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AN INSIGHT TO IMPROVED VAN DER PAUW FACTOR AND THEIR STABILITY IN THE TEMPERATURE RANGE 300 K-10 K OF LAYERED SEMICONDUCTING MATERIAL, MOLYBDENUM DISELENIDE SINGLE CRYSTALS

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Hall Effect measurement is a unique tool to provide basic material parameters needed to find the suitability of its application. The van der Pauw technique is commonly used for electrical transport measurements on solid materials and is suited to thin, arbitrarily shaped samples, with the contacts placed anywhere on the periphery. Present study reports Hall Effect measurements on grown crystals of $MoSe_2$ using van der Pauw technique by taking ohmic contacts using different methods viz contacts prepared by conducting silver paste, thermally evaporated indium dots and by diffusion of indium ingot on cleaned surfaces. We show a highly stable ohmic contacts and thereby improved value of van der Pauw factor (vdP), F = 0.999 on $MoSe_2$ single crystals in the case of diffused indium contacts. This ensures better understanding of transport properties of these materials and further device performance. The stability of the result has been verified for a temperature range of 10K – 300K.

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1. Introduction

The theoretical foundation of Hall measurement evaluation for irregularly shaped samples is based on conformal mapping developed by van der Pauw [1]. He showed how the resistivity, carrier concentration and mobility of a flat sample of arbitrary shape can be determined without knowing the current pattern, if the following conditions such as (i) the contacts are sufficiently small, (ii) the contacts are at the circumference of the sample (iii) the sample is uniformly thick and (iv) the sample contains no isolated holes are met. van der Pauw suggested different geometries such as circular, square, rectangular and cross. The cross structure generally used for films and other for bulk crystals. According to the investigations made by Daniel W. Koon [2-5] for different geometries, the preferred geometry is said to be square rather than circle to reduce the effect of contact lead placement errors in measurement of transport parameters such as resistivity and Hall coefficient. The square is the most convenient sample shape to fabricate, and by using a square shape sample it can be reduce the effect of errors in the van der Pauw method arising from either the

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size or displacement of contact leads from the edge of the sample. The lead displacement in the square sample must be near the corners in order to minimize errors. The conformal mapping will map the lines of equal potential and the current – flow lines in an electric potential problem in the square region. It is easy to show that for four contacts on the boundary of a semi-infinite plane sheet, the resistances $R_{12,34}, R_{23,41}$ satisfy the relationship $\exp\left(-\frac{\pi R_{12,34} t}{\rho}\right) + \exp\left(-\frac{\pi R_{23,41} t}{\rho}\right) = 1$.

By knowing t, $R_{12,34}, R_{23,41}$ the above equation can be solved for the resistivity of the material, [6, 7],

$$\rho = \frac{\pi t}{\ln(2)} \frac{(R_{12,34} + R_{23,41})F}{2} \qquad (1)$$

Where, $R_{12,34} = \frac{V_{34}}{I_{12}}$.

The current I enters the sample through contact 1 and leaves through contact 2 and $V_{34} = V_4 - V_3$ is the voltage between contacts 4 and 3. $R_{34,\ 41}$ is similarly defined. The quantity 'F' is a transcendental function of the ratio,

$$R_r = \frac{V_{43} I_{23}}{I_{12} V_{14}} = \frac{R_{12,34}}{R_{23,41}} \qquad (2)$$

or $$R_r = \frac{I_{12} V_{14}}{V_{43} I_{23}} = \frac{R_{23,14}}{R_{12,43}} \qquad (3)$$

Whichever is greater, and F is found by solving the equation,

$$\frac{R_r - 1}{R_r + 1} = \frac{F}{\ln(2)} ar\cosh\left\{ \frac{\exp\left[\frac{\ln(2)}{F}\right]}{2} \right\} \qquad (4)$$

F = 1, when $R_r = 1$, which occurs with symmetrical samples like circles or squares, when the contacts are equally spaced and symmetrical.

