A study of diffusion processes in Cu_xS–CdS solar cells using Rutherford backscattering

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It is now widely appreciated that solar energy can make a significant contribution to the world's future energy requirements, and research and development teams throughout the world are showing increasing interest in the development of cost-effective devices for the photovoltaic conversion of solar radiation. For large-area systems, thin-film devices have a significant cost advantage over conventional silicon wafer cells but the long-term stability of thin-film cells is generally rather poor in comparison with those fabricated using single-crystal technology. Clearly, the device lifetime has an important influence on the economic viability of solar energy collection and, accordingly, much attention is now being given to controlling the efficiency degradation processes which occur.

In the case of thin-film Cu_xS–CdS cells, lifetime tests on devices produced using commercial-scale fabrication techniques have yielded promising results [1] but until the causes of instability are thoroughly understood, the degree to which they are under control will be in some doubt and commercial exploitation of this technology will be hindered.

A key component of a front-wall Cu_xS–CdS cell is the thin Cu_xS absorber layer (~ 0.1 μm thick). The optoelectronic properties of Cu_xS are very sensitive to the stoichiometry of the material and, while Cu_2S (chalcocite) is required for high-efficiency cells, it is well known that Cu_xS can exist in a number of different phases at room temperature [2]. It follows that great care is required both in the preparation of this layer and in subsequent post-fabrication treatments which could cause a departure from the ideal stoichiometry. Possible degradation mechanisms include surface oxidation, if the Cu_xS layer is exposed to air, and interdiffusion across the Cu_xS/CdS interface. Previous studies in this laboratory [3] using Auger electron spectroscopy (AES) with argon ion etching (to yield depth profiles of the various Auger signals) provided evidence to show that significant interfacial diffusion can occur during post-fabrication annealing treatments. However, destructive techniques of this kind are not ideally suited to investigations of this kind which, preferably, require gradual changes in the structure and characteristics of the Cu_xS layer to be monitored during the course of a series of cell fabrication and post-fabrication processing events.

Of the possible non-destructive techniques available, luminescence spectroscopy has been shown to provide some useful insights [4] but in this paper we consider the application of Rutherford backscattering (RBS). It can easily be shown that the energy E_1 of protons scattered through an angle of 180° is given by

$$E_1 = E_0 (M - m)^2/(M + m)^2 \qquad (1)$$

where E_0 is the energy of the incident protons and M and m are the masses of the target atoms and the protons respectively. It follows that the maximum energy of 400 keV protons scattered through 180° is 385 keV for target atoms of Cd, 376 keV for Cu and 352 keV for S. Thus it is predicted that of the various atomic species present in a Cu_xS–CdS cell, scattering due to surface Cd should yield the highest energy backscattered protons and, therefore, that surface Cd should be clearly detected. This is of particular significance in relation to a study of cell stability as previous investigations of Cu_xS–CdS cells using destructive methods [3, 5, 6] have revealed significant concentrations of Cd at the surface of degraded cells. The predicted sensitivity of the RBS technique to the presence of Cd at the cell surface suggests that this technique should be well suited for studying the chemical stability of these Cu_xS–CdS devices. This is confirmed by the results of the exploratory study.

In the experiment, Cu_xS–CdS cells were fabricated using 30 μm thick, polycrystalline CdS films which were deposited onto Zn-coated copper foil at approximately 220 °C by thermal evaporation of CdS from a quartz crucible. The Cu_xS layer was formed by dipping the CdS film into an aqueous solution of CuCl (pH = 4) at 95 °C for a few seconds, depending on the thickness required. For RBS studies, the cells were cut into 5 × 5 mm test samples and mounted on a sample holder attached to a three-axis goniometer in the RBS chamber, which was evacuated to less than 10^{-4} Pa. A proton beam of up to 10 μA (before collimation) could be produced in this chamber using a 400 keV van de Graaff proton accelerator. For the experiments described here, an energy-stabilized and collimated beam of 10–30 nA was employed. Protons backscattered from the target cells were detected using a thermoelectrically cooled annular silicon surface barrier detector.

