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Silicon Based Cadmium Sulphide and Zinc Sulphide Heterojunction Photovoltaic Solar Cell

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ABSTRACT. The practical utilization of the photovoltaic effect in hybrid junctions between p-Si substrates and n– $(Zn_x–Cd_{1-x})$ S was observed. The performance of junctions prepared on hot substrates ($T_{sb} > 200°C$), and annealed in sulfur and air atmosphere for 20 minutes at temperature $T_a > 350°C$ is given by 0.57 V for V_{oc}, 15 mA/cm^2 for I_{sc} and 7 percent for conversion efficiency. A proper cleaning method to get rid of oxygen contaminating the Si surface is necessary.

Solutions to the energy problems on the earth using photovoltaic solar cells for the production of economical electrical power has received great scientific attentien, where much work has been devoted to the development of inexpensive systems. The interest in the growth and characterization of CdS and ZnS in the form of polycrystalline thin films has remained high for many years because of their photovoltaic potential application.

The main objective of this work is to develop the $(Zn_x–Cd_{1-x})S/Si$ hybrid system to serve as a technically viable solar cell. The utilization of CdS/Si and ZnS/Si in photovoltaic devices has been previously reported (Okimura *et al.* 1967, Cook and Christy 1980, and Abou-Elfotouh 1983). However, the addition of ZnS to CdS has improved (Abou-Elfotouh 1983) the cell performance since it increases the optical window, the diffusion potential and reduces differences in electron affinity between the film and substrate (Feucht 1977).

Thus, systematic investigations have been carried out to examine the influence of the various conditions of preparation involved in the fabrication of the system on the film properties and consequently on the operation characteristics of the resulting device. The effect of post preparation heat treatments, nature and concentration of doping of the film, and substrate temperature were also considered in this study.

Experimental

Films of $(Zn_x\text{–}Cd_{1-x})S$ were deposited with different Zn content x either by electron beam evaporation or by radio frequency sputtering on the (111) surface of p-type Si substrates. The resistivity of the Si wafers ranged between 0.2 and 3 ohm cm. The substrates were polished to optical finish, chemically cleaned and etched prior to introduction into the preparation chamber. Mixed sulphide films of thickness between 0.2 and 0.8 micron were prepared on substrates kept in a temperature range of 100° to 300°C. Indium doped films were also prepared. Post preparation isothermal and isochronal annealing in H_2, H_2S or a mixture of sulphur and air was given in the temperature range 200-400°C. The device performance was determined by I-V and ϱ-V measurements. Chemical composition of the junction was measured by SIMS (secondary ion mass spectroscopy) using 3F ion microanalyser.

Results and Discussions

Figure 1 demonstrates the variation in resistivity ϱ of the $(Zn_x\text{–}Cd_{1-x})S$ film as a function of zinc content x, annealing condition and substrate temperature T_{sb}. It is clear that ϱ decreases from 80 ohm cm to 15-20 ohm cm by raising T_{sb} from 150° to 300°C. In general, partial substitution of Zn for Cd has increased ϱ. However, this increase was much smaller after annealing. The increase in ϱ is more pronounced in the unannealed samples particularly at $x = 0.15$. The resistivity is still within the acceptable range for efficient heterojunction when the film was annealed for 20 minutes in H_2S or sulphur and air mixture at 250°C for $x = 0.15$. The resistivity of the mixed sulphide film prepared at $T_{sb} = 250°C$ and annealed at 450°C in H_2 for one hour is $\varrho \approx 5$ ohm cm for $x \approx 0.15$ while the best value obtained by other workers (Chynoweth and Bube 1980) is 1.5×10^3 for the same value of x.

The present data have demonstrated a decrease in the carrier concentration N with T_{sb} while increasing by annealing in H_2 and H_2S. On the other hand, the mobility is reduced by annealing particularly in S and air atmosphere. The value of N obtained for $(Zn_x\text{–}Cd_{1-x})S$ films with $x = 0.12$ (prepared at $T_{sb} = 250°C$) after annealing for 20 minutes in a mixture of S and air at reduced pressure 10^{-2} torr and temperature 450°C is 5×10^{16} cm^{-3}. The mobility μ is about 80 cm^2 V^{-1} Sec^{-1}. A comparison between the photovoltaic characteristics of $n(Zn_x\text{–}Cd_{1-x})S/pSi$, n CdS/pSi and Si n-p junction is shown in Fig. 2.

