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PHOTOETCHING OF III/V SEMICONDUCTORS

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Abstract—The dependence of the capacitance–potential plots and of the photocurrent–potential plots of n-GaAs(100) and p-GaAs(100) interfaces in sulfuric acid on the hydrogen peroxide concentration was investigated. Simultaneously, *in situ* Raman spectroscopy was applied. The mechanism of the photodissolution derived from the investigation suggests an intermediate formation of an As_2O_3 layer parallel to the dissolution of Ga^{3+} ions.

1. INTRODUCTION

The surface processing of semiconductors is an important step in semiconductor technology. In general, the tendency leans towards processing of semiconductors by gas phase methods; *ie* sputtering, chemical vapour deposition or plasma vapour deposition. Nevertheless, some processes still continue as "wet" processes. That means, they are connected to reactions and charge transfer at a semiconductor–electrolyte interface. An important process of this type is the photoelectrochemical etching of semiconductors which is particularly used in connection with compound semiconductors. In this paper, varying processes on III/V semiconductors will be discussed.

One important application of III/V semiconductors is the use of such materials in optoelectronic devices, *eg* it was shown in the literature that optical gratings can be produced in gallium arsenide by photoelectrochemical etching (Matz *et al.*[1]). Other applications refer to the drilling of holes in such materials using the special optical properties of gallium arsenide at 250 nm. Holes with very high aspect ratios were produced by laserelectrochemical drilling in gallium arsenide (Osgood *et al.*[2]). In both cases a sulphuric acid/hydrogen peroxide/water mixture was used as the etching medium. The processes of oxidation of the semiconductor and reduction of the oxidizing medium (hydrogen peroxide) in this medium were investigated in a number of papers. In one part of the investigations, the technological aspects were studied, *eg* Iida and Ito concentrated on the selectivity of the etching process[3]. Shaw investigated acidic H_2O_2 solutions with respect to its application for microstructuring[4]. Kinetic aspects have already been described in earlier publications by Gerischer *et al.*[5, 6] and later on by Mori and Watanabe[7] for $H_3PO_4/H_2O_2/H_2O$ electrolytes. General electrochemistry was studied by Gerischer, Müller and Haas[8]. The corrosion rate was measured analytically by Haroutiounian *et al.*[9]. Similar studies were made in alkaline H_2O_2 solutions, the most recent one by Kelly *et al.*[10]. But despite these efforts, the kinetics of the process cannot yet be completely understood. We therefore started new experiments to study the electrochemical and the photoelectrochemical behaviour of gallium arsenide in the $H_2SO_4/H_2O_2/H_2O$ electrolyte under inclusion of *in situ* Raman spectroscopy, to determine the intermediates of the process and some preliminary results were recently published[11]. Electrochemical and photoelectrochemical details are described in a separate paper[12]. In this present paper, a more general view of the processes occurring at the gallium arsenide/H_2SO_4, H_2O_2, H_2O interface are presented.

2. EXPERIMENTAL CONDITIONS

Photoelectrochemical measurements on n-GaAs and p-GaAs(100) surfaces were carried out in a three-electrode cell compartment under potentiostatic conditions, in combination with a device for capacitance measurements (EG&G lock-in amplifier 124 in combination with a two-phase accessory). The light source for the photoelectrochemical measurements was an argon ion plasma lamp used either in an all-line mode or under monochromatic conditions (Zeiss grating monochromator). Photocurrents could be measured in a chopped mode or directly under white light illumination.