In order to check that Cd could, indeed, be satisfactorily detected by means of RBS, using the kind of polycrystalline material employed in our cells, a series of trial measurements were initially made using CdS films without a Cu_xS absorber layer and, in addition, some CdS films onto which excess

Cd had been deliberately deposited (by vacuum evaporation) in order to ensure a high concentration of Cd atoms at the surface of the film. The resulting RBS spectra are shown in Fig. 1 (curves (a) and (b)). It is clear that the high-energy edge of the spectrum for the CdS layer alone (curve (a)) occurs at the same energy as the corresponding edge for the sample with a layer of Cd over its surface (curve (b)). Thus this edge can be attributed to scattering from Cd (at 385 keV) and this result was used to calibrate the energy axis for subsequent results.

The increased concentration of Cd at the surface of the layer onto which Cd had been deposited is clearly reflected in curve (b) by the enhanced yield at the high-energy edge of the spectrum, and information about the thickness of the surface Cd layer can be obtained by measuring the width ΔE of this enhanced signal. The range ΔE corresponds to the difference in energy between protons scattered from the upper and lower surfaces of the evaporated Cd film. The value of ΔE depends upon the scattering process and on the stopping power S (energy loss per unit path length for protons moving through the material). Obviously S depends on the density and composition of the material involved as well as on the proton energy. Referring to the schematic diagram in Fig. 2 it can be shown that the thickness x of the Cd layer is given by

$$x = \frac{K_{Cd}E_0 - E_4}{S^{E_3} + K_{Cd}S^{E_0}} \qquad (2)$$

where K_{Cd} is the scattering factor for Cd as defined by Equation 1 and S^{E_3} and S^{E_0} are the Cd stopping powers for protons at energy E_3 and E_0 respectively. For the small Cd thickness involved here. S^{E_3} can be approximated to S^{E_1} and using corresponding values for S obtained from tabulated data [7] the resultant thickness of the evaporated layer of Cd was estimated to be ~0.2 μm.

The third RBS spectrum shown in Fig. 1 is for a CdS layer with an evaporated surface layer of copper (curve (c)). In this spectrum, it is clear that there is a shift of the Cd edge to lower energy due to the protons losing energy in passing through the Cu layer before and after being scattered by the
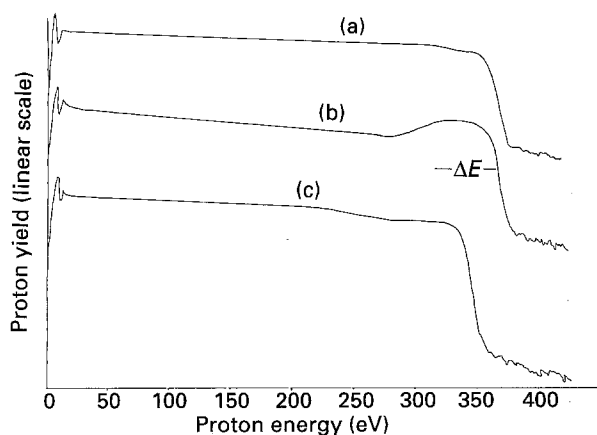

Figure 2 Schematic diagram showing the energy changes for protons interacting with a layer of Cd (of thickness x) on the surface of a CdS film. E_0 is incident energy; E_1 is energy after scattering from surface Cd; E_2 is energy of incident protons after penetrating thickness x; E_3 is energy of protons backscattered by Cd at depth x; E_4 is energy of these protons when they emerge from the upper surface of the layer.

underlying Cd atoms in the CdS film. (As previously noted, the smaller mass of Cu ensures that protons scattered by the surface Cu atoms will have significantly smaller energy than those scattered by Cd atoms.) From the observed shift in the high-energy cut-off energy, and using a similar procedure to that above, the thickness of the evaporated layer of Cu was estimated to be ~0.08 μm.

