

Electrodeposition kinetics of gallium arsenide

S MOORTHY BABU, L DURAI, R DHANASEKARAN and
P RAMASAMY

Crystal Growth Centre, Anna University, Madras 600 025, India

Abstract. A kinetic model has been developed for the electrodeposition of GaAs from solution containing reducible ions of both constituents and is based on the generalised Butler–Volmer equation. The effect of hydrogen ion concentration and activities of ions on the total current density is studied. Voltammograms corresponding to various values of hydrogen ion concentration and activities of ions are constructed by the computer simulation technique.

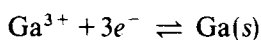
Keywords. Electrodeposition of GaAs; voltammogram; kinetic model.

1. Introduction

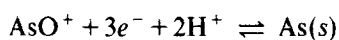
Gallium arsenide is considered to be an important semiconducting material for thin film photovoltaic and photoelectrochemical cells, lasers and in many other optoelectronic devices (Parkinson *et al* 1978, 1979; Kohl and Bard 1979; Hollan *et al* 1980; Noufi and Tench 1980; Horowitz *et al* 1984). It is a direct gap semiconductor with a room temperature energy gap of 1.43 eV and can readily be prepared in both *n*- and *p*-type form. Existing techniques for the preparation of GaAs material are complicated and expensive. Electrodeposition is a simple and inexpensive technique to prepare thin films and is successfully employed to deposit GaAs thin films (Chandra and Khare 1987). In the present work, an attempt has been made to understand the kinetics involved in the process of electrodeposition of GaAs. A simple kinetic model for the electrodeposition of GaAs from solutions containing reducible ions of both constituents has been developed and is based upon the Butler–Volmer equation (Engelken and Vandoren 1985; Durai *et al* 1987). Voltammograms have been simulated for various values of pH and activities of constituent species. The dependence of total current density on applied potential for various values of pH and activity of the species in the electrolyte has been investigated.

2. Electrochemical reactions

The primary cathode reactions and the corresponding potential versus the normal hydrogen electrode are



$$E_{\text{Ga}} = E_{\text{Ga}}^{\circ} + \frac{RT}{3F} \ln \left(\frac{a_{\text{Ga}^{3+}}}{a_{\text{Ga}}} \right) = -0.529 + 0.0197 \log \left(\frac{a_{\text{Ga}^{3+}}}{a_{\text{Ga}}} \right), \quad (1)$$



$$E_{\text{As}} = E_{\text{As}}^{\circ} + \frac{RT}{3F} \ln \left(\frac{a_{\text{AsO}^+} a_{\text{H}^+}^2}{a_{\text{As}}} \right),$$

$$E_{As} = 0.254 + 0.0394 \text{ pH} + 0.0197 \log \left(\frac{a_{AsO^+}}{a_{As}} \right), \quad (2)$$

where $a_{Ga^{3+}}$, a_{AsO^+} are the activities of Ga and AsO ions in the solution and a_{Ga} , a_{As} are the activities of the respective atoms in the electrodeposits. When the electrode potential is increased from a negative value the deposition of gallium will take place first followed by the arsenic deposition. This is due to the fact that the electrode potential of arsenic being more positive than that of gallium. In the present investigation, conditions corresponding to the simultaneous deposition of Ga and As are determined. The formation of GaAs can be written as



and occur at a bare inert (graphite, platinum etc.) potentiostat-controlled cathode immersed in an aqueous solution (pH=1.0) containing GaCl_3 and As_2O_3 . The cathodic current densities are described by a generalised Butler-Volmer equation (Antropov 1972).

$$\begin{aligned} j_i = & \frac{z_i F k_i^0 \left\{ \left[\prod_m a_{rm} \gamma_m \right] (\bar{\alpha}_i + \bar{\alpha}_i) \exp \left[\frac{-z_i F \bar{\alpha}_i}{RT} (E - E_i^0) \right] \right.}{1 + \frac{z_i F k_i^0}{j_{c,i}} \left[\prod_m a_{rm} \gamma_m \right] (\bar{\alpha}_i + \bar{\alpha}_i)} \dots \\ & \left. - \frac{\left[\prod_m a_{pm} \gamma_m \right] (\bar{\alpha}_i + \bar{\alpha}_i) \exp \left[\frac{z_i F \bar{\alpha}_i}{RT} (E - E_i^0) \right] \right\}}{\exp \left[\frac{-z_i F \bar{\alpha}_i}{RT} (E - E_i^0) \right]} \dots \quad (4) \end{aligned}$$

