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Prevention of gallium arsenide photocorrosion by an epoxy adhesion layer

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Abstract

Coating of gallium arsenide with an adhesion layer of commercial epoxy prevented its photocorrosion. A two-component room temperature curing adhesive paste (Araldite 2014) has been selected. When GaAs/Araldite was employed as an anode in a three-electrode photoelectrochemical cell the photogenerated current density decreased significantly due to epoxy coating. However, depositing of few monolayers of Pt on GaAs surface prior to epoxy adhesion increased the photogenerated current density about four times. Moreover, impregnation of the epoxy film with gold enhanced the photogenerated current density significantly. The room temperature electrical conductivity of the epoxy films increased from 10^{-8} to $10^{-4}\,\Omega^{-1}\,\text{cm}^{-1}$ due to gold impregnation. Enhancement of the photocurrent due to gold impregnation is attributed due to better conduction of the photogenerated holes into the electrolyte, also due to activating the adsorption of electrolyte ions.

Several parameters are studied with the objective of determining the stability of epoxy films: these are continuous current–voltage ($I-E$) scans, prolonged illumination, weight changes and surface topography by scanning electron microscopy. All investigations have proven that the epoxy film was quite stable under anodic potentials and illumination in aqueous solutions.

Keywords: Gallium arsenide; Epoxy adhesion; Corrosion prevention

1. Introduction

Gallium arsenide, GaAs, is unstable in O_2 and aqueous media [1]. Its corrosion has been a subject of intensive investigations [2–4]. Corrosion studies have dealt with etching [5–7], oxides [8,9] as well as porous formation [10–14]. Corrosion products depend on the pH values of the electrolyte [15–17]. In strong alkaline solutions lattice dissolution takes place, but in neutral and acidic electrolytes oxide growth is favored [2–4,16–18]. Porous GaAs surface is formed under certain conditions of electrolyte composition and applied bias [10–14,19,20]. There have been several attempts to prevent the corrosion of GaAs. One of these is metallization of GaAs [18,21–23]. These coatings have improved several of the photoelectrochemical properties of GaAs, essentially, due to altering the band bending at the metal/semiconductor interface. However, because of necessity of metal layers to be very thin to allow transparent access of light, these layers, in most cases, were porous and did not achieve the purpose of preventing aqueous electrolytes of reaching GaAs surface. Passivation of GaAs has also been achieved by treatment in aqueous sodium sulfide, Na_2S electrolyte [24,25]. It was also reported that organic thiols with various organic functional groups have passivated GaAs [26,27]. Other organic molecules [28–30] and polymeric materials [31] with particular functional groups have also been employed to achieve the same purpose.

Epoxy-based adhesives are extensively employed in many industries, in order to bond different materials substrates [32,33].

It is the objective of the present paper to investigate the possibility of using a thin epoxy film to prevent the corrosion of GaAs.

2. Experimental

Electrodes were made of Si-doped n-GaAs wafers purchased from MCP Ltd. The doping level was $2\times10^{16}\,\text{cm}^{-3}$. Ohmic contacts were made by silver

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epoxy to a copper rod, which was attached to the back of the electrode. The rod, the part of the electrode to be dipped into the electrolyte, and the edges of the electrode, except the phase to be illuminated, were covered with silicon rubber. Prior to fixing the GaAs wafer to the copper rod its active surface was mechanically polished with a 1 μm diamond paste, then rinsed in water and blown dried with nitrogen. The electrodes were etched in a mixture made of sulfuric acid (H_2SO_4) hydrogen peroxide (H_2O_2) and water (H_2O) (3:1:1 v/v). Etching time was 30 s at 298 K.

One of the electrodes was coated with 10 monolayers of Pt by a cathodic deposition on its surface from 1×10^{-3} M chloroplatinic acid, H_2PtCl_6 solution [23]. Silicone rubber was removed prior to epoxy coating. A two-component room temperature commercial curing paste was used as an adhesive film for GaAs coating (Araldite 2014). The Araldite 2014 is a structural two-component epoxy paste manufactured by Ciba Specialty Chemicals. It contains Bisphenol A resin (number average $M_w < 700$) and the hardener is diethylenetriamine. Equal masses of the resin and the hardener were mixed well before dropping the viscous mixture on GaAs surface. Gold-impregnated epoxy film was prepared by adding 0.2 ml of 0.01 M gold chloride ($AuCl_3$) aqueous solution to 1.0 g of viscous epoxy mixture that changed immediately into white paste of lower fluidity. In order to make thin and homogeneous epoxy film, the viscous adhesive mixture was spread on the electrode surface by pressing with a cylindrical metal load of 25 g cm^{-2} on the top of a paraffin wax paper. The epoxy mixture was left in ambient atmosphere to cross-link overnight. The thickness of the epoxy films as measured by a digital micrometer was in the range 50–80 μm. Thickness measurements were made on films prepared on a flat glass plate under the same conditions as that prepared on GaAs. It was easy to pull films from glass surface but not from GaAs. The whole electrode, except the Araldite-coated surface, was coated again with silicone rubber. All electrochemical measurements were performed inside a three-electrode cell with the GaAs as the working electrode, a Pt wire as the counter and a saturated calomel electrode (SCE) as the reference. All potentials refer to the SCE. The biasing potentials as well as the current–voltage curves ($I-E$) were obtained with a PAR 273 potentiostat (EG & G). Light was obtained from a 250 W quartz-halogen lamp. It has filtered from IR by water and from UV by 420 nm cut-off filters. Light intensity has measured by a Time Integrated Solar station (Pomona, CA, USA, Model 815 W). The electrolyte was made of 0.20 M cerous nitrate ($Ce(NO_3)_3$).