In order to study the cell degradation process, comparative measurements were made on Cu_xS–CdS cells immediately after fabrication and after a series of different post-fabrication treatments. Curve (a) in Fig. 3 shows the results for a sample immediately after fabrication. As expected, the main edge of this spectrum (attributed to Cd in the CdS film) occurs at an energy somewhat less than 385 keV due to the CdS being covered by Cu_xS (similar to curve (c) in figure 1) for the CdS film with a Cu overlayer). Making use of the same procedure as above (and assuming that $x = 2$ in calculating the effective stopping power for. the Cu_xS from the tabulated data for Cu and S [7], the thickness of the Cu_xS layer was estimated to be ~0.06 μm. As expected, this value for the thickness of the surface

Figure 1 RBS spectra for polycrystalline films of CdS: Curve (a)—CdS film alone; Curve (b)—CdS film with a thin surface layer of Cd; Curve (c)—CdS film with a thin surface layer of Cu.
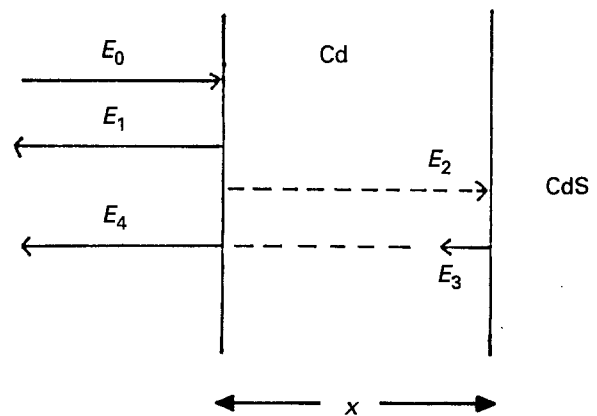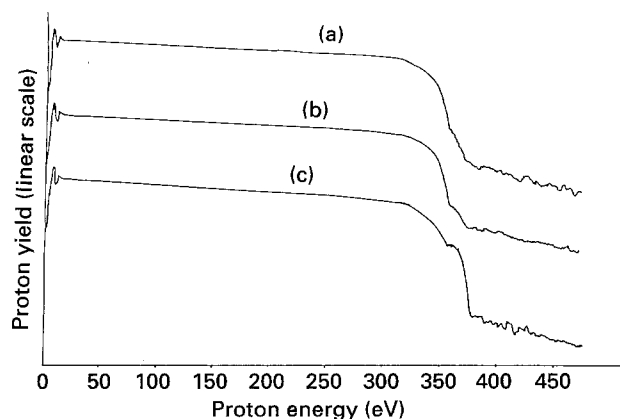

Figure 3 RBS spectra for Cu_xS–CdS cells: Curve (a)—cell immediately after fabrication; Curve (b)—cell after being annealed in air at 200 °C for 30 min; Curve (c)—unannealed cell after being left in air at room temperature for 1 year.

Cu$_x$S layer is rather small in comparison with the mean effective thickness values obtained using ECA (which includes the Cu$_x$S in the grain boundary regions of the CdS layer). A further feature which should be noted in Fig. 3 (curve (a)) is that there is a definite tail from the main edge in the spectrum, extending to higher energies up to 385 keV. It is possible that the tail is partly due to non-uniformity in the thickness of the Cu$_x$S layer, and partly due to Cd distributed throughout the Cu$_x$S layer, as would be expected to result from the chemical exchange process which is responsible for the formation of the Cu$_x$S layer. It seems probable that Cd distribution is the dominant reason for the tail as it is this feature which changes with different treatments, particularly exposure to air. This is illustrated by the curve (b) in Fig. 3 which shows the result for a sample similar to that in curve (a), which has been heated in air for 0.5 h at 200 °C. The high-energy tail is seen to be replaced by a more clearly defined shoulder with threshold at 385 keV as would be provided by a thin layer of surface Cd. The result for an unannealed sample which had been left in air for 1 year is also shown in Fig. 3 (curve (c)). This spectrum shows an even larger high-energy peak (again with a limit at 385 keV), indicating a more significant concentration of Cd at the surface. For the case of ideal, plane, parallel structures, it can be shown that a layer of Cd of thickness 0.033 μm would produce a RBS signal of width ~10 keV which would be clearly separated from the Cd signal arising from the underlying CdS layer. In practice, there would be some broadening of the signal and when Cd is also distributed through the Cu$_x$S layer, the surface peak would not be clearly resolved, as in the case in Fig. 3. Taking account of the non-uniformity of the layers involved in the polycrystalline samples studied here, it is probable that the peak in curve (c) in Fig. 3 is due to a Cd layer with a thickness less than ~ 0.033 μm. However, there is no doubt that this RBS data demonstrates very clearly the existence of Cd at the surface of degraded Cu$_x$S–CdS cells and therefore supports the evidence provided by the previously mentioned destructive techniques.

