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CHEMICAL COMPOSITION OF ANODICALLY FORMED P-TYPE POROUS GAAS IN HF BASED ELECTROLYTE

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SUMMARY

We have performed an extensive study of the porosification of p-type GaAs using electrochemical etching (EE) in a hydrofluoric acid (HF)-based electrolyte. The p-doped GaAs substrates were used to study the influence of different parameters, such as current density, porosity, and etching rate. Also, etching of p-GaAs wafers in HF was investigated and characterized through different techniques, such as cathodoluminescence (CL), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS). It was found that after electrochemical etching, the porous layer showed a major decrease in the CL intensity and a change in the chemical composition, the elemental concentration, and the crystalline phase. Contrary to previous report on p-GaAs porosification, which believe that the formed layer is composed of porous GaAs [1-2], we bring evidence that this is not the case. The porous layer is composed mainly of porous As_2O_3 . Finally, a model that explains the As_2O_3 formation on p-GaAs substrate is proposed.

1. INTRODUCTION

III-V based solar cell technology is important for concentrated photovoltaic (CPV) applications. III-V multi-junction space solar cells offer the opportunity to achieve higher efficiencies and thus a lower power-to-mass ratio. Porous GaAs nanostructures have some particular applications; it was used as an antireflective coating for GaAs solar cells [3]. It was also found that the porous GaAs showed elastic properties and acted to reduce the density of misfit dislocations, thereby increasing the epilayer critical thickness [4]. Additionally, porous GaAs-based devices are good candidates to obtain fast response to H_2O gas sensing [5]. So far, the electrochemical porosification mechanism of p-doped GaAs is different from that of the n-doped type. For n-GaAs, the pore density, the pore dimension and the layer structure depend on the doping density and the crystallographic orientation of the wafer. High-aspect-ratio triangular pore arrays of n-GaAs along the [111] crystallographic direction have been demonstrated by several groups [6-7]. However, for p-GaAs, uniformly distributed mesopores are obtained at the surface. The argument is that holes are the majority carriers in p-type substrates and are certainly omnipresent, which consequently will lead to a uniform dissolution even with backside illumination. From a morphology standpoint, electrochemical etching of p-GaAs is believed to lead to porous GaAs formation as it shows a nanometric crystallite size that looks promising for layer transfer engineering [2], but from a chemical standpoint, the p-GaAs surface that comes in contact with HF shows a brown layer that is shown to consist of elemental As that can be replaced by As_2O_3 particles [8]. In this work, we report CL, XPS, EDS and XRD characterization to reveal the chemical nature of porous the p-GaAs layer.

2. EXPERIMENTAL RESULTS AND DISCUSSIONS

Preparation of p-doped porous GaAs substrates (p-GaAs)

Porous GaAs layers were formed by an EE method, on a highly doped p-type wafer (resistivity = 2.10^{-3} ohm.cm). After immersing the GaAs wafer in an electrolyte consisting of 49% HF, a direct current was applied to form the porous GaAs layer.

Electrochemical calibration

Fig (1.a-b) illustrates the dependence of the porosity and the etching rate on the current density. Similarly to porous p-Si, the etching rate increases linearly with increasing current density. The porosity also increases with the current density before stabilizing at 80%. The scanning electron microscope (SEM) image of porous p-GaAs (Fig 1.c), shows randomly and uniformly distributed mesopores formed at the surface of the sample. We can also see the presence of small crystallites, with sharp edges, dispersed on the surface of the porous layer and having sizes of several hundred nanometers that are attributed to As_2O_3 precipitation [8].

Luminescence and Chemical composition

The CL spectra from both layers show luminescence in the near infrared region with a maximum intensity at 875 nm when excited by a 20 keV electron beam at room temperature Fig (2.a-c). After the porosification process, the CL intensity was considerably attenuated. A spatial mapping of the intensity reveals luminescence preferably around cracks. XPS spectra of porous p-GaAs after anodization in 49% HF solution at 2 mA/cm^2 is reported in Fig (2.d), the table in the inset summarises the chemical composition of the porous layer and shows a very low gallium concentration, confirming that the porous material is not GaAs.