Molybdenum dichalcogenides belongs to the large family of layered transition metal dichalcogenide compounds (TMDC's). Single crystals of these semiconducting compounds have been receiving increasing attention because of their potential electrochemical applications. Many discussions have been reported that among these layered semiconductors has excellent optical absorption in the solar spectral region and exhibit suitable properties for various optoelectronic devices such as photovoltaic solar cells and nanocrystallites etc. [8-12]. It is necessary to note, that due to the weakness of interlayer forces for the layered crystals, the presence of plenty of interlayer defects, defects of stacking faults and etc. The periodicity of wave functions in the direction of perpendicular to the layers is broken, and it leads to the occurrence localized states with the energies of layers being in the interval of band energy. As a result it turns out, that the charge carrier mobility in layer planes is considerably more, than in the direction perpendicular to layers and this leads to the anisotropy in conductivity. Hence for the understanding of the transport properties the electrical contacts with minimum measurement errors in terms of intrinsic as well as geometrical errors is very essential. We report here the conformity of chosen square van der Pauw geometry, the validity of improved van der Pauw (vdP) factor and the Hall effect measurements on molybdenum diselenide single crystals for a temperature range of 10K-300K.

2. Experiment

Crystals of $MoSe_2$ were grown by direct vapour transport (DVT) method inside a dual zone horizontal furnace [13-15]. The microstructural examination of the surfaces of the as grown crystals as well as the metal deposited surfaces was accomplished with the help of Axiotech 100 reflected light microscope, by Carl Zeiss Jena, Germany. Crystals with flat shining surfaces were chosen with the help of optical microscope. These crystals were then washed in acetone to remove adhesive contaminations and to make the surface clean. It is kept in the oven for a couple of minutes at 60^0C to dry out the crystals completely. Figure 1 shows a typical topographical image of fused indium contacts on cleaned $MoSe_2$ surface. It clearly indicates the layered growth through steps promoted by the screw dislocation process.

In the present study the ohmic contacts on crystals along the basal plane were accomplished in three different ways. First contact was made from conductive Ag paste and low strain thin Ag alloy wires painted onto the basal plane of the crystal [16-18]. The contacts were then annealed at 100^0C for 12 hours. In the conventional ohmic contact the indium metal was chosen. Initially indium metal ingot was deposited by thermal evaporation onto the four corners of the crystal with a suitable thin mica mask under a pressure of 10^{-6} torr. Further the electric contact is made possible with low strain thin Ag alloy wires and Ag paste as adhesive [19]. In the third method, direct fusing of indium metal ingot along with low strain thin Ag alloy wires onto the four corners of the crystal was done to provide van der Pauw geometry for measurements [20]. This has been done with the help of a soldering iron with fine tip, providing a constant tip temperature of 275^0C for three minutes.

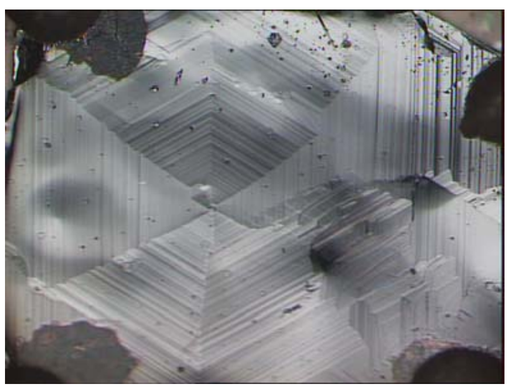

Fig. 1. Optical - Micro structure of $MoSe_2$ van der Pauw geometry, Indium fused electrical contact (5X image).