In the above equation all the quantities (defined in the list of symbols at the end) are either known or can be derived from the data available in the literature except the term activity of the reactants and products. These activities can be calculated using the thermodynamic considerations. Regular associated solution (RAS) model (Jordan 1970) has been applied to determine the activity coefficients of Ga, As and GaAs components. Accordingly the activity coefficients are given by

$$\begin{aligned} \gamma_{Ga} &= \exp \left(\frac{\beta}{RT} x_2^2 \right), \\ \gamma_{As} &= \exp \left(\frac{\beta}{RT} x_1^2 \right), \end{aligned} \quad (5)$$

$$\text{and } \gamma_{GaAs} = \exp \left(\frac{\beta(1 - 4x_1x_2)}{RT} \right),$$

where β is a compound dependent constant and x_1 , x_2 are the mole fractions of Ga and As respectively. Now the effective mole fraction equilibrium constant K' is defined as

$$K' = \frac{x_{GaAs}}{x_{Ga} x_{As}} = \exp \left(\frac{\beta'}{RT} \right), \quad (6)$$

where $\beta' = \beta/2 - \Delta G^\circ$.

The conservation of atoms in the electrode leads to

$$n_{\text{GaAs}} = n_1 - n_{\text{Ga}} = n_2 - n_{\text{As}}, \quad (7)$$

where n_1 , n_2 are the number of Ga and As atoms deposited on the electrode and n_{Ga} , n_{As} and n_{GaAs} the number of Ga and As atoms and GaAs molecules after the association.

Now

$$K' = \frac{x_{\text{GaAs}}}{x_{\text{Ga}}x_{\text{As}}} = \frac{n_{\text{GaAs}}}{n_{\text{Ga}}n_{\text{As}}}(n_{\text{Ga}} + n_{\text{As}} + n_{\text{GaAs}}). \quad (8)$$

Combining (7) and (8), it can be shown that

$$n_1 = n_{\text{Ga}} + \frac{K' n_{\text{Ga}}(n_2 + n_{\text{Ga}} - n_1)}{n_{\text{Ga}} + n_2}. \quad (9)$$

Solving for the permissible, positive values of n_{Ga} , we have

$$n_{\text{Ga}} = \frac{n_1 - n_2}{2} + \left[\left(\frac{n_1 - n_2}{2} \right)^2 + \frac{n_1 - n_2}{1 + K'} \right]^{0.5}. \quad (10)$$

From equation

$$x_{\text{Ga}} = \frac{n_{\text{Ga}}}{n_{\text{Ga}} + n_{\text{As}} + n_{\text{GaAs}}}$$

we can write

$$x_{\text{Ga}} = \frac{1}{1 + 1/(n_{\text{Ga}}/n_2)}. \quad (11)$$

By defining

$$\frac{n_1}{n_2} = h = \frac{b_{\text{Ga}}j_{\text{Ga}}}{b_{\text{As}}j_{\text{As}}}, \quad [\text{where } b_i = 1/Z_i], \quad (12)$$

one obtains

$$\frac{n_{\text{Ga}}}{n_2} = \frac{h-1}{2} + \left[\left(\frac{h-1}{2} \right)^2 + \frac{h}{1+K'} \right]^{0.5}, \quad (13)$$

$$\text{defining } M = (h-1)/2 = \frac{j_{\text{Ga}}/j_{\text{As}}}{2} - 1, \quad (14)$$

and substituting this in x_{Ga} , γ_{Ga} and γ_{As} we have

$$x_{\text{Ga}} = \frac{M + \left[M^2 + \frac{2M+1}{1+K'} \right]^{0.5}}{M+1 + \left[M^2 + \frac{2M+1}{1+K'} \right]^{0.5}}, \quad (15)$$

$$\gamma_{\text{Ga}} = \exp \left[\frac{\beta}{RT} \left(\frac{1}{2M+2} \right)^2 \right], \quad (16)$$

and

$$\gamma_{\text{As}} = \exp \left[\frac{\beta}{RT} \left(\frac{2M+1}{2M+2} \right)^2 \right]. \quad (17)$$

Substituting the above terms into the individual Butler–Volmer equation we have

$$j_{\text{Ga}} = \frac{3Fk_{\text{Ga}}^0 \left\{ a_{\text{Ga}^{3+}}^{(\bar{\alpha}_{\text{Ga}} + \bar{\alpha}_{\text{Ga}})} \exp \left[\frac{-3F\bar{\alpha}_{\text{Ga}}}{RT} (E + 0.529) \right] - \exp \left[\frac{3F\bar{\alpha}_{\text{Ga}}}{RT} (E + 0.529) \right] \right\} \left[\exp \left[\frac{\beta}{RT} \left(\frac{1}{2M+2} \right)^2 \right] \left[\frac{M + \left[M^2 + \frac{2M+1}{1 + \exp(\beta'/RT)} \right]^{0.5}}{M+1 + \left[M^2 + \frac{2M+1}{1 + \exp(\beta'/RT)} \right]^{0.5}} \right] \right]^{(\bar{\alpha}_{\text{Ga}} + \bar{\alpha}_{\text{Ga}})}}{1 + \frac{3Fk_{\text{Ga}}^0}{j_{c,l_{\text{Ga}}}} a_{\text{Ga}^{3+}}^{(\bar{\alpha}_{\text{Ga}} + \bar{\alpha}_{\text{Ga}})} \exp \left[\frac{-3F\bar{\alpha}_{\text{Ga}}}{RT} (E + 0.529) \right]}$$

