

SILICON BASED CADMIUM SULPHIDE AND ZINC
SULPHID HETEROJUNCTION PHOTOVOLTAIC SOLAR CELL

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ABSTRACT:

The practical utilization of photovoltaic effect in hybrid junction 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 for I_{sc} and 7 percent for conversion efficiency. A proper cleaning method to get rid oxygen contaminating the Si surface is necessary.

INTRODUCTION:

Solutions to the energy problems on the earth using photovoltaic solar cells for the production of economical electrical power has received strong scientific attention , 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 objectives of this work is to develop (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 [1-3] . However , the addition of ZnS to CdS has improved [3,4] the cell performance since it increases the optical window, the diffusion potential and reduce difference in electron affinity between the film and substrate [5].

Thus systematic investigation has been carried out to examine the influence of the various conditions of preparation involved for 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 to the film , and substrate temperature were also considered in this study.

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EXPERIMENTAL:

Films of $(Zn_x - Cd_{1-x})S$ 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 was ranging 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°C to 300°C. In doped films were also prepared. Post preparation isothermal and isochronal annealing in H_2 , H_2S or 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 $(Zn_x - Cd_{1-x})S$ 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°C 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 Sand air mixture at 250°C for $x = 0.15$. The resistivity of the mixed sulphide film prepared at $T_{sb} = 250^\circ C$ and annealed at 450°C in H_2S for one hour is $\rho \approx 5$ ohm cm for $x \approx 0.15$ while the best value obtained by other workers [6] 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 Sand air atmosphere. The value of N obtained for $(Zn_x - Cd_{1-x})S$ films with $x = 0.12$ (prepared at $T_{sb} = 250^\circ C$) after annealing for 20 minutes in a mixture of S and air at reduced pressure 10^{-2} torr and temperature 450°C is $5 \times 10^{16} \text{ cm}^{-3}$. The mobility μ is about $80 \text{ cm}^2 \text{ V}^{-1} \text{ Sec}^{-1}$. A comparison between the photovoltaic characteristics of $n(Zn_x - Cd_{1-x})S/pSi$, $n \text{ Cds}/pSi$ and $Si \text{ n-p}$ junction is shown in figure 2.

The dark current density J_0 of the $(CdS - ZnS)/Si$ heterojunction is shown in figure 3. It is shown that J_0 increases with x for devices prepared at low T_{sb} ($< 200^\circ C$) while it decreases slightly for devices prepared at $T_{sb} > 300^\circ C$. It is also found that J_0 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_0 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). Diode factors of 2 is considered as indication of recombination within the junction region. Recombination is attributed to deep level traps detected by [7] in polycrystalline films, other defects at the junction, and lattice mismatch.

Figures 4 and 5 represent SIMS depth profile data obtained by ion microanalyser for the $(Zn_x Cd_{1-x})S/Si$ junction before and after annealing. A complete scan was also performed in different position 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 process is required to remove native oxides from the substrate surface prior to film deposition. From figure 4 it is seen that the surface became S deficient after annealing in H_2S while accumulation is observed at the interface. The profiles has also shown that Zn is precluded from the interface due to annealing. The annealing treatment did not cause a major variations in CdS and ZnS profiles. It only improved the stoichiometry and gave rise to sharper interface.

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 proved the possibility of optimization of both material and device parameters of the $n(Zn_x - Cd_{1-x})S/pSi$ 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 figure 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 figure 5 explain the increased carrier concentration in the sulphide film due to annealing. This agreed well with the explanation given by [8,9] , since they attributed the donar formation to S vacancies which is native defects in CdS.

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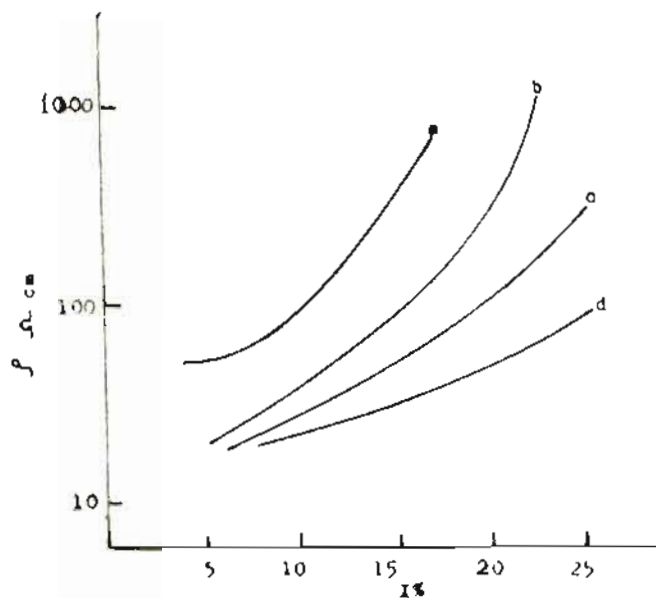


Fig. 1: The resistivity of $(Zn_x - Cd_{1-x})S$ as a function of Zn content X before annealing (a, b) and after annealing (c,d) at 250°C for 20 minutes (c) annealed in H_2 (d) annealed in H_2S .

