CADMIUM AND ZINC SULFIDE THIN FILMS-SILICON HYBRIDE PHOTOVOLTAIC SYSTEM

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ABSTRACT:

The formation of n(Zn_x - Cd_{1-x}) S-PSi heterojunction solar cell under various heat treatments is investigated in order to optimize their behaviour. The results obtained indicate that substantial improvement can be made in the conversion and quantum efficiency of cells with x about 0.75, deposited at substrate temperature of 370°C, after annealing in $H2/N_2$ atmosphere at 600°C. Under these conditions, minimum density of interface states good lattice match, and maximum electron mobility are achieved.

I. INTRODUCTION:

Cadmium sulfide and Zince sulfide films have received a considerable interest in photovoltaic applications in which these materials and their mixture have been acting as the large gap window material of a heterojunction. The primary advantage of heterostructure solar cell is the enhanced short wavelength response, reduced carrier loss from surface recombination and lower fabrication cost. In order to increase the conversion efficiency of heterojunction solar cell (1), the base material should lie in the range 1.1 - 1.9 ev, the window material should have as large gap as possible, the lattice mismatch and difference in electron affinity between the two materials should be minimum. A mixed sulfide film (Zn_x - Cd_{1-x})S could have an excellent lattice match with silicon and an energy gap in excess of 3.0 ev by adjusting the value of x. An efficiency in the range 13-15 percent is expected from such a system provided a good quality sulfide film can be deposited on a properly cleaned Si surface. In this paper we are carrying on work previously started (2, 3) which is performed as an attempt to relate the physical (electrical and optical) properties and chemical composition of the (Zn_x - Cd_{1-x})S films to the photovoltaic performance of their heterojunction with silicon. The main objective is to study the formation of n(Zn_x - Cd_{1-x})S-Psi heterojunction under various heat treatments in order to optimize their behaviour.

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II- Experimental:

Heterojunction solar cells were fabricated by applying $n(Zn_x - Cd_{1-x})S$ film of thickness 3000 to 5000Å on a cleaned (111) surface of P-Si substrates. The mixed sulfide films ($n \approx 2\text{-}5 \times 10^{17}$ cm^{-3}) were deposited by radio frequency sputtering from $(Zn_x - Cd_{1-x})S$ targets with x ranging between 0.05 and 0.85 at different substrate temperature Tsb (between 150 and 350°C) in argon or H_2S atmosphere at pressure of 10^{-2} to 10^{-4} torr.

Clean surface of the substrate is considered as a must in order to grow a sulfide film with good structure order at the interface. Therefore a thin layer was evaporated from the surface of the wafer after chemical cleaning to remove surface damages created during cutting and polishing of the wafer. Then the wafers were thermally cleaned by heating them at temperature over 950°C in a high vacuum chamber in a vacuum better than 10^{-7} torr to remove the native oxides from the Si surface. Complementary surface analysis including Auger electron scanning AES, and secondary ion mass spectroscopy SIMS were employed to study the chemical and molecular species of the surfaces and interfaces of the heterojunctions. Compositional profiling was also utilized to study the heterostructure transition layer including the initial formation of the sulfide film on the Si substrate. The crystallite grain sizes in the film were measured using scanning electron microscope, and information on the crystal structure was obtained from x-ray diffraction studies. Evaporated indium or aluminum was used as a low-resistance front contact to the sulfide film. Electrical contact to the Si base was made from Al evaporated at pressure of 10^{-5} torr and sintered at 450°C for 10 - 15 minutes. Current - voltage, capacitance - voltage measurement were done for characterization of the completed solar cell and for determination of the density of interface states respectively.

III- Results and Discussions:

The improvement in the performance of annealed $n(Zn_x\text{-}Cd_{1-x})$ S-Psi solar cell due to increasing Zn content x from 0.12 to 0.75 is demonstrated in figure 1. It is clear that the conversion efficiency of heterojunctions prepared under the same conditions and received the same annealing treatment has increased by two points by increasing x from 0.12 to 0.7.

The electrical characteristics of the as grown sulfide films are summerized in Table 1 and of the annealed films in Table 2. It is clear that the resistivity increases with x. However a drastic drop takes place after annealing in a H_2 atmosphere at temperature 550°C. Minimum value of ρ =40 ohm cm and maximum value of carrier concentration n = 5×10^{17}cm^{-3} are obtained at x = 0.12. The electron mobility μ as a function of annealing condition and x is shown in figure 2.

