

Photoelectrochemical solar cells using electrodeposited GaAs and AlSb semiconductor films

S CHANDRA, N KHARE and H M UPADHYAYA

Department of Physics, Banaras Hindu University, Varanasi 221 005, India

Abstract. Electrodeposited GaAs and AlSb thin film semiconductors were prepared under various deposition conditions. Reasonable stoichiometry could be attained as revealed by EDAX studies. The best stoichiometry was obtained are $\text{Ga}_{1.04}\text{As}_{0.96}$ and $\text{Al}_{1.12}\text{Sb}_{0.88}$. The band gap of the GaAs and AlSb films was ~ 1.5 eV and 1.6 eV respectively. The electrochemical and photoelectrochemical studies on these films are reported with different redox-couples in aqueous and non-aqueous medium.

Keywords. Photoelectrochemical cells; electrodeposition of thin films; semiconductors; GaAs films; AlSb films.

1. Introduction

Photoelectrochemical solar cells (PESC) are semiconductor/electrolyte junction solar cells (Gerischer 1979; Chandra and Pandey 1982; Chandra 1985). In recent years considerable progress has been made in the state-of-art of PESC and some high efficiency PESC have been successfully prepared using single crystals (Heller 1977; Parkinson *et al* 1979; Heller *et al* 1981; Tufts *et al* 1987; Gabouze and Gorochoy 1986; Switzer 1986; Azaiez *et al* 1986). As single crystalline solar cells are expensive, the use of wide area semiconductor thin-film is a desirable alternative for cost reduction. The optimum band gap for PESC is ~ 1.50 eV. We report PESC characteristics which use two promising materials viz GaAs ($E_g \sim 1.5$ eV) and AlSb ($E_g \sim 1.62$ eV). Both these materials were obtained by the electrodeposition technique described below.

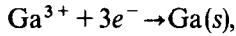
For GaAs PESC, we have used three types of redox-electrolytes: (a) aqueous $\text{S}^{2-}/\text{S}_2^{2-}$ redox-couple (b) ferrocene/ferrocenium redox-couple in CH_3CN and (c) $\text{MV}^{2+}/\text{MV}^{+}$ (methyl viologen) couple in CH_3CN . However, AlSb was found to hydrolyse faster in aqueous medium. Therefore, non-aqueous electrolyte (CH_3CN , acetonitrile) with $2\text{I}^-/\text{I}_2$ and nitrobenzene, $[\text{Ph}(\text{NO}_2)]^{0/-}$ redox-couples were used for preparing PESC.

2. Electrodeposition of GaAs

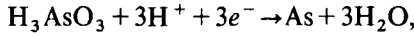
For preparing GaAs-semiconductor films, Ga-metal and As_2O_3 were separately dissolved in concentrated HCl. Dilute aqueous solutions were prepared later by adding the two solutions in the appropriate ratio. Ultrasonically cleaned Ti-substrate in trichloroethylene was used for electrodeposition. When electrolysis was carried out in the electrolysis cell, ionic species of Ga and As start moving towards cathode (Ti-substrate) and Ga/As gets deposited in different stoichiometric ratios depending on the deposition condition.

The electrochemical reactions for the deposition of Ga and As and their corres-

ponding Nernst equations are:



$$E_{\text{Ga}} = E_{\text{Ga}}^0 + \frac{RT}{3F} \ln (a_{\text{Ga}^{3+}}/a_{\text{Ga}}) = -0.529 + 0.0197 \log (a_{\text{Ga}^{3+}}/a_{\text{Ga}}),$$



$$E_{\text{As}} = E_{\text{As}}^0 + (RT/3F) \ln (a_{\text{H}_3\text{AsO}_3}/a_{\text{As}}) + (RT/F) \ln a_{\text{H}^+} \\ = 0.248 + 0.0197 \log (a_{\text{H}_3\text{AsO}_3}/a_{\text{As}}) - 0.0591 \text{ pH},$$

where the electrode potential E^0 is with respect to the normal hydrogen electrode, $a_{\text{Ga}^{3+}}$, $a_{\text{AsH}_3\text{O}_3}$ are the activities of Ga ion and H_3AsO_3 in the solutions, a_{Ga} and a_{As} are the activities of the respective atoms in the electrodeposits, which for pure metallic deposition are equal to one. It should be noted that the activity is pH-dependent.

