CHAPTER 3

SURFACE MODIFICATION OF GaAs:

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3.1 PHOTOELECTROCHEMICAL SOLAR CELL STUDIES:

3.1.1 PEC SOLAR CELL FABRICATION

A perspex cell of cylindrical dimensions (48.25 cm$^3$ with diameter 3.2 cm and height 6.0 cm) was used for the electrochemical experiment shown in Fig.3.1. The cell contained GaAs or In$_{0.53}$Ga$_{0.47}$As working electrode (WE), a graphite counter electrode (CE) and a Pt reference electrode (RE). The CE had 50 times larger area than the WE. The distance between WE and RE was 0.3 cm and that between CE and WE 1.5 cm. The WE was generally positioned adjacent to the cell window made of special optically flat thin perspex window to minimise absorption losses in the solution. During illumination care was taken to place the Pt CE in dark. The three electrode (3-E) configuration was used for dark I-V and C-V measurements.

Photoelectrodes were mounted on a teflon holder, which was found to be the best material not being attacked by any of the commonly used organic or inorganic electrolyte. The contacts and the thin copper wire connections were fully covered with silicone rubber (532 RTV Dow Corning, USA) to isolate these from electrolyte solution.

3.1.2 PREPARATION OF REDOX COUPLES AND ELECTROLYTES:

The electrolytes were aqueous solutions of alkali prepared with 18 M$\Omega$ deionised (DI) water from a Millipore Deioniser. Potassium hydroxide (KOH) or Sodium hydroxide (NaOH) of required molar concentrations were used. KOH was used as the main supporting electrolyte because of its higher
The conductivities of redox electrolytes were measured by a Systronics 303 Conductivity Meter. NaOH was used in the preparation of redox species. The redox couples $\text{Te}^{2-}/\text{Te}_x^{2-}$, $\text{Se}^{2-}/\text{Se}_x^{2-}$ and $\text{S}^{2-}/\text{S}_x^{2-}$ were prepared from their respective salts of analytical grade reagents in water. The following procedures were used:

**Te$^{2-}/\text{Te}_x^{2-}$ REDOX COUPLES**: Finely crushed tellurium powder (1 gm) was mixed with 4 gm of $\text{Na}_2\text{S}_2\text{O}_4$ (sodium dithionite) in 50 ml of argon purged 5M NaOH solution. The mixed solution was gently heated to 70 °C while stirring simultaneously by a magnetic stirrer. A purple colour appeared due to formation of $\text{Na}_2\text{Te}^{2-}$ or $\text{Na}_2\text{Te}_x^{2-}$. The colour disappeared on cooling and white crystalline powder of $\text{Na}_2\text{Te}$ was obtained. Stock solutions of $\text{Na}_2\text{Te}$ were then prepared by weighing the required amount of salt in an inert atmosphere and dissolved in argon purged water. A portion of this solution was oxidised intentionally to incorporate $\text{Na}_2\text{Te}_x$ in the solution. The solutions were preserved in argon sealed bottles. The main difficulty in maintaining equilibrium was the inability to rigorously exclude $\text{O}_2$, which rapidly oxidizes $\text{Te}^{2-}$ to $\text{Te}_2^{2-}$ and $\text{Te}_2^{2-}$ to Te.

**Se$^{2-}/\text{Se}_x^{2-}$ AND S$^{2-}/\text{S}_x^{2-}$ REDOX COUPLES**: Here preparation procedures were the same as for $\text{Te}^{2-}/\text{Te}_x^{2-}$, instead of tellurium, selenium or sulphur being taken.

### 3.1.3 pH MEASUREMENT

The pH of the redox solutions were measured by a Systronics (Model 331) expanded scale pH meter. The cell
consists of two electrodes, a glass electrode and a reference electrode. The reference electrode was typically mercury-mercurous chloride (calomel) in a saturated solution of potassium chloride.

The pH meter was standardised by calibrating in a buffer solution. This standardisation automatically compensates for the various potentials in the electrode system. Subsequent immersion of the electrodes in the test solution generates a potential that is proportional to the pH of the solution and it is directly read off in the normal or expanded scale of the meter. The pH of redox-electrolytes was kept constant at 13 ± 0.1 throughout all PEC solar cell experiments.

3.1.4 LIGHT SOURCE

A tungsten-halogen lamp is one of the most convenient light sources for simulating solar radiation in a laboratory. It consists of coil filament of tungsten mounted between two electrodes. The radiation characteristics of one sq. cm area black body and tungsten are shown in Fig.3.2a (curves A and B) at 3000 K. This illustrates that for the same amount of visible radiation tungsten radiates only 76% as much as the total radiation from a black body at the same temperature. Only a relatively small percentage of the total radiation from an incandescent source is in the visible region of the spectrum. As the temperature of a tungsten filament is raised, the intensity of radiation in the visible increases more rapidly than that at longer infrared wavelengths.
Fig. 3.1 PEC Cell.

Fig. 3.2a Comparison of spectral distribution of radiation emitted from (A) black body, (B) tungsten (both at 3000 K).

Fig. 3.2b Spectral distribution of radiation (i) solar AM 0 and AM 1, (ii) tungsten-halogen.
The advantage of tungsten-halogen lamps over the usual incandescent lamps include excellent lumen maintenance and compactness. The source can also be described as providing a whiter light (i.e. higher colour temperature) as well as having longer life at a given light intensity. There is relatively more ultraviolet radiation from tungsten-halogen lamps than from ordinary tungsten lamps due to higher filament temperature as well as due to the transparent quartz envelope. Iodine is the halogen generally used in these lamps for ensuring longer life. This is taking advantage of the formation of a tungsten-halogen compound which dissociates at high temperatures to redeposit tungsten on the filament. The regenerative cycle starts with tungsten being evaporated off the filament operating at incandescence.

