JOURNAL OF MATERIALS SCIENCE 30 (1995) 5031–5035

Schottky barrier height enhancement on n-$In_{0.53}Ga_{0.47}As$ by $(NH_4)_2S_x$ surface treatment

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$(NH_4)_2S_x$ surface treatment was found to increase the barrier height (ϕ_{Bn}) for Au/$In_{0.53}Ga_{0.47}As$ Schottky junctions from 0.26 eV to 0.58 eV at 300 K as determined from Richardson plots. The ideality factor n thus decreased from 2.7 to 1.6 and the reverse saturation current density J_o from 9.4 A cm^{-2} to 3.4×10^{-5} A cm^{-2}. The values of the effective Richardson constant were also evaluated. The chemical state of $In_{0.53}Ga_{0.47}As$ surfaces before and after $(NH_4)_2S_x$ modification, examined by X-ray photoelectron spectroscopy (XPS), indicated bond formation of S with In, Ga and As.

1. Introduction

The ternary compound $In_{0.53}Ga_{0.47}As$, lattice matched to InP, is one of the most promising materials for high speed electronic and optoelectronic devices because of its high electron mobility and a direct bandgap (E_g) of 0.75 eV at 300 K. This makes $In_{0.53}Ga_{0.47}As$ suitable for fibre optic detectors operating between 1.3 and 1.55 μm. For many devices such as metal–semiconductor field effect transistors (MESFETs) and metal–semiconductor–metal (MSM) photodetectors, it is necessary to achieve a high Schottky barrier height. Conventional Schottky diodes prepared on n-$In_{0.53}Ga_{0.47}As$ exhibit barrier heights lower than 0.3 eV for Au, Al, Ti or Nb [1–3]. The ideality factor n and the reverse saturation current density J_o are also relatively high.

Efforts to improve effective Schottky barrier height of $In_{0.53}Ga_{0.47}As$ have been mostly based on the incorporation of a thin interfacial layer between $In_{0.53}Ga_{0.47}As$ and the metal. The interfacial layers used so far are (1) insulating oxide layers [4–5], (2) counterdoped p^+ $In_{0.53}Ga_{0.47}As$ space charge layers [6–7] and higher band-gap semiconductors such as InP [8], InAlAs [9], GaAs [7] and AlGaAs [10].

Recently studies on $(NH_4)_2S_x$, Na_2S and plasma treated $In_{0.53}Ga_{0.47}As$ surfaces have been reported [11–13]. Suemasu *et al.* [11] found that the combination of surface treatment with $(NH_4)_2S_x$ followed by heating at 450 °C in pure hydrogen before metallorganic vapour phase epitaxy (MOVPE) growth was effective in improving the I–V characteristics of n-$In_{0.53}Ga_{0.47}As$/i-InP/n-$In_{0.53}Ga_{0.47}As$ tunnel diodes. Yablonovitch *et al.* [12] showed that both $Na_2S \cdot H_2O$ and NaOH treatment yielded very low surface recombination velocities (20 cm s^{-1}) at the InP/n-$In_{0.53}Ga_{0.47}As$ interfaces.

This paper describes significant enhancement of the barrier height of Au Schottky junctions formed on $(NH_4)_2S_x$ treated n-$In_{0.53}Ga_{0.47}As$. The electrical behaviour of junctions was examined by current–voltage (J–V) characteristics at different temperatures and capacitance–voltage (C–V) measurements at 1 MHz. The surfaces of the $(NH_4)_2S_x$ treated n-$In_{0.53}Ga_{0.47}As$ were analysed using X-ray photoelectron spectroscopy (XPS) to obtain physicochemical information.