GaAs(100) single crystals, n-doped and p-doped, were used as electrodes. n-GaAs was Si-doped, p-GaAs Zn-doped, both with concentrations of $N_D = 1 \times 10^{18}\,cm^{-3}$ (Wacker Chemie, Burghausen, Germany). Before insertion of the electrodes into the electrolyte, the electrodes were chemically polished in $H_2SO_4/H_2O_2/H_2O$ (1 : 1 : 1 and 3 : 1 : 1) and then oxide layers were removed by dipping shortly into HCl/HNO_3 mixtures ($HCl:HNO_3:H_2O = 2:1:2$). Electrolytes were made of p.a. chemicals and the solution was purged with nitrogen. The counter electrode was a platinum net and the reference electrode a $Hg/Hg_2SO_4/H_2SO_4$ electrode. All potentials refer to the normal hydrogen electrode. The temperature during the experiment was kept at room temperature and controlled at $23 \pm 0.5°C$.

The Raman spectra were measured *in situ* using an Ar-ion laser (Coherent, Innova 90) at 514.5 nm, typical power 100 mW, a Specs-triplemate spectrograph, an

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optical multichannel analyser as detector and a PDP 11/23 for data acquisition. A Canon lense, 80 mm/ $f = 1.2$, was used for stray light collection. The electrochemical set-up was similar to the one described above.

3. DETERMINATION OF FLATBAND POTENTIALS AND DONOR OR ACCEPTOR CONCENTRATION OF n-GaAs AND p-GaAs

Mott–Schottky plots of n-GaAs and p-GaAs in 0.2 M sulphuric acid are shown in Fig. 1. A linear behaviour of $1/C^2$ as a function of the potentials was observed in regions of neglectable Faradayic currents. Flatband potentials of -0.8 V (n-GaAs) and of $+0.6$ V (p-GaAs, mean value of various experiments) were determined in agreement with the literature (Gleria and Memming[13]). The difference of the two flatband potentials agrees with the literature value for the band gap of 1.43[14]. The flatband potential of n-GaAs is independent of the H_2O_2 concentration, but the flatband potentials of p-GaAs show a pronounced dependence on the H_2O_2 concentration (cathodic shift)[12].

The donor concentration determined from the slope of the Mott–Schottky plots gave values of 2×10^{18} cm^{-3}—in acceptable agreement with the value given by the manufacturer of the GaAs.

4. CURRENT POTENTIAL BEHAVIOUR

4.1 *n*-GaAs

Dark current and photocurrent potential plots of n-GaAs in 0.2 M sulphuric acid, 0.2 M H_2O_2 are shown in Fig. 2. For comparison, the photocurrent and dark current potential plot in pure sulphuric acid is shown in Fig. 3. The interpretation of the dark currents and photocurrents is possible on the basis of the schematic band model shown in Fig. 4. Comparing the behaviour of various redox systems in n-GaAs published in the literature[15–18], a certain similarity of all these redox systems in the potential region -0.5 to 0 V was observed. We explain this similarity by the charging and discharging of surface states in this potential range. If the potential is cathodic of the surface states, the surface states are charged and serve as electron donors to fill up photoholes generated by electron–hole pair excitation. If the potential is moved cathodically of the surface states, they become unoccupied and the recombination mechanism is blocked. The photocurrent increases until the photocurrent limit determined by the light intensity and by the diffusion processes in the semiconductor is reached.

In presence of H_2O_2, the reduction of such is observed in a small cathodic current starting at approximately -0.2 V in the dark and merging with the increase of the photocurrent under illumination con-