The spectral distributions of the radiant flux from a tungsten halogen lamp at 3400 K is shown in Fig.3.2b. The maximum intensity occurs at $\lambda = 0.62 \ \mu m$ which is different from an ordinary tungsten source. The spectrum also matches better the solar spectrum for AM1 illumination. The present experiments were conducted with a 1.5 kW tungsten-halogen light source (Thorn Lighting, U. K.). The heat generated due to the lamp was dissipated by circulating water filter. The output light was focused onto the PEC cell under investigation. The intensity of radiation which was measured by a calibrated meter consisting of Si solar cell (Surya-Mapi) was maintained at 100 mW.cm$^{-2}$ at the sample position.
3.1.5 CHEMOMECHANICAL POLISHING AND SURFACE MODIFICATION OF PHOTOELECTRODES:

The n-GaAs wafers used in the present investigations were cut into small specimens using a diamond saw crystal cutter (South Bay Technology, U. S. A.). The area of the samples varied from a minimum of 3x3 mm$^2$ to a maximum of 8x8 mm$^2$. While cutting, the diamond wheel damaged the surface to a certain depth. To remove the damage and to prepare smooth and shiny mirror finish surfaces, the following steps were found essential:

1) Lapping
2) Polishing
3) Etching

Lapping of the specimens was done using 1000 mesh carborundum on glass and then on Rodel polishing pads (Rodel Production Corpn., Arizona, U. S. A.). After about half an hour of polishing, a shiny surface was produced. Final polishing was done using fine alumina (50 µm) suspensions (Geologists India). Specimens were then thoroughly washed with triple distilled water followed by acetone, trichloroethylene (TCE) and methanol. Final mirror-finish polishing was obtained using Rodel polishing pads or soft velvet cloths impregnated with methanol and 0.01-0.1% bromine solution. The samples were then etched in a solution of 1:1, 30% H$_2$O$_2$; H$_2$SO$_4$ for 30 sec following the reaction:

$$2\text{GaAs} + 8\text{H}_2\text{O}_2 \rightarrow 2\text{Ga(OH)}_3 + 2\text{As(OH)}_5$$

(3.1)

where Ga(OH)$_3$ and As(OH)$_5$ are soluble in H$_2$SO$_4$. The samples were then degreased by rinsing in triple distilled water, acetone, TCE and methanol respectively. Samples were boiled
in CCL₄ (carbon tetrachloride) to remove oxides before loading into coating unit for deposition of contact materials.

For surface modification the samples were first matte etched by repeated dipping in 1:1, 30% H₂O₂, H₂SO₄ without etchant convection and then dipped in a solution of 0.01 M RuCl₃ or Na₂S or (NH₄)₂Sₓ in 0.1 N HNO₃. Matte etching resulted in surface roughness which increased from 0.015 to 0.075 μm as measured by a Talysurf.

3.1.6 OHMIC CONTACT:

An ohmic contact is defined as a non-rectifying metal-semiconductor contact that has a negligible contact resistance (Rₑ) relative to the bulk resistance (Rₒ) or spreading resistance (Rᵇ) of the semiconductor. Ohmic contacts with low resistance are necessary for high performance in many III-V devices e.g. LEDs, lasers, Gunn-diodes and solar cells. For example the efficiency (η) of a solar cell is strongly influenced by series resistance i.e. contact resistance (Rₑ).

For a homogeneous contact of area A having uniform current density J, the contact resistance is simply

\[ Rₑ \approx \frac{rₑ}{A} \quad (3.2) \]

where \( rₑ \) is the specific contact resistance given by

\[ rₑ \approx (\frac{\partial V}{\partial J})^{-1} \Big|_{V=0} \quad (3.3) \]

and the measured resistance (R) = \( Rₑ + Rᵇ + Rₒ \) \quad (3.4)

where \( Rₒ = 0.05 \) Ω, \( Rᵇ < 0.12Rₑ \). In case of a PEC cell \( Rₒ \) includes the bulk resistance of the sample, the electrolyte
resistance and the resistance offered by the overpotential at S-E interface.

Alloyed ohmic contacts to GaAs have been reported by many workers [1-4]. Various types of ohmic contacts on GaAs used prior to 1985 have been reviewed by G. Y. Robinson [5]. It was found that (Au-Ge-Ni) (88:10:2) alloy forms a lowest resistance contacts to n-GaAs and an alloy of Au-Zn (98:2) is best for p-GaAs.

The Au-Ge (88:12) alloy was thermally evaporated by resistive heating onto n-GaAs in a vacuum system (Hind High Vacuum, Bangalore) at 5x10⁻⁶ Torr pressure. The contacts were deposited at the back of the sample in the form of circular dots by using metal masks. These were then annealed in Ar:H₂ (volume ratio 3:1) at 450 °C for 3 min.

In the second method thermally evaporated (90:10) In-Au alloy was used which was annealed at 300 °C in Ar:H₂ for 3 min. for ohmic contacts to n-GaAs. The specific contact resistance \( r_c \) was measured by a modified four-point method as suggested by Kuphal [6]. Four equidistant contacts a, b, c and d were arranged on a straight line, ideally on an infinite plane of infinitesimal thickness. The current \( I_{ad} \) was applied between points a and d and the voltage \( V_{bc} \) between points b, c and \( V_{ab} \) between points a, b were measured. For contact 'a' of area A, one finds

\[
\rho_c = \frac{A}{I} \left[ V_{ab} - V_{bc} \left( \frac{\ln \left( \frac{3s}{2D} \right) - 0.5}{2\ln 2} \right) \right]
\]

(3.5)

where \( s \) is the spacing between two neighbouring contacts and \( D \) is the contact diameter. The following conditions were
maintained: i) $D \ll d$ i.e. no distortion of the potential by contacts $b$ and $c$ and ii) layer thickness $W \ll d$ i.e. the current is uniform with depth.

$\rho_C$ was found to be $2.8 \times 10^{-3} \ \Omega \text{cm}^2$ for Au-Ge on n-GaAs and $4.1 \times 10^{-3} \ \Omega \text{cm}^2$ for In-Au on n-GaAs. The error estimated was less than 10%. The contacts showed good adhesion, smooth surface and high mechanical stability.

