Improvement of CdS–Cu$_x$S Solar Cell Performance by CdS Etching under Illumination

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Abstract

The influence of dark and light etching of CdS single crystals on the electrical and optical characteristics of the CdS–Cu$_x$S heterojunction is investigated. It is shown through current–voltage characteristics, spectral response and junction capacitance measurements that the junction of these cells is strongly affected by the presence of light during the etching process. It is found that when the CuS is formed on an etched CdS surface under light a chalcocite phase (Cu$_2$S) is obtained. In contrast, when the CuS layer is grown on a dark etched surface a mixture phase of chalcocite and djurleite (Cu$_{1.96}$S) is found.

1. Introduction

Since the original observation of the photovoltaic effect induced by the p–n junction in CdS by Reynolds *et al.* (1954), the CdS–Cu$_2$S heterojunction has been considered an efficient photovoltaic cell for solar energy conversion over the last three decades. Many significant advances have been made in the development and understanding of these photovoltaic cells (Pande *et al.* 1983; Oktik *et al.* 1983; Al-Dhafiri *et al.* 1988). The optical and electrical characteristics of the junction are highly influenced by the various preparation conditions. Recent studies have been concerned with understanding the role of surface topography on the junction properties (Cheng *et al.* 1983; Oktik *et al.* 1983, 1987). Cheng *et al.* related the variation of the junction properties to the difference in the structure of Cu$_x$S on the CdS surface. The characteristics depends on whether one grows Cu$_x$S on the rough side of CdS or on the smooth side. Oktik *et al.* found that the specific surface features play an important role in determining the overall behaviour of the CdS–Cu$_2$S heterojunction.

However, the effect of chemical etching in the dark or under illumination of CdS on the behaviour of CdS–Cu$_x$S solar cells has never been reported. To study the effect of etching on the characteristics of CdS–Cu$_x$S solar cells, copper sulfide was grown on two different CdS single crystal substrates by the wet barrier technique. One of them was etched in HCl under illumination while the other in the dark under the same conditions. The electrical and optical characteristics of CdS–Cu$_x$S solar cells such as current–voltage characteristics, spectral response and junction capacitance were then investigated.

2. Experimental Details

The CdS–Cu$_x$S heterojunctions were fabricated on CdS single crystals grown from the vapour phase (Russell *et al.* 1985). The boules were oriented by X-ray back reflection and cut into 2 mm thick slices with the large area faces perpendicular to the *c*-axis. The slices were polished with alumina of thickness 3 μm and then with 1 μm to finish with a smooth surface, and then cut into sections with dimensions of 4×4×2 mm^3. These dices were etched in concentrated HCl for 30 s at room temperature to remove any surface damage and to identify the Cd and S polar faces. Ohmic indium contact was then made to the cadmium (000$\bar{1}$) planes by melting a small piece of indium on the back surfaces in an argon ambient. Finally, a heterojunction was formed by using a wet plating method (Oktik *et al.* 1983). Contacts were made to the Cu$_x$S surface by evaporating gold 1 mm in diameter onto the sample to provide collector electrodes.

To study the effect of light and dark etching on the characteristics of the CdS–Cu$_x$S heterojunction, two types of devices were prepared. The first was fabricated by depositing a CuS layer on a dark etched CdS, while the second was prepared on a light etched CdS surface, all other conditions being kept constant. A 200 W tungsten lamp was used as a light source. The surface topography of the etched CdS was examined by using a scanning electron microscope (SEM). The current–voltage (*I–V*) characteristics of the heterojunction were measured in the dark and under 100 mW cm^{-2} incident illumination (simulated AM1) provided by a 1·5 kW quartz–halogen strip lamp with parabolic reflector and water filter. The spectral response was measured using a Barr and Stroud prism
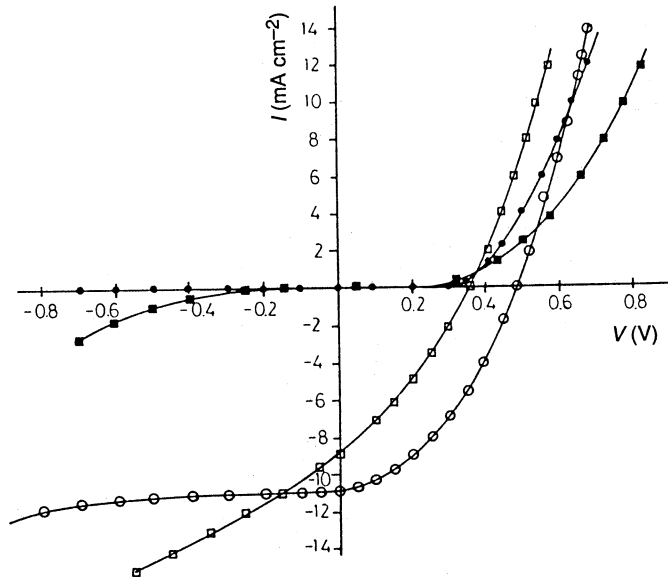