Weight change measurements were carried out to determine the stability of epoxy films in electrolytes of different pH values. These films were prepared on glass surface. After cross-linking, the film was cut into pieces of equal areas and about the same masses. The pieces were dipped into 10 ml each of 0.2 M $Ce(NO_3)_3$, 0.1 M sodium hydroxide (NaOH) and 0.05 M H_2SO_4, for various periods of time. The epoxy films did not show any sign of color change or breakage. They were dried before weighing. The electrical conductivity experiments were carried out within a cell made of two tungsten electrodes, each of 5 mm diameter. Epoxy films, of the same diameter as the tungsten electrodes, were covered on both sides with silver paint and placed between the two electrodes. The DC power to the sample was kept to values less than 0.1 W to prevent excessive joule heating. The DC current was measured by a Keithly electrometer. Scanning electron microscopy (SEM) micrographs were taken for GaAs after removal the epoxy films. When the epoxy-coated GaAs was left in a mixture of ethanol-acetone (1:1 v/v) overnight, the film was easily removed from GaAs surface.

3. Results and discussion

Figs. 1a and b represent the dark and photocurrent intensities of GaAs and Pt/GaAs both coated with epoxy films. The values of both dark and photocurrents of epoxy/GaAs are less than the corresponding values of epoxy/Pt/GaAs electrode, as shown in Fig. 2. The increased currents in the case of epoxy/Pt/GaAs are accounted by an enhanced transfer of charge across the interface. Such a transfer is retarded in the case of epoxy/GaAs, essentially, due to an insulating oxide layer existing on the interface between epoxy film and GaAs surface. Usually, an oxide layer is composed of gallium oxide (Ga_2O_3) and arsenic oxide (As_2O_3) covers GaAs surface [1,2]. This layer is removed by etching, but during exposure to air, even for a short period, the oxide grows again, though, with different thickness [30]. Etching in H_2SO_4/H_2O_2 also leaves the surface of GaAs rich in arsenic that is also oxidized. The surface of GaAs is thus composed of an oxide layer not necessarily in the same stoichiometric ratio of Ga_2O_3 and As_2O_3 [34,35]. Although, GaAs itself is a semiconductor but its oxides are insulators. It is thus expected that contact between GaAs surface and the epoxy film is not ohmic. On the other hand, Pt deposition makes such a contact relatively better conductive.

Gold-impregnated films showed the highest photoactivity, compared to the last two cases. This is clear from the ($I-E$) curves of Fig. 3. Gold metal deposition from its aqueous ionic solutions, usually takes place electrolessly, i.e. without applied external potential. This takes place on almost every surface, even on those of very inert materials like wood. The electroless deposition results in the formation of metallic gold particles, presumably, dispersed homogeneously within the

