ORIGINAL PAPER

Electrodeposition of gallium onto vitreous carbon

D. O. Flamini · S. B. Saidman · J. B. Bessone

Abstract Gallium electrodeposition onto vitreous carbon was studied in chloride solution using potentiostatic and potentiodynamic techniques. The morphology and composition of the deposits were analysed by SEM/EDX. The effects of solution pH, applied potential and the hydrodynamic conditions on the electroreduction process were investigated. Results indicate that the reduction to Ga^{+1} species takes place at the lower overpotentials, while at high overpotentials gallium deposition occurs through progressive nucleation and growth under diffusion control. The influence of the simultaneous hydrogen evolution reaction on the electrodeposition process is discussed.

Keywords Gallium · Vitreous carbon · Electrodeposition · Potentiostatic polarisation · Potentiodynamic polarisation

1 Introduction

Gallium is extracted primarily from the residue obtained during the processing of aluminium and secondly via electrolytic zinc by electrodeposition from very alkaline solutions. There are many applications of

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gallium in various fields: optoelectronics (e.g. LED's), telecommunications, aerospace, and many commercial and household items such as alloys, computers and DVD's [1]. On the other hand, it is known that gallium decreases the corrosion potential of Al sufficiently, favouring its application in primary batteries or as aluminium sacrificial anodes in sea water. In this case the active interface works at low pH [2, 3].

The electrochemical behaviour of pure Al in the presence of Ga^{3+} or when a particle of Ga was mechanically attached to Al in chloride and acetic acid solutions and in distilled water was studied in previous work [4]. This study was conducted to assess the Al activation produced by Ga on Al alloys used as sacrificial anodes. Although cathodic polarisation of Al in acidic solutions in the presence of Ga^{3+} was used as a method to generate surface conditions similar to those found in the Al–Ga alloy, in principle the study of Ga deposition onto Al is very complex due to the presence of the Al oxide.

Stock and worldwide prices for gallium are increasing [1]. Gallium recovery and purification is thus a worthwhile operation. Accordingly its electrochemical recovery (electrodeposition from alkaline solutions) calls for further attention. This process, as well as Al activation produced by Ga (low pH solutions), needs a better assessment, avoiding substrate interference. Therefore, the electrodeposition of Ga was studied onto an inert substrate, here vitreous carbon (VC). Thus, a better understanding of the influence of the electrolyte, the perturbation programme and the hydrodynamic conditions on the composition and morphology of the deposits can be obtained. In the present work, the electroreduction of Ga^{3+} onto VC was studied by potentiodynamic and potentiostatic

techniques and the deposits were characterised by SEM/EDX.

2 Experimental
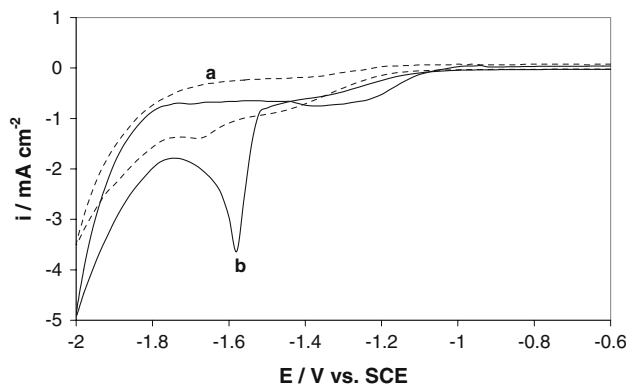
Disc electrodes of vitreous carbon rods embedded in a Teflon holder with an exposed area of 0.07 cm^2 were used as working electrodes. The discs were polished with 1000 emery paper followed by 1 μm and 0.3 μm grit alumina suspensions and then cleaned with triply distilled water. The auxiliary electrode was a large Pt sheet. Potentials were measured against a SCE reference electrode connected through a Luggin–Haber capillary tip. Electrolyte solutions were prepared from analytical grade chemicals. The pH was adjusted to 2.5 by means of HCl addition or to pH 12 or 13.3 by adding NaOH to the base 0.5 M NaCl solution.

Potentiodynamic and potentiostatic measurements were performed with a potentiostat-galvanostat PAR Model 273A. A dual stage ISI DS 130 SEM and an EDAX 9600 quantitative energy dispersive X-ray analyser were used to examine the electrode surface characteristics.