Fig. 1. Current–voltage characteristics of CdS–Cu$_x$S heterojunctions: circles, device fabricated on an etched CdS under illumination; squares, device fabricated on an etched CdS in the dark. Open circles/squares are the illuminated characteristics and solid circles/squares the dark characteristics.

monochromator type VL2 with a 250 W tungsten lamp source. The capacitance–voltage $(C–V)$ measurements were made with a Boonton 72B capacitance meter which operates at 1 MHz, together with a calibrated DC voltage source (Keithley 602 Electrometer).

3. Results

After etching in concentrated HCl, SEM examination of the $(000\bar{1})$ surface of CdS revealed the presence of large hillocks on these planes for both types. There was not much difference between the hillock sites for the dark and light etched samples, however, the topographical features of these hillocks were found to be related to the etching time of the CdS surface (Oktik *et al.* 1983).

Typical $I–V$ characteristics measured immediately after fabricating a hetero-junction device are shown in Fig. 1. Measurements were repeated on various samples prepared under identical conditions and all reveal the same behaviour. Here we present one set of curves for clarity. Measurements were made at room temperature for both types of samples. The dark etched devices exhibit relatively high series resistance which is responsible for the poor efficiency of these devices. In contrast, the light etched devices have a low series resistance even though the substrates for both types of device were nominally identical. The photovoltaic output characteristics are given as follows: the open circuit voltage (OCV), the short circuit current (SCC) and the fill factor (FF) were respectively 0·44 V, 11 mA cm^{-2} and 0·42 for the light etched device and 0·38 V, 9 mA cm^{-2} and 0·26 for the dark etched device.

The spectral response curves for both types of device are shown in Fig. 2. Measurements were made at room (295 K) and liquid nitrogen (85 K) temperatures. The light etched device shows a maximum response at 0·96 μm at both temperatures, which has been interpreted (Caswell *et al.* 1977) as representing the generation of electron–hole pairs in the chalcocite (Cu$_2$S) components of the copper sulfide layer. The dark etched device shows two peaks at about 0·96 and 0·66 μm at room temperature, while the second peak shifts to the longer wavelength of about 0·75 μm at 85 K. The second response of the OCV occurred in two bands centred near 0·75 and 0·66 μm and have been attributed to the absorption of light across the direct bandgap of djurleite (Cu$_{1\cdot96}$S) and to increased excitation from copper acceptor levels within the depletion region of the CdS (Caswell *et al.* 1977).

A plot of C versus V is given in Fig. 3. The intercept on the horizontal axis of the extrapolated line gives the diffusion voltage V_d. As can be seen, the cutoffs are 0·68 and 0·55 V for the light and dark etched devices respectively. The donor concentrations calculated from $C–V$ characteristics were $1\cdot4\times10^{15}$ cm^{-3} for the light etched and $0\cdot5\times10^{15}$ cm^{-3} for the dark etched device. The light etched device also shows a lower zero differential junction capacitance than the dark etched.