According to Bogus and Mattes [8], much improved stability can be achieved by depositing a thin layer of Cu (500–1000 nm) onto the Cu$_x$S surface of the cells and heating them to a temperature of ~ 180 °C in air. It is believed that this process leads to the formation of a copper oxide layer which acts as a protective film. In order to examine the effects of this protective-layer-formation procedure, RBS measurements were made on Cu$_x$S–CdS cells which were identical to those already discussed except for the presence of a thin layer of copper (~ 1000 nm) which was evaporated onto the Cu$_x$S surface immediately after formation. The cells were subsequently annealed in air at 180 °C for 90 min. The RBS spectrum for such a sample is shown in Fig. 4. It can be seen that this spectrum is very similar to that in Fig. 3 for the as-formed cell prior to any heat treatment. Both show a well-defined edge attributed to scattering from Cd in the CdS layer, and both
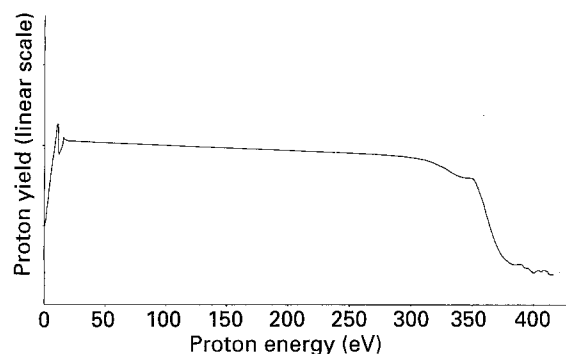

Figure 4 RBS spectrum for Cu$_x$S–CdS cell with overlayer of Cu after annealing in air at 180 °C for 90 min.

show a weak tail extending to the same high-energy threshold associated with Cd remaining in the Cu$_x$S layer at the end of the chemical exchange process. While curve (b) in Fig. 3 for the uncoated sample which had been heat-treated in air for only 30 min shows a substantial increase in the tail signal (due to Cd out-diffusion), the spectrum in Fig. 4 for the Cu-coated sample (heat treated for 90 min) shows no suggestion of an increased surface concentration of Cd. This is consistent with the results obtained by Bryant et al. [6], using the AES profiling technique, which showed that an abrupt Cu$_x$S/CdS interface was maintained when a Cu overlayer was present during heat treatment in air. Thus, there is substantial evidence to indicate that the structure and characteristics of Cu$_x$S–CdS cells can be stabilized by the formation of a copper oxide layer over the surface. Using thermodynamic considerations of the chemical reactions which might occur between the various elements at the cell surface, Partain et al. [9] have shown that the oxide required for optimum chemical stability is CuO. The same reasoning reveals that the formation of CdSO$_4$ is strongly favoured in unprotected cells and this is clearly consistent with the experimental observations of Cd on the surface of degraded cells.

In conclusion, RBS has been shown to be a very convenient, non-destructive tool for studying the stability of Cu$_x$S–CdS solar cells subject to different fabrication and post-fabrication treatments. The results obtained in this investigation confirm previous indications that out-diffusion of Cd to the cell surface is a significant degradation process in cells which are exposed to the air and that this process can be strongly inhibited by the formation of a copper oxide overlayer.

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