3.17 RESULTS AND DISCUSSION

RESULTS:

This section presents the PEC solar cell results using n-GaAs photoelectrodes before and after modification with the following cell specifications:

<table>
<thead>
<tr>
<th>Photoelectrodes:</th>
<th>Te doped (100) GaAs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Donor concentration ($N_D$):</td>
<td>$4.5 \times 10^{16} \ \text{cm}^{-3}$</td>
</tr>
<tr>
<td>Electron mobility ($\mu_n$):</td>
<td>$2990 \ \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$</td>
</tr>
<tr>
<td>Exposed area of photoelectrodes:</td>
<td>$(2 \times 2)-(5 \times 5) \ \text{mm}^2$</td>
</tr>
<tr>
<td>Redox electrolyte:</td>
<td>1.0 M KOH, 0.1 M Na$_2$Te/Na$_2$Te$_x$ or Na$_2$Se/Na$_2$Se$_x$ or Na$_2$S/Na$_2$S$_x$.</td>
</tr>
<tr>
<td>pH of electrolyte:</td>
<td>$13.0 \pm 0.1$</td>
</tr>
<tr>
<td>Conductivity of electrolyte:</td>
<td>(310-340) millimhos.</td>
</tr>
<tr>
<td>Counter Electrode (CE):</td>
<td>Graphite.</td>
</tr>
<tr>
<td>Intensity of illumination at the photoelectrode:</td>
<td>100 mW cm$^{-2}$.</td>
</tr>
</tbody>
</table>

High purity argon (IOLAR, India) was bubbled through the electrolyte before and during measurements to remove...
dissolved oxygen and to maintain an inert atmosphere. First, the solar cell characteristics were optimised for three redox electrolytes: $\text{Na}_2\text{Te}/\text{NaTe}_x$, $\text{Na}_2\text{Se}/\text{Na}_2\text{Se}_x$ and $\text{Na}_2\text{S}/\text{Na}_2\text{S}_x$. The redox levels of these three are known to be -0.90, -0.66 and -0.46 eV/NHE respectively [7]. So $\text{S}^{2-}/\text{S}_x^{2-}$ is expected to give highest $V_{\text{oc}}$. Instead it was observed that $\text{Te}^{2-}/\text{Te}_x^{2-}$ redox yielded highest $V_{\text{oc}}$ and $\eta$ followed by $\text{S}^{2-}/\text{S}_x^{2-}$ and $\text{Se}^{2-}/\text{Se}_x^{2-}$. J-V characteristics for $\text{Te}^{2-}/\text{Te}_x^{2-}$ was observed to be more stable than that for $\text{S}^{2-}/\text{S}_x^{2-}$ or $\text{Se}^{2-}/\text{Se}_x^{2-}$.

The effect of surface modification using $\text{Na}_2\text{Te}/\text{Na}_2\text{Te}_x$ redox was first investigated by studying dark (J-V) [Fig.3.3], C-V [Fig.3.4] and solar cell characteristics [Fig.3.5]. Dark J-V and C-V measurements were carried out using a Keithley (160 B, 177) DMM and a Boonton capacitance meter (72 B) at 1 MHz. For C-V measurements, the applied d.c. voltage across the junction was varied from -1 V to 2 V. The superimposed a.c. signal was 10 mV$_{\text{pp}}$. In plotting the photo I-V characteristics on an X-Y recorder, the dark component of the current was nulled by adjustment of the X-Y recorder.

Table-3.1 summarises the results obtained from these measurements. It is seen that $\text{Na}_2\text{S}$ modified n-GaAs showed highest $J_{\text{sc}}$ (22.0 mA.cm$^{-2}$), $(\text{NH}_4)_2\text{S}_x$ modified samples highest $V_{\text{oc}}$ (1.0 V) while $\text{RuCl}_3$ modified samples yielded highest FF (0.62) and $\eta$ (12.2). It is observed that the reverse saturation current density ($J_0$) decreased substantially on modification.
Fig. 3.3 InJ vs. V plot of n-GaAs photoanodes in KOH-Te\textsuperscript{2}/Te\textsuperscript{2}\textsuperscript{-} redox electrolyte.

Fig. 3.4 C\textsuperscript{2} vs. V plot at 1 MHz showing increased V\textsubscript{fb} on modification.

Fig. 3.5 Solar cell characteristics of n-GaAs photoanodes in 1.0 M KOH-0.1 M Na\textsubscript{2}Te/Na\textsubscript{2}Te\textsubscript{x} redox at 100 mW\cdot cm\textsuperscript{2}.
Table 3.1 Solar cell parameters of n-GaAs|KOH-Te²⁻/Te₂ system.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$</th>
<th>$V_{oc}$</th>
<th>FF</th>
<th>$\eta(%)$</th>
<th>$n$</th>
<th>$J_0$</th>
<th>$V_{fb}$</th>
<th>$L_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-GaAs</td>
<td>mA cm⁻²</td>
<td>V</td>
<td></td>
<td></td>
<td></td>
<td>A cm⁻²</td>
<td>V/Pt</td>
<td>µm</td>
</tr>
<tr>
<td>Unmod.</td>
<td>17.37</td>
<td>0.90</td>
<td>0.50</td>
<td>7.81</td>
<td>3.2</td>
<td>8.2$\times$10⁻⁵</td>
<td>-1.42</td>
<td>0.54</td>
</tr>
<tr>
<td>Na₂S</td>
<td>22.00</td>
<td>0.92</td>
<td>0.48</td>
<td>9.71</td>
<td>2.7</td>
<td>8.5$\times$10⁻⁶</td>
<td>-1.45</td>
<td>0.70</td>
</tr>
<tr>
<td>(NH₄)₂Sₓ</td>
<td>19.72</td>
<td>1.00</td>
<td>0.56</td>
<td>11.04</td>
<td>2.3</td>
<td>3.2$\times$10⁻⁶</td>
<td>-1.54</td>
<td>0.64</td>
</tr>
<tr>
<td>RuCl₃</td>
<td>20.30</td>
<td>0.97</td>
<td>0.62</td>
<td>12.20</td>
<td>1.8</td>
<td>3.4$\times$10⁻⁶</td>
<td>-1.50</td>
<td>0.66</td>
</tr>
</tbody>
</table>

The spectral response was studied using a Jarrell Ash monochromator whose output was calibrated using a silicon photodiode. The response curves shown in Fig.3.6 before and after modifications indicated increase of photocurrent output between $\lambda = (400-930)$ nm. It was found that $L_p$ increased from 0.54 µm to 0.68 µm as calculated using eqn 2.4 due to modification [Fig.3.7].

