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The etching behavior of n-GaP in aqua regia solutions

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Abstract

The etching of GaP, whether in strong HNO_3 or in strong HCl is severely inhibited, whereas mixtures of HNO_3/HCl are commonly employed as etchants for chemical polishing. The etching mechanism of n-GaP in aqua regia (3HCl/1HNO_3) has been investigated. Aqua regia etching may occur by accomplishing both the following two processes: (1) oxidation and (2) dissolution. First, the nascent chlorine and nitrate ions obtained from the vigorous interaction between HCl and HNO_3, may easily oxidize the surface atoms of GaP, then nucleophilic attacked by Cl^- on the electron-poor trivalent gallium ions of the oxide lattice generally takes place over the passive surface. Moreover, the remaining phosphate or phosphorus oxide is very soluble. Ga and P atoms are thus carried away from the surface by the etchant system. In HNO_3-etch, the nitrate ion formed is a weak nucleophile and the amount of its production is very small. In the HCl-etch, Cl^- causes a direct attack on GaP substrate via an $Ga^{(I)}$ chloro intermediate whose thermodynamics is very unfavorable. Thus, the experimental observations are in good agreement with the mechanistic concepts presented.

1. Introduction

In the field of metal insulator semiconductor (MIS) technology, the application of the III-V compound semiconductors to device fabrication has grown considerably in the recent decade. However, the main technological problem to be resolved is the instability of the devices, probably related to the quality of the semiconductor–insulator interface. This point is the importance of preparing clean semiconductor surfaces [1].

The mixtures $HCl/HNO_3/H_2O$ are widely used for many III-V materials [2–6]. For example, one of the most commonly employed etchants for GaP is aqua regia solution. However, very little is known about the mechanism of III-V semiconductors in such etchant systems.

X-ray wide angle diffraction (WAD) and glancing angle diffraction (GAD) techniques have been used in our previous studies [7–13] to establish a much better understanding of the chemical nature of GaP, [7–9] GaAs, [10, 11] and InP [12–14]surfaces after a variety of chemical treatments. In previous work, [7–9] the dissolution mechanisms of n-GaP in HNO_3 and in HCl have been investigated, respectively. These experiments revealed that the dissolution rates for GaP, whether in HNO_3 or in HCl, were all very low and increased little over a large acid concentration range.

In HNO_3-etch, the reduced intermediate, nitrite ions (NO_2^-), could cause nucleophilic attack on the electron-deficient gallium component and the residue of phosphate or phosphorus oxide is very soluble in water. And the electrode material was thus etched. But, an electron transfer from GaP across the interface to NO_3^- ion would preferably be weak.

In HCl-etch, Cl^- cannot participate in the dissolution intermediate because the lower valence $Ga^{(I)}$ compounds are obtained only with difficulty. In contrast, the mixture of above two acids was very widely used for polishing GaP substrate.

In this work we attempted to make a step toward a better understanding of the etching mechanism for the n-GaP (100) in the aqua regia solutions (3HCl/1HNO_3). In particular possible effects of the interaction between HCl and HNO_3 on the efficacy of the mixture as a powerful etchant are examined. To these ends, the presented mechanistic concepts are extended to illustrate the different reactivities for the individual component acid.

2. Experimental

The GaP substrates were (100) oriented n-type slices doped with Si at a concentration of 10^{17} atoms cm^{-3}. All solutions were prepared by dissolving reagent-grade chemicals from Merck in de-ionized water (resistivity of 18 MΩ). The maximum acidities available for HCl and HNO_3 were 12 M and 16 M, respectively.

The dissolution rate of the Group III and Group V constituents of the GaP samples in the solution were measured by inductively coupled plasma (ICP) emission spectrometry. Unless otherwise indicated in the measurements of dissolution rate vs. concentration of aqua regia, the aqua regia was prepared first. The reaction mixture was then left standing for 5 min. Finally, de-ionized water with GaP samples was added to the reaction mixture.

Nitrite ion concentrations before etching were analyzed by ultraviolet and visible spectroscopy (U-3410 spectrophotometer, Hitachi Company).

The n-GaP electrodes used indium solder for the back contact, and were heated for 30 min at 250 °C in air. The electrode was encapsulated in epoxy cement. All potentials were measured relative to a saturated calomel electrode (SCE) with an electrometer (Keithley 602C).

The composition of the solid oxide layer on GaP was identified at room temperature by an MXP 18 X-ray diffraction meter (XRD) (Material Analysis and Characterization Company, Japan). Two different XRD analyses were employed in this work: wide-angle diffraction (WAD) technique of the conventional θ–2θ scanning technique and glancing-angle diffraction (GAD) technique of asymmetric-Bragg diffraction. To increase intensities, a 12 kW rotating Cu anode X-ray source was used. The GAD measurement was performed using a spectrometer attached to the thin film measuring system. The bent analyzing crystal monochromator used for WAD measurements was changed by a flat graphite (0002) for GAD measurements. The thin film specimen was fixed at an incidence angle 0.5° larger than a critical value (α_c=0.33°) below which X-ray total reflection occurred.