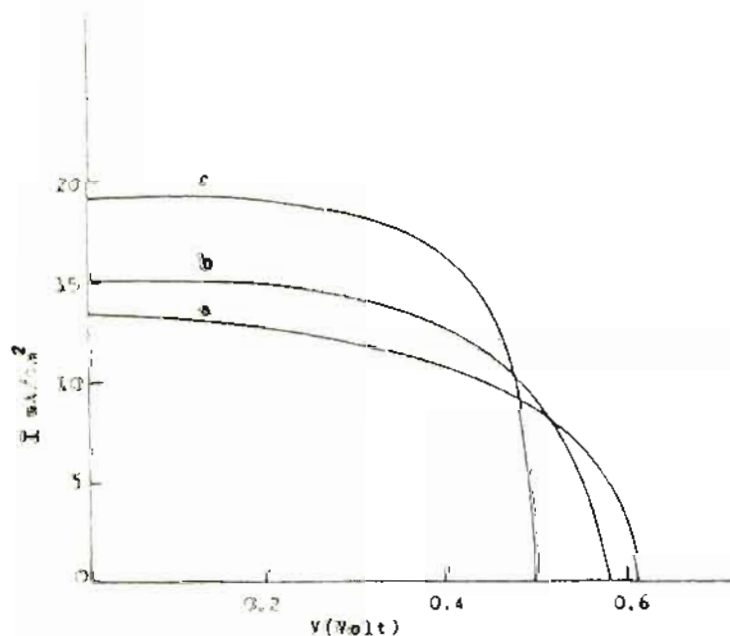


Fig. 2: Comparison between the photovoltaic characteristics of $n(Zn_x - Cd_{1-x})S/Pi$ (a), $n CdS/Pi$ (b) and Si homojunction of 10.5 percent efficiency (c).

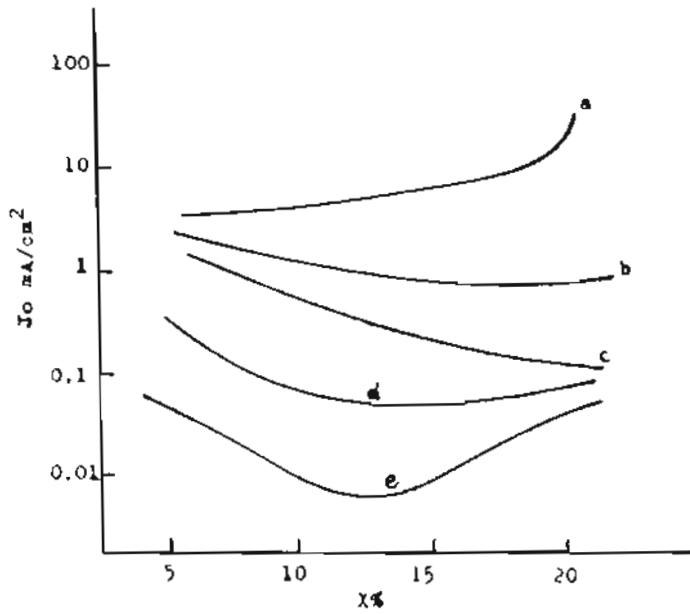


Fig. 3: Dark current density J_0 as a function of Zn Content X before annealing (a,b) and after annealing (c,d,e) at 450°C (c) annealed in H_2 , (d) annealed in H_2S (e) annealed in a mixture of S_2 and air.