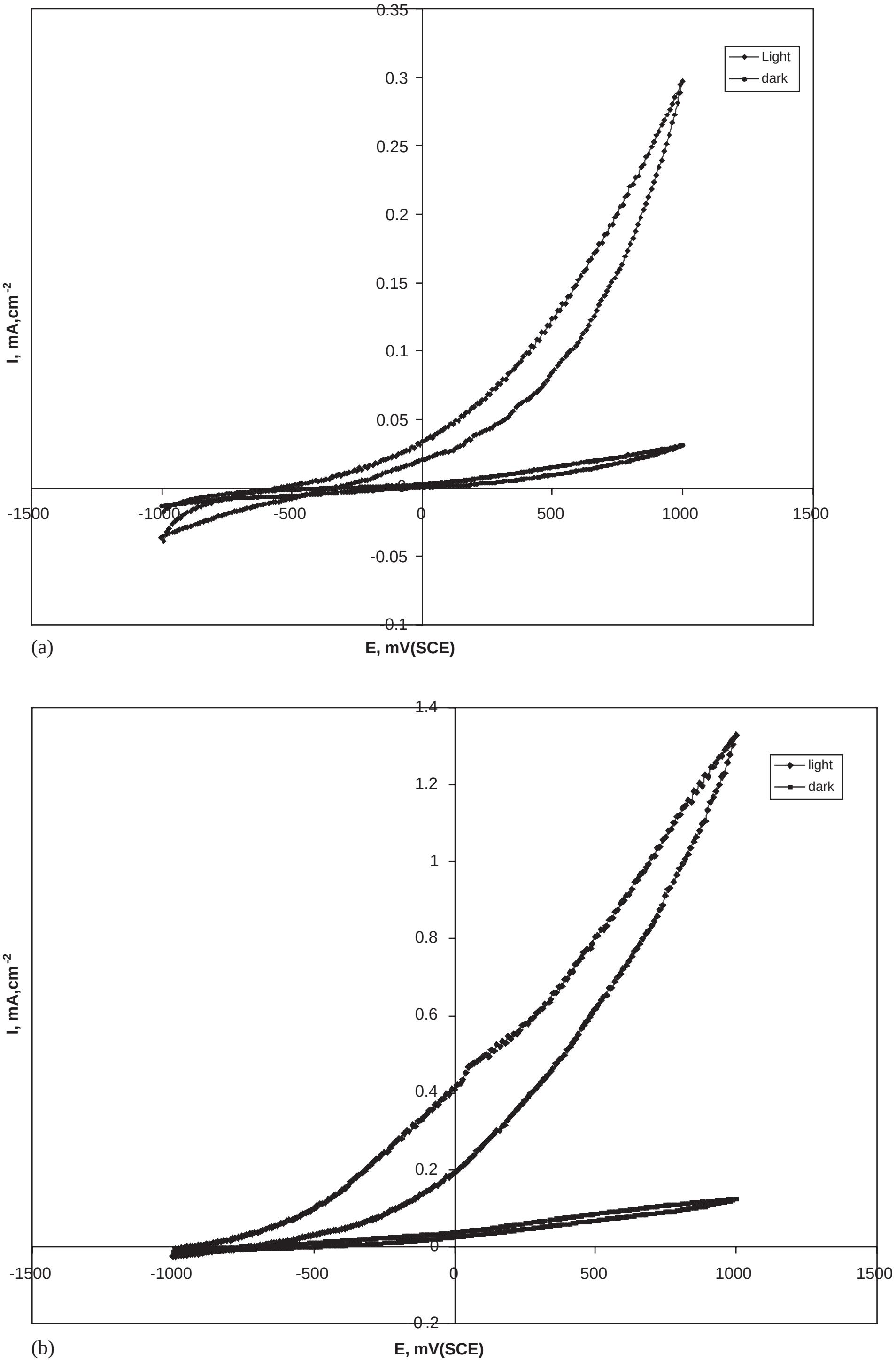

Fig. 1. Current–voltage scans in the dark and under illumination in 0.05 M H_2SO_4. Light intensity was 20 mW cm^{-2} and the scanning rate was 20mVs^{-1} (a) n-GaAs coated with an epoxy film and (b) n-GaAs coated with 10 monolayers of Pt before epoxy coating.

viscous epoxy mixture. The electrical conductivity of gold-impregnated film increased from 10^{-8} to $10^{-4}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. In addition to the electroless deposition of gold, the salt itself, i.e. $AuCl_3$ might have been impregnated within the epoxy film. Whether metallic gold particles or ionic gold chloride salt were embedded within the epoxy film, the net result is an increase in the electrical conductivity of the film either due to electronic or ionic effects, respectively. The increase in the electrical conductivity enhances the conduction of photogenerated holes into the electrolyte and thus increases both the dark and photocurrents, as shown

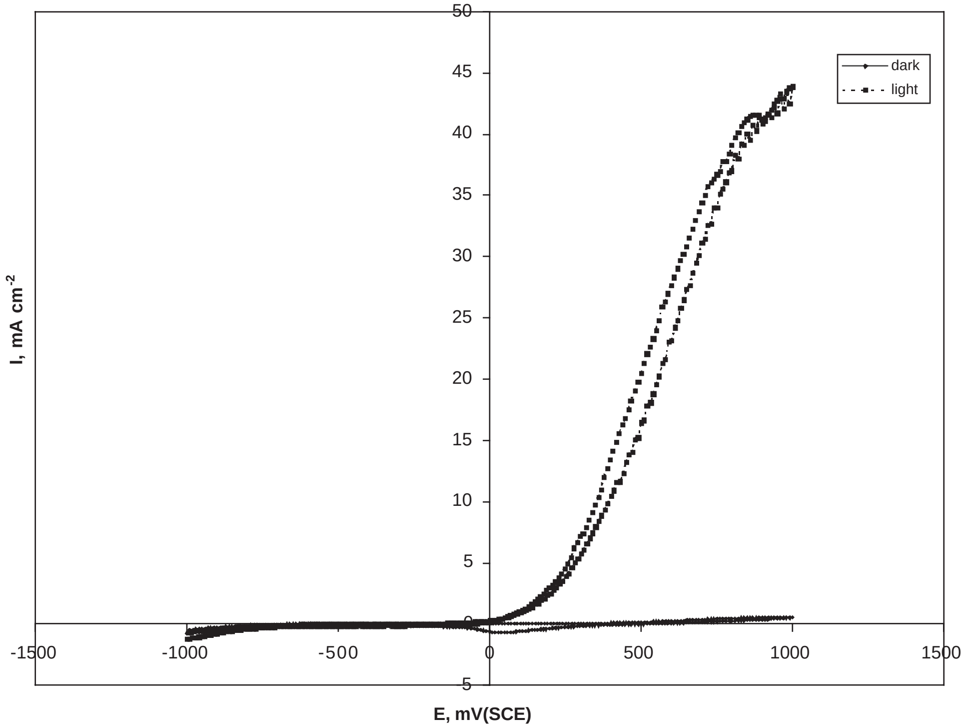

Fig. 2. Current–voltage scans of naked GaAs measured under the same conditions as in Fig. 1.