For simultaneous deposition of Ga and As, the concentration of the solutes, the pH of the solution, the temperature of the electrolyte and the electrolysis current density should be adjusted such that the electrode potential of all individual deposits come closer to each other.

There are no clear-cut methods available for fixing the deposition parameters for compound film deposition. Most of the earlier attempts failed because of this. We have, in principle, used the following two procedures for fixing the starting conditions of our trial to electrodeposit GaAs.

(i) *Pourbaix diagram approach*

These diagrams define thermodynamical immunity regions and are represented as the plot between the electrode potential and the pH. The Pourbaix diagrams of Ga and As are overlapped to find the common immunity region for Ga and As. Within this region of pH and electrode potential, one may expect simultaneous deposition of the two giving Ga_xAs_y . Chandra and Khare (1987) used this method and found that the pH range 0.3 to 4.2 at about -0.8 volt (NHE) is the common immunity region.

(ii) *Polarization curve approach*

The I - V curve is drawn at different pH. The sudden increase in current at some electrode potential indicates the onset of deposition of one species. Similarly for other species, the current increases at another electrode potential. In between, a plateau is observed in the I - V curve which indicates the region of likely simultaneous deposition of both. In this paper, we have used both these approaches.

With the initial optimization of $\text{pH}=0.7$ of the electrolysis solution by the Pourbaix diagram approach, we proceeded to plot the polarization curves of GaAs-film deposition by keeping the other deposition parameters as: $\text{pH}=0.7$, temperature = 22°C , electrolyte contained 50 mg each of Ga and As_2O_3 dissolved in HCl to which a few drops of NH_4OH were added to make the $\text{pH}\approx 0.7$.

The polarization plot is shown in figure 1. Curves A and B were taken at different sensitivities of current axis in the X-Y recorder. Curve A (low sensitivity plot) shows

one step only without a well-defined plateau. However, when the experiment was done at higher sensitivity (curve B), we could locate another step at electrode potential ≈ 0.3 V (SCE) which corresponds to Ga deposition, while the other step at 0.7 V (SCE) is for As deposition. The plateau is between these two electrode potentials (0.3–0.7 V). We tried our electrodeposition by fixing the electrode potential in this range.

2.1 Characterization of electrodeposited GaAs film

(a) Structural

The stoichiometry of various films obtained at different deposition conditions was studied by the EDAX (energy-dispersive analysis by X-rays) technique. EDAX (PW 9100) attached to an electron microscope (Phillips EM-400) was used for this study. Films were electrodeposited on Ti-foils (0.3×0.3 cm²) and were directly mounted on the stub of the EDAX sample-holder using graphite paint as a conductor between the film and the stub. The stoichiometry of the best film was Ga_{1.04}As_{0.96}. This film was obtained in 8 minutes on titanium substrate at an electrolysis current density of 2.5 mA/cm². The stoichiometry of the films obtained under different electrolysis conditions is given in figure 2. The optimized conditions for the best films obtained are listed in table 1.

Electron diffraction patterns were also recorded using an electron microscope (Phillips TEM 200) to check the crystallinity of the film. The electrodeposited films on the substrate were scraped and the material was lifted on copper grid dipped in formvar. The observed and standard d -values of GaAs film (stoichiometry Ga_{1.04}As_{0.96}) are listed in table 2 which shows a reasonable agreement.