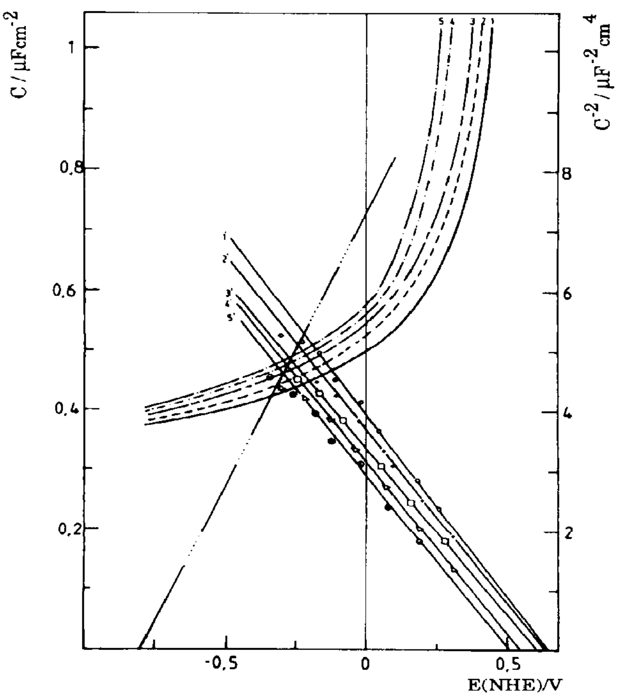

Fig. 1. Capacitance–potential (C–E) plots (curves 1–5) and Mott–Schottky plots (capacitance c as $1/C^2$ as function of potential E) (curves 1′–5′9 for p-GaAs in H_2SO_4 (0.2 M)/H_2O_2 (x M); $x = 0$ M (1), 0.02 M (2), 0.1 M (3), 0.2 M (4) and 0.5 M (5). Scan rate 10 mV/s^{-1}; results independent of scan direction. For comparison: the Mott–Schottky plot for n-GaAs is shown (——) which is independent of the H_2O_2 concentration.

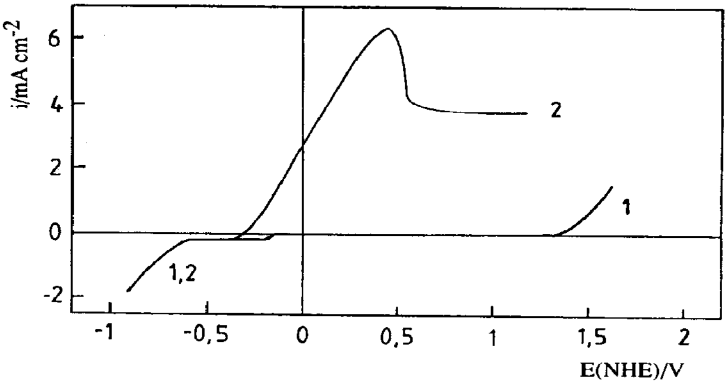

Fig. 2. Current and photocurrent (i)–potential (E) plots of n-GaAs(100) in H_2SO_4 (0.2 M)/H_2O_2 (0.2 M). Scan rate 10 mV s^{-1}.

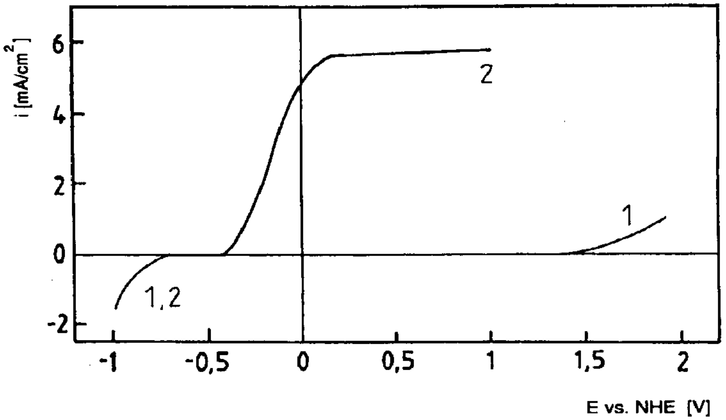

Fig. 3. Current (1) and photocurrent (2)–potential plots (i–E-plots) of n-GaAs (100) in H_2SO_4 (0.2 M) for comparison with Fig. 2. Scan rate 10 mV s^{-1}.