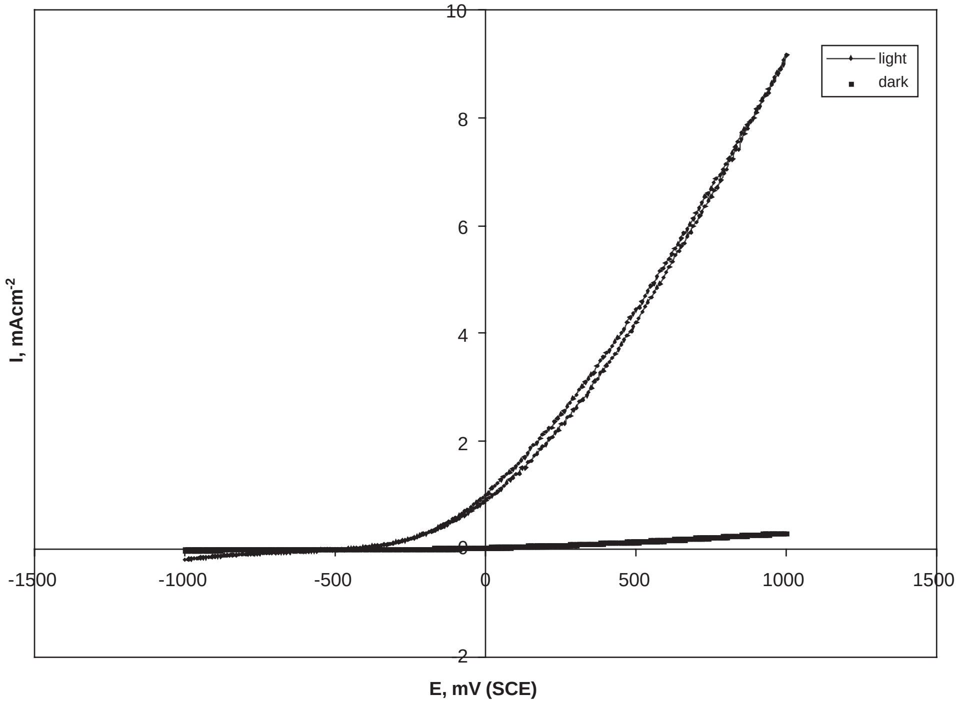

Fig. 3. Current–voltage scans of a gold-impregnated epoxy/n-GaAs measured under the same conditions as in Fig. 1. Gold impregnation took place electrolessly from 0.01 M $AuCl_3$ into the viscous epoxy mixture before dryness.

in Fig. 3 in comparison with Fig. 1a. More importantly, gold might have played an important role in the adsorption of the electrolyte and the formation of the Helmholtz double layer.

Current–voltage curves ($I-E$) in various electrolytes as well as prolonged photocurrent transients are employed to investigate the stability of GaAs due to epoxy coating. Fig. 4 shows the dark ($I-E$) of a naked