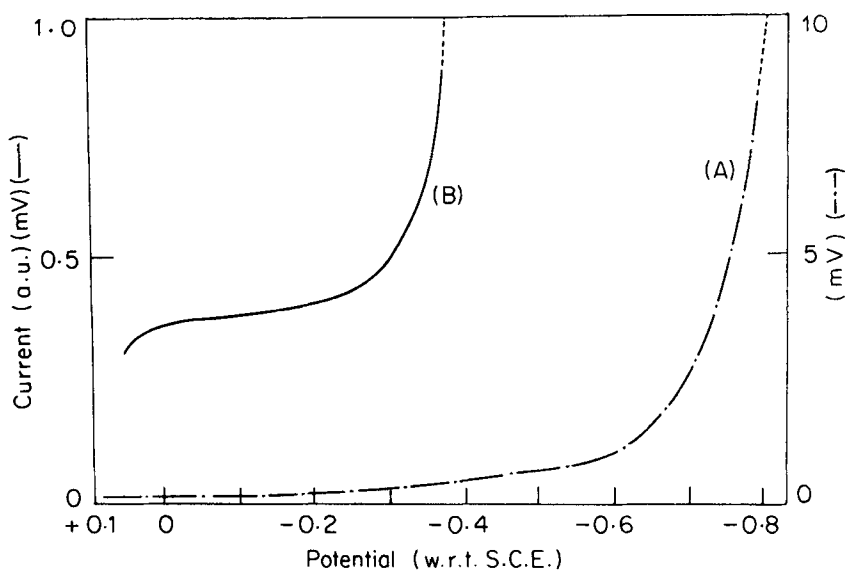


Figure 1. Polarization curve for GaAs electrodeposition.

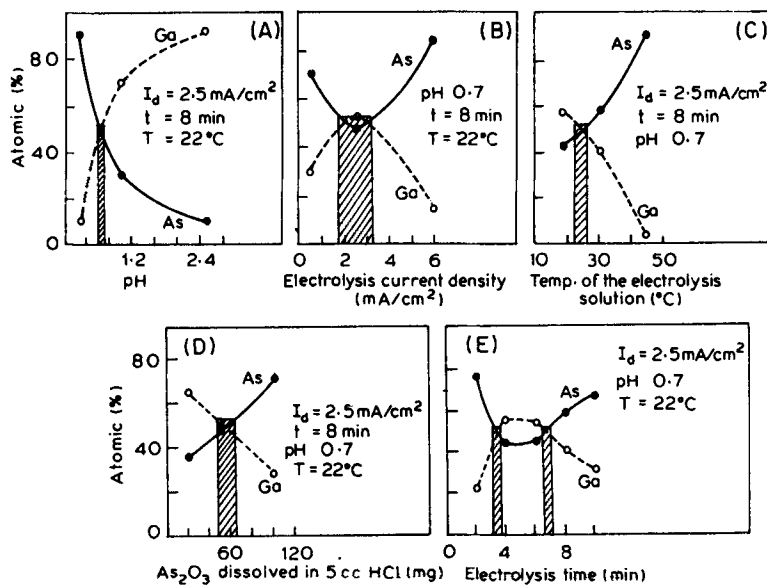


Figure 2. Relative composition of Ga and As in the electrodeposited films prepared at different (a) pH, (b) deposition current density I_d , (c) temperature, (d) concentrations of As_2O_3 and (e) deposition time. For other conditions see table 1. In all cases except (d), As_2O_3 was taken as 50 mg in 50 ml of HCl mixed into another solution of 50 mg of Ga in 5 ml of HCl. Shaded zones mark the region in which stoichiometry is approximately that of GaAs.

Table 1. Deposition conditions for obtaining various films. The best stoichiometry of the film obtained is noted in the column while the stoichiometry of other films can be seen in figures quoted in the same column.

Stoichiometry of best films	pH	As_2O_3 (mg in 5 ml)	Ga (mg in 5 ml)	Deposition time (min)	Deposition current (mA/cm^2)	Deposition temperature ($^{\circ}C$)
$Ga_{1.04}As_{0.96}$ (figure 2a)	0.3-2.5*	50	50	7	2.5	22
$Ga_{1.06}As_{0.94}$ (figure 2b)	0.7	50	50	7	0.5-6.0*	22
$Ga_{1.04}As_{0.96}$ (figure 2c)	0.7	50	50	7	2.5	22-45*
$Ga_{1.06}As_{0.94}$ (figure 2d)	0.7	20-100*	50	7	2.5	22
$Ga_{1.04}As_{0.96}$ (figure 2e)	0.7	50	50	2-10*	2.5	22

*This parameter is varied within the range given while the others were kept fixed.