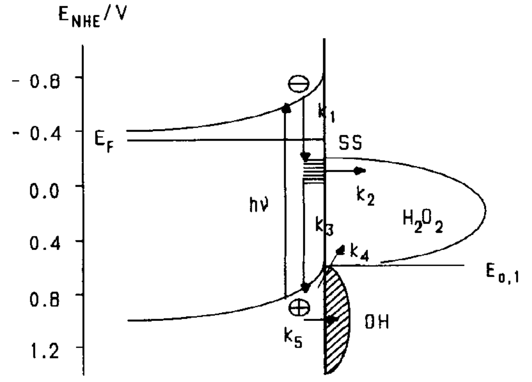

Fig. 4. Schematic band structure model for n-GaAs in H_2O_2 containing sulfuric acid.

ditions. The reduction current can either occur by direct electron transfer from the conduction band to the H_2O_2 molecules or also via surface states. Also noteworthy is the decrease of the anodic photocurrent at approx. + 0.4 up to + 0.5 V.

4.2 *p*-GaAs

Dark current and photocurrent potential plots over a large area of potential variation of *p*-GaAs in pure sulphuric acid are shown in Fig. 5. The influence of various concentrations of H_2O_2 on the dark current is shown in Fig. 6, the influence on the photocurrent is shown in Fig. 7. The influence of the hydrogen peroxide on the dark current was only observed anodically of the flatband potential in the region of GaAs oxidation. A passivation phenomenon is observed on the GaAs electrodes. Reduction of the H_2O_2 below the flatband potential was observed under illumination

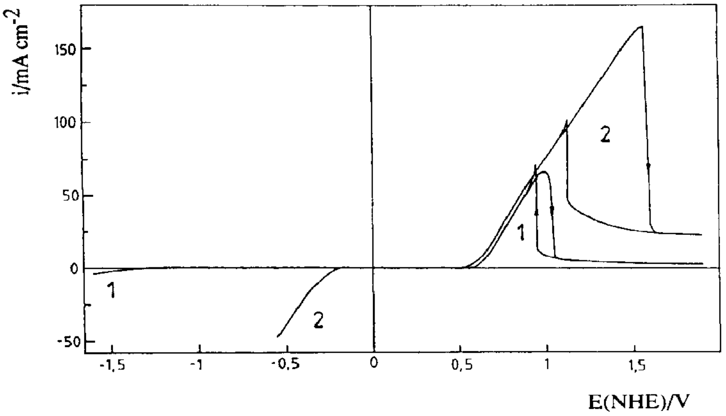

Fig. 5. Current (1) and photocurrent (2)–potential plots (*i*–*E*-plots of p-GaAs(100) in H_2SO_4 (0.2 M) for comparison with Figs 6 and 7; scan rate 10 mV s^{-1}.

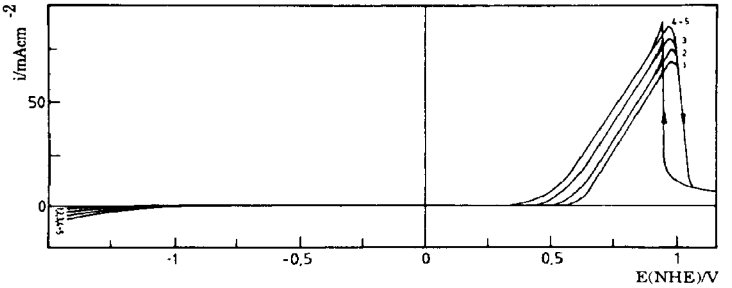

Fig. 6. Influence of H_2O_2 (x M) on the dark current–potential dependence of p-GaAs in H_2SO_4 (0.2 M); $x = 0$ M (1); 0.02 M (2); 0.1 M (3); 0.2 M (4); 0.5 M (5); scan rate 10 mV s^{-1}.