2. Experimental procedure

2.1. Schottky diode preparation

The experiments were carried out using n-$In_{0.53}Ga_{0.47}As$ ($N_D = 4.5 \times 10^{16}$ cm^{-3}), epilayers of thickness 5 μm grown on (1 0 0) oriented n-InP by the liquid phase epitaxial (LPE) method. Ohmic contact on n-$In_{0.53}Ga_{0.47}As$ was made by thermally evaporated Au–Ge alloy followed by annealing at 300 °C in argon for 1 min. For surface modification the samples were first cleaned in $Br_2:CH_3OH$ (1:1000) and then dipped in a solution of 0.01 M $(NH_4)_2S_x$ in 0.1 N HNO_3 for 10 min. The samples were then washed in deionized water, dried and immediately loaded into a vacuum chamber. For Schottky barrier fabrication Au was thermally evaporated by resistive heating through a metal mask to form a circular contact of 0.6 mm diameter and thickness 0.50 μm.

2.2. Schottky diode characterization

The J–V characteristics of Schottky barriers on n-$In_{0.53}Ga_{0.47}As$ with low carrier concentration (N_D) can be described by the thermionic emission equation [14]

$$J = J_0[\exp(qV/nkT) - 1] \quad (1)$$

where k is Boltzmann constant, T is absolute temperature and the reverse saturation current density J_o (current density extrapolated to zero bias) can be expressed as

$$J_0 = A^{**}T^2\exp(-q\phi_{Bn}/kT) \quad (2)$$

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Equations 1 and 2 can be used to evaluate the Schottky barrier height $\phi_{Bn}{}^{J-V}$. Here V is the bias voltage, n is the ideality factor ($= (q/kT)(\delta V/\delta \ln J)$ for $V \gg 3kT/q$) and A^{**} the effective Richardson constant. A^{**}(theoretical) $= 120\, m_e/m_o = 4.92\ \mathrm{A\,cm^{-2}\,K^{-2}}$ was assumed for n-$In_{0.53}Ga_{0.47}As$ for an electron effective mass (m_e) of $0.041\, m_o$ (free electron mass). A second method of determining Schottky barrier height is the measurement of J–V characteristics at different temperatures and using a plot of $\ln(J_o/T^2)$ as a function of reciprocal temperature. The barrier height $\phi_{Bn}{}^{J-T}$ was obtained from the slope of this dependence according to Equation 2 and the effective Richardson constant (A^{**}) from the intercept on the y-axis.

The barrier height was also estimated by use of the following Mott–Schottky relation

$$C_A^{-2} = (2/q\varepsilon_o\varepsilon_s N_D)(V + V_i) \quad (3)$$

and

$$\phi_{Bn}{}^{C-V} = V_i + V_n + kT/q \quad (4)$$

where V_i is the built-in voltage equal to intercept on the V-axis of C_A^{-2} versus V and $qV_n = E_C - E_F = 0.06\ \mathrm{eV}$ which was calculated from the doping concentration [14]; ε_0 and ε_s are dielectric constant of free space and relative dielectric constant of semiconductor respectively, C_A is the depletion capacitance of Schottky barrier, and E_C, E_F are the conduction band and Fermi level energies.

3. Results

From the J–V characteristics measured between 100 and 350 K the $\ln J$ versus V curves were obtained (Figs 1 and 2). The slope of each curve gave the ideality factor (n) and the intercept on the y-axis $\ln J_o$. The barrier height $\phi_{Bn}{}^{J-T}$ and A^{**} were determined from the $\ln(J_o/T^2)$ versus $1/T$ plot (Fig. 3). Fig. 4 shows the variation of n and ϕ_{Bn} with temperature. The Mott–Schottky curves for unmodified and $(NH_4)_2S_x$ modified samples are shown in Fig. 5. Table I summarizes the results obtained from J–V and C–V measurements at room temperature.