The morphology of the GaP surface after etching was examined by scanning electron microscopy (SEM) after a thin, and conducting layer of gold was deposited on all samples.

3. Results and discussion

3.1. *Dissolution of GaP*

The dissolution rate of GaP in aqua regia solutions of various dilution by de-ionized water were determined analytically by measuring the phosphorus concentration in the etching solution by ICP. Figure 1 shows the phosphorus dissolution rate as a function of the volume ratio (VR) of aqua regia (AR). The axis of the abscissa stands for the aqua regia ratio in the etching solution on a volume basis, i.e., 1/2 for 1 vol. aqua regia plus 1 vol. H_2O, e.g., solution X in Figure 1. The dissolution rate sharply drops to a very low value as the concentration of aqua regia is decreased to one-eighth of pure aqua regia.

Before the immersion of GaP wafer in these aqua regia solutions, the color of the solution changed first to light-yellow, then to reddish-yellow, and finally to dark orange-red. Presumably the color was produced by the presence of nitrosyl chloride (NOCl), and the solution foamed simultaneously. This reaction occurred rather quick as soon as HCl and HNO_3 were mixed together. Yellow fumes were observed to evolve from the solution, and they are probably NOCl too. At lower aqua regia concentrations ($<$ 1/2), inspection of this etching solution before immersing GaP test sample showed that diluted aqua regia became clear and appeared to stop the progress of the reaction.

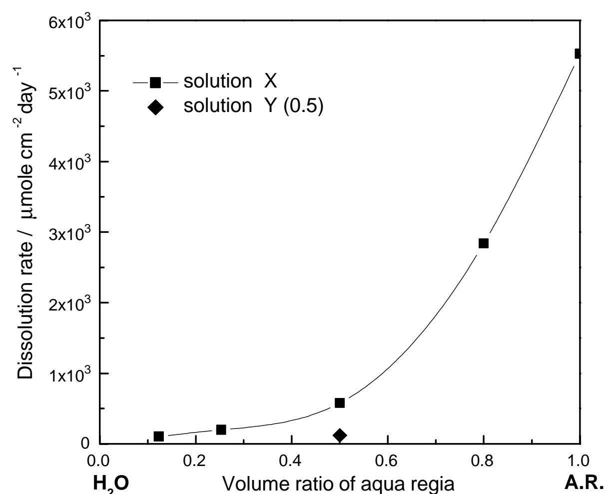
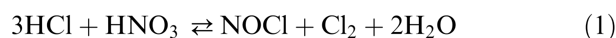


Fig. 1. Dissolution rates of GaP (measured as P) vs volume ratio of aqua regia ($3HCl/1HNO_3/4H_2O$ mixed simultaneously, then remained for 5 min. Before etching (■), $3HCl/1HNO_3$ mixed initially, then remained for 5 min, $4H_2O$ added to it finally (◆)).

One effect of the very rapid reaction between HCl and HNO_3 was found when a different sequence of dilution was carried out in the etching solution preparation at the same aqua regia concentration. For instance, 1 vol. aqua regia and 1 vol. H_2O were mixed together, and then a GaP sample was immersed in this solution, which remained clear. No yellowish color was observed as with previous solution prepared (solution X). Such solution stood for 5 min before the immersion of GaP and was designated as solution Y. It can be seen that the rate of dissolution falls off to the value close to the rate of no reaction, as shown in Figure 1. Thus, the high dissolution rates seem to be associated with the strong interaction between the etchant components and the low rates with weaker or even no such reaction.

The dissolution rates of GaP in pure aqua regia as a function of time between the preparation of aqua regia and the immersion of GaP are shown in Figure 2. A more than 20-fold increase of the dissolution rate takes place when the lapse of time is increased from 0 to 120 min. This fact proves the importance of a reaction intermediate or final product from the interaction between HCl and HNO_3 in participating in the dissolution process of GaP.

The reaction between HCl and HNO_3 in aqueous solutions has been reported to be



$$3HCl + HNO_3 \rightleftarrows NOCl + Cl_2 + 2H_2O \quad (1)$$

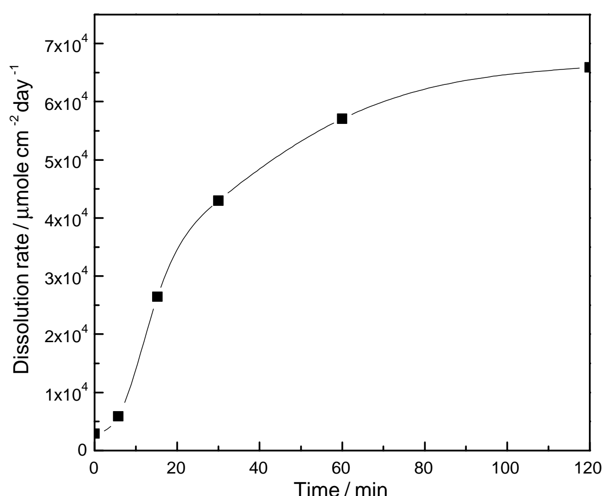


Fig. 2. Dissolution rates of GaP (measured as P concentration) vs time between the preparation of aqua regia and using it to etch GaP.