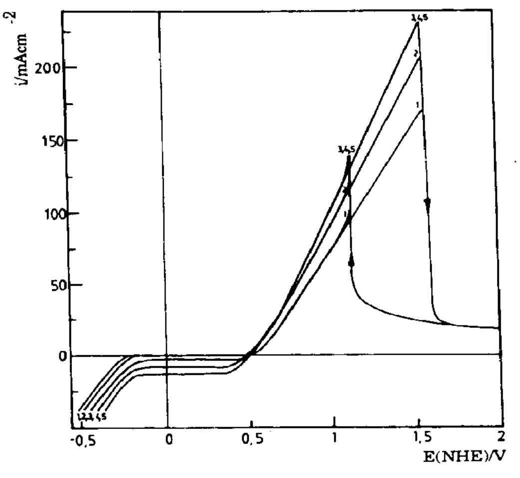

Fig. 7. Influence of H_2O_2 (x M) on the photocurrent–potential dependence of p-GaAs in H_2SO_4 (0.2 M); same conditions as in Fig. 6.

and resulted in the reduction current increasing linearly with the H_2O_2 concentration. The cathodic increase of the current on p-GaAs due to hydrogen evolution is shifted by H_2O_2 towards anodic potentials. The shift of the hydrogen evolution was opposite the cathodic shift of the flatband potential in Fig. 1.

The observed current potential plots are explained by a schematic band diagram shown in Fig. 8. Again, surface states are used to explain the features. At the flatband potential, the surface states are unoccupied and act as scavengers for photoexcited electrons which play a role as efficient catalysts for recombination of electron–hole pairs and no photocurrent is observed before the filling up of the surface states at −0.2 V. Then, the electrons accumulated at the electrode–electrolyte interface find an additional path by decharging hydrogen ions and developing hydrogen.

Hydrogen peroxide increases the onset of anodic oxidation of GaAs due to the shift of the flatband potential. The reduction of H_2O_2 cathodic of the flatband potential can only be observed under illumination. Nevertheless, corrosion was found cathodic of the flatband potential even in the dark and independent of the potential between the flatband potential

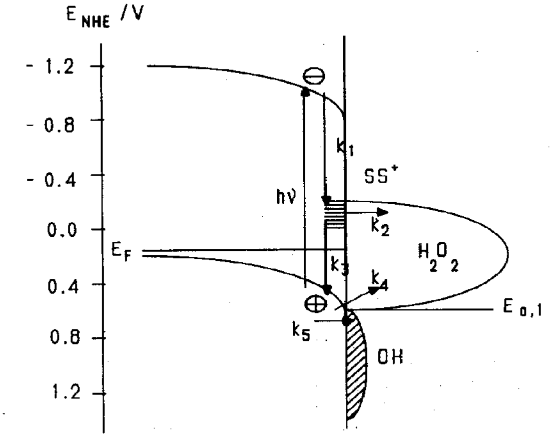

Fig. 8. Schematic band structure model for p-GaAs in H_2O_2 containing sulfuric acid.

and the H_2 evolution[9]. The corrosion current had to be compensated quantitatively by reduction of H_2O_2 to keep the net current zero. Only after excitation could the photoelectrons be transferred directly, or via surface states into the hydrogen peroxide molecules. These electrons cannot be recombined, causing a net cathodic photocurrent.

The zero point in the current potential plots of Fig. 7 is independent of the hydrogen peroxide concentration. This is explained by a stable redox equilibrium at the semiconductor–electrolyte interface[12] which, in agreement with the Raman results, could be associated with the arsenic/arsenic trioxide redox couple.

