CHAPTER III

PREVIOUS WORK

The related previous works are described in this chapter. The section 3.1 is the studies on ohmic contact of p-$CuInSe_2$. However, in our work, we used the different method, both experimental and theoretical. The measurement technique and the simple pseudo-Richardson model, are in the section 3.2. Another complex model will be described in subsection 4.3.2.

3.1 Ohmic Contact to p-$CuInSe_2$

Although p-$CuInSe_2$ is a promising semiconductor for solar cells, there are only few works on the study of the ohmic contact on p-$CuInSe_2$. The first one seems to be the study of Matson et al. (1984) who investigated several metals deposited in different ways on thin film p-$CuInSe_2$. The metalisation may be evaporated and magnetron sputtering silver, evaporated gold, electron-beam heated copper, magnetron sputtering nickel, magnetron sputtering and rf-sputtering molybdenum, and electron beam and magnetron sputtering aluminum. The I-V characteristics of the contacts were measured across pairs of contacts, in order to look for ohmic behavior. Samples showing non-ohmic behavior were then examined by the electron beam induced current (EBIC) technique. They concluded that only gold and nickel gave reproducible ohmic contacts.

Abou-Elfotouh et al. (1990) compared I-V characteristic of evaporated gold, evaporated gold-beryllium, electron beam platinum, and rf-sputtering molybdenum, contacts to p-$CuInSe_2$ single crystals with different compositions. Among these, platinum contacts had the most linear I-V. For gold, the linear I-V were obtained only for copper-rich composition crystals.

The first contact resistivity measurement and systematic work was due to Toro (1986). He used evaporated gold, and dc-sputtered molybdenum, nickel, and aluminum, on p-$CuInSe_2$ single crystals. He used a three-probe ring structure configuration to measure the I-V characteristic of the contact. This configuration gives directly the resistance of the interested contact but excludes other resistances, such as the bulk, and the back contact. The contact resistivity was calculated directly from slope of the I-V plot. He also performed EBIC measurement, the electron probe microanalysis, and the Auger electron spectroscopy. His results are :

a) according to EBIC measurement, all as-deposited metals form homojunction buried about 1 μm into $CuInSe_2$. This occurs because of the Se out-diffusion, which leaves the donor state behind and results in type conversion.

b) as-deposited Au, Ni, and Mo contacts yield the contact resistivity values of about 0.6, 0.6 , and 5 Ω-cm^2, respectively,

c) annealing in forming gas, Au contact resistance increases, while annealing at 450 ^oC the contact resistance of both Ni and Mo become less resistive. The lowest contact resistivity was about 0.008 Ω-cm^2, obtained from a Ni contact which was annealed at 450 ^oC, while the lowest value of Mo contact was about

0.02 Ω-cm^2. The change of the contact resistivity in annealing was attributed to the out-diffusion of the constituents of the semiconductor,

d) according to the sensitivity limit of AES, as-deposited Au contacts are abrupt and unreactive. For as-deposited Ni contacts, the out-diffusion and an interfacial oxide were detected, while with Mo contacts, no oxide is formed.

Recently, Moons et al. (1993), used the simple two equal probes method to investigate the contact resistivity of evaporated gold and In-Ga eutectic, onto single crystals which had different chemically etched surfaces. Fresh Br_2/ methanol, or KCN /H_2O, or the combination of these two etches were used. The best ohmic contact was obtained by evaporated gold onto a Br_2 /methanol etched crystal. The gold contacts yield contact resistivity value varying between 0.03 and 0.3 Ω-cm^2, and good stability with time (within 5 days). Although most In-Ga contacts showed linear I-V characteristics, they are more resistive (between 0.25 and 8.00 Ω-cm^2) than Au contacts and showed the degradation with time. For Au contacts, air-annealing (5 min, 200 ^oC) increased the resistivity, while argon-annealing (5 min, 200 ^oC) did not change the resistivity.

By synchrotron radiation soft x-ray photo emission, Nelson et al. (1991) investigated the development of the electronic structure at the Au /$CuInSe_2$ interface. Contradicting Toro's work, they concluded that Au reacts with $CuInSe_2$ during deposition resulting in the formation of interfacial phases. In addition, the Schottky barrier heights for Au /$CuInSe_2$ were determined to 0.5 eV for n-type and 0.6 eV for p-type.

However, it seems that contacts mentioned in the works mentioned above are ohmic only in the sense that the contacts show linear I-V relationships (mostly at room temperature), not in the sense that contact resistance is negligible when compared with the bulk. This is not serious for application as large back ohmic contact on solar cells. It is however questionable when the contacts are used for measuring bulk properties, especially at low temperature.

3.2 Determination of Low Barrier Height in MS Contacts

Tantraporn (1970) described an interesting simple measurement technique. The technique could separate the bulk and barrier effects, even for the small barrier which are normally hard to detect. In addition, he proposed a simple model, namely the pseudo-Richardson model to describe the blocking behavior of the barrier. Both the measurement technique and the pseudo-Richardson model will be briefed below.