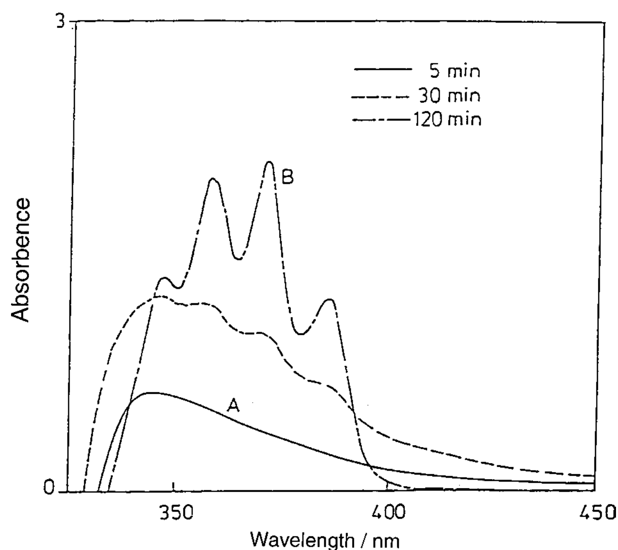
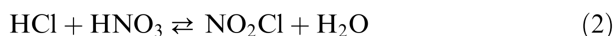


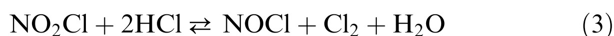
Fig. 3. Ultraviolet and visible spectra of aqua regia vs time between the preparation of aqua regia and the immersion of GaP.

which consists of two separate sequential reactions, [15]



$$HCl + HNO_3 \rightleftarrows NO_2Cl + H_2O \quad (2)$$

and



$$NO_2Cl + 2HCl \rightleftarrows NOCl + Cl_2 + H_2O \quad (3)$$

With water, the nitrosyl chloride rapidly hydrolyzes,

$$NOCl + H_2O \rightleftarrows HNO_2 + HCl \quad (4)$$

and then, HNO_2 decomposes quickly into NO and HNO_3

$$3HNO_2 \rightleftarrows 2NO + HNO_3 + H_2O \quad (5)$$

These results indicate that aqua regia not only acts as a powerful oxidizing agent but also as a nucleophile because it contains NO_2^- in addition to Cl^-. Our investigation [7] of GaP in HNO_3 has previously suggested that the nucleophile attack of the reduced intermediate (NO_2^-) on the oxidized surface leads to the dissolution of the semiconductors. Thus, the properties of the $3HCl/1HNO_3$ mixture were re-examined by UV–Visible spectrometry.

3.2. *Characterization*

3.2.1. *UV spectra*

The UV-Visible spectra of the aqua regia solution which remained for 5, 30, and 120 min, respectively, before immersing GaP samples show the characteristic peaks of N=O chromophore, as indicated in Figure 3. It clearly reveals how the transitions of $n \rightarrow \pi^*$ type shift to longer wavelength when the time is increased from 5 to 120 min, and the fine structure of the absorption band appears. The variations of dominant species indicated during the course of the reaction suggest that the formation of compound A would occur at the early stage of the chemical reaction, followed by its consumption in the subsequent reaction to produce compound B.

To help identify the peaks in Figure 3, the comparison between spectra in Figure 3 and those in the previous work [7] shows curve B is the fine structure of the same absorption band as that of the π–conjugating substituent of NO_2^- ion. Small shifts of the energy of electronic transition between these two compounds (A and B) suggest that the electronic structure for compound A is similar to that of NO_2^- presumably NOCl of the HCl/HNO_3 mixture. According to the hydrolysis reaction (Equation 4), the sequence of HCl/HNO_3 interaction is consistent with the variation of UV spectrum vs. time. The fact that the accumulation of NO_2^- concentration is in parallel with the increase of dissolution rate supports the suggestion that the large amount of nitrite ions formed must make some important contributions to enhance the etching ability of aqua regia.

Another series of experiments were performed by substituting NO_2^- ions for NO_3^- ions component of aqua regia. Namely, the original $3HCl/1HNO_3$ mixture was replaced by HCl/NO_2^-. This added NO_2^- concentration equaled that produced from $3HCl/1HNO_3$ interaction, just before the immersing of GaP test sample, by a quantitative analysis of UV–Visible spectrometry. The dissolution rate of GaP in this case was about only one-twentieth as fast as that in pure aqua regia, as shown in Table 1.

