

Corrosion Behavior and Surface Studies of GaAs in Acidic Solutions

C.A. Steer, J.L. Luo and D.G. Ivey

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

Phone: 780-492-2957; e-mail: doug.ivey@ualberta.ca

Abstract

The corrosion behavior of GaAs in various acid solutions and deionized water was studied. Potentiodynamic polarization measurements show that the factors promoting the generation of holes, or the injection of holes from the solution to the valence band, will increase the tendency of the semiconductor towards active dissolution.

During anodic polarization of n- and p-GaAs in acids, air-formed As and Ga oxides are both dissolved. The GaAs substrate is also dissolved and significant anodic segregation occurs leaving an As-rich surface layer, which gradually agglomerates and oxidizes to form As_2O_3 particles upon exposure to air. For n-type GaAs, polarized in the dark or immersed in acidic solutions at the corrosion potential for 2 hours, no As enrichment of the surface or As_2O_3 particle formation occurs. Polarization of GaAs in deionized water did not remove the surface film; instead the oxide layer thickened without the formation of As_2O_3 particles.

INTRODUCTION

Wet chemical etching is commonly used for III-V based semiconductors, both for cleaning and to etch specific features in wafers.^{1,2} Wet chemical etching is attractive because the materials are generally single crystal and the etch rate depends on crystal orientation. The etch rate can be altered significantly, however, due to galvanic effects. Semiconductor heterostructures are particularly susceptible to such effects.

The purpose of the present work is to study corrosion behavior of GaAs semiconductor electrodes in acid solutions and deionized water. The influences of the type of semiconductor and illumination on the electrochemical behavior of GaAs are investigated. Scanning electron microscopy (SEM), energy dispersive x-ray (EDX) spectroscopy in the SEM and x-ray photoelectron spectroscopy (XPS) are used to characterize the surface morphology and to analyze the composition of the surface layer before and after electrochemical tests. GaAs oxidation after electrochemical treatment is also investigated.

EXPERIMENTAL PROCEDURE

The specimens studied were n-type (Si doped at 10^{18} cm^{-3}) and p-type (C doped at 10^{18} cm^{-3}) GaAs semiconductor strips sectioned from partially metallized wafers. Prior to the tests, the specimens were cleaned in a 1%HF solution for 2 minutes, to remove the air-formed oxide layer, and then rinsed with deionized water. The electrolytes used in this work were 28.5% H_3PO_4 solutions (pH=1.19), 1%HF solutions

(pH=3.13) and deionized water (pH=7.66). All measurements were performed at room temperature (22°C) in light (daylight) unless otherwise stated.

Electrochemical measurements were conducted in a conventional three-electrode (a GaAs working electrode, a saturated calomel reference electrode (SCE) and a platinum counter electrode) cell. All potentials reported in this work were taken with reference to the SCE electrode. The electrochemical measurements were performed with a potentiostat. A potential scanning rate of 1 mV/s was used for the potentiodynamic polarization tests.

Surface morphology and oxide formation were studied using SEM, EDX and XPS.

RESULTS AND DISCUSSION

The polarization curves for n- and p-GaAs specimens in phosphoric acid are shown in Fig. 1(a). The current densities for the n-GaAs specimen, in the anodic potential range between -0.2 and 1 V, are approximately $10^{-5} \text{ A}\cdot\text{cm}^{-2}$. The current densities for the p-GaAs specimen above 0.2 V are greater than $10^{-4} \text{ A}\cdot\text{cm}^{-2}$, or about one order of magnitude greater than those for the n-GaAs specimen. Similar polarization curves were obtained for n- and p-GaAs in 1% HF.

Polarization curves measured in the dark for n- and p-GaAs specimens in phosphoric acid are shown in Fig. 1(b). The anodic current densities between 0 V and 0.8 V are less than $1 \times 10^{-7} \text{ A}/\text{cm}^2$ for n-GaAs, which is three orders of magnitude less than those for p-GaAs. Comparing Fig. 1(a) with Fig. 1(b), it is clear that the difference between the anodic current densities for n-GaAs and p-GaAs in the dark is greater than that in the light.

Polarization curves measured for GaAs in deionized water are shown in Fig. 1(c). The anodic current densities for both n- and p-GaAs are the same when the potential is above 0.5 V, indicating that both have similar stabilities in deionized water.

SEM examination indicates that a significant number of particles were formed on the surface of specimens polarized in phosphoric acid solutions, with the exception of n-type GaAs tested in the dark.

