Polarization Behavior of GaAs in Electrolyte Solutions

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Abstract

The corrosion of GaAs has received increasing attention recently. For this small band gap semiconductor, corrosion can readily occur when it is cleaned or processed in electrolytes. This work investigated the polarization behavior of both n- and p-type GaAs in acidic H_3PO_4 and basic $NH_3{\times}H_2O$ solutions with prior surface cleaning. That it took time for the electrode to be stabilized at the open circuit potential suggested that the just-cleaned GaAs surface is very reactive and the interaction between the electrode and water in aqueous solution is not very rapid. Difficulty in obtaining a linear Mott-Schottky plot of n-GaAs in $NH_3{\times}H_2O$ was explained by the dissolution of elemental arsenic, one of the anodic decomposition products, by $NH_3{\times}H_2O$. The potential distribution at the electrode surface with different distances from the ohmic contact metallization was also studied and the validity of using the applied potential as the real potential at electrode surface was assessed.

INTRODUCTION

The corrosion of GaAs has received more and more attention in recent years with the increasing use of GaAs-based semiconductor devices. At room temperature the band gap of GaAs is about 1.42 eV, which indicates that in aqueous electrolytes, GaAs may undergo anodic decomposition under anodic polarization. This anodic corrosion is undesirable in most cases because it can limit the application of GaAs. For instance, photocorrosion of GaAs electrodes in aqueous electrolytes represents a major difficulty in implementing this active solar energy material in solar energy conversion applications. In addition, GaAs is commonly cleaned in acidic solutions, which can lead to electrochemical reactions at the semiconductor/solution interface. Galvanic corrosion of metallized GaAs is one such case. The contact metal is cathodic, while GaAs behaves as an anode and is oxidized and dissolved. In some cases, corrosion may be desirable, i.e., during processing through etching or photoetching of the semiconductor to produce devices.

Corrosion of GaAs in electrolyte solutions is an electrochemical and photoelectrochemical process. The study of the polarization behavior is one of the more common and relatively easy approaches to study this phenomenon. The current-potential characteristics for n- and p-type GaAs electrodes in strong acid solutions show that anodic decomposition occurs via the valence band[1] through this reaction:

$$GaAs + 4H_2O + 8\,h^+ \rightarrow Ga^{3+} + H_3AsO_4\,(aq) + 5H^+$$

From the above equation, it is clear that anodic decomposition of GaAs requires holes from the valence band. For n-GaAs, the hole concentration is low, so the anodic dissolution current is very small in the dark, but it can be significantly enhanced by illumination.

Flatband potential is one of the most important parameters to characterize the semiconductor/electrolyte interface. In electrochemistry, it can be obtained by extrapolating a Mott-Schottky plot, which relates the capacitance of the space charge layer to the applied potential, assuming that the capacitance of the double layer at the semiconductor/electrolyte interface is much smaller. For GaAs electrodes, a change in the potential across the Helmholtz layer has been observed after anodic and cathodic prepolarization, leading to a change in the flatband potential, which was explained by the interaction of GaAs with water to form a hydroxyl or hydride surface layer[2]. It was also pointed out that linear Mott-Schottky plots for n-GaAs were only obtained at high scan rates and after anodic or cathodic prepolarization. Selective etching of GaAs was shown, through XPS and EDX analysis, to occur in strong acid solutions. Gallium dissolves faster than arsenic, resulting in an arsenic-enriched surface layer[3].

In this work, clean GaAs electrode surfaces were prepared by three-step etching and cleaning. The polarization behavior of n- and p-type GaAs electrodes was studied in both acidic and basic solutions and compared. Due to the strip shape of the specimens used in this work, the potential distribution along the semiconductor electrode surface as a function of distance from the ohmic metallization layer was also examined.