5. RAMAN SPECTROSCOPIC INVESTIGATIONS

The photoelectrochemical experiments were correlated to Raman spectroscopic investigations especially on p-GaAs. A preliminary report on these experiments was published in[12] and a more extensive paper is in preparation[21]. The first process investigated by Raman spectroscopy of GaAs interfaces was the oxide formation anodic of the flatband potential. The dependence of the Raman spectra on the potential is shown in Fig. 9. Cathodic of the flatband potential, the Raman spectra are determined by the gallium peaks at 268 and 291 cm^{-1}. These lines disappear above 0.5 V and lines attributable to amorphous As_2O_3 can be observed in the Raman spectrum with peaks at 525, 475 and 375 cm^{-1}[19]. A broadening peak at 200–250 cm^{-1} indicates that there might be amorphous arsenic in the film[20]. So far, we have not investigated the passivation process which occurs at very large anodic potentials (Figs 5 and 7), but would tentatively attribute this passivation phenomenon to the oxidation of arsenic trioxide to arsenic pentoxide. The formation of the arsenic and the oxide on the surface could also be observed in a very limited potential region of around the zero point of the current at 0.5 V (Fig. 10) and the reversible manner could be demonstrated (Fig. 11).

One of the questions of the present investigations was, what happens to p-GaAs in a sulphuric acid/hydrogen peroxide electrolyte under open-circuit conditions and no illumination. The potential is obviously adjusted to the open-circuit value (0.1 V, Fig. 6). The Raman spectrum measured under these conditions is shown in Fig. 12a. For comparison, a Raman spectrum of p-GaAs is shown in Fig. 12b. The characteristic GaAs peaks at 291 cm^{-1} were observed. In sulphuric acid/H_2O_2 electrolyte under illumination, the Raman spectrum shown in Fig. 9 indicates

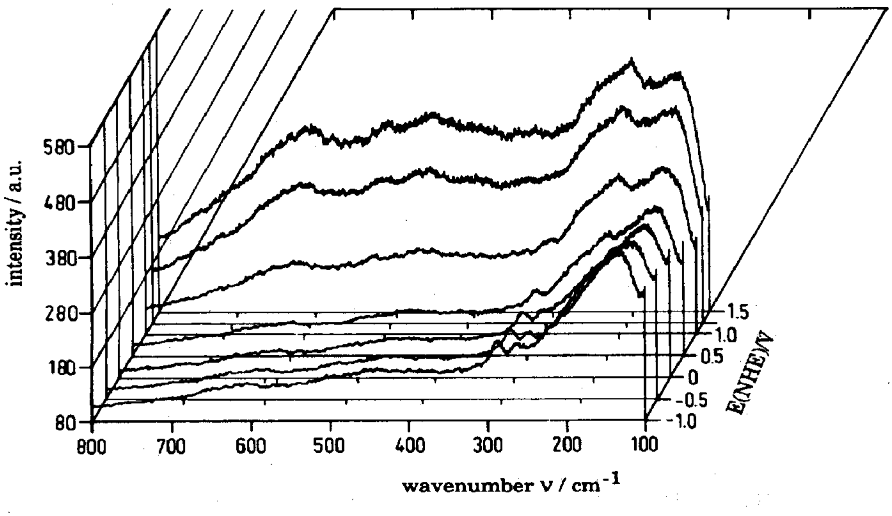

Fig. 9. Potential dependence of Raman spectra of p-GaAs(100) in H_2SO_4 (0.2 M).