To investigate the particle formation process, GaAs specimens were polarized at 0.75 V vs. SCE for 2 hours in either phosphoric acid or deionized water, followed by

SEM, EDX and XPS analysis immediately after potentiostatic testing and after exposure to air. For comparison, the same

than 10 minutes (Fig. 2(a)) and there was no apparent change compared with the morphology of the cleaned specimens before the potentiostatic tests. Crystalline particles began to appear on the specimen surface after exposure to air for about 20 hours. The number and size of particles increase with increasing air exposure time (Fig. 2(b)). EDX analysis shows that the particles are enriched with As relative to the GaAs surface. An oxygen peak is also present in the spectrum, indicating that the As has been oxidized.

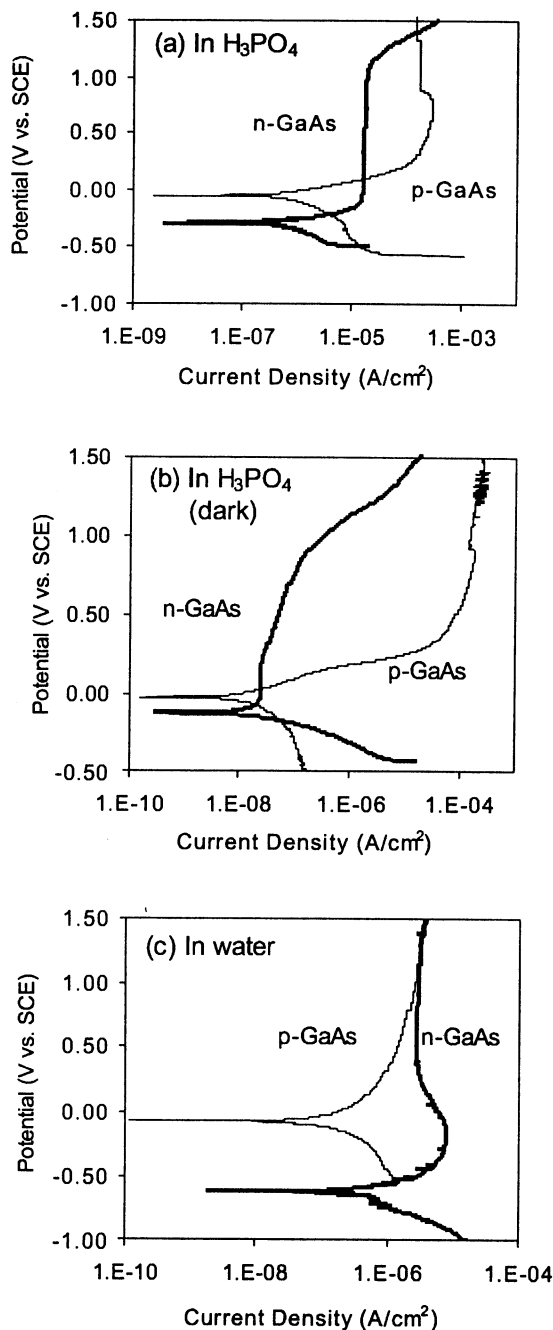


Fig. 1 Polarization curves of GaAs.

analyses were also performed on cleaned specimens before electrochemical testing and on specimens immersed in phosphoric acid at the corrosion potential.

SEM images after the potentiostatic tests are shown in Fig. 2. The surface was featureless when exposed to air for less