3 Results and discussion

### 3.1 Electrodeposition under stagnant conditions

Electrochemical aspects of the initial stages of Ga electrocrystallisation on VC were studied by means of cyclic voltammetry and choronoamperometry. First, the voltammetric technique was used to gain information about the general behaviour of the electrodeposition process. Figure 1 shows the potentiodynamic runs

in 0.5 M Cl$^-$, pH 2.5 solution in the presence of 0.01 M Ga^{3+} and that corresponding to the blank solution. The deposition of Ga occurs only at high overpotentials in acid chloride solution, considering the reversible potential corresponding to Ga/Ga^{3+} (–0.772 V$_{SCE}$) [5]. Once a particular potential is reached the deposition process produces a steep increase in current, followed by a rapid current decrease. The proton reduction that follows is known to have an overpotential of about 1.8 V on VC or metallic Ga [5]. After reaching –2 V, the electrode surface was examined and the presence of Ga was detected (Fig. 2).

Figure 1 also shows that no oxidation peak is observed when the potential sweep is reversed. No oxidation peak was obtained even if the potential was scanned to values corresponding to the oxygen evolution region while surface analysis indicates that the deposits of Ga remain at these high positive potentials.
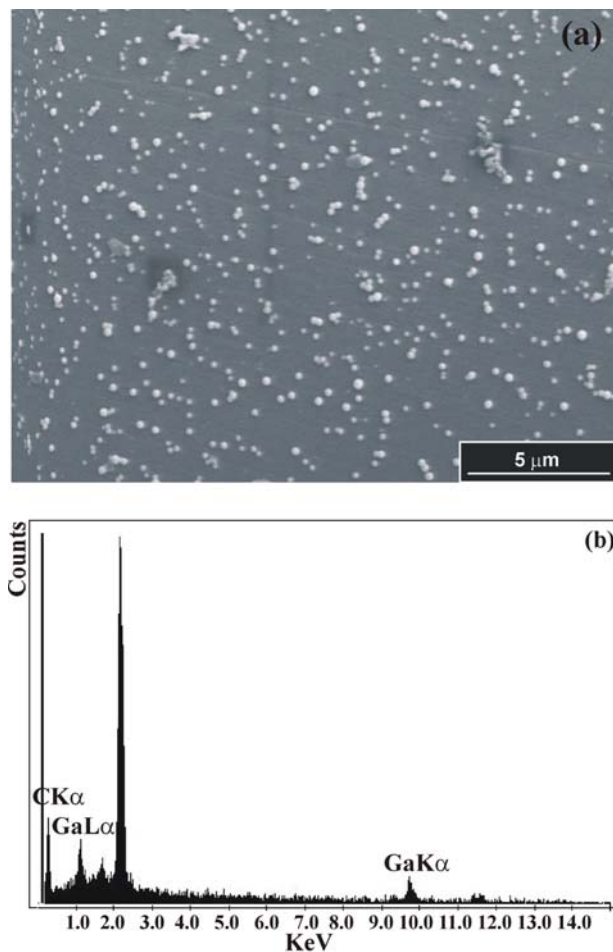

Fig. 2 (**a**) SEM micrograph showing the deposit obtained by removing the VC electrode at –2 V after potentiodynamic polarisation at 0.02 V s^{-1} in 0.5 M Cl$^-$ + 0.01 M Ga^{3+}, pH 2.5 solution. (**b**) EDX spectrum of the deposit shown in Fig. 2a

Fig. 1 Voltammetric responses of VC in 0.5 M Cl$^-$, pH 2.5 solution without Ga^{3+} (curve a) and with 0.01 M Ga^{3+} (curve b). Sweep rate: 0.02 V s^{-1}

In order to obtain more precise insight into the Ga deposition process involved in the potential range of the voltammetric peak shown in Fig. 1, potentiostatic transients were recorded on a fresh VC surface in 0.5 M Cl$^-$, pH 2.5 containing 0.01 M Ga^{3+}. Figure 3 presents the i/t transients at different potentials. After charging the double layer, a current increase to a maximum is observed for applied potentials more negative than –1.56 V. At longer times the current decayed following a linear relationship with $t^{-1/2}$. In the potential range studied a dependence of i vs. $t^{3/2}$ was found for the analysis of the increasing part of the transients which corresponds to progressive nucleation and growth under diffusion control (Fig. 4). The i vs. $t^{-1/2}$ plots obtained for the decaying part of the transients yield a straight line as expected for a diffusion limited process. The mean value of the diffusion coefficient obtained according to the Cottrell equation from the slope of the i vs. $t^{-1/2}$ lines is 1.92×10^{-5} cm^2 s^{-1}. A change in this coefficient is observed at the more negative applied potential (Table 1). This is due