Sub-bandgap response involves the optical excitation of carriers from states within the bandgap to either band and subsequent transport of the majority carriers into the bulk. The carriers crossing the surface into the electrolyte is monitored. The states involved may be at the surface / interface or in the bulk within a minority carrier diffusion length from the surface. Sub-bandgap response of GaAs PEC cell increased between $\lambda = (930-950)$ nm due to RuCl₃ modification as evident from the Fig.3.6 shown on a magnified
Fig. 3.6 Spectral response of n-GaAs photoanodes in KOH-Te$^2^+/Te_x^2^-$ redox showing increased photoresponse on modification. Inset: Shows diminished sub-band gap response.

Fig. 3.7 Plot of $\eta q^4$ vs. $\alpha(\lambda)^{-1}$ showing increased diffusion length ($L_p$).
Fig. 3.8 Showing improved solar cell characteristics for smaller area samples.

Fig. 3.9 Absorption spectra of KOH - Te$^{2-}$/Te$^{2-}_x$ redox electrolyte.
The magnitude of response would depend on the density of states and also on the excitation mechanism. Since the density of bulk states is not expected to be dependent on redox potential or surface treatment, the results indicated the role played by surface states in determining the sub bandgap response.

For smaller area (2x2) mm$^2$ samples $J_{sc}$ values increased from 17.37 to 23.49 mA cm$^{-2}$ yielding $\eta = 14.1\%$ [Fig.3.8] due to better uniformity of the sample, lower shunting and $I^2R$ effect.

Optical absorption by the electrolyte is obviously undesirable and was examined by a Shimadzu UV/VISIBLE/NIR 3100 Spectrophotometer. A typical absorption spectra of freshly prepared KOH-Na$_2$Te/Na$_2$Te$^x$ redox solution is given in Fig.3.9 which showed more than 99% transparency over the visible spectrum (>350-900 nm).

**DISCUSSION:**

The ideality factors indicate that there is a high density of interface states of the GaAs-electrolyte interface. Although larger values of ideality factors are expected in S-E junctions, no satisfactory explanation has been forthcoming. Explanations of larger $n$ factors invoked [8] mechanisms such as internal field emission, generation-recombination, tunneling through space-charge layer and recombination through surface states at S-E interface. An ideality factor of 2 is known to indicate that the generation-recombination processes in the space-charge
region predominate over other current-transport mechanism in solid state p-n junction diodes [8]. Values of $n$ far in excess of 2 have also been reported by [9] for CdSe and GaAs PEC solar cells.

The variation of junction capacitance with voltage is shown in Fig.3.4. The linearity of Mott-Schottky plots suggest uniform distribution of ionised donors both shallow and deep within the space-charge layer. The extrapolation of the straight line onto the potential axis gave an intercept at $-1.42$ V/Pt (Table-3.1) for unmodified GaAs and is equal to the flat-band potential $V_{fb}$. From the inverse slope $N_D = 4.4 \times 10^{16}$ cm$^{-3}$ was obtained assuming static dielectric constant of GaAs to be 13.1. The higher values of $V_{fb}$ with modifications correspond to a larger band bending and lower surface recombination.

The results obtained can be explained with the help of an energy band diagram shown in Fig.3.10. On the basis of flat-band potential obtained by Mott-Schottky plots, the positions of $E_{CB}$ and $E_{VB}$ were determined for pH = 13 with $V_{oc} = 0.90$ V and $V_{fb} = -1.42$ V/Pt. The conduction band-edge and valence band-edge have energies $E_{CB} = -1.48$ eV and $E_{VB} = -0.05$ eV respectively. The location of the $Te^{2-}/Te^{2-}$ redox potential was determined to be $-0.52$ V/Pt using the relation $V_{oc} = V_{redox} - V_{fb}$. $V_{oc} = 1.0$ V is in agreement with the values reported earlier [10-11]. $V_{oc} = 1.0$ V for GaAs is rarely reached in perfectly grown solid state photovoltaic junctions.
Lewis et al. [10-11] observed $V_{oc}$ values for n-GaAs in ferrocene >0.85 V and $V_{oc}$ values for p-GaAs in the cobaltocene system of >0.75 V. They thus estimate $\phi_{Bn} + \phi_{Bp}$ >1.6 eV which is in excess of $E_g$ (1.43 eV) for GaAs. Additionally, the barrier height for n-GaAs in CH$_3$CN, based on $V_{oc}$ measurement, has been proposed to be in excess of 1.1 eV.

According to N. S. Lewis [12]

$$V_{oc}^{(max)} = (k T/q) \ln(J_{ph} N_p N_D N_{DL}/q D_p N_c N_v) + E_g/q$$

(3.6)

The calculated $V_{oc}^{(max)}$ = 0.95 V for unmodified and 0.96 V for Na$_2$S and RuCl$_3$ modified GaAs. Experimentally obtained $V_{oc}$ for RuCl$_3$ modified GaAs was 0.97 V higher than $V_{oc}^{(max)}$.

According to Shockley and Queisser [13] recombination centres and traps which present deviations from the electroneutrality may be responsible for the slight disagreement in $V_{oc}$ for RuCl$_3$ modified sample, since the interaction between charge carriers is not considered when Boltzmann statistics is applied.

The spectral response showed an increase at $\lambda$ = 400 nm when the absorption due to Te$^{2-}$/Te$_x^{2-}$ is only 1%. The maximum response occurred at 620 nm (2.0 eV) which is 0.57 eV higher than the band-gap of GaAs. The wavelength for maximum intensity shifted from 620 to 680 nm due to different types of modifications. The response had a cut-off at 850 nm corresponding to the energy of 1.45 eV. The nature of the spectral response i.e. the onset of response, the wavelength of maximum response and the cut-off etc all suggests that the observed photocurrent is mainly due to the light absorption.
Fig. 3.10 Energy scheme for n-GaAs in Te$^{2-}$/Te$^x$$^{2-}$ redox (pH = 13.0).