EXPERIMENTAL

The specimens studied were n-type (Si doped, 2×10^{18} and 1×10^{17} cm^{-3}) and p-type (C doped at 1×10^{18} cm^{-3}) GaAs semiconductor strips sectioned from wafers, with about half the area covered with a standard Pd/Ge/Au (n-type) or Ti/Pt/Au (p-type) ohmic metallization layer. The backs and edges of the specimens were covered with lacquer, leaving an exposed region for experiments. Cleaning of the electrode surface was done by etching the sample in a H_3PO_4:H_2O_2:H_2O (1:1:10) solution for 15 seconds, followed by cleaning in HCl and $NH_3{\cdot}H_2O$ to remove any Ga oxides and elemental arsenic. Electrolytes used in this work were 28.5% H_3PO_4 (pH=1.2) and 1M

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$NH_3 \cdot H_2O$ (pH=11.7) solutions. All the chemicals used were analytical grade. All measurements were performed at room temperature and were open to air in daylight. The electrochemical cell used was a conventional three-electrode model, with GaAs as the working electrode and a platinum mesh as the counter electrode. A saturated calomel electrode (SCE) was used as the reference electrode and all potentials reported here were referred to SCE. A scan rate of 1 mV/s was applied in the potentiodynamic tests. For Mott-Schottky relationship measurements, a 10 mV sine wave modulated signal on a 100 mV linear potential scan was employed. All electrochemical experiments were performed on a Solartron 1287 electrochemical interface system. The potential distribution experiments were carried out by opening exposed windows at different sites at different separations with respect to the ohmic contact layer. For other polarization or Mott-Schottky experiments, the exposed windows were opened at the same distance, about 2 cm from the ohmic contact.

RESULTS and DISCUSSION

Open Circuit Potential

The cleaning procedures employed here followed those suggested in the literature[4], in which H_3PO_4 was used to remove surface metallic contaminants, HCl to remove oxides, and $NH_3 \cdot H_2O$ to remove excess elemental arsenic. The resulting clean surface is very sensitive to air and is readily oxidized in air or in aqueous solutions, as verified by the changing open circuit potential (OCP) upon immersion in the electrolytes (Figure 1).

The difference in behavior between n-type or p-type GaAs in H_3PO_4 and $NH_3 \cdot H_2O$ is due to the difference in pH of the two solutions. In acidic solutions, the equilibrium reaction with the electrode is the reduction of hydrogen ions, while the reduction of oxygen occurs in $NH_3 \cdot H_2O$. The difference in OCP for different types of GaAs, in the same solution, is due to differences in hole concentration. The greater the number of holes in the semiconductor, the easier it is oxidized and the more positive the OCP.

Potential Distribution

The GaAs specimens used in this portion of the work were partially metallized strips sectioned from wafers, which had circular,\ GaAs openings patterned with stop-off lacquer at various locations from the metallization (see inset in Figure 2). The position of these openings may lead to differences in the potential distribution. When there is a current flowing through the sample during polarization, it is expected that the potential at these different sites on the sample would not be the same due to the inherent poor conductivity of the semiconductor. Figure 2 shows examples of polarization curves of n-GaAs (1×10^{17} cm^{-3}) in H_3PO_4 at sites with different separation from the ohmic contact.

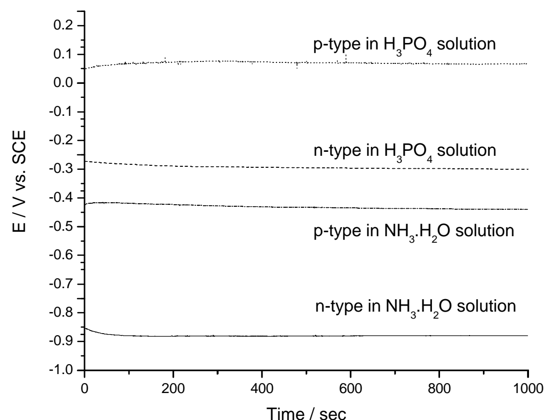

Figure 1 OCP for both n- and p-type GaAs in H_3PO_4 and $NH_3 \cdot H_2O$ solutions.