Table 1 Diffusion coefficient obtained at different potentials according to the Cottrell equation from the slope of the i vs. $t^{-1/2}$ lines

| E/V	$D \times 10^5/\text{cm}^2\ \text{s}^{-1}$
–1.56	1.79
–1.58	1.88
–1.60	2.08
–1.62	1.47
–1.64	1.15
–1.66	0.89

to the fact that hydrogen evolution occurs simultaneously with electrodeposition, blocking the available sites for Ga nucleation. For applied potentials more positive than –1.56 V a monotonic current increase was registered. A SEM/EDX examination of the electrode surface after 120 s of polarisation at –1.60 V shows the formation of spherical deposits of Ga and the formation of agglomerates (Fig. 5). In contrast, when the applied potential is more positive than the peak potential (–1.58 V) no deposits are observed, even after a polarisation time of 15 min. The measured current in
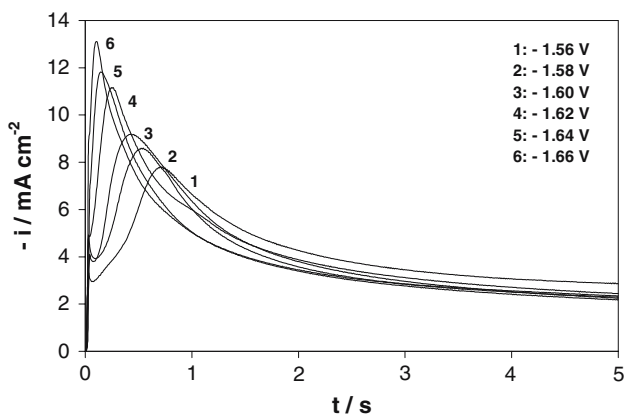
Fig. 3 Potentiostatic current transients for different potential values in 0.5 M Cl$^-$, pH 2.5 solution containing 0.01 M Ga^{3+}. $E_i = -0.8$ V
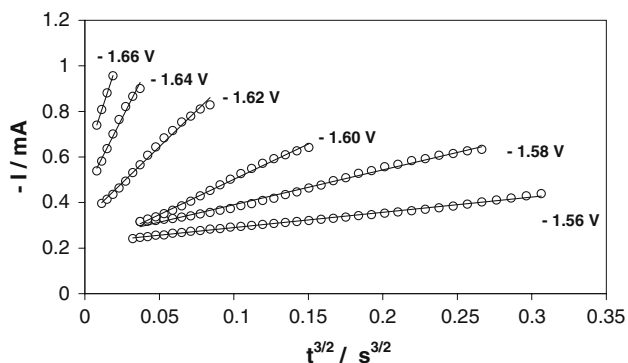
Fig. 4 I vs. $t^{3/2}$ plots obtained from the initial part of transients in 0.5 M Cl$^-$, pH 2.5 solution containing 0.01 M Ga^{3+}
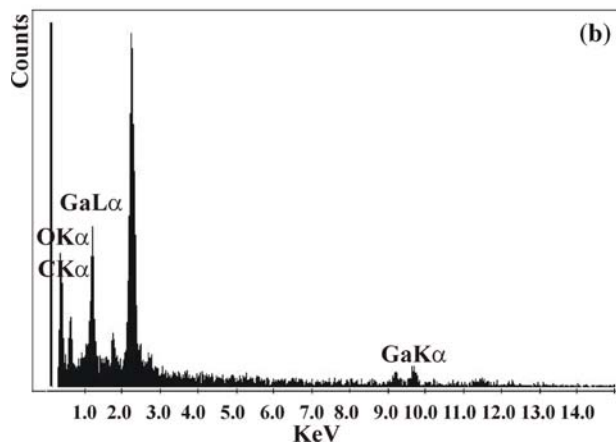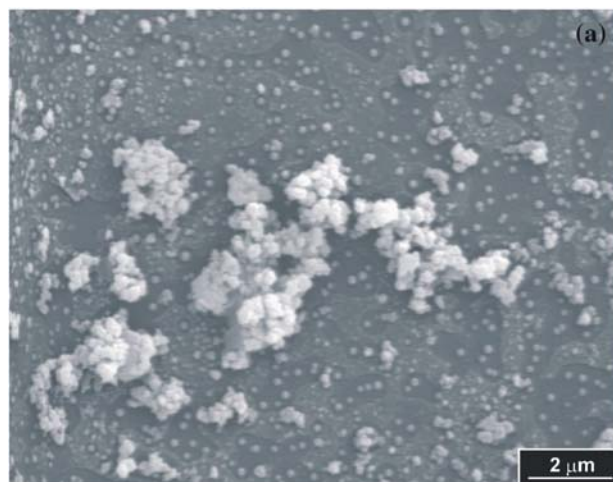
Fig. 5 (**a**) SEM micrograph of the deposit obtained in 0.5 M Cl$^-$ + 0.01 M Ga^{3+}, pH 2.5 solution after 120 s of polarisation at –1.60 V. (**b**) EDX spectrum of the deposit shown in Fig. 5a
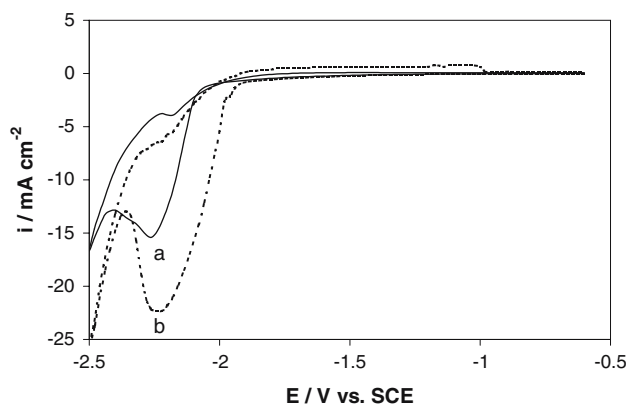
this potential range is due to the reduction of Ga^{3+} to Ga^{1+}, according to results obtained for the electrodeposition of Ga species in molten salt electrolyte [6]. Thus, the rising part of the cathodic current in Fig. 1, which has a very large slope, would be associated with the reduction to Ga^{1+} and at more negative potentials Ga nucleation initiates.

