of experiments, the PPC effect leads to a low signal-to-noise ratio. For example, Fig. 3 shows the tracing curve of sample D which has a high sheet resistance approximately up to $10^8\,\Omega/\mathrm{sq}$. Obviously, the signal of the Hall voltage almost cannot be detected in the PPC background. Therefore its conductivity type cannot be determined in this situation.
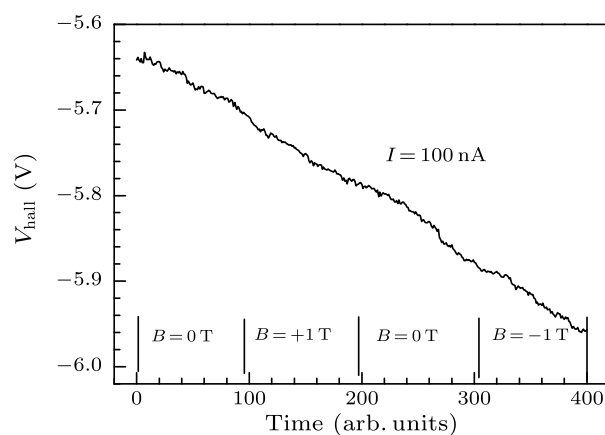

Fig. 3. A tracing curve of the Van der Pauw Hall measurement for sample D.

In summary, Van der Pauw Hall measurement has been performed on the intended doped ZnO films (Na doped ZnO) grown by using an MBE system. All of the as-grown samples show n-type conductivity and the electron concentration decreases with Na impurity density increasing in ZnO. However, for the annealed samples, the Van der Pauw Hall measurement yields an ambiguous carrier type (n- or p-type) in the same sample, and both the carrier concentration and mobility become smaller. By tracing the Hall voltage in the Van der Pauw Hall measurement, we have demonstrated that the ambiguous carrier type in intended doped ZnO films is not intrinsic behavior of the samples, but due to the persistent photoconductivity effect in ZnO. The persistent photoconductivity effect strongly affects the determination of carrier conductivity type in highly resistive intended doped ZnO samples for p-type conductivity. We suggest that the study of the self-compensating effect and deep-energy impurity states would be very important to overcome the p-doping problem of ZnO.

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