4. Discussion

The barrier height of 0.28 eV for unmodified $In_{0.53}Ga_{0.47}As$ increased to 0.60 eV for the $(NH_4)_2S_x$ treated sample. The reverse saturation current density J_o decreased by five orders of magnitude from $9.4\ \mathrm{A\,cm^{-2}}$ to $3.7 \times 10^{-5}\ \mathrm{A\,cm^{-2}}$ (Table I). The reduction of both n and J_o indicates reduction of generation–recombination centres at the surfaces. For $In_{0.53}Ga_{0.47}As$ it is calculated that at 300 K the diffusion component of the reverse saturation current density $J_d = q(D_p/\tau_p)^{1/2}(N_i^2/N_D)$ is $3.0 \times 10^{-8}\ \mathrm{A\,cm^{-2}}$ whereas the depletion layer generation component $J_g = (qN_iW/\tau_p)$ is $1.4 \times 10^{-4}\ \mathrm{A\,cm^{-2}}$ using the parameters: hole diffusion coefficient $D_p = 2.7\ \mathrm{cm^2\,s^{-1}}$ for mobility $\mu_p = 106\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$, life-time $\tau_p = 9.9 \times 10^{-9}\ \mathrm{s}$, intrinsic carrier concentration $N_i = 7.18 \times 10^{11}\ \mathrm{cm^{-3}}$, donor concentration $N_D = 4.5 \times 10^{16}\ \mathrm{cm^{-3}}$ and depletion layer width $W = 1.2 \times 10^{-5}\ \mathrm{cm}$ for

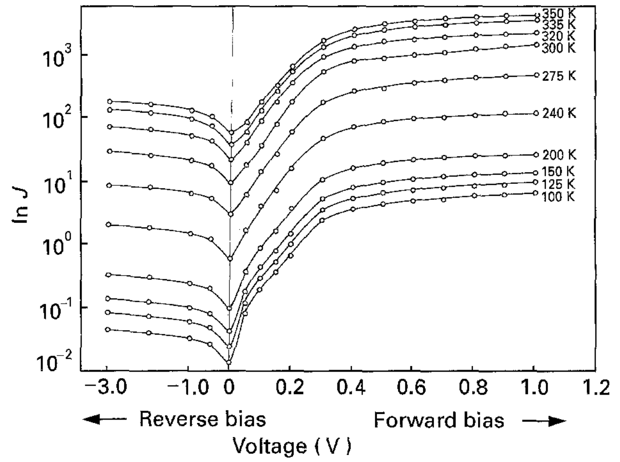

Figure 1 $\ln J$ versus V plots at different temperatures (100–350 K) for unmodified Au/n-$In_{0.53}Ga_{0.47}As$ junction.

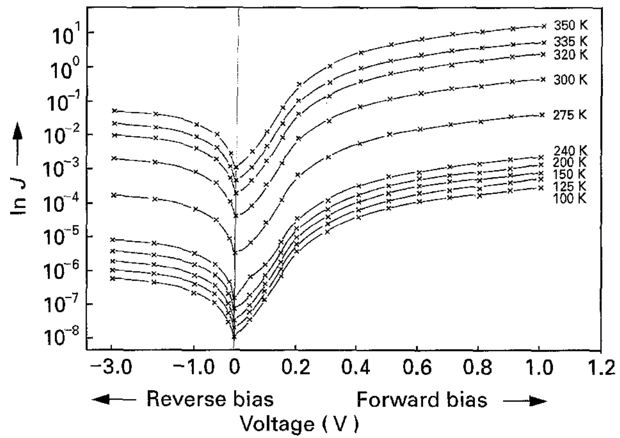

Figure 2 $\ln J$ versus V plots at different temperatures (100–350 K) for $(NH_4)_2S_x$ modified Au/n-$In_{0.53}Ga_{0.47}As$.

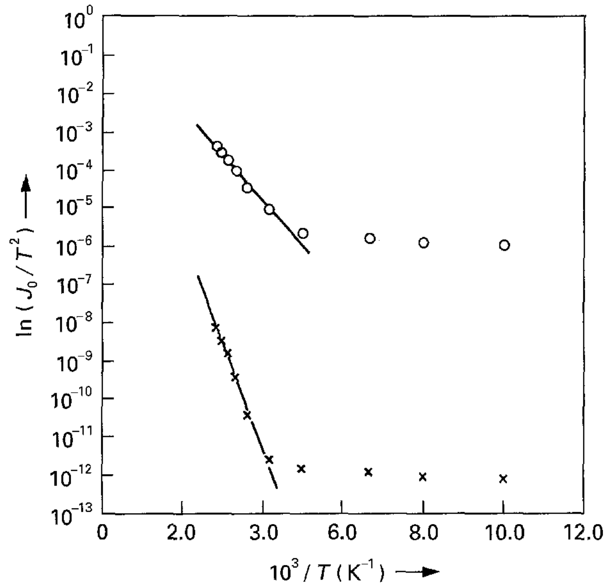

Figure 3 $\ln(J_o/T^2)$ versus $1000/T$ plots giving $A^{**} = 2.3\ \mathrm{A\,cm^{-2}\,K^{-2}}$ for unmodified (O) and $A^{**} = 2.0\ \mathrm{A\,cm^{-2}\,K^{-2}}$ for $(NH_4)_2S_x$ modified (×) samples.