Beside the pseudo-Richardson model, Tantraporn (1972) also proposed a more complex model which required numerical calculations. The latter will be described in section 4.2.

3.2.1 Different Area Constant Current Technique (DACCT)

This measurement technique is based on the fact that the barrier effect does depend on the contact area even when the conduction is only on the contact area's periphery, while the bulk does not. The Schematic drawing of this technique is shown below.

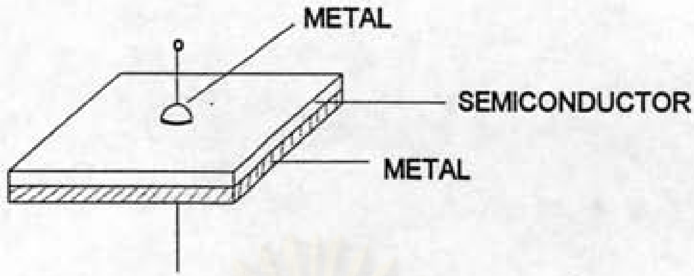

Fig.2 Schematic drawing of small area metal - semiconductor - large area metal device used in DACCT measurement (after Tantraporn, 1970).

In measurement, voltages across the device, i.e. large area metal contact-semiconductor-small area metal contact, sustaining a constant current is measured as a function of temperature for both polarities of applied voltage. The example of his measurement is shown here in Fig.3.

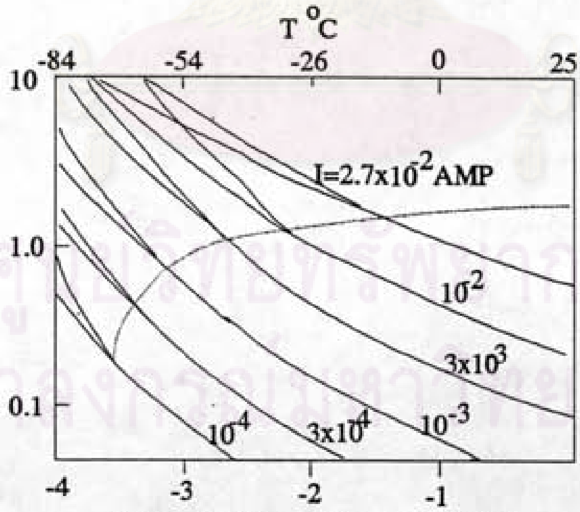

Fig.3 Absolute values of the voltage across a sample of metal-GaAs-metal device carrying a constant current as a function of the temperature as indicated by the chromel-alumel thermocouple reading, cooling toward left. Each constant current

curve at higher temperature splits into two curves at lower temperatures. The splitting indicates the existence of a blocking contact barrier, each branch for one polarity of the applied voltage. The dashed line separates the pure bulk- property region, to the right of this line the resistance is due to the bulk properties only (after Tantraporn, 1970).

Note that the DACCT needs no back ohmic contact. Furthermore it detects the existence of the barrier when the barrier is in reverse bias, when it needs a larger applied voltage. So, it can effectively detect the small barrier effect.

It will be seen later that this technique is still effective for metal-thin insulator-semiconductor contact.

3.2.2 The Pseudo-Richardson Model

In this model, any resistance which has symmetric I-V characteristic is regarded as "bulk". So, "bulk" need not be the same everywhere. This criterion is pertinent to DACCT measurement which isolates the asymetric behavior due to the barrier.

The model assumed that a metal-semiconductor contact, whether forming a sharp metallurgical discontinuity or diffused region, can be represented by an effective barrier height B_{eff}. The equilibrium flux across the barrier is given by a pseudo-Richardson equation with an effective mass m* (Tantraporn, 1970; Tantraporn and Stephens, 1980). As long as the current demand is less than the

"Richardson" current, the barrier offers no resistance and the contact is "ohmic". A semiconductor sample with two electrical contacts will sustain the same voltage for both polarities of the same current as long as both contacts are ohmic, regardless of the sample's geometry. This ohmic range is on the right hand side of the dash line in Fig.3.

At sufficiently high current demand and /or low temperature, the small contact in Fig.2, can no longer supply sufficient carrier flux unless a higher electric field near the interface is provided to suppress B_{eff} of the small contact to allow more carrier flux in order to maintain the continuity of current. While in another polarity, because of the larger contact area, the large contact still can supply sufficient current and still needs no additional applied voltage. Thus, for each current, there is the split temperature T_s that pseudo-Richardson equation can be applied, i.e. (Tantraporn, 1970)

$$I = A_c A^* T_s^2 \exp(-Beff/kT_s) \qquad (3.2.2.1)$$

where

A_c = contact area,

A^* = Richardson constant,

k = Boltzmann constant.

At temperature lower than split temperature,identifying the blocking by the small contact, there may be another temperature that pseudo-Richardson equation can be applied for the large contact as well. This latter's blocking temperature depends on the ratio of the two areas, and can be readily identified from the family of constant-current curves. The reader may recognize the powerful use of this ratio, in the case of one dot vs. five identical dots in parallel, say, when emission of current is not uniform over the dot's area.