$$j_{\text{As}} = \frac{3Fk_{\text{As}}^0 \left[(a_{\text{AsO}^+} \cdot a_{\text{H}^+}^2)^{(\bar{\alpha}_{\text{As}} + \bar{\alpha}_{\text{As}})} \exp \left[\frac{-3F\bar{\alpha}_{\text{As}}}{RT} (E - 0.254) \right] - \exp \left[\frac{3F\bar{\alpha}_{\text{As}}}{RT} (E - 0.254) \right] \right] \left[\exp \left[\frac{\beta}{RT} \left(\frac{2M+1}{2M+2} \right)^2 \right] \left[\frac{-M + \left[M^2 + \frac{2M+1}{1 + \exp(\beta'/RT)} \right]^{0.5}}{M+1 + \left[M^2 + \frac{2M+1}{1 + \exp(\beta'/RT)} \right]^{0.5}} \right] \right]^{(\bar{\alpha}_{\text{As}} + \bar{\alpha}_{\text{As}})}}{1 + \frac{3Fk_{\text{As}}^0}{j_{c,l_{\text{As}}}} (a_{\text{AsO}^+} \cdot a_{\text{H}^+}^2)^{(\bar{\alpha}_{\text{As}} + \bar{\alpha}_{\text{As}})} \exp \left[\frac{-3F\bar{\alpha}_{\text{As}}}{RT} (E - 0.254) \right]}$$

From the above equations it is apparent that all the individual current densities are functions of deposition potential, activities of ions and the temperature. Computer simulation technique has been adopted to calculate the current densities for various values of constant M at a particular potential and then finding the exact current densities for which (14) is satisfied. Similar procedure has been followed to calculate the current densities for all the potentials chosen for the system. From these calculated values voltammograms have been constructed.

3. Results and discussion

Figure 1 shows the plot of calculated total current density as a function of applied potential for various values of hydrogen ion concentration (pH = 0.5 to 4.0). For pH = 0.5 as the potential is slowly decreased from a more positive value +0.4 to -0.6 V, the total current density value remains close to zero and starts increasing at 0.29 V and as the potential is further decreased the total current density increases

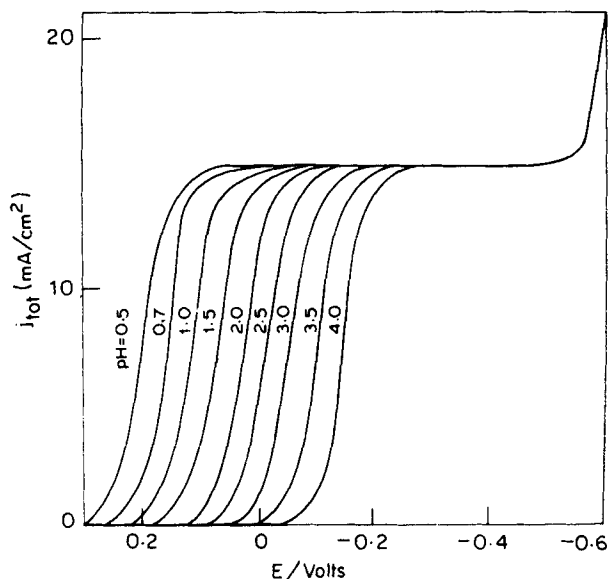


Figure 1. Plot of current density vs potential for various pH values.

and reaches the diffusion-limited current density (14 mA/cm^2) of arsenic j_c, l_{As} at the arsenic Nernst potential ($E_{\text{As}}^\circ = 0.254 \text{ V vs SHE}$). The total current density remains constant until $E = -0.35 \text{ V}$ and again increases as the potential is further reduced. For $\text{pH} = 1.0$ the total current density value starts increasing at a much negative potential and as the potential is decreased further the current density increases and approaches j_c, l_{As} . When $\text{pH} = 2.0$, the current density approaches the diffusion-limited current density of arsenic at a much reduced negative potential; after that it follows the earlier path. Now it is clear that the increase in pH decreases the current density due to arsenic and it approaches the diffusion-limited current density of arsenic at a further reduced potential.