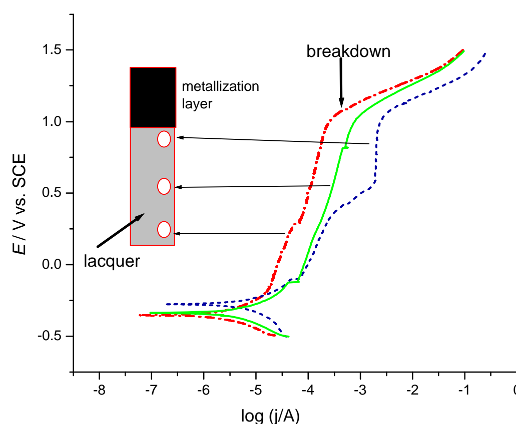

Figure 2 Polarization curves for n-GaAs (1×10^{17} cm^{-3}) in an H_3PO_4 solution at sites with different separations relative to the ohmic metallization layer, without holding for a stable OCP. The distances among these sites from the ohmic contact were 2.1 cm, 1.4 cm and 0.2 cm from the bottom to the top, respectively.

It is interesting that the closer the site is to the metallization layer, the more positive is the OCP. A possible explanation is that there is a potential drop in the bulk of the semiconductor close to the OCP. As assumed above, the surface before measurement was clean and readily oxidized. In addition, 30 minutes was needed for the electrode to stabilize in water. Therefore, for these measurements, at applied potentials close to the OCP, equilibrium between the electrode and solution had not been reached, resulting in current flowing through the electrode. On the other hand, it is clear in Figure 2 that the breakdown potentials at different sites are same, which can be explained from Figure 3. The real part of the Mott-Schottky measurement is the resistance of the electrode

and the double layer. Figure 3 shows that when the applied potential is close to the breakdown potential (about 1.0 V vs. SCE for this doping density), the resistance is much lower than for applied potentials closer to the OCP.

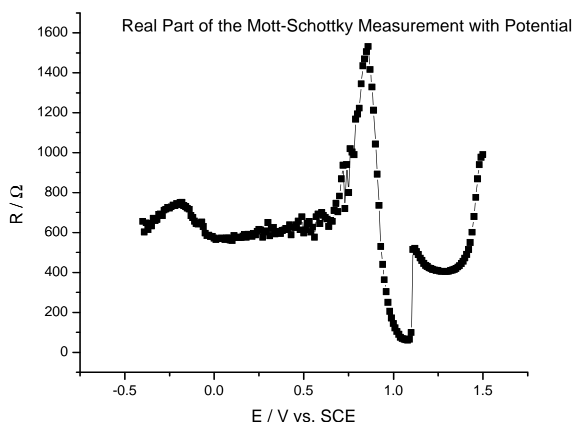

Figure 3 The real part of the Mott-Schottky measurements as a function of potential. The doping density is the same as in Figure 2.

One important problem brought up here is whether the potentials measured from the instrument are exactly the potentials at the electrode surface. Obviously, at breakdown where the resistance of the semiconductor is rather small and the semiconductor behaves like a metal (Figures 2 and 3), the potential applied can be treated as that at the electrode surface. However, for other potential regions studied here, the potential drop in the bulk semiconductor cannot be neglected. Therefore, one should be careful to examine the real potential at the electrode surface and the validity of the Mott-Schottky plot, which will be further discussed below.