(b) Band gap

Optical absorption was studied to determine the band gap of the electrodeposited GaAs film. The absorption spectra were recorded at room temperature ($25^{\circ}C$) with a spectrophotometer (Hitachi-320) in transmission mode. The electrodeposited film

was prepared on a titanium-coated semitransparent glass plate. This was used as the sample and a similar titanium coated glass plate was used as the reference.

The absorption coefficient near the absorption edge can be written as

$$\alpha = K(E - E_g)^n/E$$

where K is a constant, E the photon energy, E_g the band gap and n a constant which can be assigned values 1/2, 3/2 and 2 for allowed direct transition, forbidden direct transition and allowed indirect transition respectively. GaAs is a direct band gap material and so $n = 1/2$.

Figure 3 shows a plot between $(\alpha h\nu)^2$ vs $h\nu$ which is a straight line. This confirms the direct band gap nature of the material. The intercept of the straight line with the x-axis gives the value of the band gap, $E_g = 1.5$ eV.

Table 2. Standard d -values of GaAs and those obtained from electron diffraction pattern of $\text{Ga}_{1.04}\text{As}_{0.96}$ electrodeposited film.

hkl	Standard d values (Å)	Observed d values (Å)
111	3.26	3.28
200	2.83	2.80
220	1.99	1.94
311	1.70	1.69
400	1.41	1.42
331	1.29	—
422	1.15	1.16
333	1.08	1.08
440	0.99	—
531	0.95	—
620	0.89	—
533	0.86	0.87
444	0.81	—
711	0.79	0.78

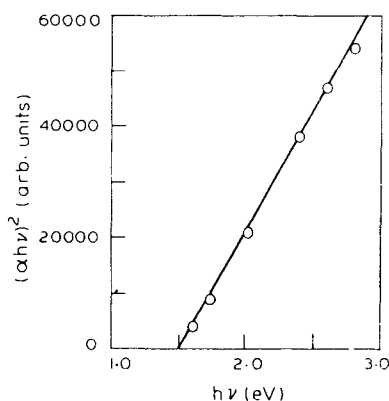


Figure 3. $h\nu$ vs $(\alpha h\nu)^2$ plot from the absorption spectral studies for determining the band gap of $\text{Ga}_{1.06}\text{As}_{0.94}$ film.

(c) Mott-Schottky studies

The Mott-Schottky study is the measurement of interface capacitance with applied bias. In this study, the electrodeposited GaAs film was one electrode, the graphite was used as the counterelectrode and a saturated calomel electrode (SCE) was the third electrode. SCE was kept near the GaAs film. The electrolyte had the redox-couple S^{2-}/S_2^{2-} consisting of 1 M-NaOH, 1 M- Na_2S and 1 M-S. The interface capacitance at different bias was measured by a Hewlett Packard LCR bridge model 4274A. The Mott-Schottky plot, as a representation of the variation of space charge capacitance C_{sc} with the applied bias V is expressed as

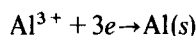
$$1/C_{sc}^2 = (2/\epsilon_s \epsilon_0 q N_D) [V - V_{fb} - (kT/e)],$$

where V_{fb} is the flat band potential, ϵ_s the dielectric constant of the semiconductors, ϵ_0 the permittivity of free space, q the electronic charge and N_D the doping density. The intercept on X-axis gives the flat band potential, V_{fb} . Further, from the slope of the straight line the value of N_D can be calculated.

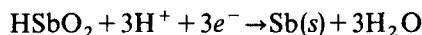
Figure 4 shows the Mott-Schottky plot of the electrodeposited $Ga_{1.04}As_{0.96}$ film dipped in S^{2-}/S_2^{2-} electrolyte. The nature of the plot indicates that the film is n -type. The values of V_{fb} and N_D were obtained as -1.4 V (SCE) and $8.7 \times 10^{15} \text{ cm}^{-3}$ respectively.