Table 1. NO_2^- effect on the etching ability of aqua regia

Etchant	Dissolution rate μmol cm^{-2} day^{-1}
HCl/HNO_3	6.6×10^4
HCl/NO_2^-	2.8×10^3
HNO_3/NO_3^-	2.6×10^2
HCl	1.2×10^2
HNO_3	0.7×10^2

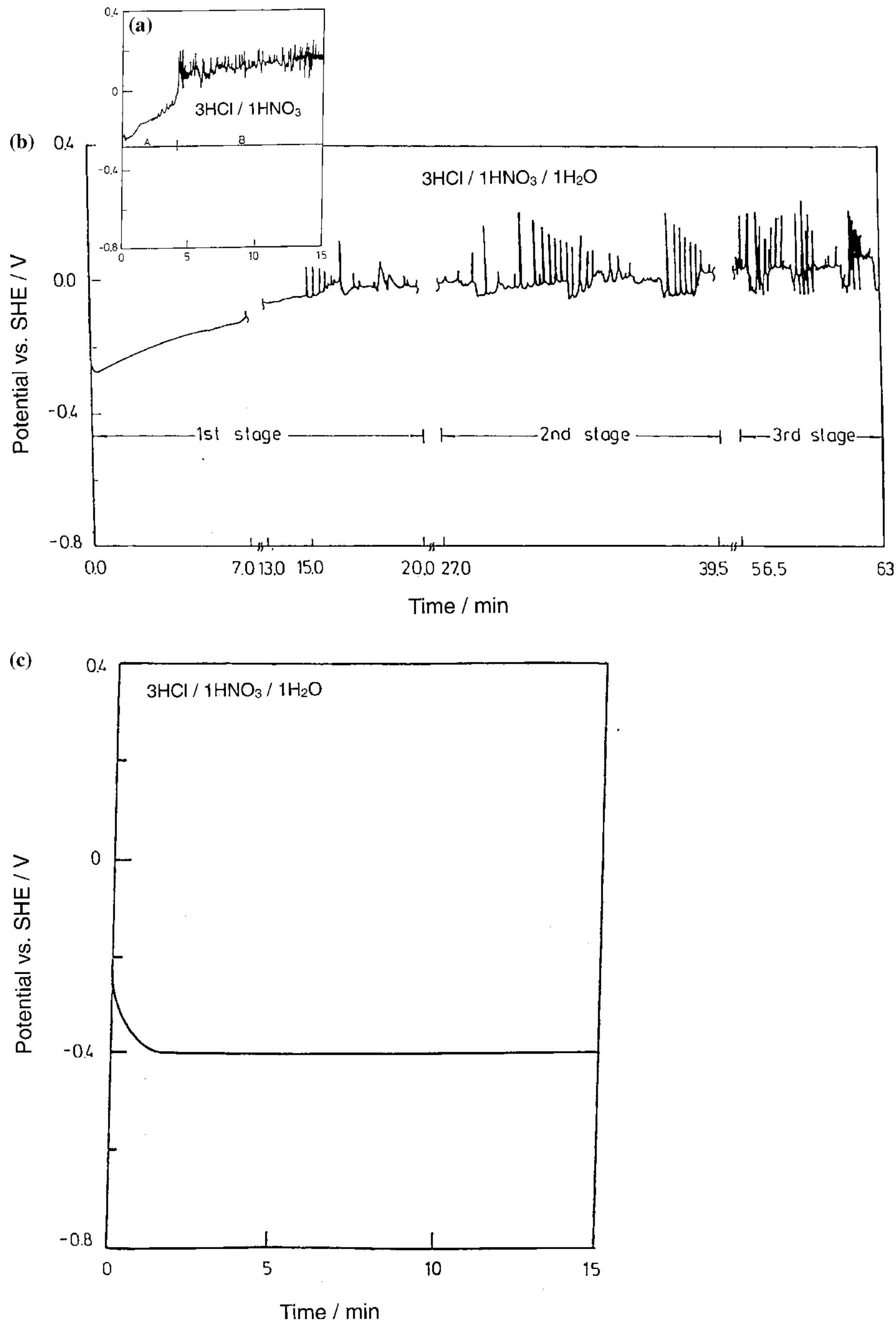


Fig. 4. Electrode potential vs time for the n-GaP electrode in: (a) $3HCl/1HNO_3$ (pure aqua regia); (b) $3HCl/1HNO_3/1H_2O$; and (c) $3HCl/1HNO_3/4H_2O$.

