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Steady-state and impedance study of *n*-GaAs in H_2SO_4 solution: Mechanism analysis

Yin Huang, Jingli Luo, Douglas G. Ivey *

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

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Abstract

In this paper, a study on the electrochemical impedance of anodic decomposition of *n*-GaAs in 0.5 M sulfuric acid, combined with steady-state polarization techniques, is presented. Both dark and daylight conditions have been investigated for comparison of their influence on polarization curves and impedance by hole injection in a potential range from open circuit to breakdown. An inductive loop appears if a high enough positive potential is applied for both conditions, while recombination resistance is only observed for the daylight case. Quantitative simulation of the impedance spectra suggests that the rate-determining step for corrosion/photocorrosion is the generation of mobile intermediates, e.g., $AsGa^+$, which are then replaced by competition between a Faradaic process involving immobile intermediate formation and a parallel chemical step to form AsGa–OH.

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1. Introduction

The anodic decomposition of GaAs has been studied for more than two decades [1]. Thermodynamically, GaAs is anodically unstable because its anodic corrosion potential resides within the bandgap [2–4]. This hampers the use of GaAs as a photoelectrochemical solar cell material [5] and it is also a problem when GaAs-based electronic/optical devices are cleaned in electrolytes, especially acidic solutions. From simple current–potential behavior, it has been found that the corrosion process occurs via the valence band. The general corrosion reaction of GaAs in a strong acid solution can be written as:

$$GaAs + 6h^+ + 2H_2O \rightarrow Ga^{3+} + HAsO_2 + 3H^+. \quad (1)$$

Although the hole concentration in *n*-GaAs is relatively low, compared with that of electrons, photocorrosion can occur when *n*-GaAs is exposed to light (photon energy >1.42 eV at room temperature).

According to Eq. (1), six charges are involved in corrosion, implying that the mechanism is very complicated. So far in the literature, two mechanisms have been proposed by Vanmaekelbergh and Gomes [5–9] and Allongue and Blonkowski [10–12], respectively. The former carried out a series of voltammetric studies of GaAs with and without stabilizing agents. From the relationship between the stabilizing coefficient, the stabilizing agent concentration and the observed current density, they concluded that the corrosion of GaAs in strong acid solution is via a mobile surface intermediate X_1, i.e., X_1 is the oxidant for further corrosion steps. The work of Allongue and Blonkowski, from band edge shift experiments, suggested that the corrosion process common to GaAs and InP is very likely to involve free holes instead.

The ac impedance technique is a powerful method for mechanism study involving multi-steps with adsorbed intermediates. During the past several years, electrochemical impedance spectroscopy (EIS) has been mainly used for the study of the recombination process for semiconductors [13] and has seldom been applied to study the dissolution mechanism. Hens and Gomes [14,15] analyzed the frequency dispersion by comparing GaAs and InP in indifferent electrolytes and concluded that surface states play a key role in the

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* Corresponding author. Tel.: +1 780 4922957; fax: +1 780 4922881.
E-mail addresses: Kent.Huang@Shaw.CA (Y. Huang), doug.ivey@ualberta.ca (D.G. Ivey).

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dispersion phenomenon. They also found that the surface states are related to the electrolyte resistivity and the electrode surface pretreatment. An impedance study on the InP dissolution mechanism, also by these authors [16], indicated that a slow oxidation step must be present as the rate-determining step. The absence of recombination impedance was explained by a rapidly oxidizing decomposition intermediate.

In this paper, EIS combined with steady-state polarization is used to examine the mobility of the intermediate X_1 after initially capturing holes through surface bonds (X_0). In addition, the slowest reactions in the overall GaAs decomposition process at different potential regions are suggested.

2. Experimental details

All electrodes used in the experiments were (100) faces of single crystal n-type GaAs. The doping density of the crystals was 1×10^{18} cm^{-3} (Si doped). The samples were cleaved into slices from a 10 cm diameter wafer, with part of the sample covered with a standard Pd/Ge/Au metallization layer as an ohmic contact. The back and edges of each specimen were then sealed by lacquer. 0.5 M H_2SO_4 solutions were prepared using reagent grade concentrated H_2SO_4 (>98%). Cleaning of the electrode surface was done by etching the sample in a $H_2SO_4:H_2O_2:H_2O$ (1 : 1 : 10) solution for 20 s, followed by cleaning in HCl (20 s) and $NH_3{\cdot}H_2O$ (2 min) to remove any oxides remaining at the surface after etching. This cleaning procedure follows the study by Z.H. Lu et al. [17], who showed that the etching rate of GaAs at this concentration ratio is ~0.32 μm/min.