It is clear that μ decreases very slightly with increasing x before annealing. After annealing in H_2S at 600°C μ has increased to a constant value for x ranging between 0.05 and 0.3 then started to decrease at higher values of x. On the other hand, annealing in H_2 at the same temperature gave rise to a slight increase in μ with x. Larger increase was obtained due to annealing in H_2/N_2 (1:1) atmosphere. The present data have shown that the dark reverse saturation current density Jo of $n(Zn_x - Cd_{1-x})S$-PSi heterojunction prepared at Tsb 350°C decreases continuously from 2.0 mA cm^{-2} to 0.02 m A cm^{-2} by increasing x from 0.05 to 0.7 due to annealing in H_2/N_2 atmosphere at 600°C. Heterojunctions annealed in H_2 or H_2S at the same temperature have shown a minimum value of Jo at x = 0.12 followed by an increase with increasing x. The values of Jo obtained at x = 0.7 are almost the same for both gases($\approx$ 0.2 m A cm^{-2}). It is well known (4) that CdS has a Wurtzite crystal structure, while as grown ZnS films is structurally impure(5) containing a cubic and hexagonal types of structures together. In this work, the proportion of the cubic phase has increased remarkably by sputtering ZnS in H_2S atmosphere (pressure 10^{-3} torr) on clean Si surface at temperature 370°C. After annealing at 650°C in H_2/N_2 atmosphere the structure was found to be mainly cubic (in which positions of the atoms in the unit cell are identical with those of the diamond cubic structure of Si). On the other hand, the crystal structure of $(Zn_x-Cd_{1-x})S$ films prepared at Tsb = 370°C in H_2S atmosphere and annealed at 650°C showed a gradual change from the wurtizite structure of CdS to the cubic structure of ZnS by increasing the Zn content x. Prolonged annealing treatment (> one hour) has increased the size in the crystallites of the $(Zn_{0.72} - Cd_{0.28})S$ films to half of the film thickness.

Auger depth profiles of $(Zn_x-Cd_{1-x})S$-Si heterojections with x = 0.15 and x = 0.8 before and after annealing in H_2/N_2 (1:1) at 650°C are shown in figures 3.a and 3.b. From figure 3.a sulfur accomulation is observed in heterojunctions with lower zinc content before annealing. Migration of sulfur has increased towards the interface of this sample after annealing. In figure 3.b junctions with x = 0.8 did not show appreciatle change in sulfur concentration at the interface due to annealing, but Zn accommulation was shown instead. It is also observed that annealing gives rise to sharper interface. Otherwise no major compositional changes were observed.

In the case of heterojunctions with high zinc content ($x \approx 0.75$) higher structure order was achieved at the transition layer, reduction in the width of the depletion layer and stability to high temperature annealing were observed. Electron microscope studies has shown that the initial bonding of the mixed sulfide films to Si surface takes place mostly through S atoms in junctions made from films with low Zn

content ($x < 0.25$). The initial bonding takes place through Zn atoms in junctions prepared from high Zn content material ($x > 0.5$) provided that the substrate temperature is higher than 350°C. Then density of interface states was reduced due to reduction in the concentration of dangling bonds. The recombination velocity was decreased from 8×10^5 cm sec^{-1} for $x = 0.2$ to 4×10^4 cm sec^{-1} for $x = 0.8$.

IV- CONCLUSION:

The present investigation has shown that significant changes in the behaviour of n(Zn_x - Cd_{1-x})S-PSi solar cell can take place by varying Tsb, annealing temperature and ambience. It was also found that Zn content x has a crucial influence on the performance of the cell. Under the same preparation and annealing conditions two cases can be distinguished.

a) In the case of sulfide films with low zinc content(x about 0.12) the efficiency obtained is 6.3 percent, the electrical characteristics (ρ and n) are optimized, the value of electron mobility is acceptable (150 cm^2 V^{-1} Sec^{-1}). However the density of interface states due to the structural discontinuity between Si and the sulfide film was so high that an appreciable recombination loss result in. Therefore a supression in Isc was observed.

b) Increasing Zn content (x about 0.75 - 0.8) give rise to an appreciable increase (about 20 percent) in both the conversion and quantum efficiency compared to the former case, in spite of the high resistivity and lower carrier concentration. This increase in efficiency is due to reduction in the density of interface states (then reduction in Jo), reduction in electron affinity difference and improved lattice match.