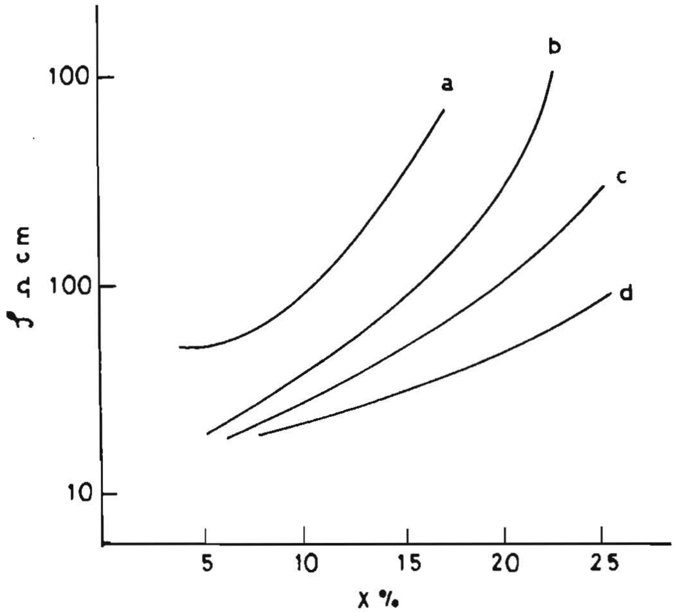

Fig. 1. The resistivity of $(Zn_x–Cd_{1-x})S$ as a function of Zn content x before annealing (a, b) and after annealing (c, d) at 250°C for 20 minutes (c) annealed in H_2 (d) annealed in H_2S.

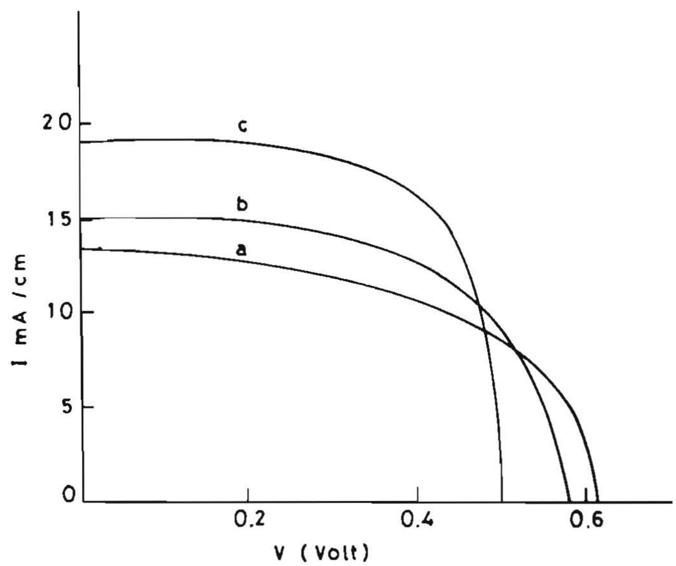

Fig. 2. Comparison between the photovoltaic characteristics of $n(Zn_x–Cd_{1-x})S/pSi$ (a), n CdS/pSi (b) and Si homojunction of 10.5 percent efficiency (c).

The dark current density J_o of the (CdS–ZnS)/Si heterojunction is shown in Fig. 3. It is shown that J_o, increases with x for devices prepared at low T_{sb} (< 200°C) while it decreases slightly for devices prepared at $T_{sb} > 300$°C. It is also found that J_o decreases at $x < 0.15$ by one order of magnitude due to annealing in H_2S and by two orders of magnitude after annealing in a mixture of sulphur and air at the same annealing temperature. The minimum value of J_o is achieved at $x = 0.12$, then it retains its original value at $x = 0.25$. The diode quality factor A of the annealed junction was slightly more than 2 (2-2.3) particularly those with $x > 0.15$. A for the unannealed junctions made from films with $x < 0.12$ are less than 2 (1.5-1.8). A diode factor of 2 is considered as an indication of recombination within the junction region. Recombination is attributed to deep level traps detected by (Besomi and Wessels 1980) in polycrystalline films, other defects at the junction, and lattice mismatch.