Vfb = -1.42 V/Pt
EcB = -1.36 V/Pt
VVB = 0.07 V/Pt
Eredox = -0.52 V/Pt

Fig. 3.11 Shows improved stability of Ru-modified GaAs electrodes, (a) photocurrent density Vs. time and (b) transient photo-response.
and e-h generation in GaAs. The increase in the area under the curves due to modifications is proportional to the increase in corresponding $J_{sc}$ values. For example in case of Na$_2$S-modified samples $J_{sc}$ [Fig.3.5] and spectral response [Fig.3.6] increased by 26%. Surface recombination, when most of the light is absorbed in the surface, is responsible for the fall in the short wavelength side. On the other hand diffusion of minority carriers holes generated inside the bulk and the depletion region is responsible for the fall in the higher wavelength side. Surface recombination velocity $S_r$ decreased from 5.0x10$^5$ cm.s$^{-1}$ (unmodified GaAs) to 2.1x10$^5$ cm.s$^{-1}$ (Na$_2$S modified GaAs).

Stability of the cell was examined by studying time dependence of photocurrent density. Typical plots for RuCl$_3$ modified GaAs are shown in Fig.3.11a. The photocurrent density remained constant at 20.3 mA.cm$^{-2}$ for 5 days and then decreased by 17.2% from the initial value in 8 days. For unmodified sample the photocurrent was stable for 3 days only after which it decreased by 40%. Dark J-V and C-V characteristics are reproducible over 15-20 days with the cells kept in dark whereas photo J-V characteristics are reproducible for 3-5 days.

The photocurrent was measured by chopping the light source (He-Ne laser) mechanically. Since the transient photocurrent response (measured across a resistor) for unmodified GaAs took only 0.7 ms compared to 0.9 ms for RuCl$_3$ modified sample [Fig.3.11b] to reach the dark current value.
after the light had been switched off, it can be concluded that the surface of unmodified GaAs must have a higher concentration of surface states. These surface states may decrease the lifetime of photogenerated carriers. Longer decay time may mean lower surface recombination. The amplitude of the photoresponse which was higher for RuCl₃ modified GaAs compared to untreated GaAs also indicated larger number of photogenerated carriers in the former case.

Impedance measurements using EG & G PAR Galvanostat/potentiostat were carried out to estimate electrical equivalent circuit of the semiconductor-liquid junction. This was done on GaAs photoelectrodes in dark and under illumination. These experiments showed greater stability of GaAs after surface modification.

From Table-3.2 it is seen that $R_s$ and $R_p$ decreased while $C_{dl}$ increased with illumination causing phase angle $\theta$ to become more capacitative ($\theta \to -90^\circ$). With different surface modifications, polarisation resistance $R_p$ was found to increase indicating higher stability (corrosion rate is inversely proportional to $R_p$ as discussed in chapter 2) e.g. $2.1 \times 10^2 \ \Omega \cdot \text{cm}^2$ (unmod.) to $4.2 \times 10^2 \ \Omega \cdot \text{cm}^2$ (Ru-modified GaAs). The GaAs photoelectrodes as expected showed less stability under illumination than in the dark.
Fig. 3.12 Impedance spectra of GaAs-KOH-Te$_2^+/Te_x^-$ PEC cells.
(a) Niquist or Cole-Cole plots, (b) Bode plots.
- Unmod. (dark), x-(NH$_4$)$_2$S$_x$ mod., △-RuCl$_3$ mod., ◦-Na$_2$S mod.,
- unmod. (20 mW·cm$^2$).
Table 3.2: $R_s$, $R_p$, and $C_{dl}$ of GaAs photoelectrodes in KOH-Na$_2$Te/Na$^+$Te$_x$ redox electrolyte from Impedance Spectroscopy.

<table>
<thead>
<tr>
<th>Sample Condition</th>
<th>$R_s$ $\Omega$.cm$^2$</th>
<th>$R_p$ $\Omega$.cm$^2$</th>
<th>$C_{dl}$ F.cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmod. dark</td>
<td>4.2</td>
<td>2.1x10$^2$</td>
<td>2.8x10$^{-8}$</td>
</tr>
<tr>
<td>RuCl$_3$-mod.</td>
<td>2.0</td>
<td>4.2x10$^2$</td>
<td>3.2x10$^{-8}$</td>
</tr>
<tr>
<td>Na$_2$S-mod.</td>
<td>2.7</td>
<td>3.7x10$^2$</td>
<td>3.5x10$^{-8}$</td>
</tr>
<tr>
<td>(NH$_4$)$_2$S$_x$-mod</td>
<td>2.9</td>
<td>3.0x10$^2$</td>
<td>3.8x10$^{-8}$</td>
</tr>
<tr>
<td>Unmod. 20 mW.cm$^{-2}$</td>
<td>1.9</td>
<td>6.5x10$^1$</td>
<td>9.3x10$^{-8}$</td>
</tr>
</tbody>
</table>

3.2 Au/GaAs SCHOTTKY DIODES:

INTRODUCTION:

In GaAs photoelectrochemical solar cells, it was found that $V_{oc}$ increased from 0.90 V to 0.97 V due to Ru surface modification together with an increase in $J_{sc}$ and FF to yield a conversion efficiency $\eta$ of 12-14%. In this section the effect of Ru surface modification on the properties of Au/n-GaAs Schottky barriers is examined. It was found that both the ideality factor $n$ and the reverse saturation current density $J_0$ decreased while the barrier height $\phi_B$ increased. Possible reasons for such behaviour are discussed.

3.2.1 DIODE FABRICATION:

(100) n-GaAs LEC grown single crystal samples were used with donor concentration $N_D = 4.5x10^{16}$ cm$^{-3}$ and mobility $\mu_n = 2990$ cm$^2$.V$^{-1}$.s$^{-1}$. The samples were cleaned to mirror-finish by Br$_2$-methanol and then etched in a solution of 11:30%
H$_2$O$_2$;H$_2$SO$_4$ followed by rinsing in deionised water. For surface modification the samples were first matte etched in the above solution without etchant convection and then dipped in a solution of 0.01 M RuCl$_3$ in 0.1 N HNO$_3$ for 1 min. For Schottky barrier fabrication, Au was thermally evaporated through a metal mask to a thickness of 0.79 μm on both unmodified and Ru-modified specimens. A guard ring electrode geometry was used with a 1.5 mm diameter central electrode and a 2.5 mm diameter guard ring. Thermally evaporated Au-In (weight ratio 10:90) annealed at 350 °C for 3 min in Ar:H$_2$ (volume ratio 10:1) was used as the ohmic contact.