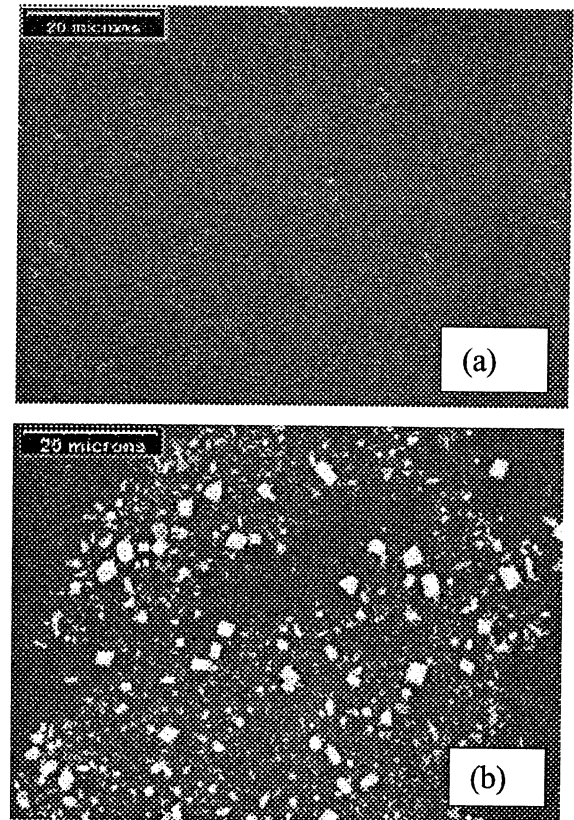


Fig. 2. SEM micrographs of the n-GaAs surface: (a) 10 min. and (b) 17 days after polarization at 0.75 V for 2 hours in 28.5% H₃PO₄.

To investigate whether the formation of the surface particles is independent of potential, similar experiments were performed at the corrosion potential in phosphoric acid. SEM images taken from these samples showed featureless surfaces, even after several days of exposure to air; no As-rich particles were detected.

For specimens polarized in deionized water in both light and dark, the surface was generally featureless with no particle formation after exposure to air for several days. To further study the particle formation process in acid solutions, n-GaAs specimens were analyzed with XPS prior to testing, immediately after testing and after 7 days of exposure to air. XPS spectra for these three conditions are shown in Figs. 3 (Ga 3d) and 4 (As 3d).

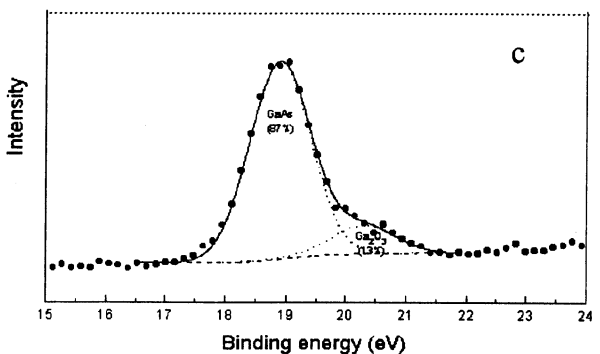
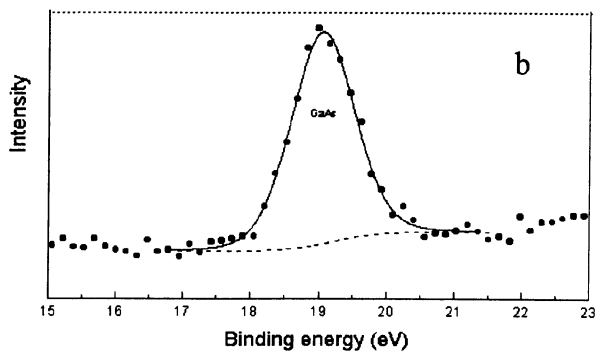
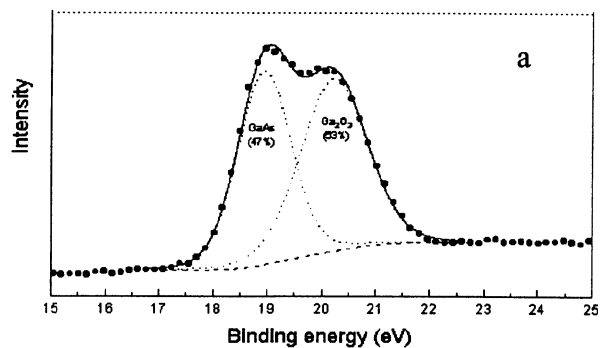


Fig. 3. Ga 3d spectra for an as-received GaAs specimen (a), immediately after polarization at 0.75V in H_3PO_4 (b) and after exposure to air for one week (c).

The spectra from the as received specimens are shown in Figs. 3(a) and 4(a). Peak deconvolutions were performed on the spectra. The Ga 3d spectrum showed two merged peaks with binding energies at about 18.9 eV and 20.3 eV, respectively. The peak at about 18.9 eV can be identified as GaAs and the one at about 20.3 eV is from Ga_2O_3 . The As 3d spectrum consists of 3 peaks: As 3d from GaAs at about 40.9 eV, As 3d from As_2O_3 at about 44.5 eV and As 3d from As_2O_5 at about 45.8 eV. These spectra indicate that the as received surface was covered with a surface oxide layer consisting of As_2O_3 , As_2O_5 , and Ga_2O_3 . The GaAs peaks observed in Ga 3d and As 3d were from the substrate.