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Table-1. Resistivity ρ and electron mobility μ and carrier concentration n of the as grown sputtered $(Zn_x-Cd_{1-x})S$ films as a function of substrate temperature Tsb and Zn content x.

x	ρ ohm cm			μ cm^2 V^{-1} Sec^{-1}			$nx10^{-16}$ cm^{-3}		
	Tsb °C			Tsb °C			Tsb °C		
	150	250	350	150	250	350	150	250	350
0.0	200	300	450	110	120	125	8	12	15
0.15	500	450	350	120	110	125	15	25	35
0.25	600	550	500	110	115	120	15	20	35
0.5	800	780	750	100	105	110	12	18	30
0.72	1000	1000	950	80	80	75	10	18	20
0.85	1100	1050	1050	50	55	50	8	12	15

Table 2. ρ and of $(Zn_x-Cd_{1-x})S$ films prepared at Tsb=350°C after annealing at temperature Ta=600°C in H_2(a), (H_2/N_2) (b), and H_2S (c).

x		0.0	0.15	0.25	0.5	0.72	0.85
ρ	a	60	40	190	280	300	320
	b	70	115	250	350	400	400
	c	85	120	260	400	450	450
n	a	28	60	55	40	30	30
	b	18	45	40	30	20	20
	c	15	40	35	30	20	20

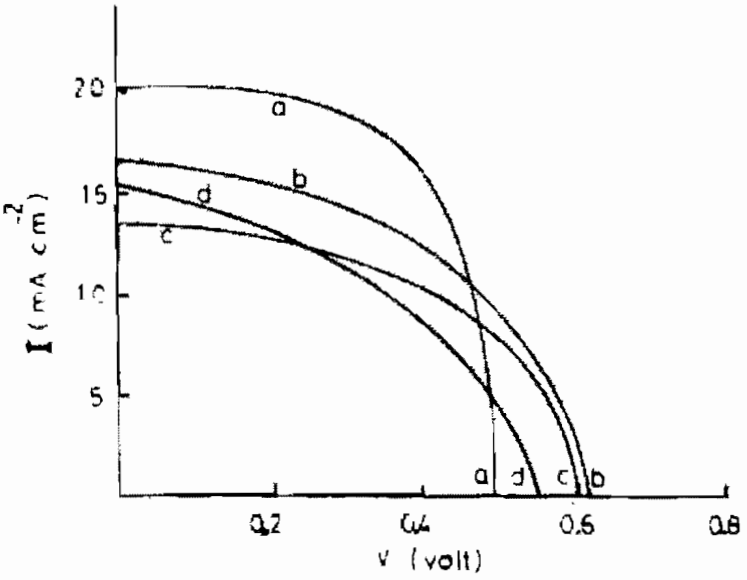

Fig.(1): I-V characteristics of (a) Si homojunction solar cell (10 percent efficiency), (b) n(Zn_x-Cd_{1-x})S-pSi heterojunctions with x + 0.75 and (c) for x + 0.12, and nCdS - pSi.

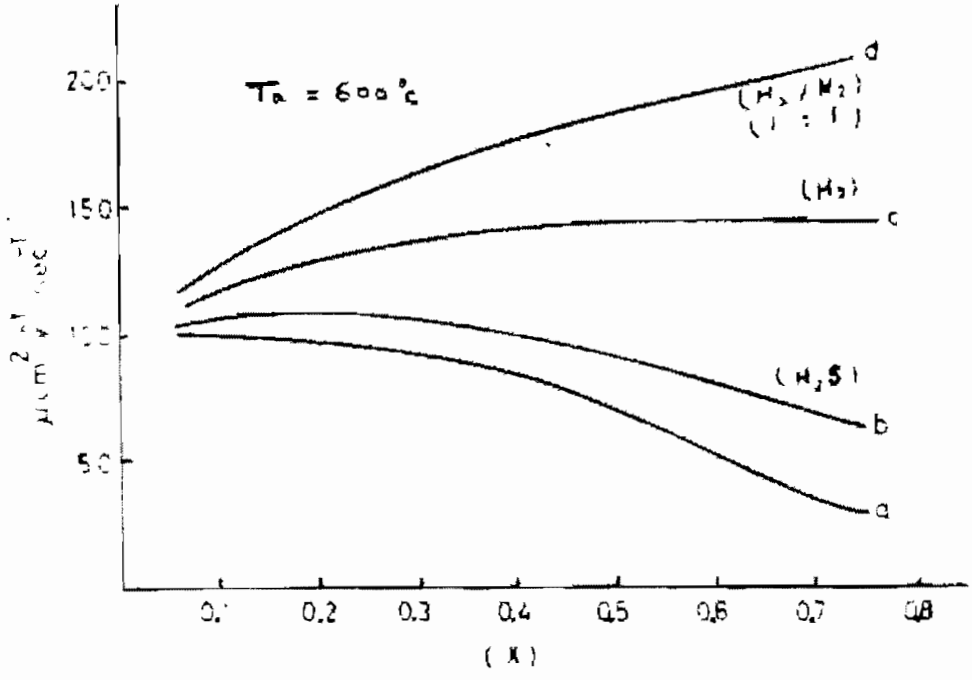

Fig.(2): Electron mobility μ of n(Zn_x-Cd_{1-x})S films sputtered at T_{sb} = 350°C as a function of x, before annealing (a) and after annealing (b, c, and d).