3.2.2 RESULTS AND DISCUSSION:

RESULTS:

The J-V characteristics were measured between 108 K and 358 K from which lnJ versus V curves were obtained [Fig.3.13a & b]. The slope of each curve (forward bias) gave the ideality factor n and the intercept on the y-axis lnJ. The barrier height (φ$_{bn}$) and the Richardson constant A$^{**}$ were determined from the ln(J$_0$/T$^2$) versus 1/T plot [Fig.3.14]. Fig.3.15 shows the variation of n and φ$_{bn}$ with temperature. The Mott-Schottky curves for unmodified and modified samples are shown in Fig.3.16. Table–3.3 summarizes the results obtained from J-V and C-V measurements at room temperature. A significant result along with the increase in φ$_{bn}$ is the decrease of J$_0$ by two orders of magnitude due to Ruthenium surface modification.
Fig. 3.13 InJ vs. V plots at different temperatures (108–358 K) for a) unmodified; b) RuCl₃ modified Au/n-GaAs junction.
Fig. 3.14 \( \ln \left( \frac{J_0}{T^2} \right) \) vs. \( \frac{1}{T} \) plots giving \( A^* = 4.3 \times 10^{-2} \text{ cm}^{-2} \text{ K}^{-2} \) for unmodified (○), \( A^{**} = 3.6 \times 10^{-2} \text{ cm}^{-2} \text{ K}^{-2} \) for Ru-modified (△) samples.

Fig. 3.15 Ideality factor \( (n) \) vs. \( T \) and barrier height \( (\Phi_{Bn}) \) vs. \( T \) plots of Au/n-GaAs junctions.

Fig. 3.16 \( C_A^{-2} \) vs. \( V \) curves of Au/n-GaAs junctions at 300K showing \( V_j = 1.5 \text{ V}, N_D = 4.3 \times 10^{16} \text{ cm}^{-3} \) for unmodified sample (○) and \( V_j = 1.13 \text{ V}, N_D = 4.7 \times 10^{16} \text{ cm}^{-3} \) for Ru-modified samples (△).

Fig. 3.17 Band diagram of metal-semiconductor junctions at zero bias showing difference between \( \Phi_{Bn}(J-V) \) and \( \Phi_{Bn}(C-V) \).
Table 3.3 Summary of J-V and C-V data for Au/n-GaAs Schottky diode for unmodified, RuCl₃, Na₂S and (NH₄)₂Sₓ modified GaAs (303 K).

<table>
<thead>
<tr>
<th>Sample</th>
<th>J₀ (A cm⁻²)</th>
<th>n</th>
<th>A** (A cm⁻² K⁻²)</th>
<th>qΦ_Bn(J-V) (eV)</th>
<th>qΦ_Bn(C-V) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unmodified</td>
<td>2.1x10⁻⁸</td>
<td>1.34</td>
<td>4.3</td>
<td>0.80</td>
<td>1.14</td>
</tr>
<tr>
<td>Ru-mod.</td>
<td>1.5x10⁻¹⁰</td>
<td>1.16</td>
<td>3.6</td>
<td>0.92</td>
<td>1.22</td>
</tr>
<tr>
<td>Na₂S-mod.</td>
<td>3.6x10⁻¹⁰</td>
<td>1.20</td>
<td>3.5</td>
<td>0.89</td>
<td>1.20</td>
</tr>
<tr>
<td>(NH₄)₂Sₓ-mod.</td>
<td>1.3x10⁻¹⁰</td>
<td>1.19</td>
<td>3.6</td>
<td>0.92</td>
<td>1.30</td>
</tr>
</tbody>
</table>

DISCUSSIONS:

From the lnJ versus Vₚ plot [Fig.3.13] it is seen that lnJ is linearly proportional to qV/kT up to 0.4 V. ln(J₀/T²) versus 1/T is linear for higher temperatures (242-358 K) [Fig.3.14]. This indicates that the current transport mechanism follows Bethe's thermionic theory in the above temperature range and thermionic field emission at lower temperatures. At these temperatures (108-242 K) the leakage current dominated and the ideality factor n increased, indicating recombination-generation in the depletion region.

The ideality factor n was 1.34 for unmodified and 1.16 for Ru-modified samples at 300 K. It was found that n increased with decrease in temperature. A poor ideality factor can be due to a variety of reasons. Amongst them, the effect of tunneling at room temperature can be excluded.
because of low carrier density \( (4.5 \times 10^{16} \ \text{cm}^{-3}) \).

Generation-recombination is known to cause ideality factors greater than unity and also give rise to high reverse saturation current density \( J_0 \). The reduction of both \( n \) and \( J_0 \) indicates reduction of generation-recombination centres at the surface. For GaAs it is known that at 300 K the diffusion component of reverse saturation current density is \( 10^{-13} \ \text{A cm}^{-2} \) whereas the generation component is \( 10^{-9} \ \text{A cm}^{-2} \). The value of \( J_0 \) on unmodified surfaces indicates that the contribution is probably due to the latter process.

The value of the Richardson constant \( A^{**} \) was found to be [Fig.3.14] \( 4.3 \ \text{A cm}^{-2} \text{K}^{-2} \) for unmodified and \( 3.6 \ \text{A cm}^{-2} \text{K}^{-2} \) for Ru-modified samples, nearly the same as that reported by Ashok et al. [14]. An explanation of the lowering of \( A^{**} \) from the theoretical value of \( 8.6 \ \text{A cm}^{-2} \text{K}^{-2} \) for GaAs can be obtained [15] by taking into account the presence of a thin oxide layer of thickness \( \delta \) (Å) such that

\[
A^{**} = \frac{A^{** \ \text{theoretical}}}{\exp(-0.26\lambda_s^{1/2}/\delta)}
\]  

(3.7)

where \( \lambda_s \) is the mean barrier height of the oxide-semiconductor interface in eV. Taking \( \lambda_s \) to be 0.08 eV [14] for both types of samples, \( \delta \) is found to be 9.42 Å for the unmodified and 11.84 Å for Ru-modified surfaces.