3. Electrodeposition of AlSb

$Al_2(SO_4)_3$ and Sb_2O_3 were the starting material for the preparation of electrodeposited AlSb thin film. The compounds were dissolved in conc. HCl solution, then a well-polished Ti-substrate was rinsed and cleaned in trichloroethylene by putting it in an ultrasonic cleaner tank. When the titanium substrate is dipped in the electrolyte containing $Al_2(SO_4)_3$ and Sb_2O_3 , deposition reaction of Al and Sb takes place as given below:



$$E_{Al} = E_{Al}^0 + (RT/3F) \ln(a_{Al^{3+}}/a_{Al}) = -1.662 + 0.0197 \log(a_{Al^{3+}}/a_{Al}),$$



$$E_{Sb} = E_{Sb}^0 + (RT/3F) \ln(a_{HSbO_2}/a_{Sb}) + (RT/F) \ln a_{H^+} \\ = 0.23 + 0.0197 \log(a_{HSbO_2}/a_{Sb}) - 0.0591 \text{ pH}.$$

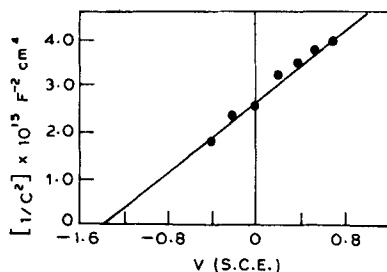


Figure 4. Mott-Schottky plot for electrodeposited GaAs film.

Antimony is a more noble metal than aluminium and its deposition tendency is greater than Al. Also, Al being a greater non-reducible metal, the deposition of Al at room temperature and low current electrolysis is difficult. Thus, for a balance of situation, we have taken the concentration of $\text{Al}_2(\text{SO}_4)_3$ much higher than the conc. of Sb_2O_3 , typically in the ratio of 1000:1. The above approach of fixing deposition parameters does not permit deduction of enough guidelines to fix the electrode potential and the electrolysis current density. For this, we use the polarization curve as for GaAs. A typical I - V curve is given in figure 5. The pH of the solution plays an important role for the AlSb system. AlSb, by nature, is chemically highly corroding in the aqueous medium. The pH range of 3.0 to 4.0 gives a good quality of deposition.

The stoichiometry of AlSb films prepared under different conditions is given in figure 6. All depositions were done at electrolysis current density = 2 mA/cm^2 at 32°C . The best film had the stoichiometry $\text{Al}_{1.12}\text{Sb}_{0.88}$.

4. Results on PESC's and discussion

The photoelectrochemical solar cells of GaAs and AlSb were fabricated by depositing these films on the Ti-electrode as one electrode and platinum plate as the counterelectrode dipped in a suitable redox-electrolyte.

The PESC of GaAs were studied both under the aqueous and non-aqueous redox-couples. The aqueous $\text{GaAs}/\text{S}_2^{2-}, \text{S}^{2-}$ system yielded a typical open circuit voltage, V_{oc} , of 195 mV and a short circuit current J_{sc} of 2.2 mA/cm^2 for 60 mW/cm^2 illumination intensity for the film of stoichiometry $\text{Ga}_{1.04}\text{As}_{0.96}$. It was found that

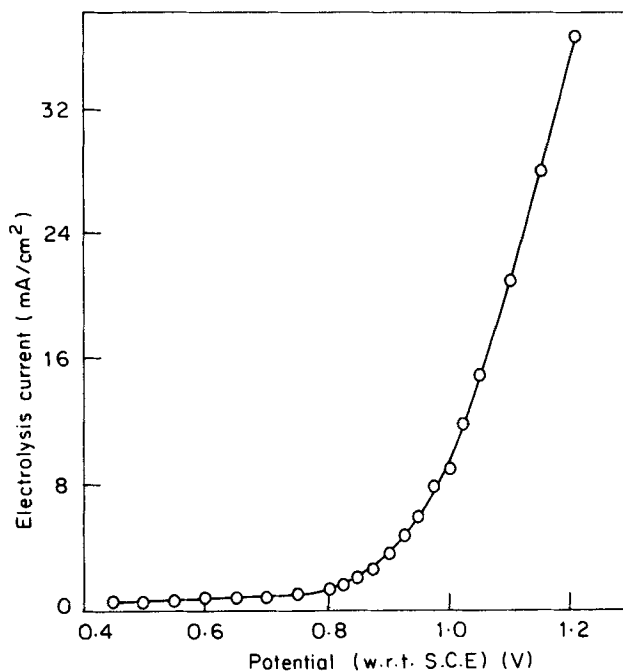


Figure 5. Polarization curve for AlSb electrodeposition.

