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Corrosion of n-GaAs/aqueous Photoelectrochemical Cell

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تآكل n-GaAs في الأوساط المائية في خلية فوتوالكتروكيميائية

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تمت دراسة تآكل GaAs في محاليل الكتروليتية مختلفة بواسطة جمع قياسات الكتروكيميائية والميكروسكوب الالكتروني وقياسات الضوء المنعكس. نتائج عملية التآكل تتأثر بالكيمياء الكهربية لـ GaAs وهذا يؤثر علي مقدار التيار الضوئي المتولد. وجد أن نتائج عملية التآكل تتغير في مدى تكون طبقة مسامية علي سطح GaAs إلي طبقة من الأكسيد علي السطح، وذلك يعتمد علي نوع الالكتروليت المستخدم. الطبقة المسامية تتكون في محلول حمض الهيدروكلوريك (HCl) وهي تقوي من التيار الضوئي المتولد نتيجة لانخفاض الضوء المنعكس. الأكسيد المتكون يتلف من كثافة التيار الضوئي نتيجة لتكون طبقة عازلة من الأكسيد، حيث أنه يتكون أكسيد ثابت في محلول محمض من فوق أكسيد الهيدروجين (H_2O_2). تم بحث تأثير فيلم الأكسيد علي التيار- فولت، وتم حساب سمك فيلم الأكسيد من قانون فاراداي.

Keywords: *Gallium arsenide, corrosion, oxide formation.*

ABSTRACT

A combination of electrochemical studies, scanning electron microscopy, SEM, and light reflectivity measurements reveals information about the corrosion of enlightened n-GaAs in various aqueous electrolytes. The corrosion products influence the electrochemistry of GaAs and thus affect the magnitude of the photogenerated current. It is found that the corrosion products range from the formation of porous layers within GaAs surface region to oxide layers on top of surface depending on the electrolyte composition. Porous layer, forms in HCl solution, enhances the generation of the

photocurrent due to decreasing the reflectivity of the incident beam. On the other hand, oxide films deteriorate the photocurrent density, presumably, due to the insulating properties of the oxides. A stable oxide film is formed in an acidic solution of H_2O_2. The effect of an oxide film on the current –voltage characteristics is investigated. The oxide film thickness is calculated by means of Faraday's law.

Introduction

The anodic oxidation of n-GaAs electrodes in aqueous solutions leads to lattice dissolution [1-4], porous layer formation [5-10] and oxide formation [11-13]. As the charges involve in these oxidation are the valence band holes, their rates, thus increase with illumination. The pH of the electrolyte is an essential parameter in determining the product of oxidation. Lattice dissolution takes place within strong alkaline solutions [14,15]. On the other hand, acidic electrolytes, particularly those containing chloride ions, produces porous layer on electrode surface [5, 9, 10]. Oxide layer formation takes place in neutral and acidic H_2O_2 solutions [11-13]. The oxide film is composed of Ga_2O_3 and As_2O_3, not particularly in stoichiometric ratio [16]. The growth of thick oxide layers in different electrolytes, mainly, for the sake of device passivation, has been the objective of several studies [11-13, 17]. The kinetics of this growth is complicated by the partial dissolution of the oxide film at the oxide/electrolyte interface. In some cases, parabolic law has described the formation of the oxide [11]. In some other cases, an exponential dependence is found [12, 13]. The discrepancy between these findings could be attributed to the partial dissolution of the oxide during its growth.

The presence of a thin insulating oxide layer on GaAs could hinder charge transfer across the semiconductor/electrolyte interface. Moreover, it could change the position of the band edges at the electrode surface, consequently, the semiconductor's properties of the electrode could be altered. It has been reported that the rates of several redox reactions decreased due to the growth of oxide films on GaAs [18-20].

The purpose of this paper is to investigate some of the electrochemical properties of n–GaAs electrodes due to its corrosion in various electrolytes.