Figures 4 and 5 represent SIMS depth profile data obtained by the ion microanalyser for the $(Zn_x–Cd_{1-x})S/Si$ junction before and after annealing. A complete scan was also performed in different positions of the junction to detect any contamination if present. Figure 6 shows the scan obtained at the interface before and after annealing. In this figure, oxygen is found contaminating the interface in the form of silicon oxide and molecular oxygen. This means that a careful cleaning

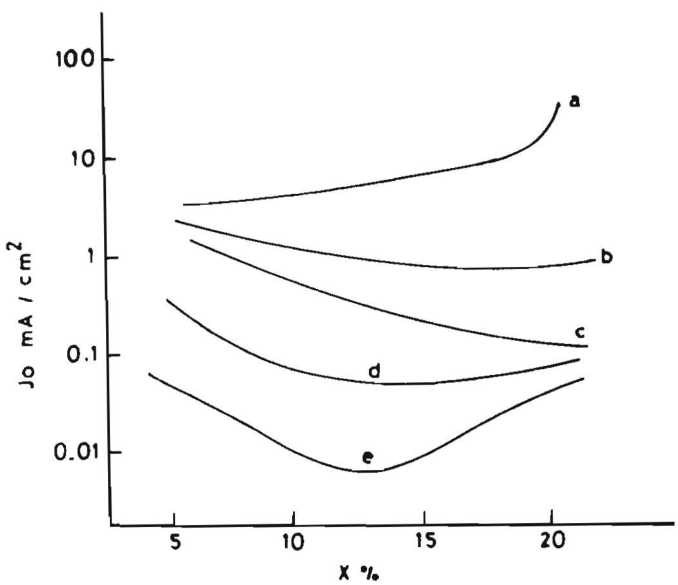

Fig. 3. Dark current density J_o as a function of Zn Content x before annealing (a, b) and after annealing (c, d, e) at 450°C (c) annealed in H_2, (d) annealed in H_2S (e) annealed in a mixture of S and air.

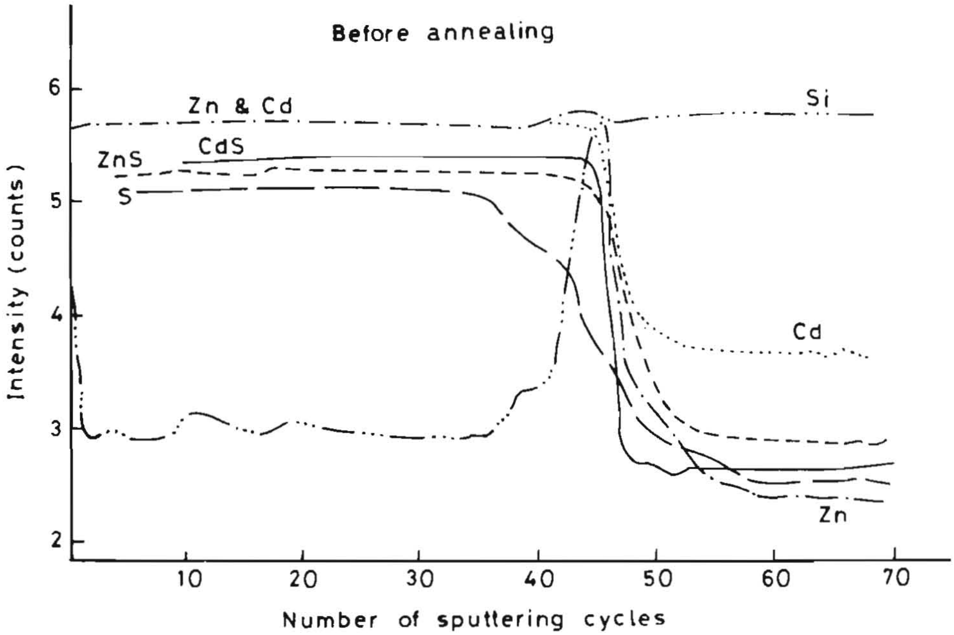

Fig. 4. SIMS depth profiles of the as grown (Zn_x–Cd_{1-x})S on Si substrate.

