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Selective etching of GaAs grown over AlAs etch-stop layer in buffered citric acid/H_2O_2 solution

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ABSTRACT

Selective etching of a GaAs layer over AlAs etch-stop layer using citric acid and hydrogen peroxide unbuffered and buffered with a potassium citrate has been carefully investigated. We show that resistivity of the AlAs etch-stop layer to chemical attack strongly depends on the layer thickness making the standard description based on the selectivity unusable. By considering the influence of stirring and analysing the diffusion/reaction rate limitation of the etching processes, as well as the composition of the etch-stop layer, we propose a new description of the chemical processes taking place at the AlAs etch-stop layer/etching solution interface. We also propose the best way of the etch-stop layer design for precise fabrication of electronic and optoelectronic devices grown on GaAs substrates.

1. Introduction

Selective etching is a crucial step in fabrication of the devices based on modern semiconductor heterostructures. In the case of photonic devices the heat extraction can be strongly enhanced by simply removing the substrate. Such approach results in an exceptionally high rise of the output power as it can be observed in the case of Vertical External Cavity Surface-Emitting Lasers [1]. Substrate removal is also required in Quantum Cascade THz laser technology when a double side metal waveguide has to be fabricated [2] or in the case of other devices like Field Effect Transistors (FETs) [3,4] which require uniform gate-recess process. The selective etching is also a key point in fabrication of modern devices of complex architectures [5].

Selective "dry" Reactive Ion Etching (RIE) plasma [6] has been successfully used in mentioned above applications providing high feature resolution and low reagent consumption. However, dry etching has also some disadvantages, which are inherent to this technique. These are for instance increased surface damage [7], relatively narrow window of selectivity and high cost of the equipment. This explains why a wet selective etching, being relatively cheaper and offering superiority of surface quality as well as ability to dissolve thick layers, is often chosen by process engineers.

The standard procedure for precise control of the in depth etching of multilayer heterostructure is deposition of a special sacrificial layer or layers with composition different from the etched ones. Such layers are easily introduced during the deposition of the heterostructure by any modern epitaxial technique such as Molecular Beam Epitaxy (MBE) or Metal Organic Chemical Vapour Deposition. In the case of devices grown on a GaAs substrate by MBE the etch-stop layer of choice is AlAs (different cation) [8–10]. The apparent advantage of such a layer is low lattice mismatch between AlAs and GaAs, simplicity of deposition of a binary compound and availability of Al source in any epitaxial system. AlAs is a convenient alternative for lattice matched GaInP (different anion) etch-stops. In MBE systems phosphorus is often avoided due to its accumulation on the chamber walls and possible ignition during the system venting.

Selective etching of GaAs over the AlAs etch stop layers turns out to be difficult mostly due to change of AlAs volume when this compound is subject to oxidation [11,12]. Despite considerable efforts the chemical processes taking place are still not well understood. A standard mixture of (citric acid/H_2O_2 4:1) is reported to have high selectivity for AlAs layer over GaAs [13,14]. However, usually no specific parameters of the etching process are given in the literature besides an exact chemical recipe of the etching solution. Also, the data is provided for etching of very thin layers for which the total time of process is rather short thus the resistivity of etch-stop layer to chemical attack is not verified in a long time scale. The resistivity of the etch-stop layer over extended times is required whenever the thick layers have to be chemically removed. The presence of crystal defects, possible wedge of the etched layer impose constrains not present when very thin layers are processed.

A citric acid/hydrogen peroxide solution has been reported [15–17] to preferably dissolve GaAs over AlAs, which is used as an etch-stop layer. According to the available data this solution has a narrow

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window of selectivity, which happens to be sensitive to concentration of each component, solution pH, temperature, hydrodynamic regime of etching as well as thickness and fraction of Al, in the case of AlGaAs [18,19]. However, in the literature there is a lack of systematic analysis and deep chemical understanding of why a particular combination of parameters is responsible for sudden increase in selectivity and what makes its window to be narrow. Moreover, often there is lack of information about exact hydrodynamic conditions of etching.

In this paper we show that the effect of buffering of citric oxide mixture dramatically increases apparent selectivity of GaAs etching over AlAs and AlGaAs etch-stop layers of a set thickness and propose a physicochemical mechanism which can explain such behaviour.

2. Experimental details

The test heterostructures were grown using molecular beam epitaxy (MBE) in Riber Compact 21T chamber. The heterostructures consisted of a thin AlAs etch-stop layer with thickness varied between 3 to 60 nm. This thickness was precalibrated using special test samples and High Resolution X-ray Diffraction method. The AlAs layers were deposited directly on a 500 nm thick GaAs buffer and covered with 400 nm thick GaAs cap. All the heterostructures were undoped and deposited on a GaAs: Si, n=2e18 cm^{-3} substrate. The standard growth conditions were applied: substrate temperature was 580 °C and As_2/Ga ratio was adjusted for stable (2×4) surface reconstruction. The As_2 was produced by cracking at 900 °C. In etching experiment the dissolution of the epilayers was investigated. For comparison, also unprocessed GaAs substrate samples were etched.