Experimental

1. Porous electrodes

Electrodes were made of Si-doped n-GaAs wafers purchased from MCP Ltd. The doping level was 2×10^{16} cm^{-3}. Ohmic contacts were made by silver epoxy to a copper rod, which was attached to the back of the electrode. The epoxy coated 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 1μm diamond paste, then rinsed in water and blown dried with nitrogen. Square wafers of GaAs of side ~4 mm and thickness 1mm were employed for measuring light reflection and studying SEM. A wafer for measuring light reflectivity and SEM was held in an aluminum clamp and fully immersed in the electrolytes while anodized for 1 hr at 0.6V in various electrolytes. A porous layer was formed by illuminating GaAs in 0.1 M HCl under an anodic bias of +0.6 V [5, 9, 10]. Normal incident helium-neon laser beam of wavelength 632.8 nm was reflected from the surface of different GaAs samples. The intensity of the reflected beam was measured by a photocell (Newport Coorp.). At this wavelength, reflectivity of GaAs is not the highest but still appreciable, ~ 30% [21] and can be easily measured. The GaAs sample was mounted at an angle of 45° with

respect to both the incident and reflected beams. In this way both the incident and reflected beams were perpendicular to each other that gives maximum reflectivity of light. The intensity of the reflected beam is proportional to the photocurrent generated within the photocell that was measured by a Keithley electrometer. Absolute reflectivity, R was calculated from the formula: $R = (I/I_o)$, where I and I_o are the currents generated by the photocell due to reflected beam from the sample and that of the incident beam, respectively. The reflectivity of different GaAs samples is tabulated in Table 1.

2. Preparation of anodic oxides on n-GaAs

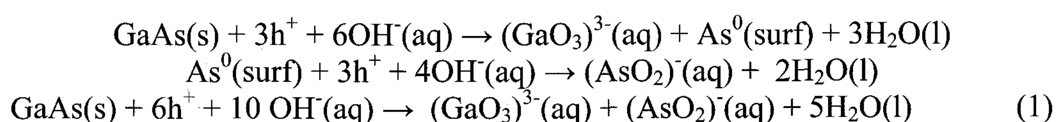
The anodization bath for the oxides formation consisted of 30% H_2O_2 solution buffered to pH 2.0 with H_3PO_4 [13]. Anodization of an enlightened electrode took place at 0.6 V for various periods of time. Prior to anodization the electrode was biased at –1.5V for 3 min and instantaneously biased at +0.6V to form the oxide.

All electrochemical measurements were performed inside a three-electrode cell. All potentials refer to the saturated calomel electrode (SCE). The biasing potentials as well as the current-voltage curves (I-E) were obtained with a PAR 273 potentiostat (EG&G). The light was obtained from a 250W quartz-halogen lamp. The light was filtered from IR by water filter and from UV by 420 nm cut-off filter. Light intensity was measured by a Time Integrated Solar station (Pomona, Ca. USA, Model 815 W).

Results and Discussion

Stationary polarization of enlightened n-GaAs electrode at +0.6 V was carried out in electrolytes of 0.1 NaOH, 0.1 M HCl and 30% H_2O_2 buffered with H_3PO_4 at pH 2. Typical current transients during these polarizations are shown in Figure 1a, b and c, for NaOH, HCl and H_2O_2 electrolytes, respectively. In NaOH electrolyte the photogenerated current did not change significantly during illumination. On the other hand, in HCl solution the photogenerated current increased from 18 mA cm^{-2} continuously, rather nonlinearly, and reached about constant value of ~ 30 mA cm^{-2}. To the contrary of this behavior, in H_2O_2 electrolyte the photogenerated current dropped slowly from 18 to ~6 mA cm^{-2} during a period of ~ 2hrs. After anodization in NaOH solution the electrode surface reserved its shiny luster. On the other hand, in both HCl and H_2O_2 electrolytes the electrode was not shiny anymore, indeed its color turned into black with the appearance of some roughness on the surface.