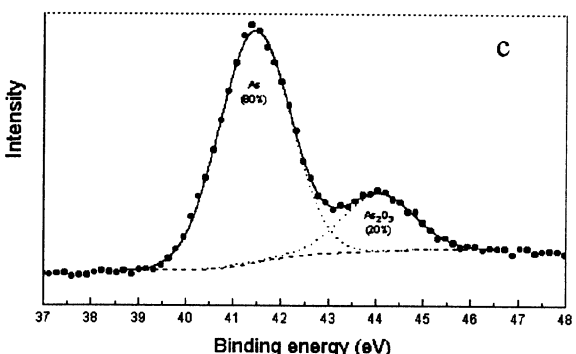
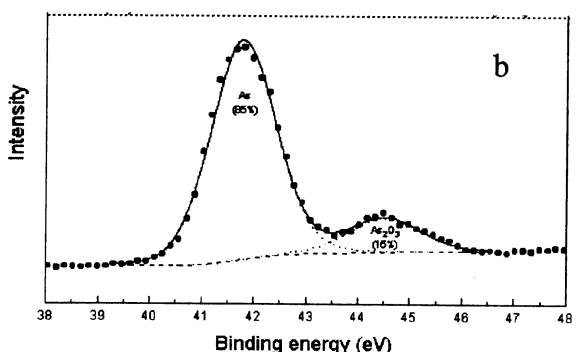
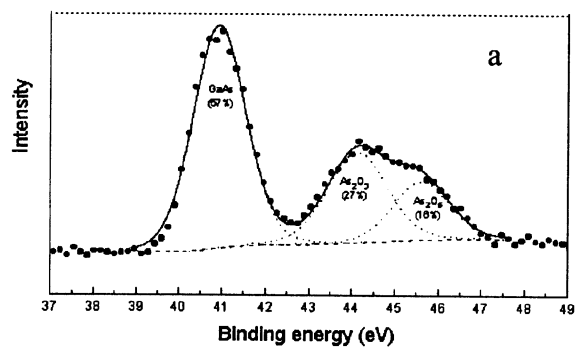


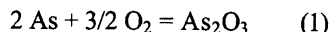
Fig. 4. As 3d spectra for an as-received GaAs specimen (a), immediately after polarization at 0.75V in H_3PO_4 (b) and after exposure to air for one week (c).

The XPS spectra for the sample immediately after polarization testing are shown in Figs. 3(b) and 4(b). The prominent Ga_2O_3 peak in Fig. 3(a) has disappeared, indicating that Ga_2O_3 is completely dissolved in phosphoric acid. Comparing the intensity of the signal in Fig. 4(b) with that in Fig. 4(a), it is clear that As_2O_5 was also dissolved in the acid. As_2O_3 is the only oxide remaining on the surface after polarization testing. The GaAs peak in Fig. 4(a) (as received sample) at about 40.9 eV for the as-received specimen disappears after testing (Fig. 4(b)) and a new peak at a binding energy of about 41.7 eV is clearly observed after testing. This peak can be identified as As. The As peak is so strong that it is difficult to pick out the weak As 3d peak contributed

from the substrate GaAs without ambiguity. The Ga 3d peak from the GaAs substrate can still be seen clearly in the Ga 3d spectrum (Fig. 3(b)) because the surface is depleted in Ga and, therefore, the Ga 3d photoelectrons from the substrate become the main contributors to this spectrum. This indicates that the outermost surface layer after polarization testing is rich in As with a small amount of As₂O₃, which formed in air during rinsing and transfer to the spectrometer.

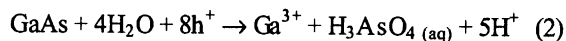
The XPS spectra for Ga 3d and As 3d, for specimens exposed to air for 7 days following electrochemical testing, are shown in Figs. 3(c) and 4(c). Comparison of the As 3d spectrum obtained on the freshly polarized specimen (Fig. 4(b)) with that obtained for the aged specimen (Fig. 4(c)) indicates that the As₂O₃ peak intensity has increased after exposure to air. No detectable As₂O₅ was found on the aged surface. The Ga 3d spectrum (Fig. 3(c)) has a shoulder in the higher binding energy side (about 20.3 eV). This peak is from Ga₂O₃, the same as that seen in the Ga 3d spectrum obtained from the as-received specimen (Fig. 3(a)).