From Table-3.3 it is seen that \( \phi_{Bn}^{(C-V)} \) is greater than \( \phi_{Bn}^{(J-V)} \) for both unmodified and modified samples. This can be explained by invoking a thin interfacial layer of thickness \( \delta \) which reduces [5, 16-17] the potential energy barrier under forward bias \( J-V \) measurements [Fig.3.17].
values of $\phi_{Bn}$ reported here are in good agreement with earlier reports [14]. Another explanation for $\phi_{Bn}(C-V) > \phi_{Bn}(J-V)$ is the lateral non-uniformity [18] of $\phi_{Bn}$ across the Au-GaAs interface due to surface roughness and variation in interfacial layer thickness. The average thickness variation is $10 \AA$.

In an earlier section for GaAs PEC system we have found that the sub bandgap response decreased together with a reduction in the surface recombination velocity from $5 \times 10^5$ to $2.4 \times 10^5$ cm.s$^{-1}$. The latter was inferred from a measured increase in the effective minority carrier diffusion length $L_p$ from 0.54 $\mu$m to 0.66 $\mu$m on Ru-modification. In the present study reduction in $n$ and $J_o$ indicated decrease in surface state density and partial unpinning of the Fermi level. Similar behaviour had been reported earlier for Au/InP Schottky barriers by Bose et al. [19]. It is thus found that the modification favourably alters the surface properties of GaAs which is evident in both electrolyte-semiconductor as well as metal-semiconductor systems. The results can be interpreted on the basis of reduction of surface state densities.

3.3 INTERPRETATION OF SURFACE MODIFICATION:

Based on experiments performed at temperatures in excess of 500 °C and using thermodynamic calculation Thurmond et al. [20] have derived the Ga-As-O ternary phase diagram as shown in Fig.3.18.
Using the thermodynamical phase diagrams, Schwartz [21] has analysed the oxides on III-V semiconductors. They have shown that the only stable phases that can exist in the thermodynamic equilibrium with GaAs are $Ga_2O_3$ and elemental As. This is evident by the presence of the tie line between $Ga_2O_3$ and GaAs in the ternary phase diagram. Similarly the absence of a tie line between $As_2O_3$ and GaAs shows that a reaction can occur between these two. Further, using the Gibb's free energy change ($\Delta G$) of these compounds, thermodynamics predicts that GaAs will reduce the $As_2O_3$ to form elemental As and $Ga_2O_3$ via the reaction (\(\Delta G\) in kcal/mol is given in parenthesis) [22],

$$As_2O_3 + 2GaAs \rightarrow Ga_2O_3 + 4As \quad (3.8)$$

$$(-137.9) \quad (-238)$$

The success of passivating technique depends on choosing a species that makes the surface repel approaching oxygen and
at the same time has a lower heat of oxide formation than \( \text{Ga}_2\text{O}_3 \) to take away oxygen from oxides. To satisfy the first requirement the chemical species should have strong chemisorption to occupy the active surface sites to prevent oxidation. \( \text{RuCl}_3 \) is more highly chemisorbed than \( (\text{NH}_4)_2\text{S}_x \) or \( \text{Na}_2\text{S} \) of the same concentration. Similarly hetero-valent \( \text{S} \) ions (valency 1 or 2) of \( (\text{NH}_4)_2\text{S}_x \) can form bond more easily than single-valent \( \text{S} \) ions (valency 2) of \( \text{Na}_2\text{S} \).

Improvement due to modification depends on the surface morphology and the distribution of the modifying ions; \( \text{Ru} \) multivalent from 0 to +8, \( \text{Cl}^{-1} \), \( (\text{NH}_4)^{+1} \), \( \text{S}^{-1,-2} \), and \( \text{Na}^{+1} \) at the interface. Best results were obtained with \( \text{RuCl}_3 \) treated \( \text{GaAs} \).

It has been reported that the \( (\text{NH}_4)_2\text{S}_x \) or \( \text{Na}_2\text{S} \) solutions are effective in eliminating the oxides of III-V semiconductors [23-31] forming a passivating sulfur layer, which prevents the surface from oxidising.

Using XPS Sandroff et al. [23] and Cowans et al. [28] observed As-S and S-S bonds while Spindt et al. [29] confirmed Ga-S bonds on sulfide treated \( \text{GaAs} \). Sugahara et al. [30] showed Ga-S, As-S and S-S bonds.

In case of \( \text{RuCl}_3 \), the growth of a passivating oxide layer \( \text{RuO}_2 \) [32] helps to reduce the interface state density and the surface recombination velocity, leading to increase in effective diffusion length by controlling hole capture. The effect of \( \text{Ru} \) was interpreted by Heller et al. as forming bonds with free As on the surface thus removing the
As-related bonds out of the band-gap. Bose et al. [33] showed that Ru modification of CdTe led to the growth of a thin interfacial layer of TeO₂ on both n & p CdTe which was responsible for surface passivation.

3.3.1 SCANNING ELECTRON MICROSCOPY

A significant contribution to the increase of J_sc is the increase of effective surface area on matte etching. Matte etching of (100) GaAs also produced (111) faces. Also a textured surface produces optical confinement allowing multiple reflection from the surface and hence decreasing the reflectivity of the material. It was observed that both matte etching and surface treatment were essential for the reported improvement.

3.3.2 CONTACT POTENTIAL DIFFERENCE (CPD)

The exact mechanism of surface modification however remains intriguing in view of the suggestion of Aspnes [34] that an alternate explanation may lie in the shift of the surface Fermi level. CPD measurements showed [Table-3.4] that the effect of chemical modification indeed alter the surface Fermi-level of GaAs.

Table-3.4: CPD results for modified GaAs surfaces.

<table>
<thead>
<tr>
<th>Surface condition</th>
<th>CPD (Volt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-GaAs</td>
</tr>
<tr>
<td>Unmodified</td>
<td>0.76</td>
</tr>
<tr>
<td>RuCl₃-modified</td>
<td>0.90</td>
</tr>
<tr>
<td>Na₂S-modified</td>
<td>0.86</td>
</tr>
<tr>
<td>(NH₄)₂Sₓ-modified</td>
<td>0.89</td>
</tr>
</tbody>
</table>
Fig. 3.19: SEM micrographs of modified GaAs.
The change in CPD given in Table-3.4 can obviously be used to derive the corresponding changes in barrier height say for Ru-modification using eqn.2.6. Assuming the work function of the gold reference electrode to be 5.10 eV and $\phi$ & $E_g$ of GaAs to be 4.07 eV and 1.43 eV respectively the barrier height ($\phi_{\text{En}}$) of n-GaAs was found to change from 0.82 eV to 0.96 eV. The CPD values were negative for p-type samples and decreased with the chemical modification.