$V_i = 0.58\ \mathrm{eV}$. The value of J_o on modified surfaces ($3.7 \times 10^{-5}\ \mathrm{A\,cm^{-2}}$) indicates that the contribution is mainly due to the latter process excluding the tunnelling owing to low carrier concentration. For $V_i = 0.26\ \mathrm{eV}$, J_g is only $9.8 \times 10^{-5}\ \mathrm{A\,cm^{-2}}$. So surface

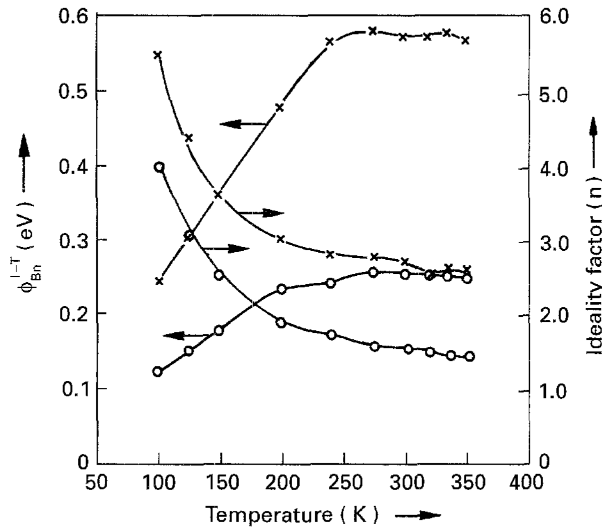

Figure 4 Ideality factor (n) versus T and barrier height ϕ_{Bn} versus T plots of Au/n-$In_{0.53}Ga_{0.47}As$ junctions. (O) unmodified; (×) $(NH_4)_2S_x$ modified.

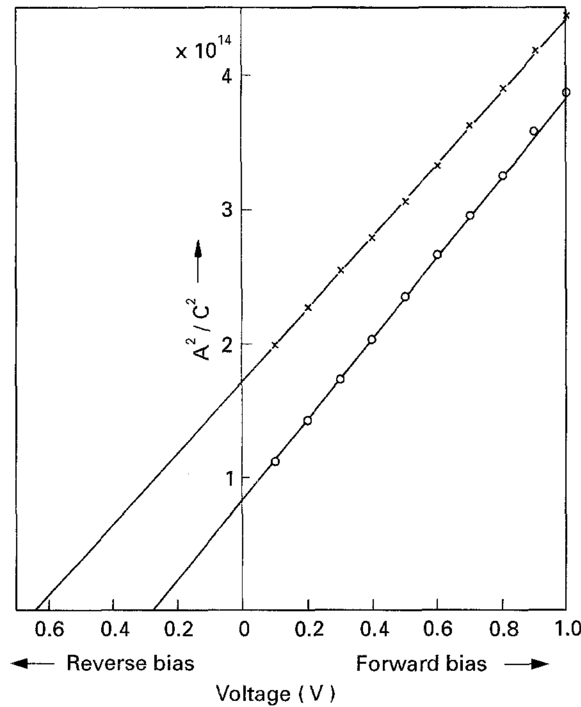

Figure 5 C_A^{-2} versus V curves of Au/n-$In_{0.53}Ga_{0.47}As$ junctions at 303 K showing $V_i = 0.28$ V, $N_D = 4.1 \times 10^{16}$ cm^{-3} for unmodified sample (O) and $V_i = 0.63$ V, $N_D = 4.6 \times 10^{16}$ cm^{-3} for $(NH_4)_2S_x$ modified (×) samples.

leakage dominates for unmodified surfaces where $J_o = 9.4$ A cm^{-2}. This value can be compared with the earlier reports [2] of $J_o = 45.9$ A cm^{-2}.