The crystals with contacts developed using methods mentioned above were fixed on a mica piece and then soldered on a sample holder PCB for the verification of ohmic nature of different pairs of contacts for all the three types of samples. Further for studying the low temperature stability the crystals were mounted on the sample mount stage inside the Closed Cycle Refrigerator (CCR 75014) and contacts were soldered for external connections. Then the whole assembly was arranged suitably between pole gaps of Hall effect measurement system model 7504 supplied by Lakeshore Cryotronics, Inc., USA. The experiment over a range of temperatures was made possible with the help of Lakeshore temperature controller (Model 340), which balances the cooling power provided by a Closed Cycle Refrigerator (CCR 75014) against two heater circuits. The first control loop consists of a temperature sensor and heater attached to the cold end of the refrigerator. The sample is located near the bottom of the copper sample well and is at a significant distance from the cold end. A temperature sensor mounted directly to the sample provides a much more accurate measure of the actual sample temperature. When the variables were set correctly, temperature was also set constant at the desired value using Lakeshore temperature controller and closed cycle cryostat. After stabilizing the set temperature, measurements were started and the data were stored as spreadsheet in the computer memory. The experiments were repeated from room temperature to cryogenic temperature of around 10K. To minimize extrinsic errors caused by geometrical factors and temperature variations the Hall Effect measurements are required to be done in the following sequence. For each measurement point in a Hall experiment, up to 32 individual resistance measurements were made for both A and B type of geometries. Where geometry A corresponds to R12,43 & R23,14 and B corresponds to R34,21 & R41,32. Each van der Pauw resistivity requires 8 measurements, and the Hall resistance requires 4 measurements. The sequence of the temperature dependence measurement is as follows:

(i) Zero field resistance measurements (8 measurements).
(ii) Hall resistance measurements for +ve magnetic field, +B (4 measurements).
(iii) Resistivity measurements for +ve magnetic field, +B (8 measurements).
(iv) Hall resistance for –ve magnetic field, –B (4 measurements).
(v) Resistivity measurements for –ve magnetic field, -B (8 measurements).

In the present investigation the experiment has been conducted for a magnetic field of $\pm 1kG$ and for a temperature range of 300-10K.

3. Results and discussion

Fig. 2 shows the V-I characteristics of all three types of contacts at room temperature. The Ag painted contact shows ohmic nature after annealing the contact around 125^0C for 10 hours. Then the contact resistance is found to be 25kΩ. The average value of vdP factor for geometry A(R12,43; R23,14) and B(R34,21; R41,32) is found to be 0.73 and 0.75 respectively. Samples with evaporated Indium, contacts also shows a ohmic nature with a contact resistance of 50 kΩ. The average vdP factor for geometry A (R12,43; R23,14) and geometry B(R34,21; R41,32) respectively is found to be 0.98 and 0.984.

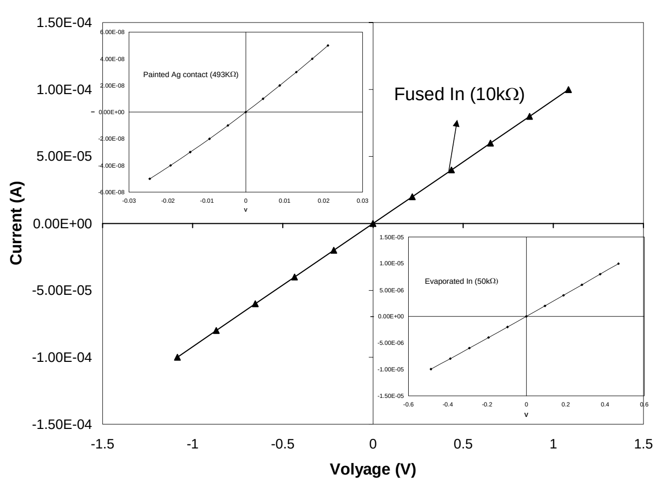

Fig. 2 Room temperature I-V Characteristics of as prepared contacts.