Referring to HCl/HNO_3 reaction scheme, it was possibly the nascent chlorine which resulted in the large difference of these two rates. This difference is consistent with the wide spread belief that the efficacy of aqua regia when used as an oxidizing agent is due to the chlorine. Furthermore, the exceedingly active properties of aqua regia are not only active in nature but also in the nascent state. The importance of this powerful oxidizing agent to the etching ability is strongly suggested to the fact that GaP dissolution requires some oxidation processes. Nitrous acid (HNO_2), a good passivator known to several metallic materials, is thus believed to participate in the GaP reaction. This suggestion is supported by the fact that the etching rate of GaP in HCl/NO_2^- was more than 20-fold which increases as fast as that in HCl etch.

Subsequently, the other possibly effective parameters that affect the dissolution of GaP were also studied. For example, the action of chloride ions of aqua regia alone was investigated. In this experiment with the absence of Cl^- ions, NO_2^- mixed with HNO_3 was likewise treated with GaP. The dissolution rate in such etching solution dropped to a very low value and was slightly higher than that in pure HNO_3 solution, as shown in Table 1. The fact that GaP dissolution was susceptible to Cl^- ions was clearly indicated.

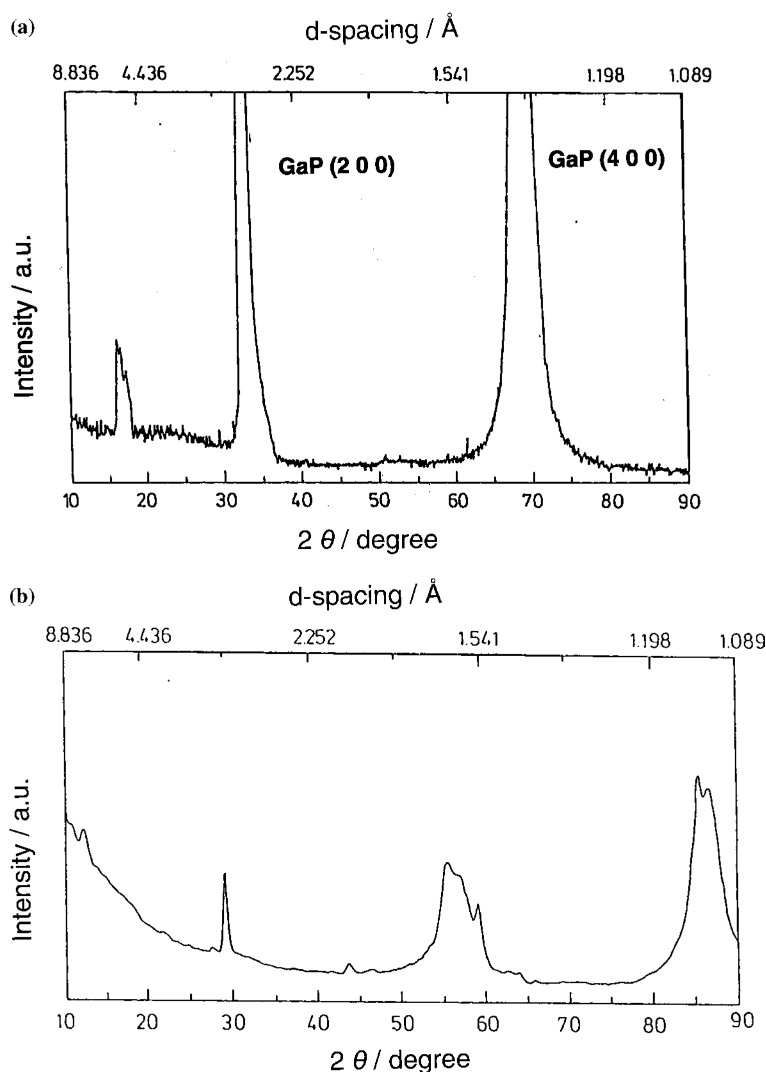


Fig. 5. (a) Wide-angle and (b) glancing-angle X-ray diffraction patterns of the oxidized GaP (100) surface in $3HCl/1HNO_3$ etchant.

3.2.2. *Open circuit potentials*

The E–t characteristics of GaP in varying diluted aqua regia solutions were investigated. The I–E curves for 1, 0.8, and 0.5 VR are shown in Figures 4(a), (b), and (c), respectively. In Figure 4(a), there are two characteristic regions A, during the first 5 min of the experiment, and B, thereafter. The shift of potential to noble direction in region A indicates that a surface film with etching resistance has grown sufficiently. Following the formation of a passivation layer intense potential oscillations appear as shown in region B. These electrochemical noises imply that this passive film is undergoing alternate breakdown and repassivation in pure aqua regia.

In order to further ascertain the etching mechanism of GaP in concentrated aqua regia, the E–t curve of GaP in 0.8 VR was also measured (Figure 4(b)). GaP in 0.8 VR aqua regia dissolved more slowly but still observed adequate reactivity (Figure 1). Owing to the slower change of potential characteristics with time the three representative partial curves are illustrated. The first stage, occurring during the first 15 min, corresponds to progressive film growth. The second stage, occurring within 35 min from the first stage, reveals that the film is momentarily broken, possibly by Cl^- ions, and is capable of repassivating. A gradual reduction in the time between two adjacent oscillation peaks, the repassivation time, is usually found in this potential range. As the oxidation with aqua regia becomes more vigorous, indicated by the increasing rate of GaP dissolution in Figure 2, the potential fluctuations occur more quickly, shown schematically in the third stage.