Figure 2 shows the plot of total current density as a function of pH for various values of applied potential. From the curves, it is apparent that the total current density is well-influenced in pH ranges $0.5\text{--}2.0$ at $E = 0.1 \text{ V}$, $1.5\text{--}3.5$ at $E = 0 \text{ V}$, $2.0\text{--}4.0$ at $E = -0.1 \text{ V}$ and $3.0\text{--}4.5$ at $E = -0.2 \text{ V}$. The pH has no influence over the current density as the potential is decreased below -0.4 V . This abrupt increase in current density is accounted for the gallium deposition.

Figure 3 shows the plot of total current density as a function of applied potential for various values of arsenic activities. From the curves it is found that low arsenic activities lead to reduced values of current density. As the arsenic activity is increased the diffusion-limited current density of arsenic also increases proportionally and the point of inflection of the diffusion-limited current density shifts to the positive side of the applied potential.

4. Conclusion

A kinetic model for the electrodeposition of GaAs has been developed. From the results, it is concluded that in the process of electrodeposition of GaAs the pH has a

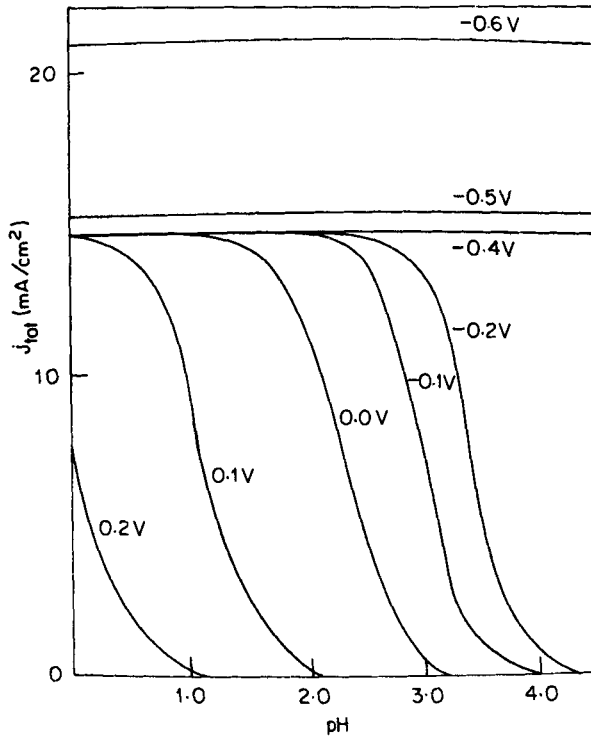


Figure 2. Plot of total current density vs pH for various values of applied potential.

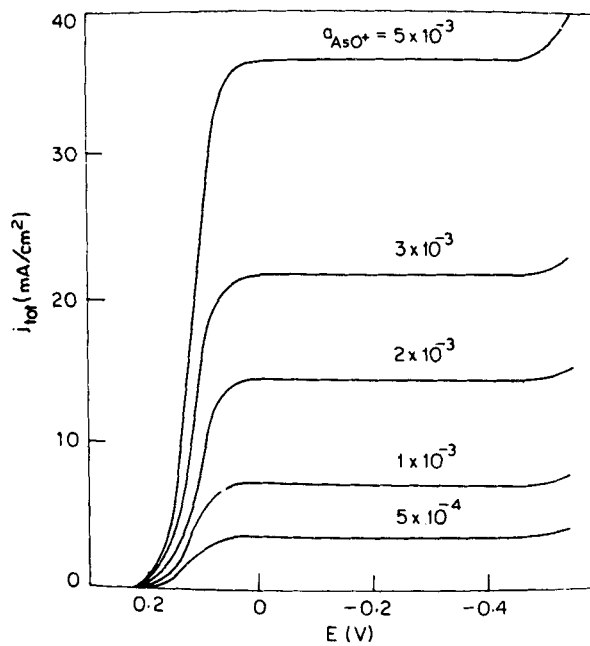


Figure 3. Plot of total current density vs potential for various values of arsenic activities.

strong effect upon the total current density at the positive side of the potential and that the arsenic deposition can be controlled by adjusting the pH of the electrolyte

solution. Also, the arsenic deposition is controlled by adjusting the activity of arsenic for simultaneous deposition of Ga and As.

List of symbols

a_i	= activity of constituent ion i ($i = \text{Ga}$ or As);
E	= applied potential;
F	= Faraday constant;
ΔG°	= free energy;
j_i	= current density of constituent i ;
j_c, j_i	= diffusion-limited current density of i ;
k_i	= fundamental rate constant;
p	= chemical product indicator;
R	= universal gas constant;
r	= chemical reactant indicator;
T	= temperature;
z_i	= number of electrons required to reduce ion i to the element;
α_i	= cathodic transfer coefficient of i ;
$\bar{\alpha}_i$	= anodic transfer coefficient of i ;
β	= solid state activity coefficient parameter;
β'	= $\beta/2 - \Delta G^\circ$;
γ	= stoichiometric coefficient.

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