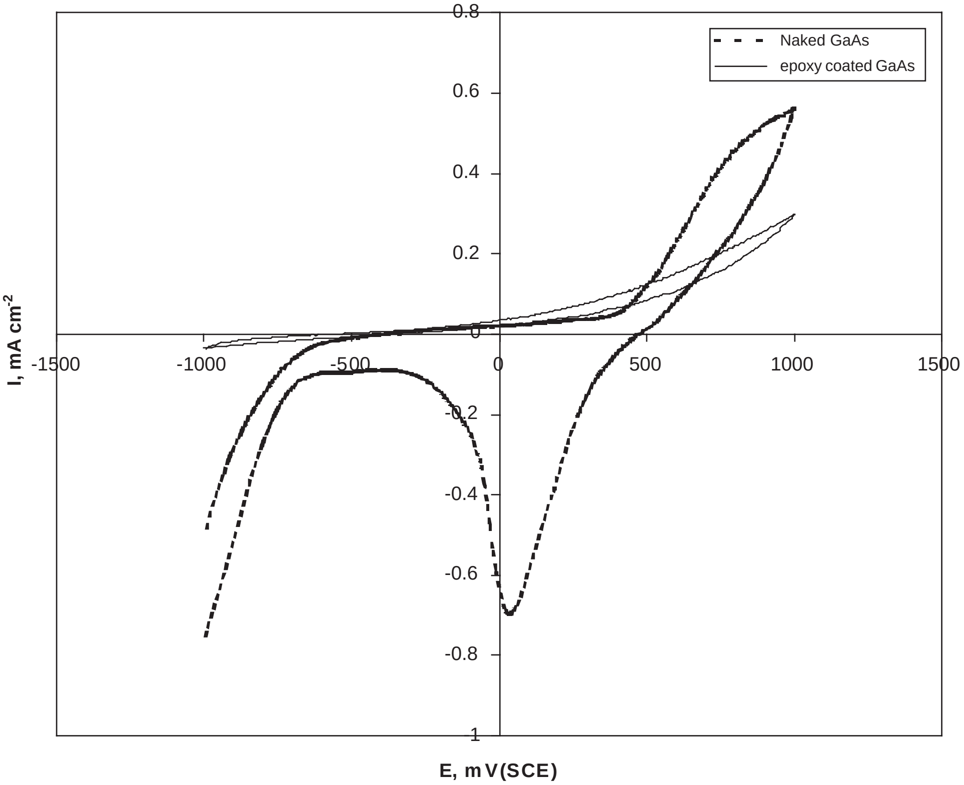

Fig. 4. Current–voltage scans measured in 0.05 M H_2SO_4 in dark at a scanning rate of $20\,mV\,s^{-1}$ for naked GaAs and gold-impregnated epoxy/GaAs.

GaAs and that of an epoxy-coated GaAs. In the case of uncovered GaAs electrode an anodic current is shown that increases significantly at potentials positive of +500 mV and a cathodic wave centered at ~+100 mV is also seen. In H_2SO_4 solution the electrode reactions result in H_2 evolution at the Pt electrode due to reduction of H^+ ions by the photogenerated electrons and the oxidation of GaAs by the photogenerated holes. The oxidation of GaAs in H_2SO_4 by the holes generated at its surface due to illumination results in the corrosion currents shown in Fig. 4. As these currents are not seen in the case of the epoxy/GaAs in H_2SO_4 solution, therefore it is expected that the epoxy coating prevents the corrosion of GaAs. An alternative electrolyte was chosen with the objective to pick up the photogenerated charges, i.e. the positive holes from GaAs surface and the negative electrons from the Pt electrode. For this purpose cerric–cerous (Ce^{4+}/Ce^{3+}) redox couple was selected. The photogenerated electrons are expected to reduce Ce^{4+} on the Pt electrode surface and the photogenerated holes to oxidize Ce^{3+} on GaAs surface. These redox reactions proceed in accordance to the two half redox reactions of Eqs. (1) and (2), respectively. In an aqueous electrolyte containing Ce^{4+}/Ce^{3+}, in addition to oxidation of Ce^{3+} ions on GaAs surface, corrosion of GaAs material due to oxidation by the photogenerated holes is expected to proceed. In order to further test the passivity effect of the epoxy film, successive scanning of both the coated and naked GaAs is recorded. The results of these scans are shown in the $(I-E)$ curves of Figs. 5a and b. In both cases the voltage was swept from −1.0 to +1.0 V and back to −1.0 at a scan rate of $20\,mV\,s^{-1}$. The cell contained 0.2 M $Ce(NO_3)_3$ aqueous electrolyte. It is clear from Fig. 5a for the uncoated electrode that the dark currents during the forward and backward sweeps increase with each successive sweep, indicating continuous changes in GaAs surface with each sweep. This is due to the continuous corrosion of the surface, i.e. in addition to oxidation of Ce^{3+} the electrode surface is oxidized as well. To the contrary of this behavior, an epoxy-coated electrode shows constant dark currents during all sweeps, Fig. 5b; that is another indication of corrosion prevention.

The effect of prolonged illumination on a gold-epoxy/GaAs electrode is shown in Fig. 6. Again the electrode was operated in $Ce(NO_3)_3$ electrolyte. During the first 15 min of illumination H_2 gas was evolved on the Pt counter electrode. The rate of hydrogen evolution was decreasing with time until completely stopped after about 30 min of illumination. The expected electrode reactions are:

At the Pt electrode (initially):