For the purpose of comparison, the etching process occurring in solution Y has also been investigated (Figure 4(c)). The constant and very negative electrode potential with respect to the potential of passivation reveals that GaP is in the active region and appears to be in a level of low activity.

Thus, according to Figures 4(a), (b), and (c), the high dissolution rate appears to be associated with the formation, alternate oxidative breakdown, as well as repassivation of a passive film, and the low rate with the absence of a passive film. It is interesting to note that,

Table 2. Comparison of the observed d spacings (Å) in aqua regia etchant with X-ray standard values from JCPDS cards for P_2O_5, $(NH_4)_3H_2P_3O_{10} \cdot H_2O$, P_4O_{10}, $GaPO_4 \cdot 2H_2O$, α-GaOOH, and GaP

		$GaPO_4 \cdot 2H_2O$	$(NH_4)_3H_2P_3O_{10} \cdot H_2O$	α-GaOOH	GaP	P_4O_{10}	P_2O_5
WAD	~5.38		5.36				
	3.057	3.061					
	2.854		2.85	2.85			
	2.723				2.726		
	2.383					2.384	
	2.229					2.229	
	2.177	2.175					
	1.793						1.79
	1.747						1.74
	1.571			1.573			
	1.509					1.512	
	1.361				1.3624		
GAD	7.28		7.25				
	3.154						3.15
	3.019		3.02				3.02
	2.067		2.07				
	1.929	1.931					
	1.6486	1.6475					
	1.6231	1.6211					
	1.5602						1.56
	1.4866						1.149
	1.4232					1.421	1.14
	1.1385						1.13
	1.1273						

from the point of view of metal oxide film theory, breakdown of passivity by Cl^- results in the lack of film protection and the exposed fresh metal atoms could thus easily dissolve into acid solution. However, the GaP lattice itself appears not to be susceptible at all to dissolution in a halogenated solvent without any change in the chemical nature of the material [16].

3.2.3. *XRD*

Figures 5(a) and (b) show the WAD and GAD patterns of the GaP (100) surface etching in the aqua regia, respectively. Table 2 lists the *d*-spacings of the peaks shown in Figures 5(a) and (b). The composition of each reaction product was determined by comparing these spacings with the X-ray standard values. This observation indicates that GaP surface is indeed covered with some oxidized compounds. As compared with previous work [8] on the oxidized GaP surface in HNO_3-etch, they showed almost the same mixture of reaction products except $(NH_4)_3H_2P_3O_{10} \cdot H_2O$ in aqua regia substituting for $Ga(NO_3)_3 \cdot 8H_2O$ in HNO_3. Nitrate ions apparently obtain electrons to be reduced to ammonium ions, which come from the reaction $NO_2^- + 8H^+ + 6e^- \rightarrow NH_4^+ + 2H_2O$, under etching in aqua regia.

On the other hand, it has been implied that Cl^- ions in GaP dissolution seemed to play a different role from those in the passive metal dissolution. This aspect is to be further examined by SEM.

3.2.4. *Morphology*

A scanning electron micrograph of the GaP (100) surface after etching in aqua regia for 60 min is shown in Figure 6(a). The surface is quite smooth and shows no preferential featuring of the crystal planes. In fact, a great majority of this specimen has been etched away, as shown in Figure 6(b). The surface in Figure 6(b)

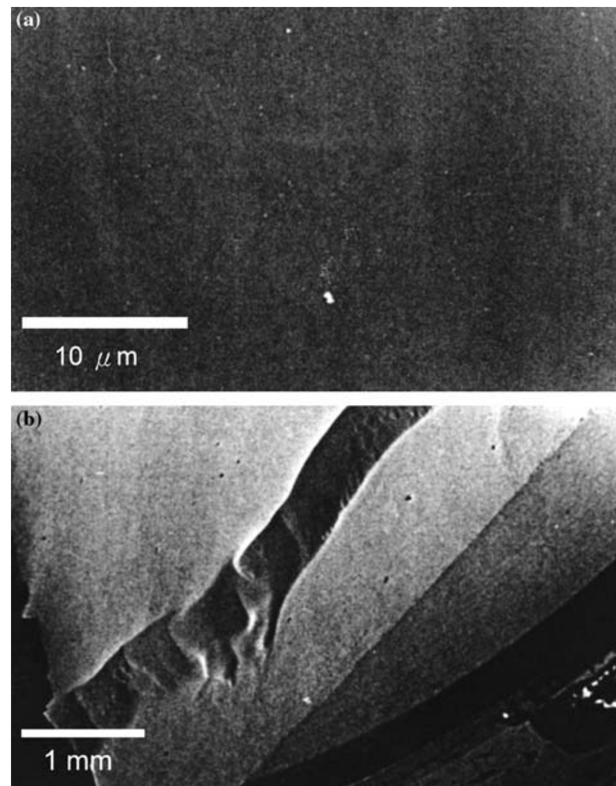


Fig. 6. Scanning electron micrograph of n-GaP (100) after etching in $3HCl/1HNO_3$ for 60 min. (a) 2500 × and (b) 20 ×.

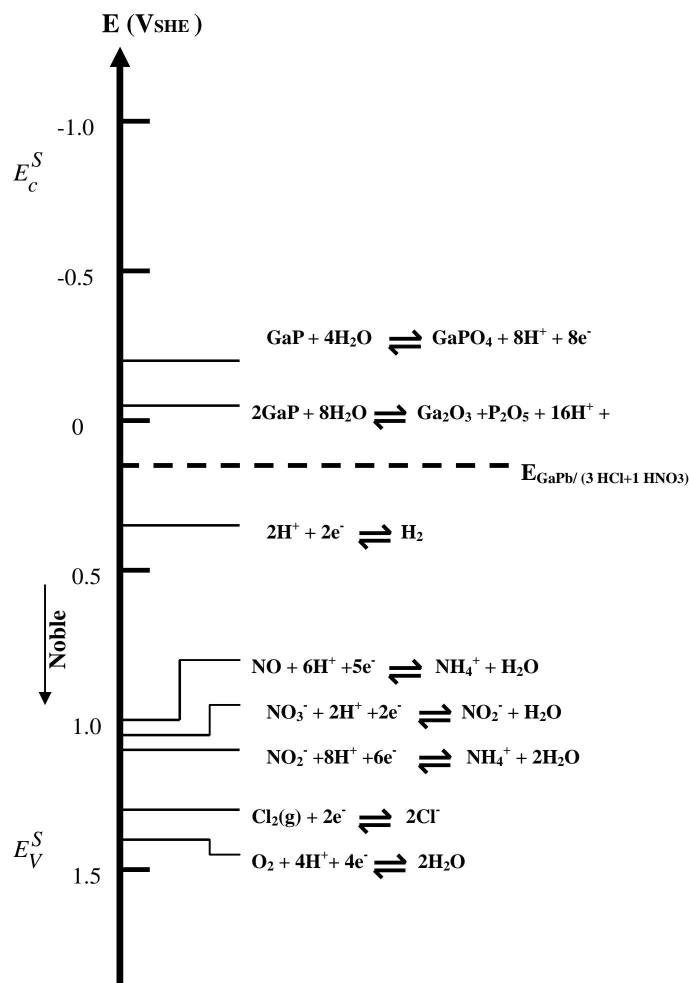


Fig. 7. The energy levels at the interface of GaP/(3HCl + 1HNO$_3$) at pH −2.1 (the natural abundance of $H_2 = 5 \times 10^{-7}$ atm).

contains two parts which are partitioned by a deep step. The upper part of the surface in the photograph was not exposed to the etching solution by covering with a layer of bees wax and GaP was thus prevented from etching completely. The lower part is the bare GaP surface after etching.

From the bulk of evidence, it can be concluded that GaP dissolution is initiated by the formation of an oxide layer on the surface, which can be rapidly achieved by the nascent chlorine and nitrite ions resulting from the vigorous interaction between HCl and HNO_3. Subsequently, a general nucleophilic attack on this oxide, mainly by chloride ions, leads to oxidized Ga and P being removed from the lattice.

3.3. *Interfacial electrochemical reactions*

In accordance with the above mechanism for the dissolution of GaP, the thermodynamic data for the energetics of the n-GaP/(3HCl + 1HNO$_3$) interface could explain the energetic tendency of such processes [17–23]. Figure 7 shows the energy levels at the interface of GaP/(3HCl + 1HNO$_3$) at pH −2.1 (the natural abundance of $H_2 = 5 \times 10^{-7}$). The electrode potential of pure aqua regia, using Pt as an electron conductor, is +1.2 V_{SHE}. The potential is so positive that the oxidation of chloro compounds with −1 valence to chlorine becomes possible. After substituting n-GaP for Pt, the electrode potential rapidly drops to −0.24 V_{SHE}, and increases to +0.16 V_{SHE} after 10 min reaction. According to the energy scheme, the reason for the driving force for the oxidation of GaP accompanied by other reduction reactions, is well illustrated. For example, chlorine, especially in the nascent state, with higher driving emf can oxidize GaP to Ga^{3+} and P^{5+}.

4. Conclusions

In previous work, whether with HCl or with HNO_3-etchants, GaP was not susceptible to dissolution attack due to etching. It is known that aqua regia-based systems are very popular in device processing for their powerful cleaning efficacy. In this study, their actions on GaP surfaces have been presented and it can be inferred why the mixture of these acids is effective as an etchant whereas the component acids are not. The results are consistent with the mechanism proposed for the kinetics of GaP in HCl or HNO_3 [7–9]. A few important conclusions can be drawn from the results:

1. Aqua regia is more effective than HNO_3 or HNO_2 owing to the mass production of chlorine and nitrite ions, obtained from HCl/HNO_3 interactions.
2. Etching of GaP in aqua regia involves two processes. Lack of either one stop the occurrence of etching. The GaP surface is rapidly oxidized to form a passive film, and subsequently, chlorine and NO_2^- ions proceed with a nucleophilic attack on this oxide. GaP is thereby removed from the lattice to the solution.
3. The bonding of the GaP semiconductor belongs to the sp^3 hybrid orbital type, which is in contrast to the purely ionic bonding between the two elements of its oxidized compounds. For GaP in HCl-etches, the formation of $Ga^{(III)}$ via a $Ga^{(I)}$ chloro intermediate is thermodynamically forbidden and thus the nucleophilic attack by Cl^- does not occur. For GaP in HNO_3-etches, firstly there is, much less production of nitrite ions than in HCl/HNO_3-etches. And secondly, the poor performance of nitrite ions as a nucleophile, results in its low etching ability for GaP. However, for GaP in HCl/HNO_3-etches, trivalent gallium oxides, easily obtained by oxidation with chlorine and NO_2^-, could directly be attacked and dissolved by Cl^-.
4. For GaP, nucleophilic attack by Cl^- generally occurs over the passive surface. Hence, the observed etched surface is much more uniform than those of the passive metals.

References

1. H.H. Wieder, *J. Vac. Sci. Technol.* **A2** (1984) 97.
2. M.I. Val'kovskaya and Y.S. Boyarskaya, *Sov. Phys. – Solid State* **8** (1967) 1976.
3. R.H. Saul, *J. Electrochem. Soc.* **115** (1968) 1185.
4. N.E. Schumaker, M. Kuhn and R.A. Furnage, *IEEE Trans. Electron Devices* **ED-18** (1972) 627.
5. T. Uragaki, H. Yamanaka and M. Inoue, *J. Electrochem. Soc.* **123** (1976) 580.
6. H.C. Gatos and M.C. Lavine, *Prog. Semicond.* **9** (1965) 38.
7. H.F. Hsieh, C.C. Yeh and H.C. Shih, *J. Electrochem. Soc.* **139** (1992) 380.
8. H.F. Hsieh, C.C. Yeh and H.C. Shih, *J. Electrochem. Soc.* **139** (1992) 1897.
9. H.F. Hsieh, C.C. Yeh and H.C. Shih, *J. Electrochem. Soc.* **140** (1993) 463.
10. H.F. Hsieh and H.C. Shih, *J. Electrochem. Soc.* **138** (1991) 1965.
11. H.C. Liu, S.H. Tsai, J.W. Hsu and H.C. Shih, *Mater. Chem. Phys.* **61** (1999) 117.
12. H.F. Hsieh and H.C. Shih, *J. Electrochem. Soc.* **138** (1991) 1304.
13. H.F. Hsieh and H.C. Shih, *J. Appl. Phys.* **66** (1989) 3542.
14. H.C. Liu, S.H. Tsai, J.W. Hsu and H.C. Shih, *J. Electrochem. Soc.* **146** (1999) 3510.
15. C.C. Kuo, Robert A. Wilkins, Jr. and I.C. Hisatsune, *Ind. Eng. Chem. Fundam.* **15** (1976) 236.
16. H.C. Gatos and M.C. Lavin, *Prog. Semicond.* **9** (1965) 1–46.
17. G.P. Schwartz, G.J. Gualtieri, J.E. Griffiths, C.D. Thurmond and B. Cshwartz, *J. Electrochem. Soc.* **127** (1980) 2488.
18. I.N. Levine, Physical Chemistry, (McGraw-Hill Inc., New York, 1978), p. 243.
19. C.W. Wilmsen, 'Physics and Chemistry of III-V Compound Semiconductor Interfaces', (Plenum Press, New York, 1985).
20. M. Gleria and R. Memming, *J. Electroanal. Chem. Interface Electrochem.* **65** (1975) 163.
21. D.D. Wagman, W.H. Evans, V.B. Parker, I. Halaw, S.M. Baily and R.H. Schumm, 'Selected Values of Chemical Thermodynamic Properties', (NBS Technical Note, 270—3, Washington, 1968).
22. Marcel Pourbaix, 'Atlas of Electrochemical Equilibria in Aqueous Solution', 2nd edn., (NACE, Houston, TX, 1974).
23. D.R. Lide and H.P.R. Frederikse, 'CRC Handbook of Chemistry and Physics', 78th edn., (CRC Press, New York, 1997).