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Multi Fermi level pinning at metal/Cu(InGa)(SeS)$_2$ interfaces

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Metal contacts to chemically etched Cu(InGa)(SeS)$_2$ layers have been investigated using current–voltage and capacitance–voltage techniques. Oxidising chemicals enhance the Fermi level pinning at metal/Cu(InGa)(SeS)$_2$ interfaces. The formation of a Schottky barrier at metal/p-Cu(InGa)(SeS)$_2$ interface is dominated by Fermi level pinning at one of the four levels, 0.77 ± 0.02, 0.84 ± 0.02, 0.93 ± 0.02 and 1.03 ± 0.02 eV above the valence band maximum. These observed levels determined from current–voltage measurements show a good agreement with some of the previously published photoluminescence, deep level transient spectroscopy and photo acoustic spectroscopy observations. The capacitance–voltage measurements showed that this material has near ideal doping concentration of $1.0 \times 10^{16}\,\mathrm{cm}^{-3}$ for fabricating solar cell devices.

1. Introduction

Copper indium diselenide (CuInSe$_2$) based materials have attracted intensive research over the past two decades to produce low-cost and high-efficiency solar cells due to their high optical absorption and suitability of bandgap. In order to improve solar cell performance, Ga and S have been incorporated to produce Cu(InGa)(SeS)$_2$ graded bandgap material layers. The work has been successfully progressing and recent publications have reported a 13.4% [1] conversion efficiency for 3600 cm^2 solar modules. The detailed understanding of these materials and interfaces will allow researchers to further improve the efficiency, and the investigation of metal/Cu(InGa)(SeS)$_2$ interfaces will be of paramount importance in this respect. Ohmic contacts with the lowest resistances are crucial in solar cell production, and reliable high Schottky barrier contacts allow researchers to investigate materials further using techniques such as current–voltage (*I–V*), capacitance–voltage (*C–V*) and deep level transient spectroscopy (DLTS). In addition, any solar cell device requires two metal (or electrical) contacts to extract electric current produced within the device structure by absorption of light. Cu(InGa)(SeS)$_2$ is used in PV cells, in both substrate and superstrate configurations, where in both situations, electrical contacts play an important role in device performance. This communication reports the initial work on metal contacts to Cu(InGa)(SeS)$_2$, the material which produced 11.6% efficiency for (30 × 30) cm^2 sub-modules.

2. Experimental procedure

Cu(InGa)(SeS)$_2$ layers grown by Showa-Shell Sekiyu K.K., Japan, have been used in this metal/semiconductor contacts work. The layers were grown by a two-stage method consisting of a selenization process followed by sulphidation of Cu/Ga/In precursor stacked layers in a reaction furnace. The Cu/Ga/In precursor stacked layers were grown by DC magnetron sputtering on Mo sputter-coated soda-lime-glass substrates. The precursor layers were then annealed in low concentrations of H$_2$Se and H$_2$S gases at temperatures above 450 and 500 °C, respectively. The temperature ramp-up rate was adjusted to enable a good adhesion between the absorber layers and the Mo substrate. Further details concerning the two-stage method for growing Cu(InGa)(SeS)$_2$ thin films can be found elsewhere [2].

As received material layers were cut into ~(1 × 2) cm^2 samples in order to make a large number of 2 mm diameter metal contacts, after etching in different chemicals. A range of common chemicals was used for etching as described in Table 1, and the samples were transferred immediately after chemical etching, to a high vacuum chamber for metallisation. The metals were thermally evaporated through a mask with 2 mm diameter apertures at a pressure of ~10^{-6} Torr, in order to perform conventional *I–V* and *C–V* measurements on metal/Cu(InGa)(SeS)$_2$ interfaces at room temperature.

3. Experimental results

3.1. Current– voltage (I–V) measurements

The *I–V* measurements were performed using a fully automated *I–V* system incorporating a Keithley 619 electrometer and a 230 programmable voltage source. For each chemically etched sample, a large number in excess of 20 metal contacts were measured, analysed and the results are summarised in Table 1 for Ag contacts. The results of XPS studies on chemically etched

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Table 1
The nature of electrical properties of 2 mm diameter Ag contacts made on chemically etched glass/Mo/Cu(InGa)(SeS)$_2$ thin film structures

Etch no.	No. of ohmic contacts out of ~20	R_s in (Ω) in (Ω cm^2)	No. of rectifying contacts out of ~20	ϕ_b (eV)	Comments
As received	~14	(18–50) (0.56–1.55)	~6	(0.84–0.85)	R_s is high due to presence of native oxides
1	~8	(20–28) (0.62–0.87)	~12	(0.82–0.87)	–
2	~11	(12–20) (0.37–0.62)	~9	(0.82–0.87)	–
3	~10	(17–38) (0.53–1.18)	~10	(0.82–0.87) or (1.01)	–
4	~18	(11–13) (0.34–0.40)	~2	(0.82–0.87)	Most suitable etch for making ohmic contacts
5	~0	–	~20	(0.82–0.87) or (1.03–1.04)	Most suitable etch for making rectifying contacts
6	~0	–	~20	(0.82–0.87) or (0.93–0.95)	Most suitable etch for making rectifying contacts
7	~17	(17–19) (0.53–0.59)	~3	(0.82–0.87)	Toxic nature of the etchant