4. Discussion and Conclusions

Although SEM studies show there is no obvious correlation between surface topography and light and dark etching, the $I–V$ characteristics show the effect of the etching conditions. There is a variation in the OCV, SCC and FF. Generally, etching is a very important stage of cell fabrication. Our study shows that the
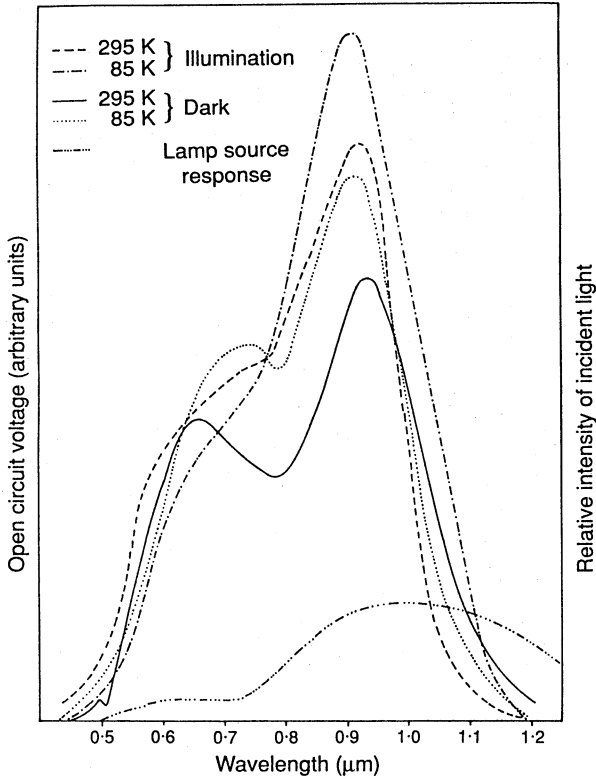
Fig. 2. Spectral response of the open circuit voltage measured at 295 and 85 K for CdS–Cu$_x$S heterojunctions where the etching has been under illumination or in the dark.
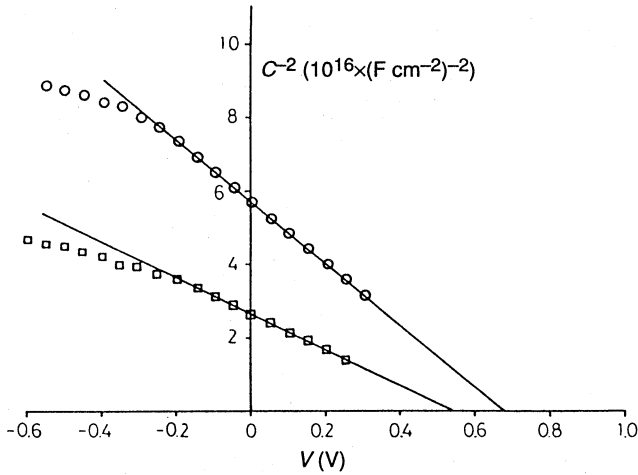

Fig. 3. Capacitance–voltage characteristics of CdS–Cu$_x$S: circles, device fabricated on etched CdS under illumination; squares, on etched CdS in the dark.

presence of light during etching of the CdS surface leads to better photovoltaic operation parameters for the CdS–Cu$_x$S heterojunction. This could be attributed to a low density of surface states of CdS due to a photoreaction taking place when the etching is carried out in the presence of light. The reverse leakage current was observed in the dark etched device when I–V measurements were carried out in both the dark and light and the cross-over between them was clearly pronounced. On the other hand, the light etched device show a less pronounced cross-over behaviour. It is important to emphasize that the cross-over effect which is usually attributed to copper diffusion during heat treatment was observed here for the as made devices. The leakage current in the dark etched device indicates that the tunnelling probability is high with a narrow depletion region in the CdS.