Richardson plots between 100 and 350 K gave the barriers ($\phi_{Bn}{}^{J-T}$) 0.26 eV for unmodified and 0.58 eV for $(NH_4)_2S_x$ treated diodes. $\phi_{Bn}{}^{J-T}$ (0.26 eV) compares favourably with the 0.23 eV deduced by Kajiyama *et al.* [1] and $\phi_{Bn}{}^{C-V} = 0.34$ eV with the 0.3 eV by Morkoc *et al.* [3]. The barrier height of 0.58 eV for the $(NH_4)_2S_x$ treated junctions is very close to the value 0.59 eV, expected for the ideal junction, for which the barrier height is given by the difference between Au work function (5.1 eV) and the electron affinity of the $In_{0.53}Ga_{0.47}As$ (4.51 eV). The value of $q\phi_{Bn}$ due to modification can be compared with those of refs [7, 12, 13]. Loualiche [4] obtained $q\phi_{Bn} = 0.65$ eV (from J–V) with ideality factor $n = 1.1$ and $J_o = 8.0 \times 10^{-6}$ A cm^{-2} for Au/$In_{0.53}Ga_{0.47}As$ by producing native oxides on n-$In_{0.53}Ga_{0.47}As$. Sugino *et al.* [13] obtained 0.70 eV (from J–V) and 0.55 eV from Richardson plot on n-$In_{0.53}Ga_{0.47}As$ treated with phosphine plasma. Kordos *et al.* [7] reported extremely low $J_o = 5.8 \times 10^{-6}$ A cm^{-2}, an ideality factor $n = 1.12$ and $\phi_{Bn} = 0.63$–0.68 eV for Nb/n-$In_{0.53}Ga_{0.47}As$ structures with a counterdoped p^+-layer.

It has been shown in previous studies on photoelectrochemical solar cells that $(NH_4)_2S_x$ surface modification of n-$In_{0.53}Ga_{0.47}As$ increased the conversion efficiency from 7.5 to 9.5% [15]. Spectral response measurements confirmed that such surface treatments increased the minority carrier hole diffusion length (L_p) of $In_{0.53}Ga_{0.47}As$ from 1.65 to 1.85 μm due to decrease in surface recombination velocity S from 9.3×10^3 to 2.4×10^3 cm s^{-1}. The contact potential difference (CPD) measured with respect to gold electrode was 0.42 eV for unmodified and 0.70 eV for modified $In_{0.53}Ga_{0.47}As$. Hence $\Delta V_{CPD} = 0.28$ eV which is in good agreement with the $\Delta\phi_{Bn} = 0.30$ eV.

The barrier heights obtained from C–V characteristics were 0.34 eV for unmodified and 0.69 eV for modified samples. Higher $\phi_{Bn}{}^{C-V}$ than $\phi_{Bn}{}^{J-V}$ can be explained by invoking (1) the thin interfacial layer oxide or sulphide which reduces the potential energy barrier under forward bias J–V measurements and (2) the charging and recharging effect of interface states during C–V measurements [16]. The free carrier concentration (4.3–4.6×10^{16}) determined from C–V measurements at room temperature was cm^{-3} in agreement with the Hall effect.

4.1. XPS study of surface modification

Of the components in $In_{0.53}Ga_{0.47}As$, Ga is more prone to oxidation than In or As as shown by the Gibb's free energy change (ΔG) . The presence of O_2 causes oxidation of $In_{0.53}Ga_{0.47}As$ to Ga_2O_3 ($\Delta G = -238.6$ kcal mol^{-1}, $E_g = 4.4$ eV), In_2O_3 ($\Delta G = -198.55$ kcal mol^{-1}, $E_g = 2.6$ eV) and As_2O_3

TABLE I Summary of J–V and C–V data for Au/n-$In_{0.53}Ga_{0.47}As$ Schottky diode at 300 K