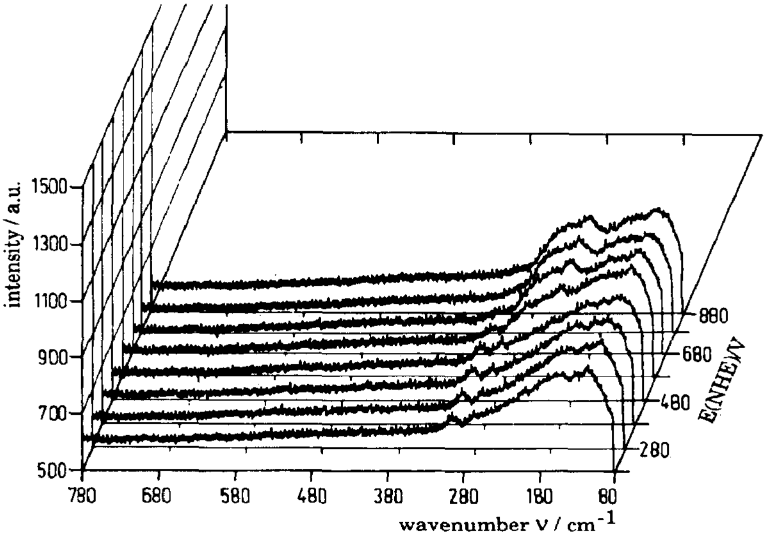

Fig. 10. Potential dependence of Raman spectra p-GaAs(100) in H_2SO_4 (0.2 M). The potential is *increased* from 0.4 V to 0.6 V (*vs nhe*).

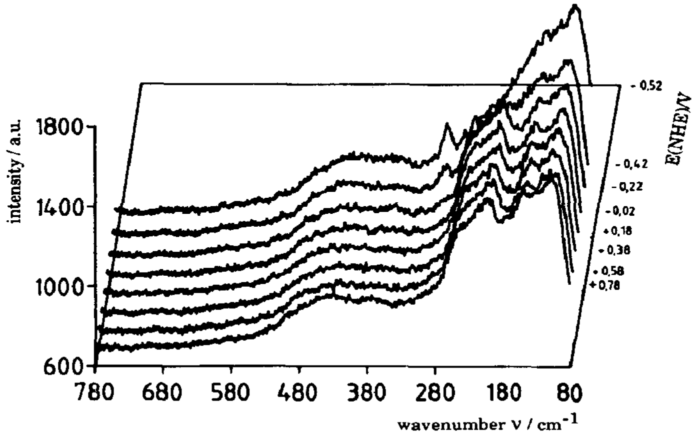

Fig. 11. Potential dependence of Raman spectra of p-GaAs(100) in H_2SO_4 (0.2 M). The potential is *decreased* from 0.6 V to 0.4 V (*vs nhe*).

the formation of arsenic/arsenic trioxide on the surface. Therefore, under open-circuit conditions, GaAs is oxidized to Ga^{3+} $+As_2O_3$ under reduction of hydrogen peroxide in the vicinity of the flatband potential. It was necessary to bring the potential as close as possible to the flatband condition in order to obtain a sufficient corrosion rate of the GaAs sample.

An additional feature is presented in Fig. 12c showing the Raman spectrum of p-GaAs after treating the electrode in sulphuric acid/hydrogen peroxide solution and then dipping it into an HCl/HNO_3 electrolyte ($HCl:HNO_3:H_2O=2:1:2$). The Raman spectrum again shows the characteristic features of GaAs and only residual features of arsen trioxide. The known activating action of a hydrochloric acid electrolyte on gallium arsenide electrodes is therefore connected with the removal of oxide films from the surface.

6. CONCLUSIONS

III/V semiconductors form a much more complicated electrochemical system than electrode–electrolyte interfaces of homogeneous electrode composition. This, in connection with the semiconductor properties of the electrode material and a very complicated redox system (the hydrogen peroxide system)