Etch 1: HCl+HNO$_3$ etch [10 ml of HCl (37%)+10 ml of HNO$_3$ (70%)+80 ml of water) for 1 min.
Etch 2: hydrogen peroxide solution.
Etch 3: ammonia solution.
Etch 4: Na$_2$S$_2$O$_3$+NaOH etch (0.5 g of NaOH and 0.5 g of Na$_2$S$_2$O$_3$ in 100 ml of water) for 2 min.
Etch 5: K$_2$Cr$_2$O$_7$ etch (1 g of K$_2$Cr$_2$O$_7$ in 10 ml of H$_2$SO$_4$ (95–98%)+490 ml of water) for 20 s.
Etch 6: etch 5 followed by etch 4.
Etch 7: dilute KCN aqueous solution.

CuInGaSe$_2$ layers have been reported in our previous publication [3]. It should be noted that there will be some stoichiometry differences due to sulphur inclusion on this material surface. However, most of the chemical changes occurring during chemical etching should be similar for both materials.

Table 1 summarises the observed *I–V* characteristics for Ag contacts fabricated on differently etched Cu(InGa)(SeS)$_2$ surfaces. In most cases, a mixture of both ohmic and rectifying contacts was observed. The series resistance of the Mo/Cu(InGa)(SeS)$_2$/Ag structure was determined using ohmic contacts and the specific contact resistance values are also presented in Table 1. The lowest series resistance values were also used to estimate the electrical resistivity of the Cu(InGa)(SeS)$_2$ material. The *I–V* characteristics of typical rectifying contacts are shown in Figs. 1(a) and (b) in both linear–linear and log–linear scales. Negatively biased Ag contacts produce forward currents, which is a strong evidence of overall p-type nature of the Cu(InGa)(SeS)$_2$ layer. Both ideality factor, n and the barrier height, ϕ_b were estimated using log–linear curves following a conventional analysing method [4].

Similar experimental work was carried out using different electrical contacts. Table 2 summarises the range of ideality factors and the barrier heights observed for Ag, Cu/Au and Au contacts fabricated on this material. Ag ($\phi_{Ag} = 4.26$ eV) and Au ($\phi_{Au} = 5.10$ eV) contacts were selected to represent low and high metal work functions in order to test the Schottky barrier height dependence on metal work function. For accurate determination of barrier heights, the diodes with the lowest ideality factors were used. It is apparent that the formation of barrier height is independent of the metal work function, and the chemical etchant used, and is due to Fermi level pinning at specific values.

3.2. Capacitance– voltage measurements

Metal/Cu(InGa)(SeS)$_2$ contacts showing good rectification properties were selected for capacitance–voltage (*C–V*) investigations. The measurements were carried out at 1 MHz frequency using a fully automated *C–V* system, while diodes were kept in dark condition. Many diodes tested showed varying capacitance as a function of applied bias voltage indicating that they were not fully depleted.

Fig. 2(a) shows the *C–V* relation for a typical contact, which showed a gradual variation of capacitance as a function of bias voltage. The capacitance varied from 900 pF to about 500 pF as the bias voltage varied from 0 to 2.0 V reverse bias voltage. The usual Schottky–Mott plots can be used in this case to estimate the doping concentration of the material layer. Fig. 2(b) shows a typical Schottky–Mott plot for the *C–V* data shown in Fig. 2(a). If this plot is a straight line, then it will indicate a uniform doping concentration of the material. The best straight line of the graph produces a value of $1.0 \times 10^{16}\,\mathrm{cm^{-3}}$ for the acceptor concentration of the material and 1.00 eV for the diffusion voltage. This indicates a presence of Schottky barrier height of ~1.03 eV at the metal/Cu(InGa)(SeS)$_2$ interface.

Close inspection of the Schottky–Mott plot shows that the graph is not one straight line, but has two straight line portions. The calculations of gradients at low reverse bias and high reverse bias produce different values estimating acceptor concentration values of 1.2×10^{16} and $9.8 \times 10^{15}\,\mathrm{cm^{-3}}$. Since this diode exists at Au/p-Cu(InGa)(SeS)$_2$ interface, the low reverse bias N_A value shows the doping concentration close to the Ag contact and the high reverse bias N_A value shows the doping concentration close to Mo contact. This indicates a slight variation of doping level across the material layer.

It is important to note that the material layers studied here in this work have average doping concentration of $1.0 \times 10^{16}\,\mathrm{cm^{-3}}$, which provides a depletion width of ~0.3 μm (assuming $\varepsilon_r = 10$ for Cu(InGa)(SeS)$_2$) for active area of the device. With these properties, this material has produced 11.6% conversion efficiency for $(30 \times 30)\,\mathrm{cm^2}$ solar modules [1]. However, common doping concentration of Cu(InGa)(SeS)$_2$ materials are $\sim(1–3) \times 10^{15}\,\mathrm{cm^{-3}}$, nearly a one order of magnitude less than that of Showa-Shell material. These results are consistent since low $10^{15}\,\mathrm{cm^{-3}}$ doping levels should produce ~3 μm wide depletion region, comparable