Sample n-$In_{0.53}Ga_{0.47}As$	J_0 (A cm^{-2})	n	$q\phi_{Bn}{}^{J-V}$ (eV)	A^{**} [a] (A cm^{-2} K^{-2})	$q\phi_{Bn}{}^{J-T}$ (eV)	$q\phi_{Bn}{}^{C-V}$ (eV)
Untreated	9.4×10^0	2.7	0.28	2.3	0.26	0.34
$(NH_4)_2S_x$ treated	3.7×10^{-5}	1.6	0.60	2.0	0.58	0.69

[a] $A^{**} = 4.92$ A cm^{-2} K^{-2} was used for $q\phi_{Bn}{}^{J-V}$.

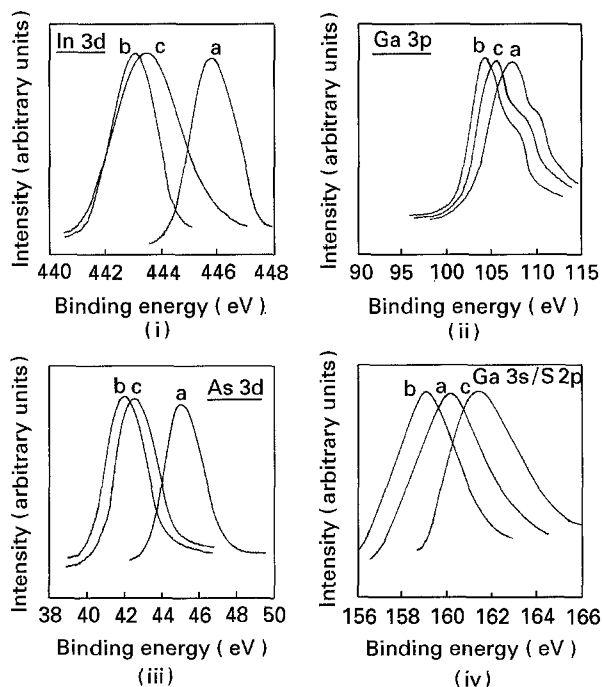

Figure 6 X-ray photoelectron spectra for (i) In 3d, (ii) Ga 3p, (iii) As 3d and (iv) Ga 3s/S 2p for (a) unetched, (b) etched and (c) $(NH_4)_2S_x$ modified $In_{0.53}Ga_{0.47}As$.

($\Delta G = -137.91$ kcal mol^{-1}, $E_g = 4.0$ eV) where the values of E_g give the oxide band-gaps [17]. Oxides formed by moist air exposure are usually non-stoichiometric. Earlier reports [18] of XPS on $In_{0.53}Ga_{0.47}As$ revealed a Ga-deficient surface and the segregation of elemental As. The dangling bonds or the incomplete bonds of As and/or Ga or In atoms in these oxides and elemental As are the cause of the interface states which increases in amount with oxidation. These oxides must be removed from the surface so that the sulphide ions can react with the virgin surface.

In the present studies Br_2-methanol etching was used to remove native oxides, after which the samples were dipped in the $(NH_4)_2S_x$ solution forming a passivating sulphur layer which prevents the surface from oxidizing. Considering the heat of formation of binary compounds (In–S > Ga–S > S–S > As–S), sulphur atoms are expected to form bonds mostly with In and then Ga.

XPS measurements were carried out to investigate the surface chemistry of sulphide-passivated and air-exposed $In_{0.53}Ga_{0.47}As$ as well as the corresponding etched surface. In Fig. 6 are presented the XPS spectra of (i) In 3d, (ii) Ga 3p, (iii) As 3d and (iv) Ga 3s/S 2p, observed at each step of the sample treatment. A special problem in characterizing the $In_{0.53}Ga_{0.47}As$ surface by XPS is due to the overlap of the In 4d peak at 16.0 eV with the Ga 3d peak at 18.0 eV. Therefore the Ga 3p doublet (104 eV, 108 eV) was used.