$$2H^+(aq) + 2e^- \rightarrow H_2(g), \tag{1}$$

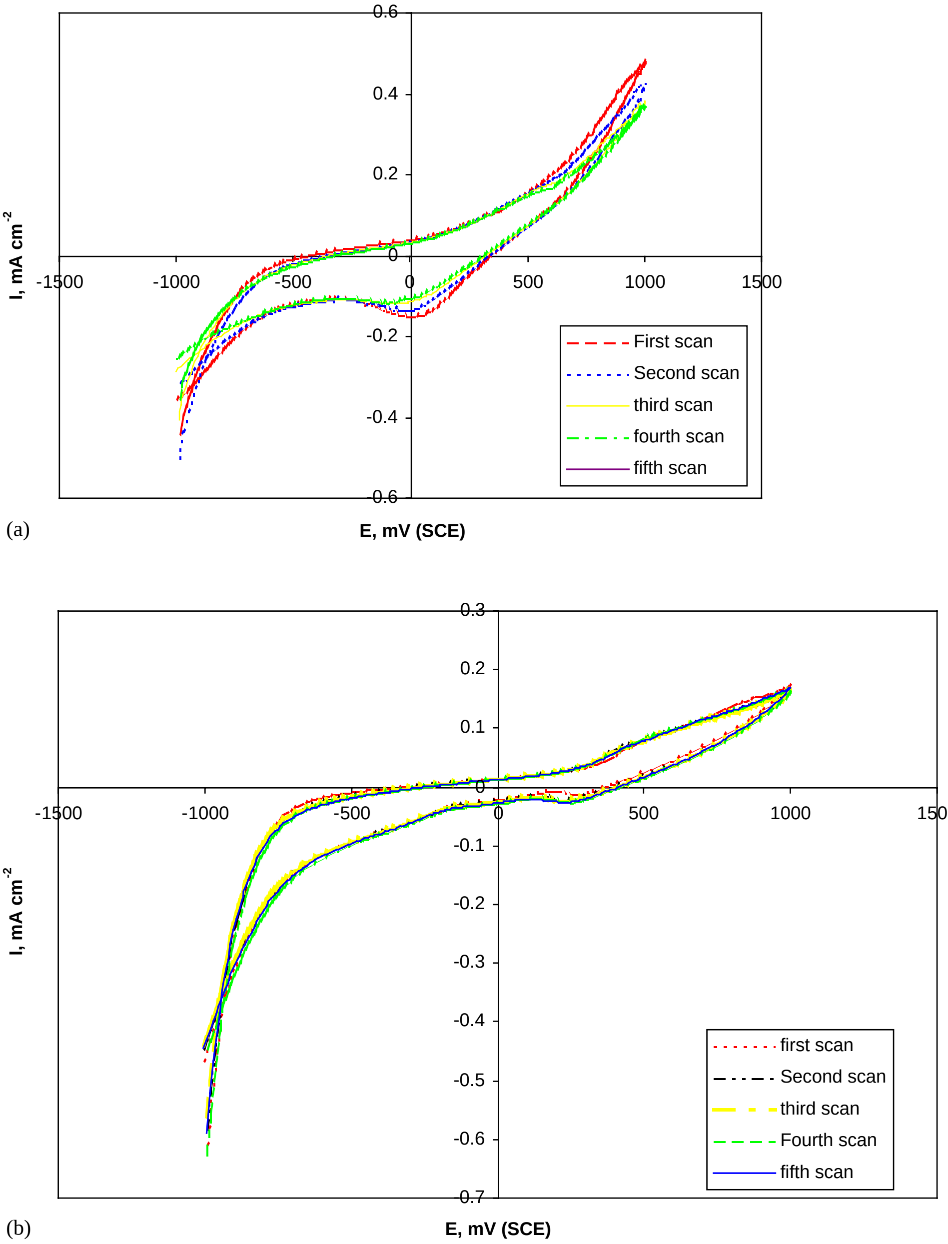

Fig. 5. Successive scans in 0.01 M $Ce(NO_3)_3$ at a scan rate of 20 mV s^{-1}: (a) naked GaAs and (b) gold-impregnated epoxy/GaAs.

where e^- is an electron photogenerated at the bulk of GaAs and transferred under the anodic bias to the Pt counter electrode.

At GaAs:

$$Ce^{+3}(aq) + h^+ \rightarrow Ce^{+4}(aq), \quad (2)$$

where h^+ is a positively charged hole forms on GaAs surface due to illumination.

The produced ceric ions (Ce^{+4}) are diffused to the Pt electrode and reduced back to Ce^{+3}. This reduction competes with the hydrogen ion reduction until the Ce^{+4} concentration becomes high enough that consumes the photogenerated electrons totally, the hydrogen evolution then stops. The photocurrent generated by the cell is thus due to the redox reactions of the Ce^{+3}/Ce^{+4} system. The steady-state photocurrent shown in Fig. 6 indicates that the GaAs electrode is quite stable and does not show any kind of corrosion. Again this is an important indication of stability of GaAs due to epoxy coating.

The stability of epoxy films in aqueous media of various pH values was further studied by weighing pieces of films after keeping them in these solutions for various periods of times. Fig. 7 represents the mass gain as a function of time. It is obvious that none of the electrolytes causes any weight loss; to the contrary, there are significant mass gains from all electrolytes. In all cases mass gains stopped