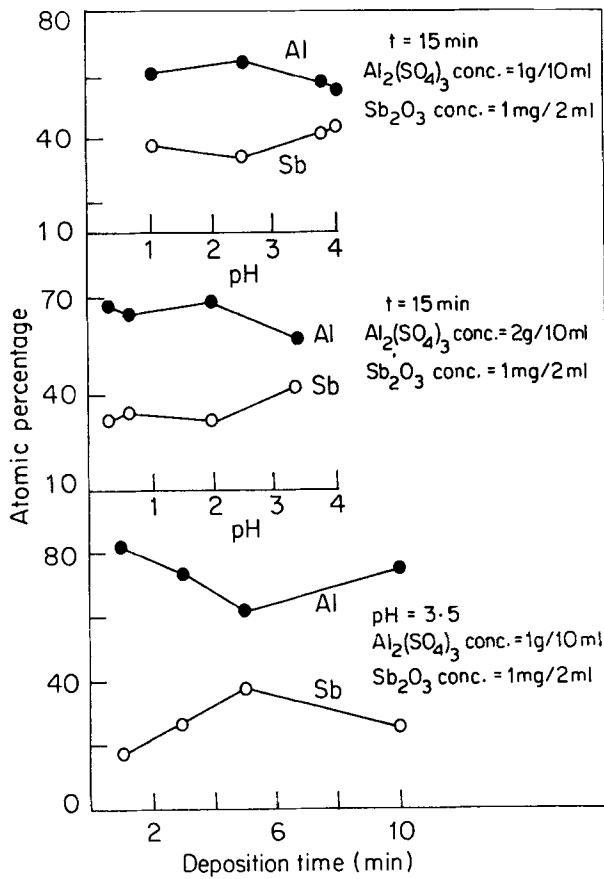
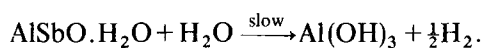
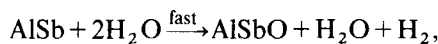


Figure 6. Relative composition of Al and Sb in the electrodeposited AlSb films at (a) and (b) different pH and (c) different deposition times.

V_{oc} and J_{sc} of the PESC depend on the stoichiometry of GaAs-film. A marked decrease of photoresponse was observed for the variation of film stoichiometry in either direction. However, the PESC of GaAs/S₂²⁻, S²⁻ is not stable, as V_{oc} and J_{sc} deteriorates with time which indicates the chemical corrosion of the film.

The non-aqueous redox-couples like GaAs/MV^{2+/+} and GaAs/ferrocene, ferrocenium in CH₃CN as non-aqueous electrolyte make the PESC stable. However, no significant change in the photoresponse of the film is seen. Table 3 summarizes the solar cell characteristics of GaAs film in different redox-electrolytes.

Similar studies were carried out for AlSb films. However, AlSb films hydrolysed quickly in aqueous medium as follows (Rudorff and Kohlmeier 1954):



Hence, the use of non-aqueous redox-couples becomes an essential requirement for the fabrication of AlSb-based PESC.

Table 3. Solar cell characteristics of GaAs and AlSb films in different redox electrolytes.

Electro-deposited photoelectrode	Electrolyte/couple	Illum. intensity (mW/cm ²)	V _{oc} (mV)	J _{sc} (ma/cm ²)	Stability
Ga _{1.04} As _{0.96}	Aqueous/S ₂ ²⁻ , S ²⁻	60	195	2.2	Unstable
Ga _{1.04} As _{0.96}	CH ₃ CN/MV ^{2+ / +}	100	200	2.0	Stable (slow response)
Ga _{1.04} As _{0.96}	CH ₃ CN/ferrocene, ferrocenium	80	150	0.3	Stable (slow response)
Al _{1.12} Sb _{0.88}	CH ₃ CN/2I ⁻ , I ₂	100	210	0.35	Stable (slow response)
Al _{1.12} Sb _{0.88}	CH ₃ CN/[Ph(NO ₂)] ^{0/-}	100	240	0.1	Stable (slow response)