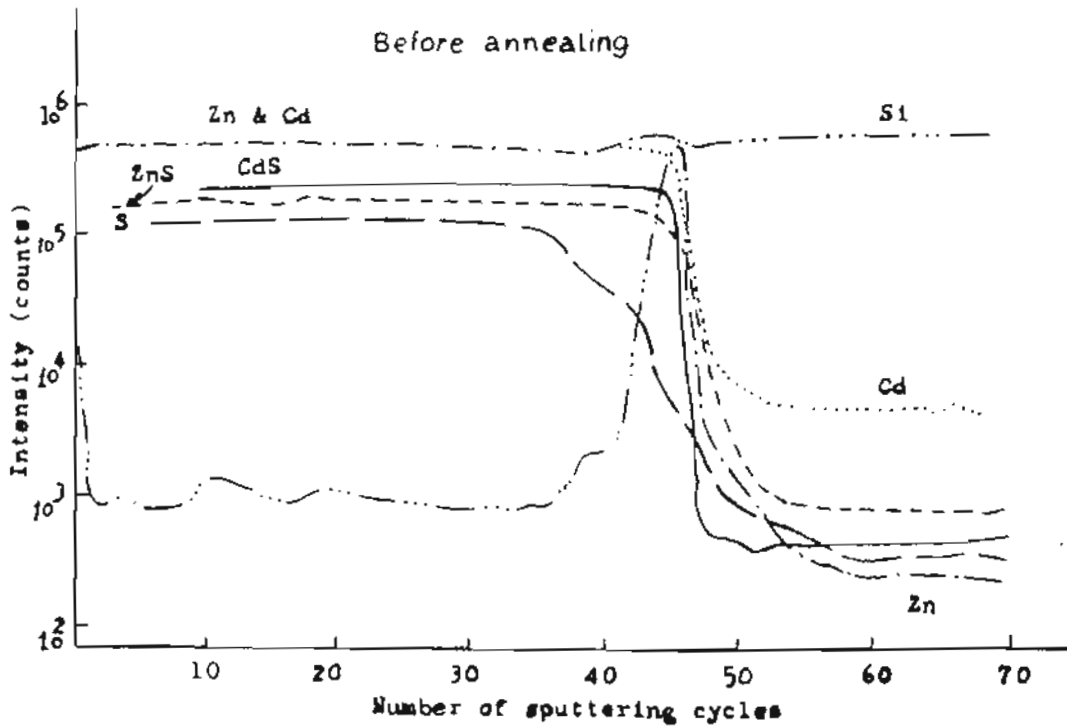


Fig. 4: SIMS depth profiles of the $(Zn_x - Cd_{1-x})S$ as grown on Si substrate.

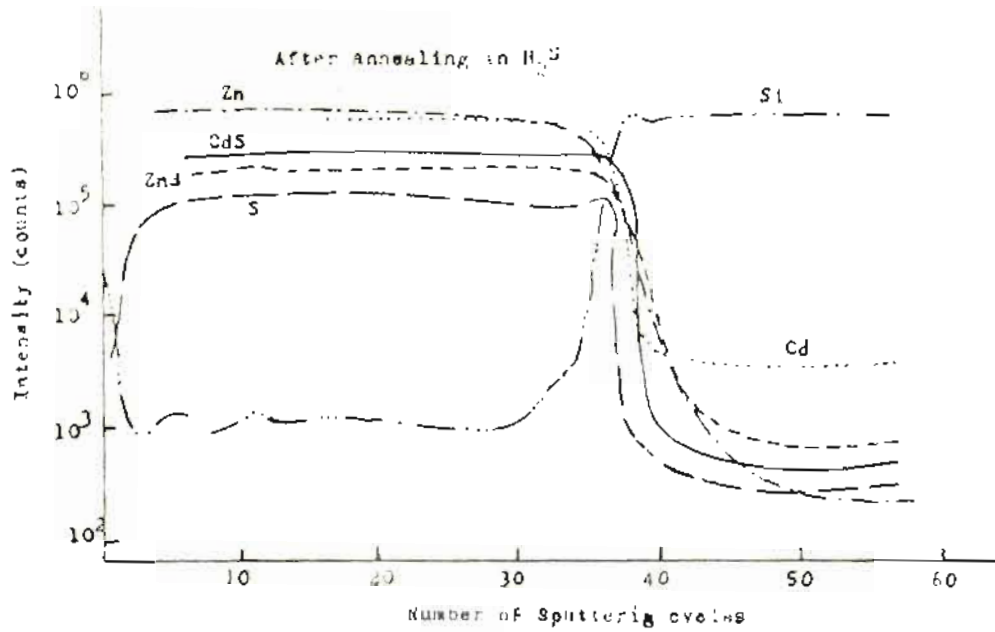


Fig. 5: SIMS depth profiles of $(Zn_x - Cd_{1-x})S/Si$ heterojunction after annealing in H₂S at 350°C for 20 minutes.

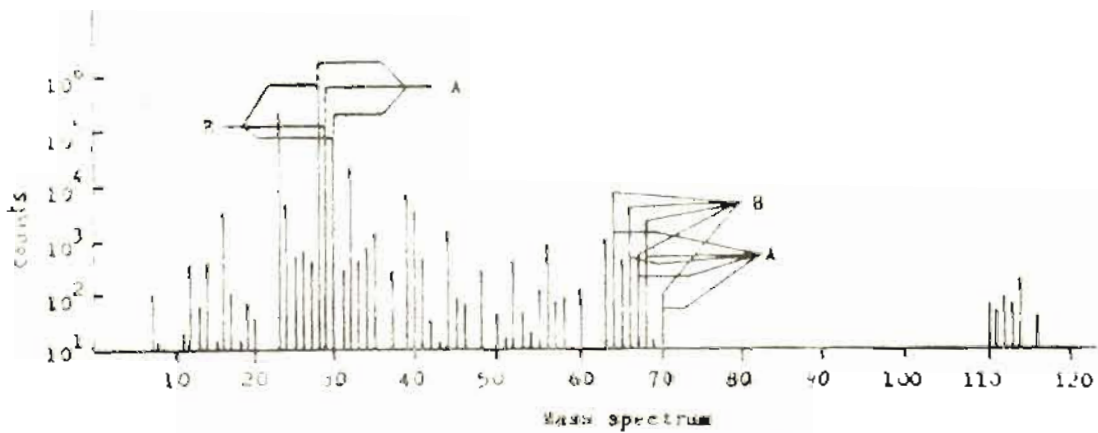


Fig. 6: Mass spectra at the interface of the $(Zn_x - Cd_{1-x})S/Si$ junction.
 B Intensity of S and Zn before annealing
 A Intensity after annealing.