The absence of oxidation peaks in the positive scan indicates that deposited Ga is already oxidised. This oxidation is a consequence of the local pH variation caused by hydrogen evolution, especially at potentials more negative than –1.8 V. It was found that Ga_2O_3 may be formed even in acid chloride solutions with pH values higher than 1 [7]. The alkalinisation produced favours Ga_2O_3 precipitation on already deposited Ga and a passive state is attained. On the other hand the formed oxide film would offer resistance to the transport of Ga^{3+}.
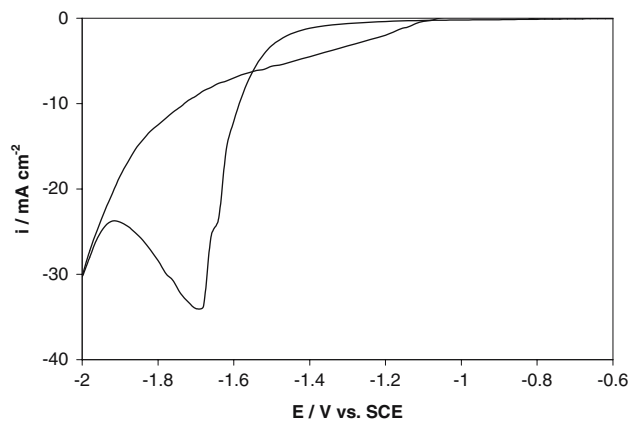
In order to study the effect of pH on Ga electrodeposition, the process was also analysed in alkaline media. At pH 12 a precipitate-free solution of Ga^{3+} was obtained as a result of the well known amphoteric nature of the Ga oxide. The hydrolysed species are of the type $HGaO_3^{2-}$ or GaO_2^- [8]. Clearly, the potential range where the hydrolysed Ga species are discharged does not match that found at pH 2.5 (Fig. 6). Thus, the high overvoltage for Ga deposition at pH 2.5 cannot be explained considering the reduction of hydrolysed species formed as a consequence of local alkalinisation due to hydrogen evolution.