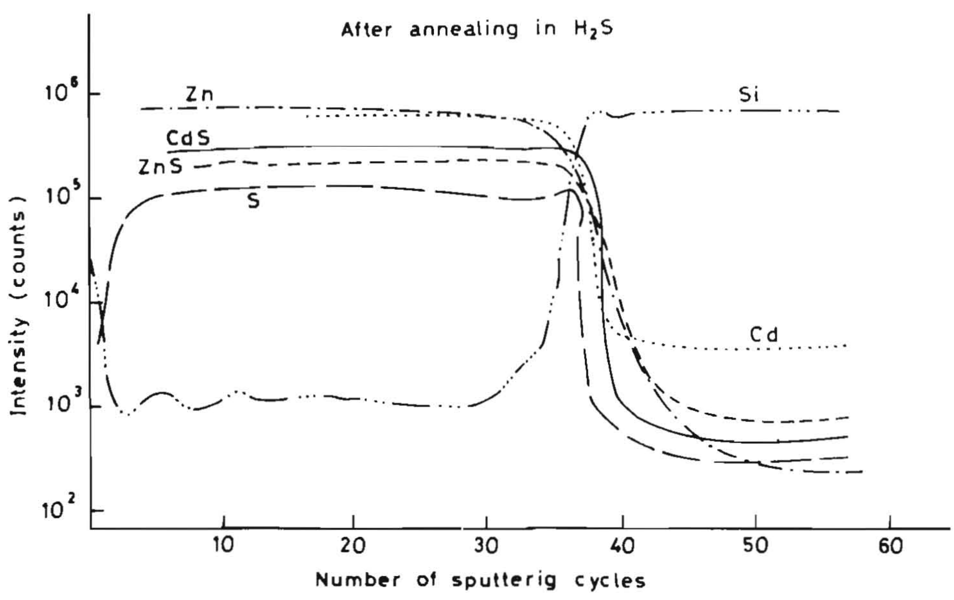

Fig. 5. SIMS depth profiles of (Zn_x–Cd_{1-x})S/Si heterojunction after annealing in H_2S at 350°C for 20 minutes.

process is required to remove native oxides from the substrate surface prior to film deposition. From Fig. 4 it is seen that the surface became S deficient after annealing in H_2S while accumulation is observed at the interface. The profiles have also shown that Zn is precluded from the interface due to annealing. The annealing treatment did not cause a major variation in CdS and ZnS profiles. It only improved the stoichiometry and gave rise to a sharper interface.

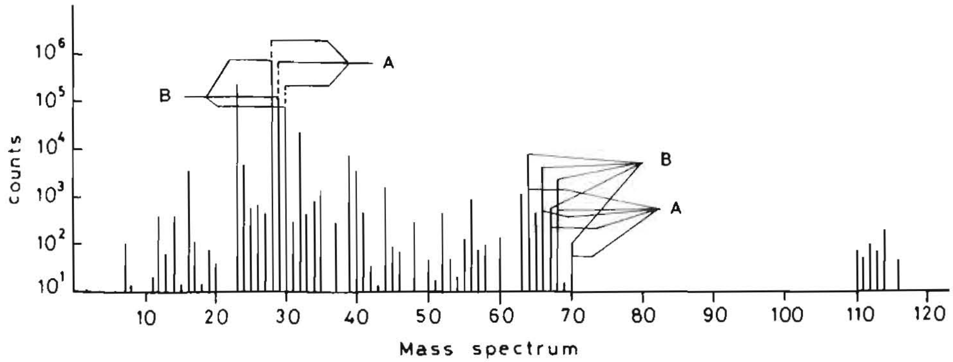

Fig. 6. Mass spectra at the interface of the $(Zn_x\text{–}Cd_{1-x})S/Si$ junction.
B Intensity of S and Zn Before annealing
A Intensity after annealing.

The degradation effect in the annealed devices is correlated to the S accumulation at the interface. It may be responsible for the recombination centers at the junction region, as well.

Conclusion

The results obtained from this work have proven the possibility of optimization of both material and device parameters of the $n(Zn_x\text{–}Cd_{1-x})S/pSi$ solar cell through proper choice of T_{sb}, Zn content x, and post preparation annealing conditions. The improved performance of this cell with respect to the n CdS/pSi cell (see Fig. 2) is attributed to the improved lattice match and reduction in the electron affinity difference between the sulphide film and substrate. In addition, improved values of N, and μ have also played a role.

The S deficiency observed in Fig. 5 explains the increased carrier concentration in the sulphide film due to annealing. This agreed well with the explanation given by Hershman and Kröger 1970, since they attributed the donor formation to S vacancies which are native defects in CdS.

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خليــة شمســية فوتوفولتيــة من كبريتيد الكادميوم وكبريتيد الزنك على قاعدة من السليكون

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تمت دراسـة إمكـانيـة الاستفادة العملية من التأثير الفوتوفولتي خلال وصلة غير متجانسة بين السليكون (المستقبل) ومخلوط كبريتيد الزنك وكبريتيد الكادميوم (المانح) . وقد أوضحت النتائج أن أداء الوصلة التي حُضرت على قاعدة ساخنة (عند درجـة ٢٠٠مْ) بعـد تحميصها في جو من الهواء والكبريت لمدة عشـرين دقيقة عند درجة ٣٥٠مْ هو على النحو التالي : جهد الـدائـرة المفتـوحـة = ٥٧ر. فولت ، تيـار الـدائرة المغلقة ١٥ مللّيأمبـير لكـل سم٢ و٧ بالمائة لكفاءة تحويل الطاقة . كما وجد أن استخـدام وسيلة منـاسبـة للتخلص من الأكسجين العالق بالسليكون يعتبر ضرورياً .