The fused indium bonded with Ag alloy wires gives a good ohmic behavior between the pairs of contacts and the average resistance between the contact pairs is found to be 10kΩ. The vdP factor for geometry A and B for this method is 0.999 and 0.999 respectively. The high value of resistance in the first two methods can be attributed to the inhomogeneous deposition of indium through the layers of the semiconductor along with poor adhesion of Ag paste bonded with the contact. On further thermal annealing, the I-V characteristics show the improvement of Ohmic behavior along with the decrease of total contact resistance. The observed significant decrease in contact resistance magnitude of around 75 percent can be attributed to (i) curing of Ag paste with heat treatment and (ii) the diffusion of indium in to the layers of the crystal. Thus the inhomogeneous deposition of Ag paint or indium the resistance ratios mentioned in equations 3 and 4 changes and lead a considerable variation in the vdP factor. In the case of fused indium contacts the low contact resistance and high vdP factor may be attributed to the high diffusion of indium onto the layers of the crystal causes the narrowing of depletion width and there by an easy tunneling of electron across the metal semiconductor junction.

The low temperature experiments carried out for the first two samples viz. evaporated indium and painted Ag contacts showed the deterioration of vdP factor with temperature At low temperatures below 70K the leakage current starts developing and the contact resistance increases substantially. But for samples of fused indium contact, the ohmic behaviour of the contact (figure 1) pairs remains the same and there is only a little change in vdP factor. Since the fused indium contacts provide adequate bonding between metal and semiconductor, the resistance ratios between the pairs (eqns. 3 and 4) does not change considerably with temperature and gives high value of vdP factor. Fig.3 shows the dependence of the temperature on vdP factor from 10K-300K. The vdP factor is about 0.999 (nearly 1) for almost all temperature ranges and slightly departing as temperature reaches to 10K. The measured Hall parameters from all the three methods of preparation of ohmic contacts are tabulated in table 1.

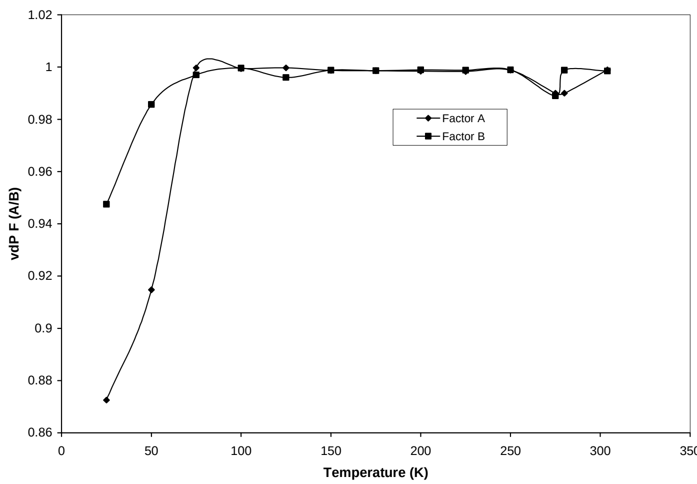

Fig..3 Stability curve of van der Pauw factor with respect to temperature of $MoSe_2$ crystals ranging from 300-10K.

Table 1. Measured Hall parameters of $MoSe_2$ crystals at 300 K.

Ohmic contact type	Resistivity (Ω-cm)	Density (1/cm³)	Mobility (cm²/V s)
In evaporated + Ag paste	22	9.84×10^{15}	68
Direct Ag paste	20.6	4.46×10^{15}	65
Fused In	4.5	3.34×10^{17}	75.58
Reported			
1. [18]	25	3.5×10^{16}	31.4
2. [13]	0.47	1.3×10^{17}	126
3. [21]	1	1.6×10^{17}	40
4. [22]	11.5	1.8×10^{16}	30.30
5. [19]	1.5	5.0×10^{16}	100

4. Conclusion

In spite of being inhomogeneities in the sample thickness due to growth spirals and steps like structure the fused indium contacts in vdP geometry provides reliable Hall effect measurements. The value of vdP factor depends on the metallization methods to $MoSe_2$ crystals and the Hall parameters are strongly influenced by the vdP factor. An increase of carrier density by a power of two has been observed with a change vdP factor from 0.73 to 0.999. This is the maximum density ever reported for this type of material. Further the stability of the vdP factor to the cryogenic temperature of 10 K helps the evaluation of Hall parameters with more accuracy.

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