The spectral response of the OCV is similar to that of the SCC. The results described here demonstrate conclusively that a good stoichiometry was found for devices made on a CdS surface etched under light. Thus, for these devices the peak was at $0\cdot96$ μm showing the response of the chalcocite phase (Cu$_2$S) only, which is the phase yielding high conversion efficiency when combined with CdS (Te Velde 1975; Soriano *et al.* 1985). Two peaks at $0\cdot96$ and $0\cdot75$ μm appearing in the dark etched devices indicate the presence of mixture phases of chalcocite and djurleite. When the experiment is carried out at room temperature the second peak shifts to $0\cdot65$ μm. This response could be attributed to a combination of the response from the djurleite phase and the copper acceptor level formed by the diffusion of copper into the CdS layer (Al-Dhafiri *et al.* 1988). On the other hand, when the experiment is carried out at 85 K, the second peak ($0\cdot65$ μm) is shifted to $0\cdot75$ μm which is due to djurleite alone, without the copper acceptor layer response. This is well established because the responses in the region $0\cdot60$ to $0\cdot70$ μm resulting from the copper levels in CdS diminish at low temperature, whereas those due to the Cu$_x$S phases are enhanced (Pande *et al.* 1983; Al-Dhafiri 1988). The small peak at $0\cdot50$ μm for the dark etched device confirms that the copper sulfide phase is djurleite (Cu$_{1\cdot96}$S) rather than chalcocite (Cu$_2$S). This is simply because the consequent reduction in the absorption coefficient of the Cu$_x$S allows more light to reach the CdS (Mulder 1972; Elizalde and Rueda 1986).

In conclusion, the heterojunctions fabricated on the light etched CdS surfaces lead to high Cu$_x$S stoichiometry, while the dark etched devices contain low phases. It is possible that the presence of light during etching causes atoms to form a CdO layer on the surface which prevents the penetration of Cu$_x$S into the CdS. This appears likely since it has been found that CdO plays a major role in controlling solar cell stability by reducing the diffusion of Cu (Partain *et al.* 1985). From spectral response studies, it seems that the copper is grown at greater depth in the CdS and hence no more ions are incorporated in the bulk of the Cu$_x$S layer in the case of light etched devices, as can be seen in Fig. 2.

The observed lower zero differential capacitance for a CdS–Cu$_x$S heterojunction fabricated on a light etched CdS arises because the Cu$_2$S layer forms predominantly on the outer surfaces of the CdS single crystal. However, in the case of a heterojunction formed on dark etched CdS, the Cu$_x$S layer penetrates more deeply and a higher capacitance is found. This is in agreement with earlier findings that chalcocite has a low capacitance at zero voltage (Razykov *et al.* 1984).

Acknowledgment

References

Al-Dhafiri, A. M. (1988). Ph.D. Thesis, Durham University.

Al-Dhafiri, A. M., Pande, P. C., Russell, G. J., and Woods, J. (1988). *J. Crystal Growth* **86**, 900.

Caswell, B. G., Russell, G. J., and Woods, J. (1977). *J. Phys.* D **10**, 1345.

Cheng, C. H., Merritte, B., Tu, C. W., and Jones, K. A. (1983). *Solar Cells* **10**, 287.

Elizalde, E., and Rueda, F. (1986). *J. Phys.* D **19**, 1563.

Mulder, B. J. (1972). *Phys. Stat. Sol.* **13**, 79.

Oktik, S., Russell, G. J., and Woods, J. (1983). *Sol. Energy Mat.* **1**. 77.

Oktik, S., Russell, G. J., and Woods, J. (1987). Proc. Seventh Photovoltaic Solar Energy Conf., Sevilles, p. 630 (Reidel: Dordrecht).

Pande, P. C., Russell, G. J., and Woods, J. (1983). *J. Phys.* D **16**, 2307.

Partain, L. D., Schneider, R. A., Donaghey, L. F., and McLeod, P. S. (1985). *J. Appl. Phys.* **37**, 5056.

Reynolds, D. C., Leies, G., Antes, L. L., and Marburger, R. E. (1954). *Phys. Rev.* **96**, 533.

Razykov, T. M., Viality, V. I., and Khodjaeva, A. (1984). *Thin Solid Films* **121**, 1.

Russell, G. J., Thompson, N. F., and Woods, J. (1985). *J. Crystal Growth* **71**, 621.

Soriano, L., Leon, M., Arjona, F., and Camarero, E. G. (1985). *Solar Energy Mat.* **12**, 149.

Te Velde, T. S. (1975). *Energy Conversion* **15**, 111.