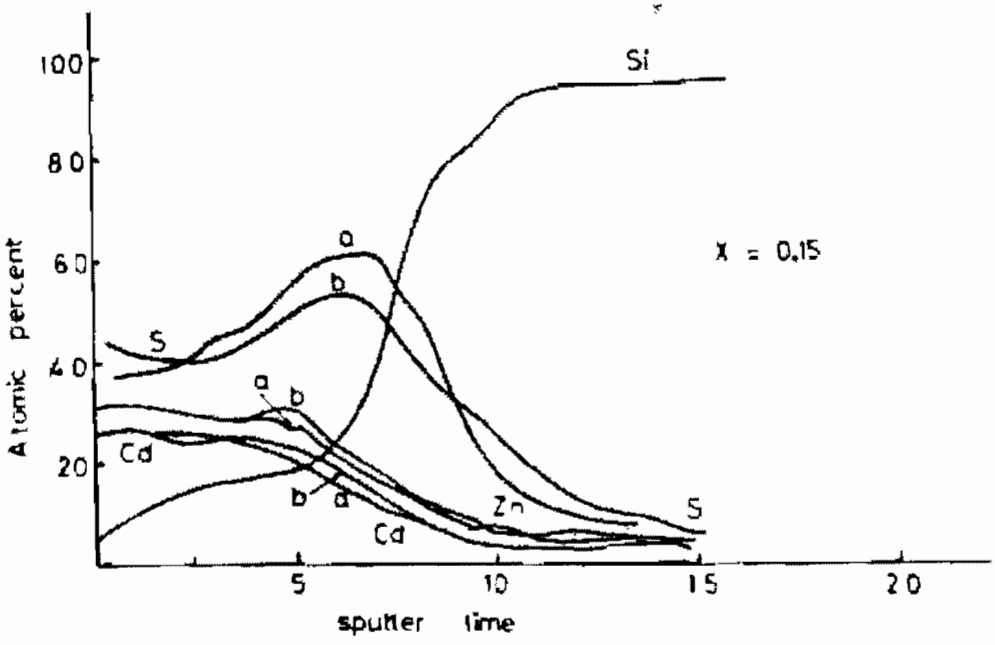

Fig.(3 a): Auger depth profiles of $n(Zn_{0.15} - Cd_{0.85})S$ - pSi heterojunction before (lines b) and after annealing (lines a).

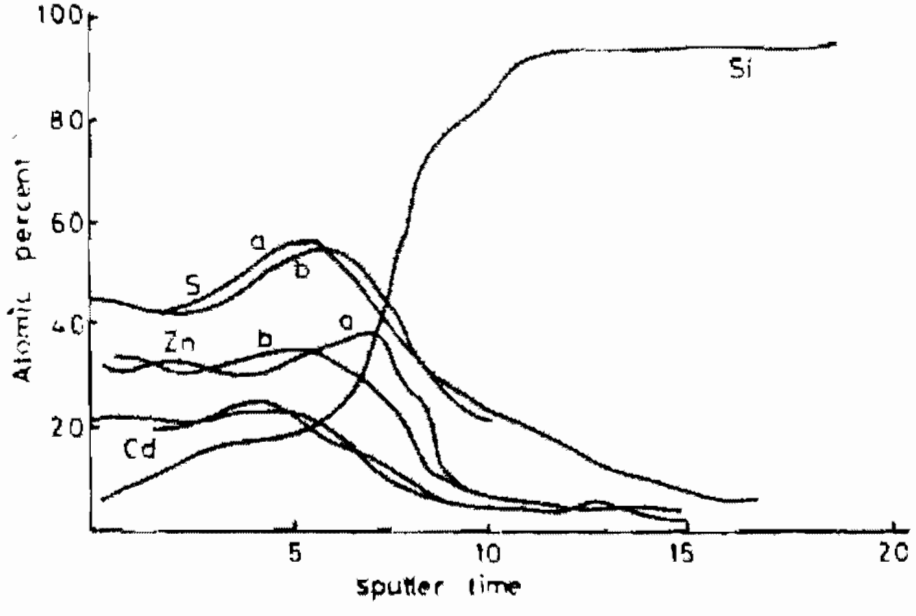

Fig.(3 b): Auger depth profiles of $n(Zn_{0.8} - Cd_{0.2})S$ - pSi before (lines b) and after annealing (lines a).