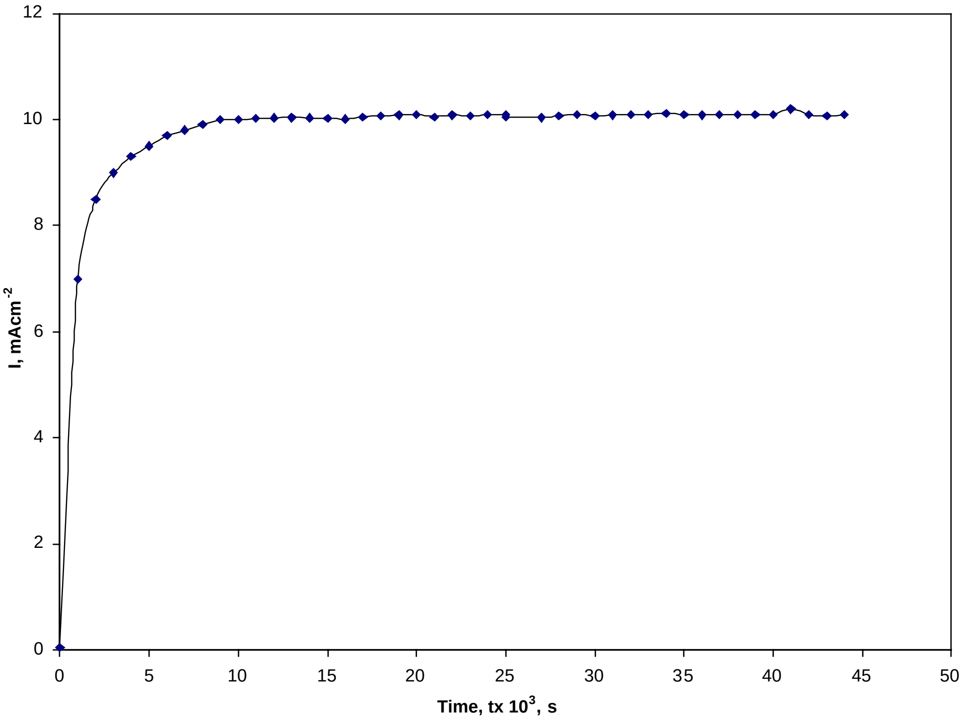

Fig. 6. Photogenerated current transient in 0.05 M H_2SO_4 of an n-GaAs electrode coated with an epoxy film impregnated with gold. The electrode was biased at $+1.0$ V (SCE) and illuminated by white light of intensity $20\,mW\,s^{-1}$.

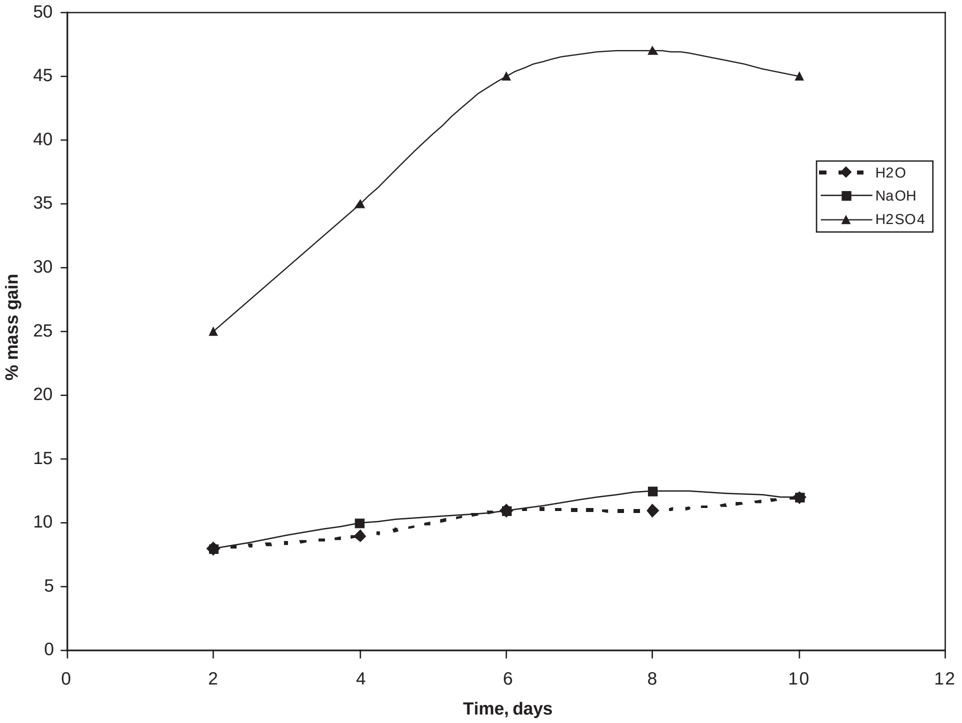

Fig. 7. Mass gain of epoxy films from H_2O, 0.1 M NaOH and 0.05 M H_2SO_4. Films were grown on a flat slide of glass.

after ~10 days of exposure to aqueous solutions. The mass gain of epoxy films is highest from H_2SO_4 electrolyte and much lower from both distilled water and NaOH solution. Because the Araldite 2014 was cured with diethylenetriamine as a hardener, it is thus plausible to account for the high weight gains from H_2SO_4 solutions, Fig. 7, due to the formation of diethylenetriamine sulfates. In the case of water and alkaline solution, the mass increase could be due to swelling of the polymer due to water adsorption. Although the weight change experiments did not show any weight loss due to the exposure of the Araldite films to different aqueous solutions, but these results do not exclude the possibility of dissolution of some of the film components in the aqueous solutions. As the solutions were not analyzed after the weight gain experiments, no conclusion can be driven about the possibility of dissolution of the Araldite films; however, it is concluded that the rate of water absorption is higher than that of film dissolution, if any.