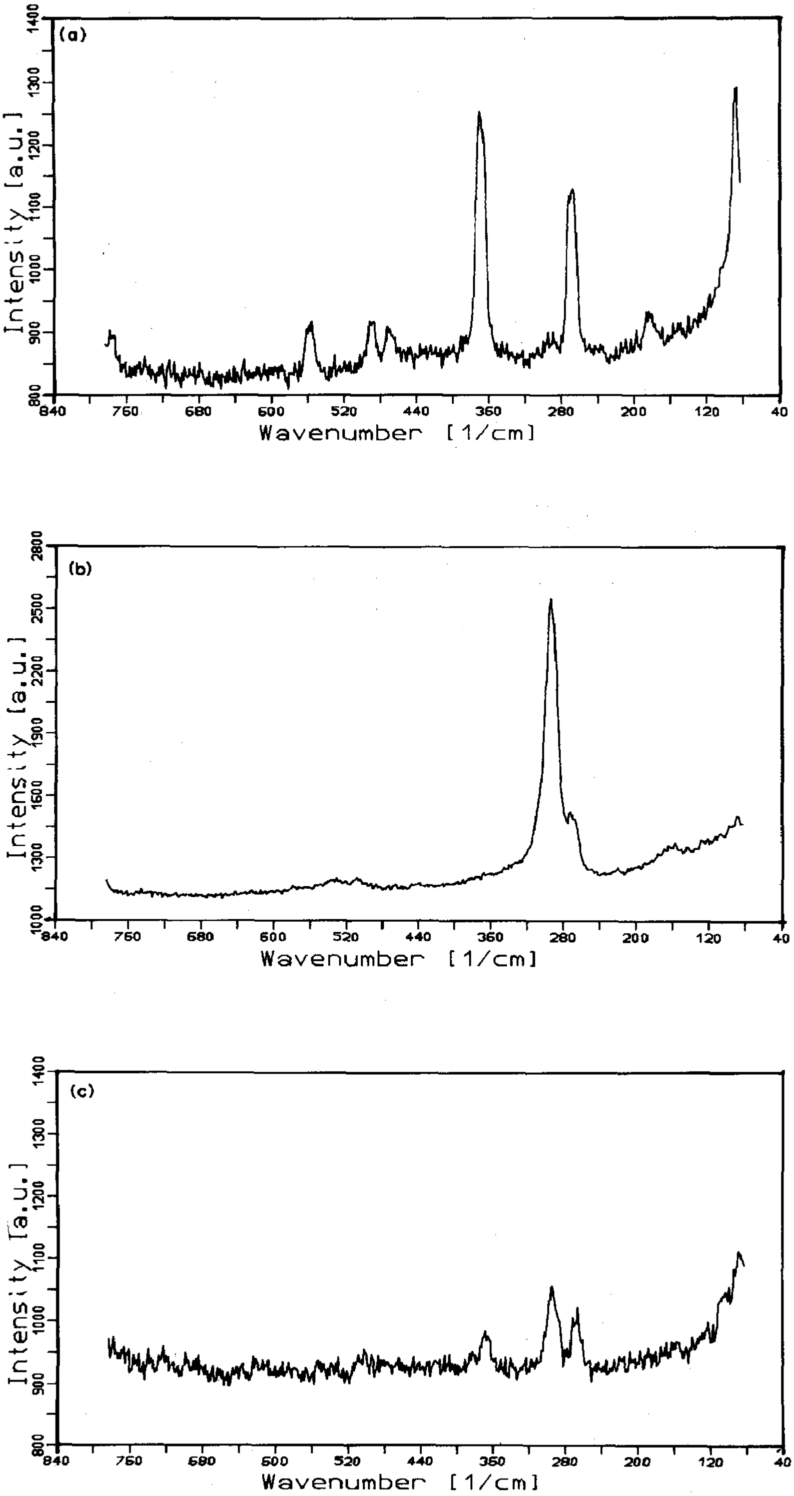

Fig. 12. Raman spectra of p-GaAs: (a) in air; (b) after etching in $H_2SO_4/H_2O_2/H_2O$ (1:1:1) for 1 min; (c) same treatment as in (b) but after additional dipping into $HCl/HNO_3/H_2O$ (1:1:1).

makes the situation of such an etching electrolyte much more difficult than etching electrolytes of a simpler nature such as iron(II)/iron(III) systems. The combination of electrochemical and new optical surface *in situ* techniques is necessary to enable a better understanding of the various processes taking place at the electrode–electrolyte interface. From such experiments, it becomes obvious that this interface might need a more sophisticated model than the simple band models shown in Figs 4 and 8. For example, the changes of the simple model due to the presence of oxide films are not taken into account. They might play an even more important role in other compounds such as for instance, indium phosphide[17].

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