Mott-Schottky Plot and Polarization Behavior

Mott-Schottky plots for both n- and p-type GaAs in H_3PO_4 and p-type GaAs in $NH_3{\cdot}H_2O$ exhibit regions of linear behavior, as shown in Figure 4. The valid potential region for the Mott-Schottky relationship for n-type GaAs was determined to be from about the OCP to the breakdown potential, while that for p-type GaAs was where no anodic decomposition occurred (below the OCP). The potential region below the OCP is not valid for n-type because of the reduction of oxygen at the surface and because the current is not negligible, compared to the anodic saturation current. It is worthwhile to point out that before the measurement of these curves, the electrodes were held in the solution until a stable OCP was reached. Mott-Schottky plots, obtained without holding the electrode for a stable OCP, were not reproducible. Waiting for a stable OCP results in equivalent effects to prepolarization. By holding the electrode at the OCP, the electrode surface interacted with water, forming a hydride or hydroxyl layer at the surface depending on the pH of the solution. The typical time required for a stable OCP was about 30 minutes, implying that this process is not very rapid. The flatband potentials from Mott-Schottky plots of n-type GaAs in acid solution were -1.0±0.1 V vs. SCE, and those for p-type GaAs were about +0.4±0.2 V for the same doping density. The difference between these two flatband potentials was reasonable since it was close to the band gap, 1.424 eV. (The samples used here have Fermi level close to the band edge.) The flatband potential of p-GaAs in $NH_3{\cdot}H_2O$ was about -0.25 V.

Linear Mott-Schottky plots for n-GaAs in $NH_3{\cdot}H_2O$ could not be obtained. This may be due to the formation of decomposition products on the GaAs surface. As indicated in the literature[3,5,6], one of the anodic decomposition products for GaAs in acid solutions is elemental arsenic. As mentioned above, elemental arsenic can only be dissolved in $NH_3{\cdot}H_2O$ solutions. Oxidation of n-type GaAs is much slower than for p-type, since there are significantly fewer holes in n-GaAs even under illumination. In $NH_3{\cdot}H_2O$ solutions, during oxidation of GaAs, elemental arsenic generated is stripped away by $NH_3{\cdot}H_2O$ resulting in an unstable surface. At the p-GaAs surface, the generation of arsenic is so fast that the electrode surface can remain stable with some arsenic coverage. Other evidence supporting this explanation is that the oxidation current density for p-GaAs is about two orders of magnitude higher than that for n-GaAs.

Polarization curves for n-GaAs in both solutions are shown in Figure 5. The two curves differ in corrosion potential and breakdown potential, while the corrosion current densities in the saturated region are similar. The difference in the breakdown potential can be inferred from the difference in the flatband potential. The flatband potential for n-GaAs in $NH_3{\cdot}H_2O$ was not attainable; however, the difference for p-GaAs in $NH_3.H_2O$ and H_3PO_4 was ~0.6 V. Based on this result, a similar value can be assumed for n-GaAs. The value of 0.6 V is slightly larger than the measured difference in breakdown potential (~0.5 V from Figure 5). The reason might be that the elemental arsenic formed at the electrode surface in acidic solutions pins the band edge of the semiconductor. The result would be reduced band bending compared with the case without Fermi level pinning and therefore higher potential/electric field would be required to break the semiconductor down.

As stated above, the potential at the electrode surface is not exactly that applied due to the potential drop in the bulk semiconductor. Fortunately, the potential region used in this work to determine the flatband potential from Mott-Schottky plots has a nearly constant resistance (Figure 3). Furthermore, from the polarization curves (Figure 5), in the region of interest for Mott-Schottky measurements, the anodic current density is also nearly constant. Thus, the Mott-Schottky relationships in Figure 4 should still apply,