3.2 Electrodeposition under non-stagnant conditions

Figure 7 shows the voltammetry performed on VC in 0.5 M Cl^-, pH 2.5 solution in the presence of 0.01 M

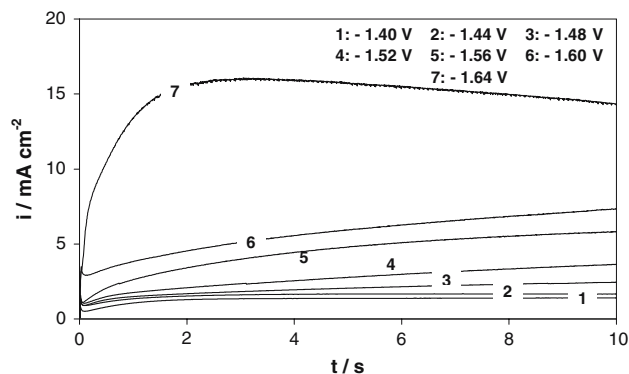**Fig. 7** Voltammetric responses of VC in 0.5 M Cl^-, pH 2.5 solution containing 0.01 M Ga^{3+} with electrode rotation (800 rpm). Sweep rate: 0.02 V s^{-1}

Ga^{3+} at a rotation speed of 800 rpm. The current peak initiates at the same potential as in stagnant solution, following the same shape but the charge involved is one order of magnitude higher than that obtained without rotation. Nevertheless a large amount of Ga is deposited. Comparing the potentiodynamics runs (with and without Ga^{3+} ions) hydrogen discharged is hindered when Ga^{3+} ions are present in solution as a chloride complex. According to a nucleation model for indium electrodeposition onto VC from acid chloride solution [9], chloride electrosorption initially facilitates electron transfer through an "electron bridge" and blocks active sites for proton reduction.

For potentials more positive than –1.64 V the i/t transients show that the current response increases monotonically with time (Fig. 8) and surface analysis does not reveal deposits. For –1.64 V, a significant current increase is observed and the shape of the transient again indicates that nucleation of electrode-

Fig. 6 Voltammetric responses of VC in 0.5 M Cl^- + 0.01 M Ga^{3+} solution at: pH 12 (curve a) and pH 13.3 (curve b). Sweep rate: 0.02 V s^{-1}

Fig. 8 Potentiostatic current transients for different potential values in 0.5 M Cl^-, pH 2.5 solution containing 0.01 M Ga^{3+} with electrode rotation (800 rpm). E_i = –0.8 V
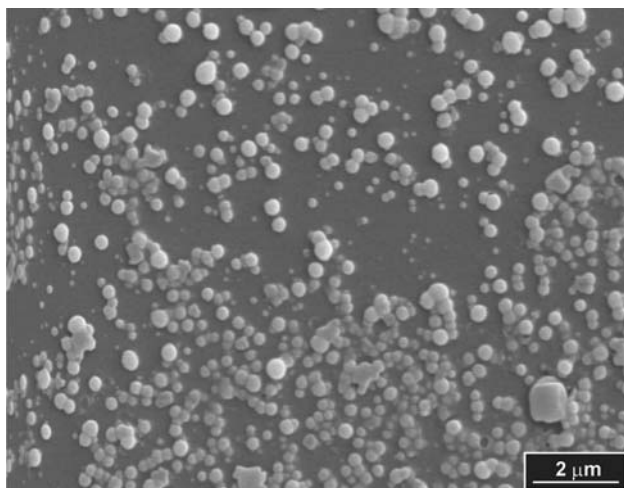
Fig. 9 SEM micrograph of the deposit obtained in 0.5 M Cl^- + 0.01 M Ga^{3+}, pH 2.5 solution after 120 s of polarisation at –1.64 V with electrode rotation

posited Ga is controlled by mass transfer of Ga^{3+}. A larger amount of deposited Ga was obtained under rotation (Fig. 9). There are at least two effects under non-stagnant conditions on the electrodeposition process. Forced convection overcomes the mass-transfer limitations and alkalinisation is hindered. Therefore, the possibility of a large local pH rise is minimised and the formation of hydrolysed species of Ga is not favoured, corroborating the fact that these species are not involved in the deposition process.

No oxidation of deposited Ga was detected under non-stagnant conditions. This can be explained considering that a very low local alkalinisation on the interface would be enough to passivate the deposited gallium.

4 Conclusions

The electrodeposition of gallium onto vitreous carbon requires high overvoltages. At low potentials reduction to Ga^{+1} species takes place and at more negative potentials the nucleation of Ga initiates. The nucleation is progressive controlled by diffusion. The shape of the transients is disturbed by simultaneous hydrogen evolution. This reaction also provokes local alkalinisation which promotes the oxidation of the deposited Ga. Measurements done in solutions of high pH and under rotation show that hydrolysed species of Ga are not involved in the discharge process.

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