According to the Pourbaix diagram for the GaAs-H₂O system at 25°C,² the stable species at 0.75 V and pH of 1.19 are Ga³⁺ and H₃AsO₄(aq) which are soluble. However, it appears that selective dissolution of gallium results in anodic surface segregation of a pure layer of As. The As is initially distributed uniformly as a thin layer over the entire surface. Upon exposure to air, the arsenic oxidizes and forms crystalline particles:



Schmuki et al.³ have also found that an outer As₂O₃-rich layer was formed on p-GaAs in a borate buffer solution. The formation of As₂O₃ leaves the underlying GaAs exposed to air, which causes it to oxidize. The fact that no As-rich crystal particles were detected by SEM on the surface for specimens tested in phosphoric acid at the corrosion potential indicates that the formation of the crystalline particles is potential dependent. At the corrosion potential, the dissolution rate is very low, leaving the substrate intact with no As enrichment at the surface.

The corrosion mechanism of a semiconductor involves the anodic dissolution of GaAs. The nature of the reaction product depends on the pH and the composition of the electrolyte. According to the Pourbaix diagram for GaAs-H₂O system at 25°C,² the electrochemical reaction for the GaAs electrode in a 28.5% H₃PO₄ solution (pH = 1.19) at an applied potential of 0.75 V vs. SCE is:



Arsenic is oxidized to form a dissolvable compound H₃AsO₄ accompanying the dissolution of GaAs semiconductor. The GaAs corrosion process depends on the presence or injection of holes into the interface.⁴ For n-type GaAs, reaction (2) depends on the generation of minority charge carries in the valence band. Several possible mechanisms exist, including electron tunneling, light absorption or injection by oxidant present in the electrolyte. Of these, photon absorption is clearly operating, as is evident by comparing the anodic current densities in Figs. 1(a) and 1(b). Holes produced by electron tunneling are possible when the field strength is high enough to permit emission of electrons from the valence band

edge at the surface of GaAs into the conduction band in the bulk. This phenomenon is observed when n-GaAs is polarized at potentials above 1 V (Figs. 1(a) and 1(b)). If surface states exist, hole generation by internal field emission of electrons occurs readily on the surface. The third mechanism, injection of holes by the oxidant in solution, requires the oxidant to have vacant energy levels near the valence band edge of GaAs. This principle may be able to explain the differences in anodic behavior for GaAs in different solutions. When holes are generated, they remain at the interface and are consumed by oxidation of the semiconductor.

For p-type GaAs, the rate of the reaction (2) will not be controlled by holes because the holes in the valence band are the majority charge carries. This can be seen from the polarization curves presented in Figs. 1(a) and 1(b). There is a characteristic difference between the polarization curves for n- and p-type GaAs in acid solutions. The anodic current densities for p-GaAs are much greater than those for n-GaAs.

The dissolution processes for oxides on the GaAs surface during polarization in deionized water were different from those in acid. Polarization in deionized water did not remove the surface film; instead the oxide film thickened. Selective dissolution of As oxide occurred resulting in a minor decrease in the As/Ga ratio of the surface oxide. The thick oxide formed during polarization testing in water may have prevented further oxidation of the surface. However, the stabilities of the oxides are potential dependent. It has been reported³ that Ga₂O₃ is much more stable than As₂O₃ in water when no external potential is applied to the specimen.

SUMMARY

Polarization in phosphoric acid can effectively remove the surface oxide previously formed on GaAs in air. However, the remaining surface is rich in As, which suggests that selective dissolution occurred during polarization. As₂O₃ particles formed on the surface after exposure to air. Polarization in deionized water resulted in the thickening of the pre-existing surface oxide and a decrease in the As/Ga ratio in the oxide layer. Anodic dissolution of GaAs in acids depends on the availability of holes. Illumination increases the tendency of n-GaAs towards active dissolution because of photo-generated holes.

ACKNOWLEDGEMENTS

This research was supported by Nortel Networks and NSERC of Canada.

REFERENCES

1. J.J. Kelly, J.E. A.M. van den Meerakker, P.H.L. Notten and R.P. Tijburg, Philips Tech. Rev, **44**, 61 (1988).
2. D. Tromans, G.G. Liu and F. Weinberg, Corrosion Science **35**, 117 (1993).
3. P. Schmuki, G.I. Sproule, J.A. Bardwell, Z.H. Lu and M.J. Graham, J. Appl. Phys. **79**, 7303 (1996).
4. R.D. Turner, J. Electrochem. Soc. **107**, 810 (1960).