Scanning electron microscopy, SEM, investigated surfaces of GaAs electrodes, after anodization in various electrolytes. The obtained SEM micrographs are presented in Figures 2a, b, c and d, for a fresh GaAs wafer and electrodes treated in NaOH, HCl and H_2O_2 electrolytes, respectively. The SEM micrograph of GaAs treated in NaOH is similar to that of a fresh GaAs, Figures 2a and b, respectively. Indeed, this is compatible with the results of the corrosion mechanism of GaAs in alkaline medium. According to this mechanism, the surface of the electrode is continuously etched and a fresh GaAs surface is always maintained [22,23]. Etching of GaAs in an alkaline electrolyte proceeds via the following reactions [14, 15, 24]:



$$\mathrm{GaAs(s) + 3h^+ + 6OH^-(aq) \rightarrow (GaO_3)^{3-}(aq) + As^0(surf) + 3H_2O(l)}$$
$$\mathrm{As^0(surf) + 3h^+ + 4OH^-(aq) \rightarrow (AsO_2)^-(aq) + 2H_2O(l)}$$
$$\mathrm{GaAs(s) + 6h^+ + 10\,OH^-(aq) \rightarrow (GaO_3)^{3-}(aq) + (AsO_2)^-(aq) + 5H_2O(l)} \qquad (1)$$

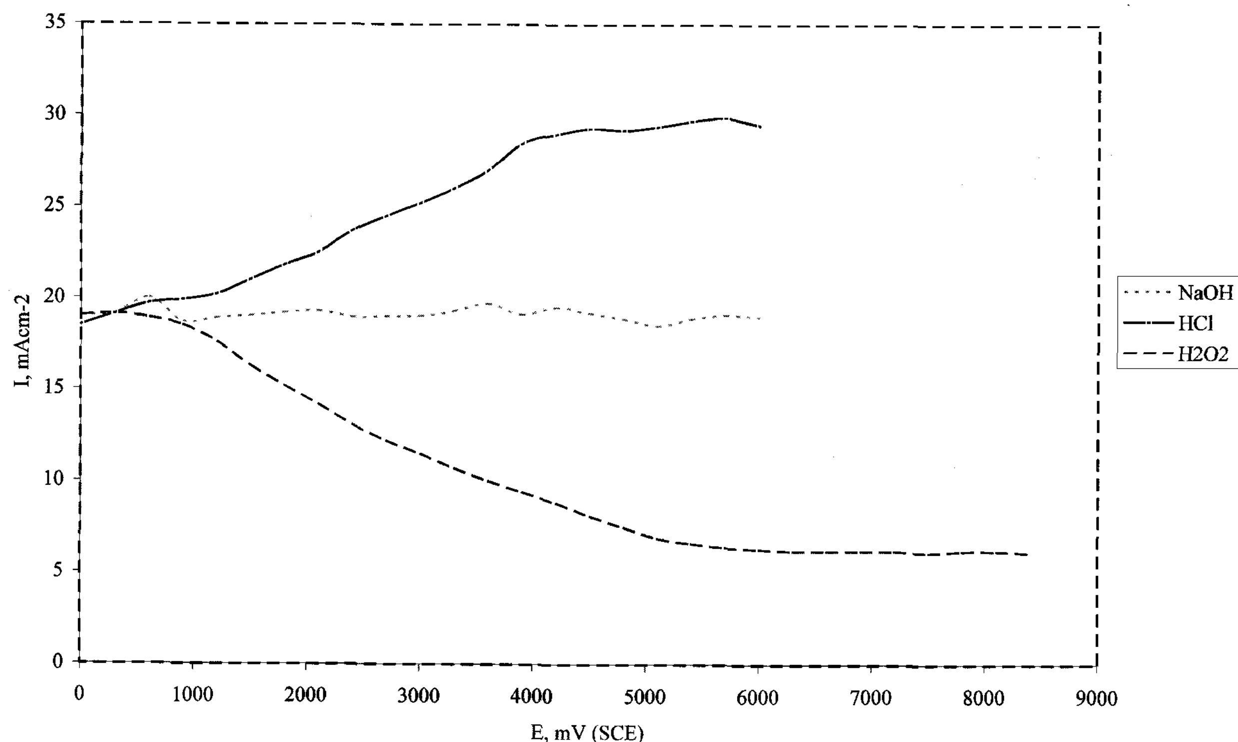
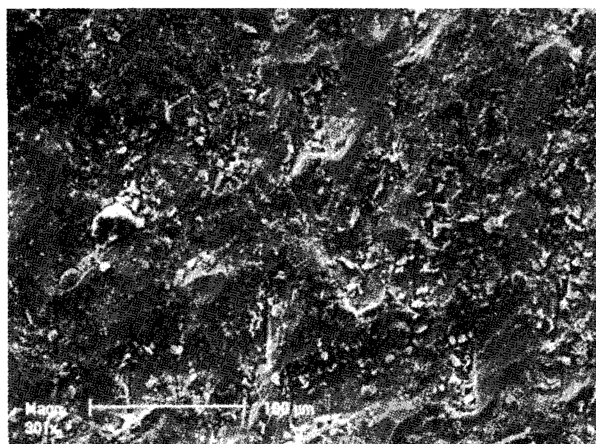


Figure 1: Photocurrents transients of n-GaAs biased at +0.6V and enlightened by 25mW cm^{-2} of white light in electrolytes of: a) 0.1 M NaOH, b) 0.1 M HCl and c) 30% H_2O_2 (pH 2).

According to Eq. 1, there is no solid product left over GaAs surface due to corrosion in NaOH, therefore the SEM micrograph of the NaOH treated electrode resembles that of a fresh GaAs sample as shown in SEM micrographs of Figures 2a and b. Moreover, the corrosion results of Eq. 1 can also account for the constant photocurrent during illumination in NaOH, Figure 1 a. In addition, Table 1 shows that the light reflectivity by GaAs, treated in NaOH, at a wavelength of 632.8 nm is comparable to that of untreated GaAs. This result along with the result from the SEM indicate that the surface of GaAs treated in NaOH and that of fresh GaAs are similar, at least, from the view point of roughness. On the other hand, the SEM micrograph of figure 2c demonstrates the formation of a porous surface layer on GaAs in HCl solution.

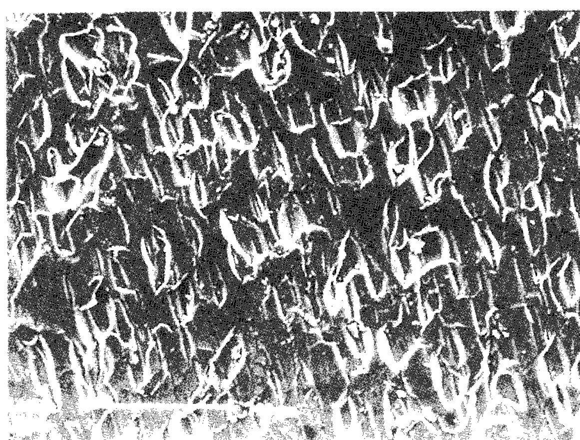
Furthermore, Table 1 shows also that the reflectivity of light of wavelength 632.8 nm decreased significantly.

This is as explained previously [5], due to the formation of porous GaAs. The formation of porous layer decreases light reflection and thus enhances the absorption of light; leading to increasing the photogenerated current density as shown in figure 1b. Working in acidified H_2O_2 decreased the photogenerated current slowly from ~18 to ~6 mA cm^{-2} in an illumination period of ~ 2hrs. Afterwards, the photocurrent stayed at about constant value. Presumably, an insulating layer of Ga_2O_3 and As_2O_3 was formed on the electrode surface [13]. The formation of the oxide layer is revealed from SEM micrograph of Fig. 2d and from light reflectivity of Table 1.



2a

2b



2c

2d

Figure 2: Scanning electron micrographs of n-GaAs biased at 0.6V and enlightened by 25 $mWcm^{-2}$ of white light in electrolytes of:
a) Untreated fresh electrode, b) 0.1 M NaOH, c) 0.1 M HCl and d) 30% H_2O_2 (pH 2).

Table 1: Light reflectance [(a)] of n-GaAs wafers treated in various electrolytes

Electrolyte	% Light reflectivity
Polished untreated sample	43
0.1 M HCl[(b)]	27
0.1 M NaOH[(b)]	45
H_2O_2[(b)]	33

(a) Reflectance of laser beam at 632.8 nm.
(b) Biased for 1 hr at +0.6 V.

Moreover, the formation of the oxide film is also revealed from the current-voltage scans of the oxidized GaAs in the dark and under illumination as shown in figures 3 and 4, respectively.

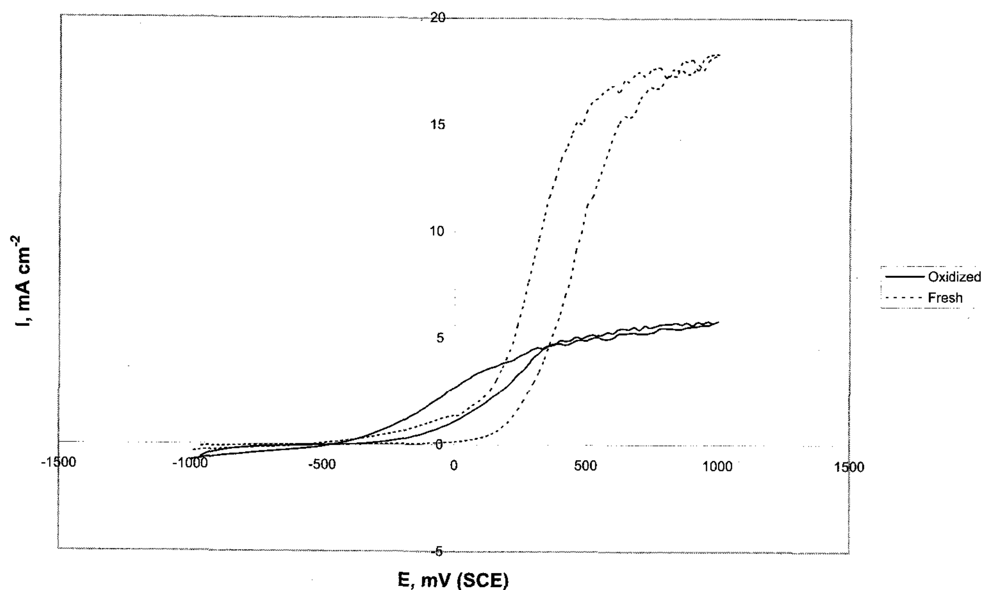


Figure 3: Current voltage curve (I-E) of n-GaAs measured in the dark in 30% H_2O_2 (pH 2) instantaneously and after 1hr of biasing at +0.6V in the same electrolyte.

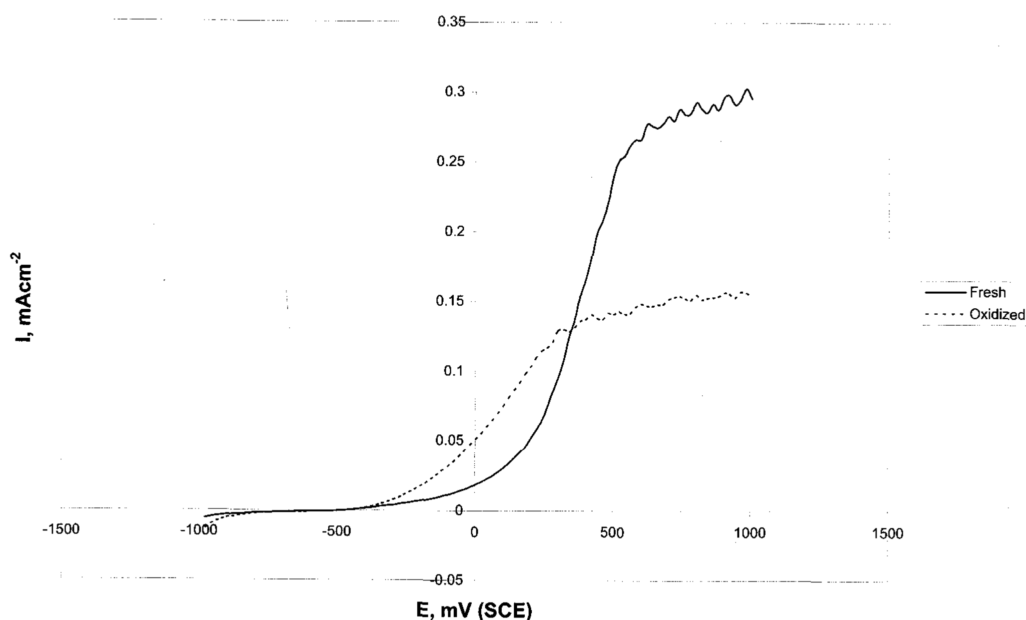
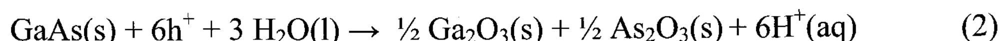


Figure 4: As in Figure 3 but under illumination by 25 mW cm^{-2} of white light.

Apparently both the dark and photocurrents decreased significantly due to the formation of an oxide layer. The decrease in the currents is attributed due to the insulating properties of the oxide layer that hinders the charge transfer across the semiconductor/electrolyte interface. Besides being insulating, the morphology of the oxide layer is shown to be rough as shown from the lower reflectivity of the laser beam, Table 1. Roughness of the oxide film is also confirmed by the SEM micrograph of Fig. 2d. Although the oxidized GaAs surface caused a significant reduction in the reflectivity of the laser light it also resulted in a remarkable decrease in the photogenerated light density presumably because of the insulating property of the oxide layer. The layer did not only

decrease the currents but also shifted the onset potential of both the dark and photocurrent towards more negative values as shown in figures 3 and 4, respectively. This negative shift in the onset potentials could be explained by the possibility that the oxides of GaAs have more negative work functions than that of GaAs itself [25-27]. The oxides are formed according to the following corrosion reaction:



$$GaAs(s) + 6h^+ + 3\,H_2O(l) \rightarrow \tfrac{1}{2}\,Ga_2O_3(s) + \tfrac{1}{2}\,As_2O_3(s) + 6H^+(aq) \qquad (2)$$

The formation of these solid products on GaAs surface accounts for the deterioration of photocurrents during anodization in acidic H_2O_2, Fig 1c. The rate of oxide growth could be related to the quantity of electricity by Faraday's law as:

$$dn = (J / ZF)dt \qquad (3)$$

Where n is the number of moles of formed oxides (Ga_2O_3 and As_2O_3) by anodic current J, ZF is the number of coulombs per moles of oxide. The overall amount of oxide formed at time, t, could be given by the empirical formula

$$\int_{n=0}^{n} dn = (1 / ZF) \int_{t=0}^{t} Jdt \qquad (4)$$

or

$$n - n_0 = (1/ZF) \int_{t=0}^{t} Jdt \qquad (5)$$

where n_o is the number of moles of oxide on fresh GaAs. If it is assumed that the electrode etching and polarization at –1.5V, before anodization at +0.6V, have produced clean surface, then n_o could be neglected. Thus, Eq. 5 is modified to

$$n = (1/ZF) \int_{t=0}^{t} Jdt \qquad (6)$$

The number of moles of oxides formed after different periods of time is determined by measuring the corresponding areas under the current-time relation of curve C in Fig. 1. Taking 190 g mol^{-1} as the average molecular weight and 5 g cm^{-3} as the density of the oxide, the average thickness of the oxide, δ can be obtained. When the oxide film thickness was drawn as a function of the square root of anodization time, a straight-line relationship was obtained, however, with a changing slope at a particular time. This relationship is shown in figure 5.