Two different solutions were used for etching in order to compare their chemical properties and selectivity. These were: (1) 50% weight solution of citric acid (CA) in water mixed with 30% H_2O_2 in 4:1 vol ratio, (2) a buffered equimolar solution of citric acid and potassium citrate (each having 0.44 M concentration) mixed with 30% H_2O_2 in a 5:1 vol ratio. Test samples of 1 cm^2 size used in all experiments were first glued to a similar area glass slide by means of red wax in order to protect the substrate side, placed horizontally on a Teflon holder and submerged in the large volume of solution. A new solution was always prepared and etching always took place using the same beaker and Teflon holder to avoid any random scattering of data. The etch time of any particular layer was precisely registered. A small spot on the top heterostructure surface was covered by wax to provide a reference level for a profilometer scan. Before the etching, the samples were always submerged in HCl for 30 s in order to remove natural surface oxide of GaAs. The etching was performed in a dynamic regime using magnetic stirrer permitting for rotation rate up to 200 rpm. Temperature of etching solution controlled by a thermocouple was set to 22 °C and stabilized for at least 30 min. The solution pH was measured by an electronic pH meter with a 0.01 unit precision. Exclusively for calculation of the etch solution activation energy the process was performed in a static regime (rpm=0) with a test sample covered by photolithographic emulsion with repeating pattern of 200 μm to create a reference level. Etched surface was observed by an optical microscope (Olympus BX51, Japan). After removing the wax or emulsion protection layer, a spot with a reference level was obtained and the depth measurements and surface roughness were investigated with a stylus profilometer (KLA Tencor P-16+, USA). The procedure permitted to measure the etch depth with an accuracy in the range of single nanometres provided that the surface was smooth. For surfaces with high roughness the etch depth value was averaged over a large length by the equipment software. Same samples were also investigated by Scanning Electron Microscopy (Zeiss Merlin, Germany).

3. Results and discussion

First we investigated whether the etch selectivity of the solutions depends on the AlAs etch-stop layer thickness. During the etching in

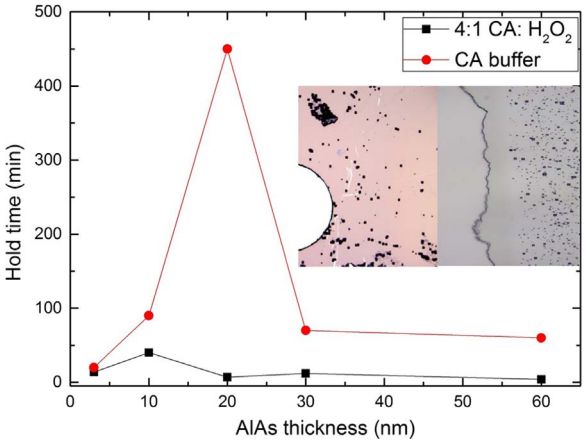

Fig. 1. Hold times of AlAs etch stop layers of different thickness in 4:1 CA:H_2O_2 standard solution (black squares) and CA:H_2O_2 buffered with potassium citrate (red circles). In the insert there are shown optical images of the surfaces of 10 nm etch stop layer several minutes after the moment of etch pits formation in 4:1 CA:H_2O_2 solution (right, ~50 min) and buffered solution (left, ~100 min).

CA H_2O_2 4:1 solution (pH < 1) of the GaAs cap layer the heterostructure surface was mirror like (dull grey for buffered mixture). Upon reaching the etch-stop layer the surface would become smooth and for some samples with a distinct colour. The colour light to deep blue is due to light interference and thus depends on the etch-stop layer thickness.

For all samples the etch time was equal in the case of the GaAs cup layers and substantially different in the case of AlAs. The etch rate of GaAs was calculated to be 0.4 μm/min. This value was confirmed also using an additional sample consisting of an unprocessed substrate. During the etching the samples surface was observed. After a certain time small etch pits would appear which would indicate the layer perforation. We define that time as the hold time and plot it versus different etch-stop layer thickness as shown in Fig. 1 (black squares). The maximum hold time of about 40 min is observed for the 10 nm thick layer which is counterintuitive as etch-stop chemical robustness was expected to increase with thickness. Moreover, we have observed that etching rate of the AlAs etch-stop layer was not uniform across the sample, but rather small randomly placed perforations were observed after a given period of time as it is shown in the insert of Fig. 1, right. The etch-stop layer between the spots was intact and perfectly smooth. These observations suggest some thickness dependent mechanism of the etch-stop layer dissolution.

In order to elucidate that mechanism further we prepared a buffered equimolar (0.44 M) solution of citric acid and potassium citrate in water mixed with H_2O_2. For this solution the etch rate of GaAs was slightly lower (0.3 μm/min), but the etch-stop perforation appeared similar to that of 4:1 solution (Fig. 1. left insert). However, the increase in hold times was considerable for all AlAs thicknesses, whereas specifically for 20 nm it was dramatic - reaching more than 7.5 h (Fig. 1, red circles). This thickness dependency of the etch rate of the AlAs layers makes the standard definition of chemical selectivity coefficient (or just selectivity) [20]:

$$S = (GaAs\ etching\ rate)/(AlAs\ etching\ rate) \quad (1)$$

unusable so the hold time is used instead. Here, for instance, according to standard definition, the selectivity for 20 nm thick AlAs layer would be higher than 6480 suggesting that AlAs dissolution rate is less than 0.4 Å/min. However, in the perforated sites it was much faster whereas unperforated areas were completely intact. Thus selectivity is misleading and should not be used for this case.

Further, the influence of fluid dynamics on the surface morphology was investigated. The data for the etching in buffered solution of CA/H_2O_2 is summarized in Fig. 2. Here optical microscope images together