Experiments were carried out in a conventional, three-electrode electrochemical cell using a saturated calomel electrode (SCE) as the reference electrode and a platinum mesh as the counter electrode. Polarization curves and impedance measurements were performed with either a Solartron 1287 Electrochemical Interface System or a Gamry 105/300 System. The amplitude of the small superimposed sinusoidal signal was set to 10 mV. The scan rate for the polarization curves was 1 mV/s. The frequency range for impedance spectroscopy was from 100 kHz to 0.01 Hz.

3. Results

3.1. Steady-state polarization curves

The results of the steady-state polarization measurements in both dark and daylight conditions are shown in Fig. 1. The polarization curve under daylight conditions shows three different regions for the anodic part. In region L1, the current density is small due to the recombination of photo-injected holes and electrons in the conduction band and the small overpotential. The current reaches a plateau in region L2 (mid potential region), where recombination effects can be excluded. The semiconductor breaks down in region L3, which may be due to tunneling through the space charge region or inversion layer formation. Tests have shown that the electrode surface pretreatment directly influences how “vertical” region L2 is. Region L2 tilts when specimens have rough surfaces, e.g., during long term etching, as shown in Fig. 2. The limiting current density in daylight conditions is about 30 μA cm^{-2}, much lower than that reported in the literature (>1 mA cm^{-2}) [6,18]. Three regions can also be observed for the dark condition curve, marked as D1 to D3. The low current density in region D1 can be attributed to the small overpotential. The mid potential region before breakdown (~1.0 V), region D2, has a linear shape (Tafel relationship between current density and potential), differing from the illumination curve. The hole concentration at the surface (p_s) accounts for the difference in the two curves. The Tafel slope measured from the dark curve is about 0.3–0.45 V/decade, which is much higher than the standard Tafel slope for a single-electron charge transfer reaction, 0.06 V/decade. This value is even markedly larger than that observed for p-GaAs (0.09–0.15 V) [19,20]. Regions D3 and L3 almost overlap, which suggests that the mechanism for breakdown may be the same for the two conditions.

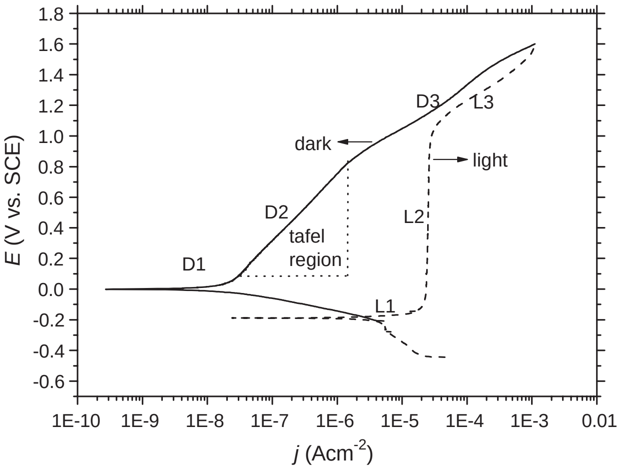

Fig. 1. Polarization curves for n-GaAs (1×10^{18} cm^{-3}) in 0.5 M H_2SO_4 under dark (solid line) and daylight (dotted line) conditions. The anodic portion can be divided into three regions, D1, D2 and D3 for dark conditions and L1, L2 and L3 for illumination conditions. Descriptions of these regions are given in the text.

3.2. Impedance spectroscopy

3.2.1. Dark conditions

A series of impedance spectra was recorded for n-GaAs electrodes in 0.5 M H_2SO_4 under dark conditions, in the potential range from open circuit potential (OCP) to breakdown (Fig. 3). Under dark conditions, charge carrier recombination is not expected, because it is assumed that the surface concentration of minority charge carriers (holes) is in quasi-equilibrium with that of the bulk and there is no external hole injection. Empirically, the impedance spectra before breakdown (Fig. 3a and b), with just one loop, can be fit to a Randles equivalent circuit $R_s(R_{ct1}C_{sc})$ (Fig. 4a). The data after breakdown (Fig. 3c) shows two capacitive loops and one inductive loop and can be fit to the equivalent circuit in Fig. 4b. The significance of the circuit elements is described below.

In EIS analysis, a common problem encountered is the physical significance of the elements in the equivalent circuit