Thus the CPD measurements demonstrate directly that i) the shift in surface Fermi-level does indeed occur, ii) it is in opposite directions for n and p-GaAs but such as to cause an increase in barrier height in both cases and iii) the magnitude of the shift is in fairly good agreement with the increase in $\phi_{\text{En}}$.

3.3.3 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

A chemisorbed ion may change the position of a surface state either by electrostatic interaction with the surface species or by forming a bond in which electrons are shared. So XPS was employed to elucidate the chemical nature of the GaAs surfaces subjected to different surface treatments. Mainly Ga 3d, As 3d and Ga 3s / S 2p were examined for unetched, etched and treated surfaces [Fig.3.20]. The binding energies (BE) and full width at half-maximum (FWHM) are given in Table-3.5.
Fig. 3.20 X-ray photo electron spectra for (i) Ga 3d, (ii) As 3d, (iii) Ga 3s/S 2p, and (iv) Ru 3d for (a) unetched, (b) etched, (c) RuCl₃ modified, (d) Na₂S modified, and (e) (NH₄)₂Sₓ modified GaAs.
### Table 3.5: XPS data for GaAs with different surface treatment.

<table>
<thead>
<tr>
<th>GaAs</th>
<th>BE(eV)</th>
<th>FWHM(eV)</th>
<th>Compounds</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unetched</td>
<td>21.8</td>
<td>2.10</td>
<td>Ga$_2$O$_3$</td>
<td>[27]</td>
</tr>
<tr>
<td>Etched</td>
<td>19.4</td>
<td>1.90</td>
<td>Ga</td>
<td>[28]</td>
</tr>
<tr>
<td>Ga 3d RuCl$_3$-mod.</td>
<td>21.0</td>
<td>2.50</td>
<td>Ga-Ru</td>
<td></td>
</tr>
<tr>
<td>Na$_2$S-mod.</td>
<td>20.0</td>
<td>2.34</td>
<td>Ga-S</td>
<td>[29]</td>
</tr>
<tr>
<td>($\text{NH}_4$)$_2$S$_x$-mod.</td>
<td>20.3</td>
<td>2.43</td>
<td>Ga-S</td>
<td>[29]</td>
</tr>
<tr>
<td>Unetched</td>
<td>44.9</td>
<td>2.20</td>
<td>As$_2$O$_3$</td>
<td>[30/27]</td>
</tr>
<tr>
<td>Etched</td>
<td>41.5</td>
<td>2.00</td>
<td>As</td>
<td></td>
</tr>
<tr>
<td>As 3d RuCl$_3$-mod.</td>
<td>43.3</td>
<td>2.40</td>
<td>As-Ru</td>
<td></td>
</tr>
<tr>
<td>Na$_2$S-mod.</td>
<td>42.1</td>
<td>2.30</td>
<td>As$^0$/AsS</td>
<td>[28/30]</td>
</tr>
<tr>
<td>($\text{NH}_4$)$_2$S$_x$-mod.</td>
<td>42.1</td>
<td>2.41</td>
<td>As$^0$/AsS</td>
<td>[28/30]</td>
</tr>
<tr>
<td>Unetched</td>
<td>160.2</td>
<td>3.40</td>
<td>Ga$_2$O$_3$</td>
<td>[31]</td>
</tr>
<tr>
<td>Etched</td>
<td>159.9</td>
<td>3.15</td>
<td>Ga</td>
<td></td>
</tr>
<tr>
<td>Ga 3s/ Na$_2$S-mod.</td>
<td>161.1</td>
<td>3.84</td>
<td>Ga-S</td>
<td>[28]</td>
</tr>
<tr>
<td>S 2p: ($\text{NH}_4$)$_2$S$_x$-mod.</td>
<td>162.0</td>
<td>3.60</td>
<td>Ga-S</td>
<td>[28]</td>
</tr>
</tbody>
</table>

'--' indicates bond formation.

The Ga 3d spectra [Fig.3.20.i] for the unetched sample (a) exhibited a peak at 21.8 eV attributable to Ga$_2$O$_3$. The peak at 19.4 eV for the etched samples (b) is considered to be due to Ga bonded in GaAs. The peak at 21.0 eV for the RuCl$_3$ treated sample (c) may indicate formation of bonds...
between Ga and Ru. The XPS peaks at 20.0 eV and 20.3 eV for Ga 3d peak confirmed sulfide formation of Ga atoms on the surface. The FWHMs increased from 2.10 eV for unmodified to 2.50 eV for RuCl₃ modified samples. Weling et al. also observed increased FWHMs after sulfide modification of GaAs.

Fig.3.20.ii shows As 3d spectra for different surface treated GaAs. The lower energy peak observed at 41.5 eV for etched sample is separated from the peak at 44.9 eV attributable to As₂O₃ for unetched sample. The peak due to As₂O₃ was not detected for treated samples even after 2-3 weeks aging.

Formation of S bonds with Ga is distinct from Fig.3.20.iii. The peaks at 161.1 eV and 162 eV respectively for Na₂S and (NH₄)₂Sₓ treated samples are indicative of sulfide bonds with the surface Ga atoms. Formation of S-O bond was detected by a peak at 170.0 eV for Na₂S modified sample. This S-O bonding may reduce oxides of GaAs surface. A XPS peak at 31.4 eV attributable to Na was also detected.

Fig.3.20.iv shows Ru peaks at 279.2 eV and 284.0 eV. Poor resolution coupled with C 1s peak prevented determination of the chemical state of Ruthenium.

Throughout the XPS study of GaAs it was found that both Ga-Ru / Ga-S and As-Ru / As-S bonds were formed on the as treated surfaces. This result is similar to that of Sugahara et al [30]. The reduction in the oxide content of the surface was confirmed by comparing the XPS peaks for unmodified and etched samples. Reduction of oxides and bond formation of the host atoms with the modifying ions are responsible for passivating the GaAs surface.
REFERENCES: