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Electrochemical characteristics of the n^+ -type GaAs substrate in HCl electrolyte and the morphology of the obtained structure

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Gallium Arsenide; Porous semiconductors; Electrochemical etching **Abstract** The anodic etching of n^+ -type GaAs (1 0 0) substrate in HCl aqueous solution has been investigated experimentally using an in situ current–voltage J(V) and capacitance–voltage C(V) measurements. In situ current–voltage, J(V), characteristics of the n^+ -GaAs/HCl interface exhibit the presence of three potential regions, which are attributed to different reaction mechanisms between HCl and n^+ -type GaAs surface. Also, current peaks appear in the J(V) characteristics which delimit the different potential regions. According to the Mott–Schottky relation, the characteristic $C^{-2}(V)$ exhibits the presence of two linear regions separated by a shoulder at about 1.15 V. This shoulder indicates the formation of porous GaAs/HCl interface. Scanning electron microscopy (SEM) images shows that GaAs etched in HCl can produce various surface morphologies depending on the anodization current density. Reasonable assumptions on the dissolution mechanisms according to the variety of morphologies are given.

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1. Introduction

Pore formation is a well-known feature of many semiconductors under anodic conditions in different electrolytes, where the majority of research efforts have been concentrated on porous silicon (Foll et al., 2002). In recent years, III–V compound semiconductors, essentially InP, GaAs and GaP have been rendered porous in spite of the few and limited available data (Takizawa et al., 1994; Langa et al., 2001; Schmuki et al., 1996a,b; Sabataityte et al., 2002; Beji et al., 2003a,b, 2005; Belogrokhov et al., 1994; Mayerink et al., 1996). Electrochemical studies of the interface n^+ -type GaAs/HCl provide necessary information about the anodization process and also some insight into the fundamentals of the charge transfer and dissolution process. Moreover, the in situ J(V) measurements offer information about the range of potentials and current densities over which current flows and anodic films evolve, and/or dissolution takes place (Schmuki et al., 1996a,b; Jonathan et al., 2001; Clausen et al., 2003). However, in order to take full advantage of the formation of porous GaAs, we need a good understanding of the process which is taking place at the semiconductor/electrolyte interface. The aim of this work is to elucidate the electrochemical conditions under which local dissolution and pore formation occur and the factors controlling this process.

2. Experimental

Electrochemical etching was performed on commercialized epi-ready n^+ -type GaAs (Si-doped) substrate with a carrier concentration of $1.8 \times 10^{18} \text{ cm}^{-3}$ and $(1\ 0\ 0)2^{\circ}$ off toward (1 1 0) orientation. Prior to each experiment, the samples were degreased with acetone, propanol, and methanol, extensively rinsed with deionized water, and then blown dry in N₂. Electric contact to the samples was established by smearing Ga-In eutectic onto the backside of the cleaved samples. The samples were then pressed against an o-ring in a Teflon electrochemical cell, with a platinum electrode, leaving 0.5 cm^2 exposed to the etching solution prepared from 37 wt.% HCl. The samples were then maintained in the etch solution for 12 s to remove the native oxide. A Teflon coated magnet stirred the etch solution to maintain uniform distribution of the electrolyte. J(V)measurement of n^+ -type GaAs substrate in HCl solution is recorded using a computed SR310 Voltalab. The working electrode is our semiconductor sample whereas the counter electrode is the platinum electrode and the reference electrode is a saturated calomel electrode (SCE). Scanning electron microscopy (SEM) images were acquired using a PHILIPS XL30 equipped with a digiscan image acquisition archiving system and energy dispersive X-ray analysis (EDX).

3. Result and discussion

3.1. In situ electrical characteristics

Fig. 1 shows the schematic representation of the band diagram of n^+ -type GaAs in contact with HCl aqueous solution at zero bias voltage. When a semiconductor is in contact with an electrolyte solution, a charge transfer occurs through the interface providing equilibrium between the Fermi level of the semiconductor and the redox potential of the electrolyte. In the case of the n^+ -type GaAs ($n = 1.8 \times 10^{18} \text{ cm}^{-3}$) in contact with HCl aqueous solution with redox potential (4.5 eV) higher than the n^+ -type GaAs Fermi level (4.11 eV) (Beji et al., 1998), represents an electron transfer from the semiconductor to the electrolyte (Fig. 1a). Furthermore, an electrically charged layer (ionic in the electrolyte and electronic in the semiconductor) will be formed. This situation induces the formation of an electric field in the space charge region, leveling the semiconductor Fermi level and the potential redox of the electrolyte solution, producing a band bending close to the electrolyte boundary (Fig. 1b). At the surface, the n^+ -type GaAs becomes depleted of majority carrier (electron) and a depletion layer, W, is formed (Fig. 1b). Under anodic bias, an excess electric field is induced and is responsible for electron transport at the interface. The electron transfer with the surface is limited by tunneling through the depletion layer or by carriers that overcome the barrier by thermal activation (Sze, 1981; Oscam et al., 1997). Furthermore, the space charge layer in the n^+ -type



Figure 1 Schematic band diagram of the n^+ -type GaAs (100) substrate in HCl electrolyte.



Figure 2 Polarization curves of an n^+ -type GaAs (1 0 0) in HCl electrolyte acquired in the dark, under ambient conditions. Sweep rate 5 mV/s. The potential was reported versus the saturated calomel electrode (SCE).

GaAs is an important current limiting factor in the electrochemical cell. Fig. 2 shows the current density, J, as a function of the applied potential, V, for an n^+ -type GaAs in hydrochloric acid solution (HCl). The potential was scanned from -1 V, at a rate of 5 mV s⁻¹. Four distinctive regions are observed. At negative potential, the band bending is too small to allow interband tunneling and the n^+ -type GaAs/HCl solution behaves as a reverse–biased diode. Nevertheless, between potential values of 0 and 1.15 V, the magnitude of the anodic current is too small, which can be attributed to the reduction of H⁺ ion according to the following equation (Nozik, 1981).

$$2\mathrm{H}^{+} + 2e^{-} \to \mathrm{H}_{2} \tag{1}$$

The plateau range is followed by a distinct current increase at a potential value of about 1.15 V, called the breakdown potential and also called the pore formation potential (PFP) (Schmuki et al., 1996a,b). This value of the PFP is consistent with other published work for a similar concentration of HCl (Schmuki et al., 1996a,b). The occurrence of a threshold potential at PFP can be explained by considering the n^+ -type GaAs/aqueous HCl junction under anodic bias. Due to the sufficiently high doping level of the n^+ -type GaAs, the width of the space layer was thin enough. In fact, the tunneling breakdown occurred easily. Above the PFP, an anodic current begins to flow and the current increases markedly as the potential is varied and reaches a first maximum at about 2.62 V (see Fig. 2). This region was attributed to the generation of the porous GaAs layer, where the first pores are formed at a potential of about 1.15 V. This occurred when GaAs was dissolved according to Eq. (2) (Willer et al., 1994; Khader, 1995), where a sufficient concentration of hole (h^+) has to be provided at the surface,

$$AsGa + 6h^+ \to Ga^{3+} + As^{3+} \tag{2}$$

The holes will generate six incomplete bonds which can be saturated by the species from the electrolyte. However, the GaAs substrate does not dissolve in pairs but atom by atom, and then eight holes will be required for dissolving a GaAs unit, i.e., four holes for each atom. Thus depending on the etching conditions, six or eight holes are needed for dissolving a Ga-As pair of atoms.

For the occurrence of the material dissolution processes a sufficient concentration of holes (h^+) has to be provided at the surface. This was preceded through trapping of valence band holes in surface bonds, nevertheless, in n^+ -type GaAs the holes are minority carriers and their density is very small. As a consequence, dissolution processes occur significantly at relatively high anodic bias where sufficient hole density is generated by breakdown mechanism. At relatively high anodic potential (extended from PFP to the first potential peak), an electron at the surface can be thermally excited from the valence band to the conduction band via the surface state (originating by chemical oxidation mechanism). Under high electric field, the electron created at the surface can generate electronhole pairs and hence, generate free holes, which can contribute to the GaAs dissolution process. In addition, a valence band electron can tunnel to the conduction band and create free holes in the valence band. According to the reported data for n^+ -type GaAs, the electron field at the surface during electrochemical etching is of about $1.5 \times 10^6 \,\mathrm{V \, cm^{-1}}$ (Sze, 1981; Oscam et al., 1997) which is sufficiently high to allow electron tunneling.

At a more positive potential a second current maximum is observed, which is located at 3.62 V. The second maximum has not been reported before for *n*-type GaAs or *p*-type GaAs, but has been observed in silicon–hydrofluoric acid contact (Patel and Sahu, 2001; Huang et al., 2006). Above the observed first current maximum, the current density increases rapidly as the anodic potential is raised (Fig. 2). This region is attributed to the electropolishing and dissolution of the n^+ -type GaAs.

Above the second maximum the current decreases rapidly to a low value which shows a weak potential dependence. This region was suggested to be attributed to the passivation process of the n^+ -type GaAs by the formation of arsenic oxides according to the following equation.

$$GaAs + 3H_2O + 6h^+ \iff Ga(III) + H_3AsO_3 + 3H^+$$
(3)

Such I–V behavior above the second maximum, which is typical of semiconductor passivation due to oxide formation, have not been reported before for *n*-type and *p*-type GaAs, but have been reported for *n*-type GaP in H₂SO₄ and Si in HF (Foll et al., 2002, 2003; Tjerkstra et al., 2002). The dependence of the capacitance versus polarization was presented in the form $C^{-2}(V)$ in Fig. 3. This figure shows an inversion zone extended from the negative bias to almost 0.25 V. This was followed by a depletion zone and an accumulation zone. This behavior is almost the same as a metal/semiconductor contact and allows the use of the simple depletion layer theory (Morrison, 1980).

$$\frac{1}{C_{sc}^2} = \frac{2}{e\varepsilon\varepsilon_0 N} \left(V - V_{FB} - \frac{k_B T}{e} \right)$$
(4)

where C is the interface capacitance per unit area, e the electron charge $(1.6 \times 10^{-19} \text{ C})$, ε the semiconductor dielectric constant, ε_0 the vacuum permittivity, N the donor density, V the applied potential, V_{FB} the flat band potential, T the ambient temperature and k_{B} the Boltzmann constant. Furthermore, a shoulder appears at the end of the depletion zone at about 1.15 V which limits two slopes. The first slope is higher than the second one where the first shows a higher doping density. This is due to the surface modifications caused by the porosity, and hence a lack of material, in accordance with the second



Figure 3 Mott–Schottky plot of an n^+ -type GaAs in HCl (5 M) acquired in the dark, under ambient conditions. Sweep rate 25 mV/s.

region of the J(V) characteristic which is attributed to the dissolution process. The presence of the shoulder may indicate the formation of a new interface which is porous GaAs/HCl-electrolyte. This suggestion is in accordance with the predicted pore formation potential from J(V) characteristic. From the extrapolated intercept on the voltage axis, two flat band potentials, $V_{\rm FB1} = 1.08$ V and $V_{\rm FB2} = 1.68$ V are observed. The value of the first flat band potential is almost equal to the barrier potential at the interface n^+ -GaAs/HCl-electrolyte (Fig. 1) the second flat band potential is suggested to be associated to the barrier potential at the interface *n*-type porous GaAs/HClelectrolyte.

3.2. Etched GaAs surface morphologies

A porous GaAs structure can be observed at the anodization current densities correspondent to the potential range between the breakdown potential and the potential where the current reaches the first maximum. This was proved by the SEM micrograph in Fig. 4a where the first pores are observed just after the breakdown potential. This SEM image shows the morphology of n^+ -type GaAs (1 0 0) anodized with a current density of 10 mA cm⁻² in HCl (5 M) solution. It is clear that the anodized GaAs surface has a porous appearance with pores of various sizes and directions, the pore shapes are mainly oval as seen in Fig. 4a.

The pore openings are small and less clearly defined, indicating the progressive dissolution of the GaAs at the surface. In fact, with increasing of the current density to 60 mA cm⁻² (Fig. 5a), the distribution density of the pores increased, and almost the entire surface was converted into a porous structure. Also, the diameter and the shape of the pores varied with the current density and the anodization time. The SEM crosssection (Fig. 4b) shows elongate cylindrical pores and when increasing current density, pores with a helicoidal structure are sometimes observed and the proportion of helical pores seems to increase with current density (Fig. 5b). Fig. 6a shows the morphology of n^+ -type GaAs (1 0 0) anodized with a current density of 100 mA cm⁻² (located above the first maximum of the J (V) characteristics) in 5 M HCl solution. Some macropores separated by large flat surfaces appear on the surface



Figure 4 (a) SEM plan view image, (b) SEM cross-section image (45°) and, (c) EDX spectra of the porous GaAs layer produced by HCl (5 M) electrolyte at anodization current density of 10 mA cm⁻² for 60 s.

of this sample. The large flat surface was caused by the electropolishing process and the pores by the dissolution process. Those two processes compete to govern the surface morphology of the porous structure in the mentioned region, and statistically the flat area on this surface and the very low intensity of the $O(K_{\alpha})$ peak of oxygen in Fig. 6c prove that the electropolishing is predominant. Furthermore the SEM



Figure 5 (a) SEM plan view image, (b) SEM cross-section image (45°) and, (c) EDX spectra of the porous GaAs layer produced by HCl (5 M) electrolyte at anodization current density of 60 mA cm⁻² for 60 s.

cross-section (Fig. 6b) shows that the inner structure is highly porous with no defined form.

Energy dispersive X-ray analysis (EDX) (Figs. 4c, 5c and 6c) reveals that the spectrum is that of As + Ga, where the intense bands are related to Ga (L_{α}) and As (L_{α}) peaks. The low intense band located at 0.52 keV is attributed to $O(K_{\alpha})$ due to superficial oxidation during the electrochemical anodization



Figure 6 (a) SEM plan view image, (b) SEM cross-section image (45°) and, (c) EDX spectra of the porous GaAs layer produced by HCl (5 M) electrolyte at anodization current density of 100 mA cm^{-2} for 60 s.

process. The amount of gallium, arsenic and oxygen depend on the electrochemical anodization conditions. Arsenic and oxygen amount increased and decreased, respectively with increasing current density. Furthermore the variation of the amount of gallium element was random with the electrochemical conditions and lower than that of arsenic. Indeed, the obtained porous structures are arsenic-rich as a result of dissolving Ga. Because, it is known that, Ga is preferentially dissolved during the anodic etching in acidic media (Alqaradawi et al., 2003).

Before corrosion takes place, the surface of GaAs after etching and cleaning is arsenic-rich. Furthermore, the outermost exposed layer will be an As $(1\ 0\ 0)$ plane with dangling bonds.

The first oxidation step is a hole captured by the surface bond with one Ga–As bond being broken. This process leaves a positive charge on the Ga instead of the As, since Ga has a lower electronegativity. AsGa⁺ is easily attacked by water molecules from aqueous solution because of the positive charge located at Ga. Two kinds of interactions may be involved.

One is the general interactions between the positive charges and the dipole from water molecules and/or the cation in the solution, i.e., non-specific adsorption. The other is the much stronger chemical reaction between water and the positive charge on the Ga atom. AsGa–OH can be formed and H^+ is generated.

$$AsGa + h^+ \to AsGa^+ \tag{5}$$

$$AsGa^{+} + e^{-} \to AsGa \tag{6}$$

$$AsGa^{+} + H_2O \iff AsGa - OH + H^{+}$$
(7)

We can suggest that this selective removal of Ga leaves an elemental arsenic-rich surface. More quantitatively, we can write the following reactions to describe the chemistry of Ga and As in 5 M HCl. For the spontaneous dissolution of Ga we have:

$$Ga + 3H^{+} + 4Cl^{-} \iff GaCl_{4}^{-} + \frac{3}{2}H_{2}$$
(8)

In fact, the reaction will proceed to the right. In the case of As, which has known simple As^{3+} aqueous chemistry, we may write Eq. (9):

$$As + 2H_2O^- \iff HAsO_2 + \frac{3}{2}H_2$$
(9)

We can suggest, that the arsenite species is the dominant form of arsenic in the (+3) state in aqueous solution, and the protonated species HAsO₂ will dominate in our HCl experiments (Frese and Morrison, 1981). Therefore, the favoured pathway for dissolution of GaAs by HCl is the formation of GaCl₄⁻, and elemental arsenic.

$$GaAs + 3H^{+} + 4Cl^{-} \rightarrow GaCl_{4}^{-} + \frac{3}{2}H_{2} + As$$
 (10)

In fact, we can suggest that an excess of metallic arsenic will be present on or near the surface of the GaAs semiconductor. Then, for thin oxide layers a large electronic current may flow parallel with ionic current. Certainly, they must involve an oxidation process at the semiconductor electrode. This process may be either runaway anodic etching of the GaAs or oxidation of an electrolyte component. It is not known why regions that may be etching do not passivate, but it is shown that conditions for the formation of a good passivating anodic layer are reasonably critical and may not be met once elemental arsenic is formed. The presence of elemental arsenic may for example, catalyze a reaction route involving anodic etching with continued generation of elemental arsenic.

4. Conclusions

Pore growth can be initiated on n^+ -type GaAs (100) in HCl solution using electrochemical in situ characterization techniques like J(V) and C(V). The anodization process at the GaAs surface is governed by three regions including pore formation, electropolishing and passivation. Furthermore, anodic polarization of GaAs in acidic solution resulted in selective dissolution of GaAs leading to the formation of As-rich porous surface. Mott-Scottky plot shows the formation of a new interface porous GaAs/HCl-electrolyte and this suggestion is in accordance with the predicted pore formation potential from J(V) characteristics. Some chemical reactions which take place during the electrochemical anodization process are suggested and as demonstrated by SEM investigation, the morphology of the porous layers depends strongly on the electrochemical conditions. The chemical surface composition of the porous structures are analyzed by energy dispersive Xray analysis (EDX) and discussed on the basis of suggested reaction mechanisms at the interface between n^+ -GaAs HCl based electrolyte.

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