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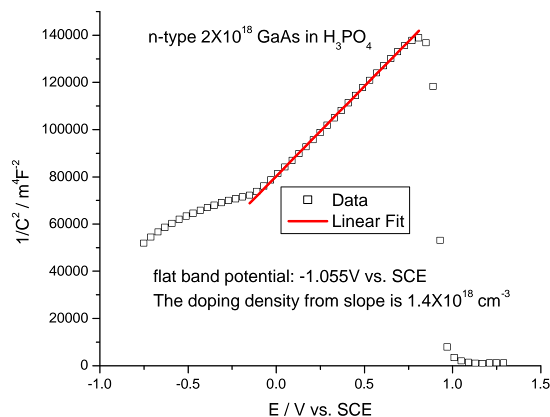
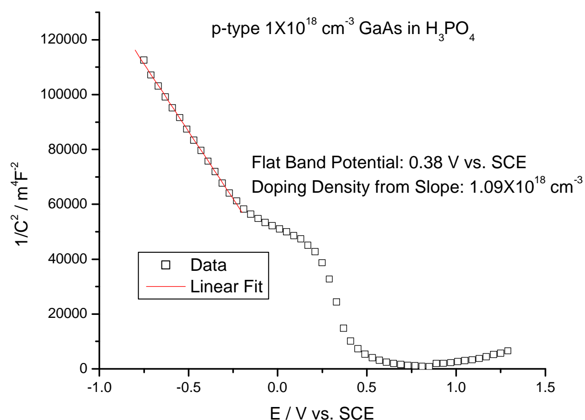
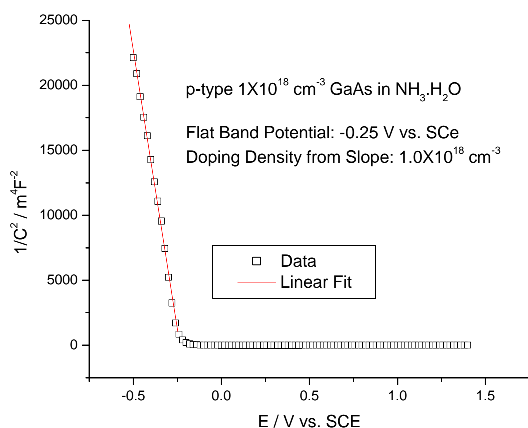
while requiring a correction or offset in the constant potential value.



(a)



(b)



(c)

Figure 4 Mott-Schottky plots for both n-type GaAs (a) and p-type GaAs (b) in H_3PO_4 solutions and p-type GaAs in $NH_3{\cdot}H_2O$ (c).

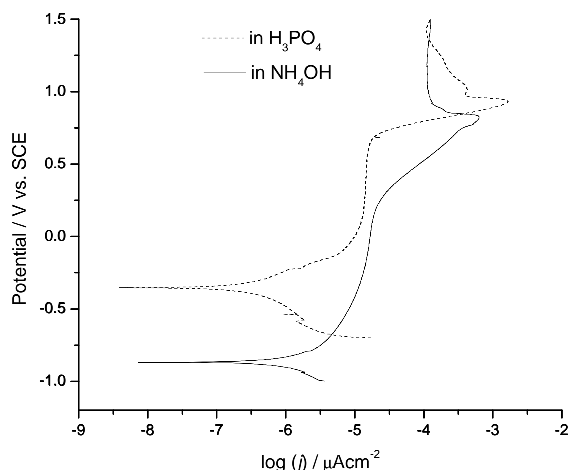


Figure 5 Polarization curves for n-type GaAs in the two solutions.

CONCLUSIONS

The polarization behavior of both n- and p-type GaAs was studied in acidic and basic solutions. The results including the open circuit potential, flatband potential from Mott-Schottky plots and the breakdown potentials were compared. The differences among these results were explained by the difference in decomposition products. In acidic solutions, GaAs was oxidized to produce elemental arsenic, enriched on the surface, while in the ammonium solution, arsenic was further dissolved and therefore a linear Mott-Schottky plot of n-GaAs in ammonium solution could not be obtained.

The investigation of the potential distribution at the electrode surface indicated that the potential at the electrode surface might not be the same as the applied potential due to the poor conductivity of the semiconductor. Discussion on the validity of flatband potential suggests that an offset should be applied to correct the value from the extrapolation of Mott-Schottky plot.

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