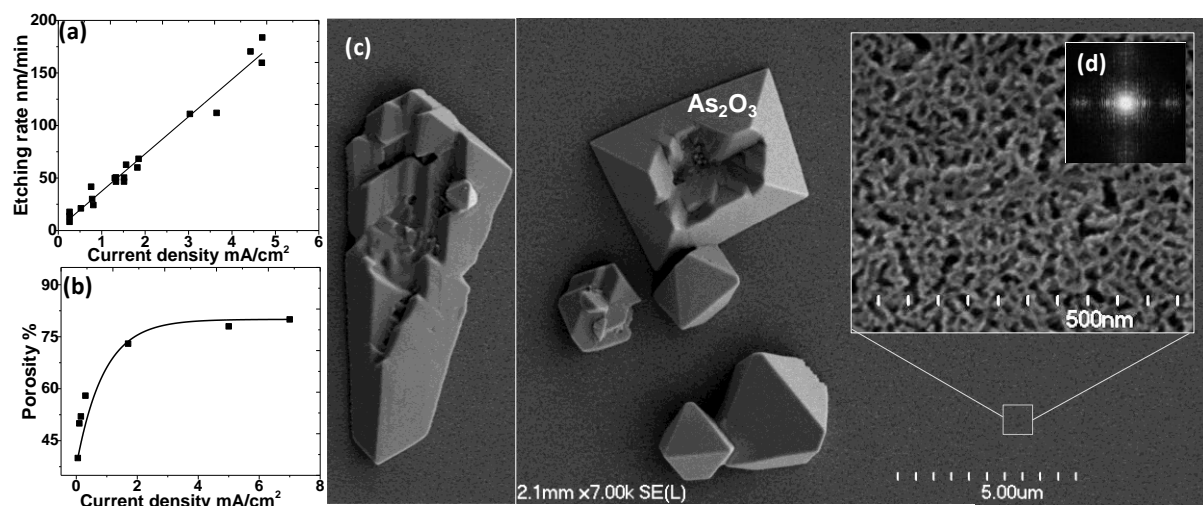


Figure 1: (a) etching rate and (b) porosity evolution versus the current density. (c) SEM images of porous p-GaAs layers formed in 49% HF solution at 2mA/cm² by electrochemical etching (d) The FFT power spectrum calculated from the SEM image.

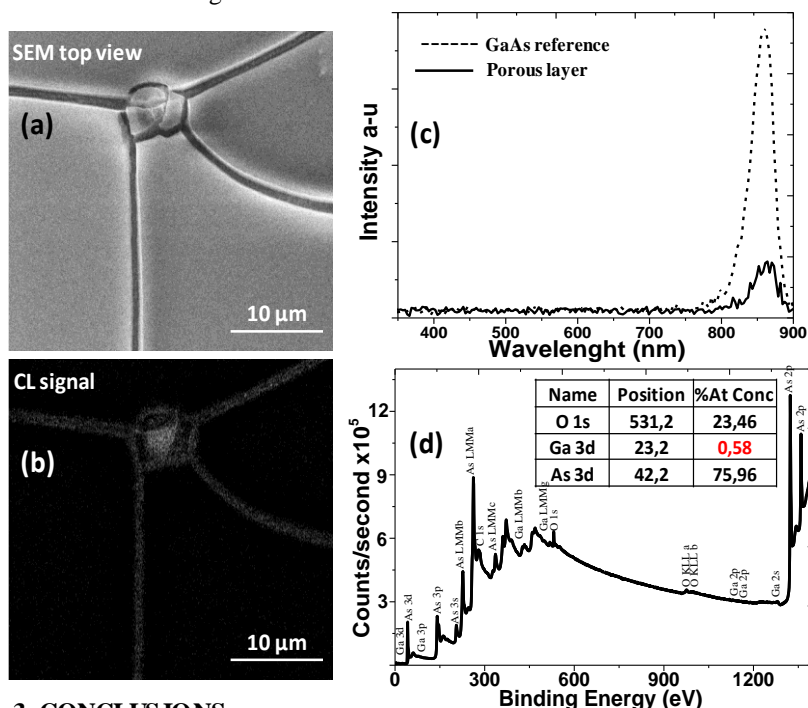


Figure 2: SEM image (a) and CL micrographs (b) taken from the top surface of porous p-GaAs with 20keV at room temperature formed in 49% HF solution at 2mA/cm² by electrochemical etching.

(c) Cathodoluminescence spectra at room temperature for p-GaAs reference substrate and porous p-GaAs and (d) XPS spectrum of porous p-GaAs immediately after anodization in 49% HF solution at 2 mA/cm².

3. CONCLUSIONS

Electrochemical etching of p-type GaAs in HF yields a porous layer that is highly gallium deficient, with only a couple atomic percent of Ga, As oxide is making up for the rest of the layer.

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