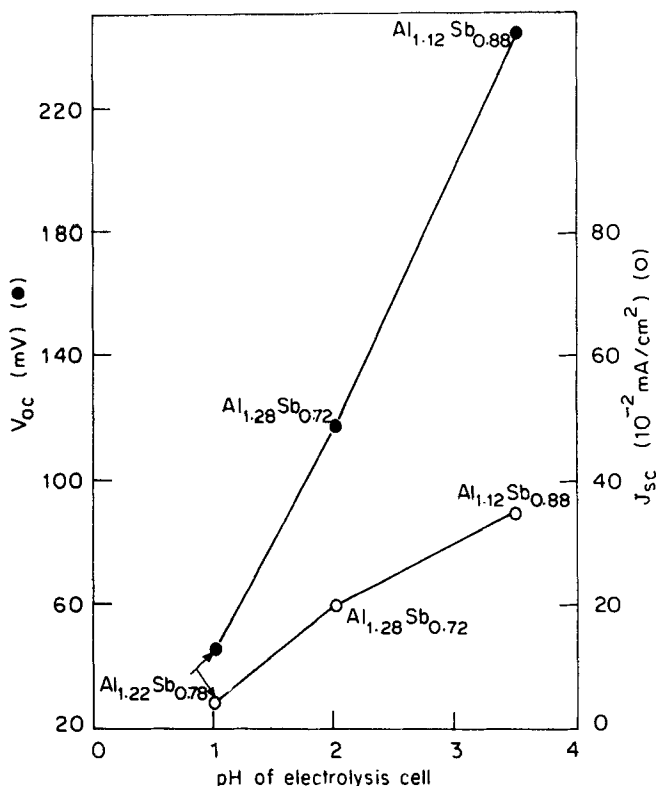
**Figure 7.** Photovoltage and photocurrent of the electrodeposited PESC system using semiconducting Al_xSb_y films electrodeposited at various pH values (for other conditions see the text).

Figure 7 shows the V_{oc} and J_{sc} of different PESC which used AlSb films prepared under different pH conditions. The corresponding stoichiometries are also given in the figure. As pointed out earlier, the best film had the stoichiometry Al_{1.12}Sb_{0.88}. The characteristics of PESC using this film as photoelectrode are listed in table 3 for two different redox-couples.

The detailed J - V characteristics of PESC showed that the GaAs film PESC had an efficiency of $\sim 1\%$ with a fill factor ~ 0.5 . It is hoped that if the films are prepared to bring better stoichiometry and uniformity, the GaAs film PESC can be a competitive

and economically viable system. However, AISb system is not recommended for terrestrial use as it is likely to hydrolyse if perfect sealing is not attained.

Acknowledgement

Thanks are due to DNES (Govt. of India) for financial assistance.

References

- Azaiez C, Levy F, Campet G and Claverie J 1986 in Report on: *The sixth International conference on photochemical conversion and storage of solar energy, July 21–25, Paris* (ed.) G V Subba Rao
- Chandra S 1985 *Photoelectrochemical solar cells* (New York: Gordon & Breach)
- Chandra S and Khare N 1987 *Semicon. Sci. Technol.* **2** 214, 220
- Chandra S and Pandey R K 1982 *Phys. Status Solidi* **A72** 415
- Gabouze N and Gorochov O 1986 in the Report on: *The sixth International conference on photochemical conversion and storage of solar energy, July 21–25, Paris* (ed.) G V Subba Rao
- Gerischer H 1979 in *Solar energy conversion and storage* (ed.) B O Seraphin (Berlin: Springer Verlag) **31** 115
- Heller A 1977 in *Semiconductor liquid junction solar cells* (Princeton: Electrochem. Soc.) **77–3**
- Heller A, Miller B and Trieb F 1981 *Appl. Phys. Lett.* **38** 282
- Parkinson B A, Heller A and Miller B 1979 *J. Electrochem. Soc.* **126** 954
- Rudorff W and Kohlmeier E J 1954 *Z. Metall.* **45** 608
- Switzer 1986 *J. Electrochem. Soc.* **138** 722
- Tuffs B J, Abraham I L, Santangelo P G, Ruba G N, Casagrande and Lewis N S 1987 *Nature (London)* **326** 861