This relation implies that the limiting step during the oxide growth could be the diffusion of the oxide ions from the electrolyte towards the interior of the electrode [28, 29]. Therefore, a simple parabolic law of the following formula could describe the kinetics of oxide film formation:

$$\delta = \sqrt{kt} \qquad (7)$$

Where the constant k includes all parameters assumed to be constant, such as the activity of oxygen ions at the oxide layer/electrolyte interface and the geometrical factors. The constant k includes also the diffusion coefficient of oxygen ions, which may vary from the surface of the electrode to its bulk. The values of k, as taken from the two slopes of figure 5 are 4×10^{-6} and 6×10^{-7} cm^2 s^{-1} for the short time and longer time oxidations, respectively. It seems that, at short time oxide ions diffused from the electrolyte into GaAs surface until it was completely oxidized, i.e. a thin oxide film was formed on the surface. Then it is suggested that oxide ions diffused through this oxidized surface film towards the bulk of the electrode. Therefore, the first diffusion process, i.e. the short time oxidation could be assigned to the diffusion of oxide ions from the electrolyte into GaAs

surface. On the other hand, the second process could be due to the diffusion of the oxide ions through the oxidized film. As the slope of the second step is ~ 7 time less than the slope of the first step, it is predicted that that the formation of a surface oxide film on GaAs passivated the material towards further corrosion.

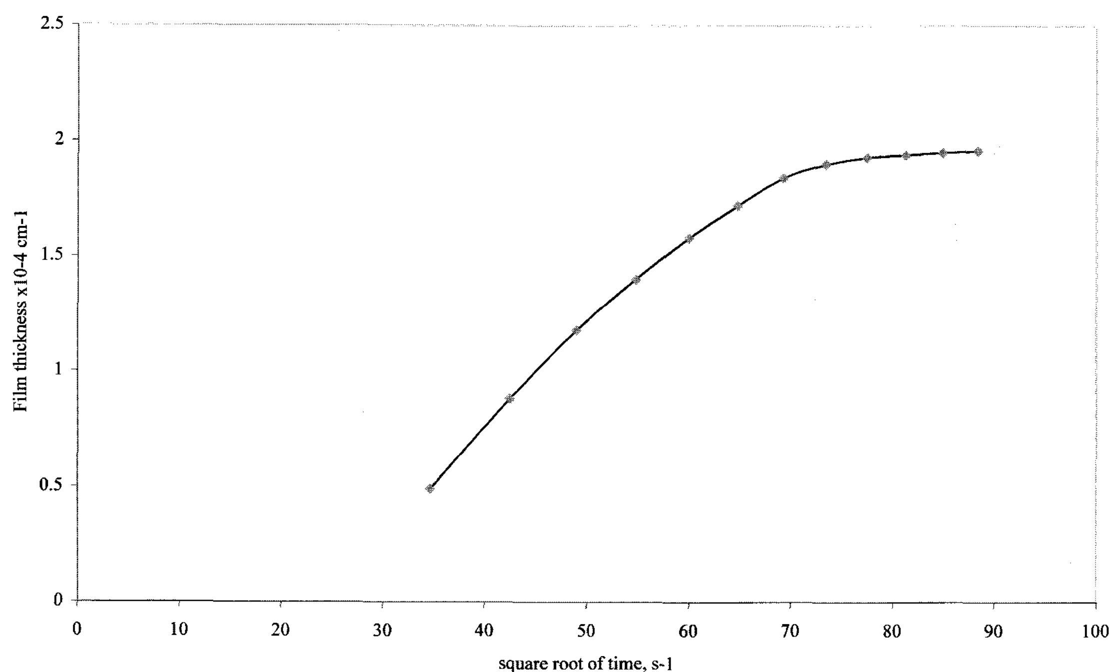


Figure 5: The relationship between the oxide film thickness, as calculated from equation 6, and the square root of oxidation time in accordance to equation 7.

Conclusions

1. Porous layer formed on GaAs in HCl solution enhanced the generation of the photocurrent density due to decreasing the reflectivity of incident light.

2. The photogenerated current density stayed constant while GaAs was illuminated in NaOH because the corrosion products were continuously etched off the surface.

3. In acidified H_2O_2 an oxide film was formed that deteriorated the photogenerated current density.

4. The results from Faraday's law for the oxide film thickness implies that diffusion rate of oxide ions from the electrolyte into GaAs surface is faster than that into oxidized surface; indicating that the oxide film decreased the rate of corrosion.

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