Curves (a) in Fig. 6 show the spectra from an unetched surface covered with the native oxides. This is the classical oxidation behaviour of $In_{0.53}Ga_{0.47}As$ surface, which presents oxidised In, Ga and As contributions respectively. Curves (b) show the spectra of the etched surface. This is the initial surface of $In_{0.53}Ga_{0.47}As$ sample subjected to $(NH_4)_2S_x$ treatment. Curves (c) describe the spectra obtained after $(NH_4)_2S_x$ treatment and a typical air exposure of 10–20 min before loading into the ultrahigh vacuum measurement chamber for XPS. The chemical shifts as well as binding energies (BE) and full width at half-maximum (FWHM) are given in Table II.

The As 3d spectra for the unetched sample had a strong peak at 45.0 eV attributable to As_2O_3. The peak at 41.0 eV due to As in $In_{0.53}Ga_{0.47}As$ was absent. However a peak at 42.0 eV indicated segregated elemental arsenic (As^{o}) [20]. The removal of oxides is seen by noting the absence of the 45.0 eV peak in the etched samples as well as the samples treated with $(NH_4)_2S_x$. The peak at 42.5 eV in the sulphide-treated samples can be reasonably attributed to AsS phase [20], because the binding energy of arsenic (As^{3+}) in As_2S_3 is 43.5 eV. The peak due to As_2O_3 did not appear for the treated samples even after two weeks' ageing.

In 3d and Ga (3s, 3p) spectra showed peaks corresponding to In_2O_3 or Ga_2O_3 for the unetched samples. The treated samples showed the presence of In and Ga sulphides (Table II).

TABLE II XPS data for $In_{0.53}Ga_{0.47}As$

$In_{0.53}Ga_{0.47}As$		BE (eV)	FWHM (eV)	ΔE (eV)	Compounds	Ref.
In 3d	Unetched	445.8	2.0	2.8	In_2O_3	
	Etched	443.0	1.8	0.0	In	[18]
	$(NH_4)_2S_x$	443.5	2.6	0.5	In_2S_3	[19]
Ga 3p	Unetched	106.8 110.0	6.0	2.3	Ga_2O_3	
	Etched	104.5 108.0	5.3	0.0	Ga	[18]
	$(NH_4)_2S_x$	105.4 109.0	6.0	0.9	Ga_2S_3	
As 3d	Unetched	45.0	2.3	3.0	As_2O_3	
	Etched	42.0	1.9	0.0	As	[20]
	$(NH_4)_2S_x$	42.5	2.4	0.5	AsS	
Ga 3s/ S 2p	Unetched	160.0	3.3	1.0	Ga_2O_3	
	Etched	159.0	3.0	0.0	Ga	[20]
	$(NH_4)S_x$	161.2	3.4	2.2	Ga_2S_3	

The S 2p/Ga 3s spectra were more helpful in studying the incorporation of S. The peak at 161.2 eV suggested that sulphide treatment shifted the Ga 3s peak (159.0 eV) indicating the formation of Ga_2S_3. No separate peak at 164 eV or 165 eV for elemental S was detected. Also no S–O bonding which would be at about 168 eV was observed. From the values of ΔE for sulphides (Table II), it is difficult to determine the dominant phase. However for the compounds In_2S_3, Ga_2S_3 and AsS it is evident that S atoms are bonded more strongly to In and Ga than As.

Thus the reduction in oxide content of the $In_{0.53}Ga_{0.47}As$ surface atoms together with the formation of sulphide phase was responsible for improved Schottky properties.

5. Conclusions

Passivation of $In_{0.53}Ga_{0.47}As$ surface by $(NH_4)_2S_x$ has been studied using XPS and Schottky diode characteristics. A significant enhancement of the barrier height from 0.26 eV to 0.58 eV was observed for Schottky junctions formed on $(NH_4)_2S_x$-treated n-$In_{0.53}Ga_{0.47}As$. XPS studies showed that this was due to replacement of native oxides by strong S bonds with the surface atoms.

Acknowledgements

The authors gratefully acknowledge the Department of Non-Conventional Energy Sources (DNES), India for project support.

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Received 11 January 1994
and accepted 22 March 1995