In order to test whether electrolyte materials penetrate the epoxy film, SEM investigated surface topography of the used GaAs electrodes. The SEM micrographs of coated and naked GaAs are shown in Fig. 8a and b, respectively. The SEM micrograph of Fig. 8a resembles that of a fresh GaAs sample; revealing that the epoxy film prevents penetration of the electrolyte into GaAs surface and thus prevents corrosion. On the other hand,

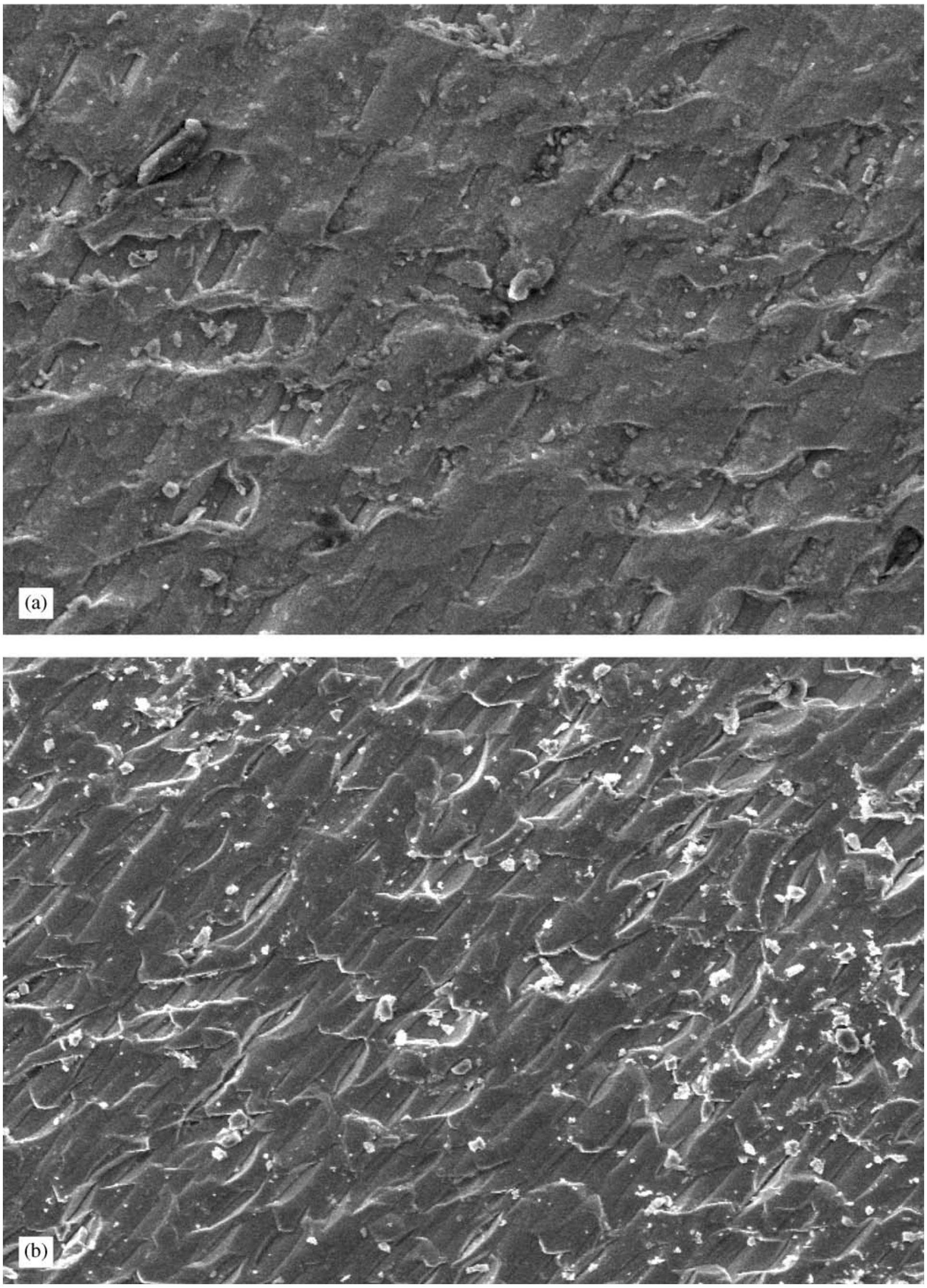

Fig. 8. Scanning electron micrographs (SEM) of n-GaAs after illumination for 1 h in 0.05 M H_2SO_4 at 1.0 V: (a) GaAs was coated with a gold-impregnated epoxy, the film was detached off GaAs surface before taking the SEM image, the magnification factor is 400 and (b) naked GaAs, the magnification factor is 400.

the SEM micrograph of the uncoated electrode shows that the electrode surface was porous; essentially due to photocorrosion [10,13,14].

4. Conclusions

1. Photocorrosion of n-GaAs is prevented by coating with a thin film of a commercial epoxy adhesive that allows conduction of charges but prevents penetration of electrolyte ions.
2. Conduction of the epoxy film is achieved by impregnation with gold via electroless deposition.
3. The stability of epoxy films in aqueous media is revealed from continuous current–voltage scans, prolonged illumination, SEM of GaAs and weight gains from various electrolytes.

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