# $H_2O_2$:HF:$C_4O_6H_6$ (Tartaric Acid):$H_2O$ Etching System for Chemical Polishing of GaSb

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## ABSTRACT

We present the results of a study of $H_2O_2$:HF:$C_4O_6H_6$(tartaric acid):$H_2O$ solution for chemical polishing of GaSb wafers. The influence of etching solution composition on surface morphology was studied. The solutions investigated varied in $H_2O_2$ (2.0-3.0 mol) and HF (0.0-5.0 mol) concentrations, but contained a constant concentration of tartaric acid (0.7 mol). It was found that the etchant has excellent polishing properties for GaSb wafers when the HF concentration was less than 1.5 mol. For HF concentration larger than 1.5, the etchant solution produced rough surfaces. The dependencies of the etching rate on solution composition, temperature, and etching time were studied.

Gallium antimonide (GaSb) is an interesting material for the fabrication of different optoelectronics devices, such as laser diodes, light emitting diodes, and photodetectors for the middle infrared spectrum area. It is used as a substrate for multilayer heterostructures (GaSb/AlGaAsSb, GaSb/InGaAsSb, GaSb/InAsSbP).

In contrast with Si, GaAs, and InP, for which a number of etchants are known and widely used, only a few etchants for GaSb have been reported.[1-6] Detailed studies of chemical polishing of GaSb have been performed with $H_2SO_4$:$H_2O_2$:$H_2O$,[1,2] HCl:$H_2O_2$:NK (tartrate),[1,3] HF:$HNO_3$:$CH_3COOH$,[1,4,5] and Br-methanol[1] etching systems.

Because GaSb easily oxidizes, during wet etching the resulting oxides are hardly soluble in aqueous acids or alkali solutions, which leads to difficulties in obtaining highly polished surfaces. Therefore, a study of other chemical etching systems to prepare polished GaSb wafers is very important for epitaxial growth, as well as for surface physics experiments.

We present the results obtained from etching GaSb wafers with a solution $H_2O_2$:HF:$C_4O_6H_6$(tartaric acid):$H_2O$.

The samples used in this work were as received monocrystal wafers of GaSb (100), Te-doped with a carrier concentration of $N = 1 \times 10^{17}$ cm$^{-3}$. Before etching, the wafers were mechanically mirror-like polished with 0.3 $\mu$m alumina powder, rinsed and degreased in boiling organic solvents. Then, photoresist stripes with a width of 1 mm and with a distance between them of 2 mm were patterned on the specimen surface parallel to the [110] direction. To determine the etching rate ($V_{ETCH}$), we measured the depth of the etched groove between two stripes by observing the cleaved edge with a high resolution optical microscope. The depth of grooves did not exceed 50 $\mu$m. Before chemical etching, a water solution of tartaric acid was prepared, then all components of the etchant were mixed. We investigated the dependence of $V_{ETCH}$ on etchant composition, temperature, and etching time. The resulting morphology of the surface was observed and registered optically with Nomarski interference contrast.

The dependencies of $V_{ETCH}$ *vs.* etchant composition are shown in Fig. 1. Note, that in the solution of only $H_2O_2$:$C_4O_6H_6$(tartaric acid):$H_2O$ in any concentrations, there was no etching of GaSb, and no change in the surface was observed. When the concentration of HF was increased, two kinds of surface morphology were observed. In one case, represented by open marks on Fig. 1, when the concentration of HF was lower than approximately 1.5 mol, the resulting surface was excellent, mirror-like, without any traces of oxide layer or reaction products. An important point is that in this region of etchant composition, there was no observable difference in resulting surface morphology (mirror-like, no reaction products), whether or not the samples had been in contact with air before etching. This point is very critical for such etching systems as Br-methanol and HCl:$H_2O_2$:NaK(tartrate), because the etching in corresponding solutions results in a rough surface if the sample had been exposed to air before etching.[1] In the second region, represented by black marks on Fig. 1, we observed a dark layer on the surface of all samples. This layer was insoluble in acids, and probably was formed by antimony oxide $Sb_2O_5$.[3] The morphology of the surface on these samples was very rough. The microphotographs of surface morphology for both cases are shown in Fig. 2A, B, and C, respectively.

The dependence of $V_{ETCH}$ on time is shown in Fig. 3. Excellent surface morphology was achieved after removing a thin damaged layer that was introduced by the mechanical polishing. It can be seen from Fig. 3 that $V_{ETCH}$ decreases very fast in the first minute of etching in a solution with small concentration of HF (0.25 mol) and becomes constant after 1.5 min, when mechanically polished wafers were used. The same etching experiment was performed on wafers previously chemically polished. The results obtained showed that the etching rate is independent of time for pretreated wafers. We suggest that the high rate of GaSb etching in the first minute of reaction can be caused by the crystal damage in the surface layer of mechanically polished wafers.

Regions 1 and 2 in Fig. 1 refer to the low and high HF concentration experiments, respectively. In region 1, $V_{ETCH}$ is not very dependent on $H_2O_2$ concentration, which is the oxidizing component, and the reaction rate is primarily limited by the concentration of HF. When the concentration of HF is higher than 1.5 mol, the etching rate shows a somewhat stronger dependence on the concentration of $H_2O_2$. In this area of composition, the rate of oxide removal is

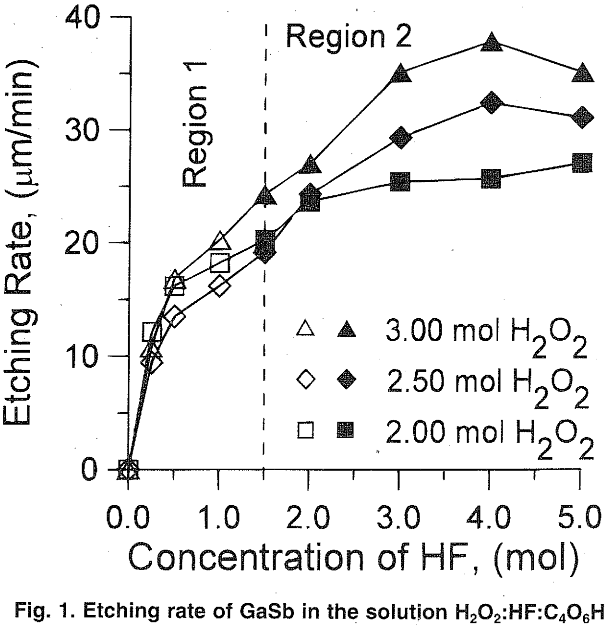

**Fig. 1. Etching rate of GaSb in the solution $H_2O_2$:HF:$C_4O_6H_6$ (tartaric acid):$H_2O$ as a function of HF concentration for three different concentrations of $H_2O_2$ and constant tartaric acid concentration of 0.7 mol, at room temperature. Open marks correspond to the mirror-like surface after etching (region 1), dark marks show the presence of the dark layer on the surface of etched wafers (region 2).**

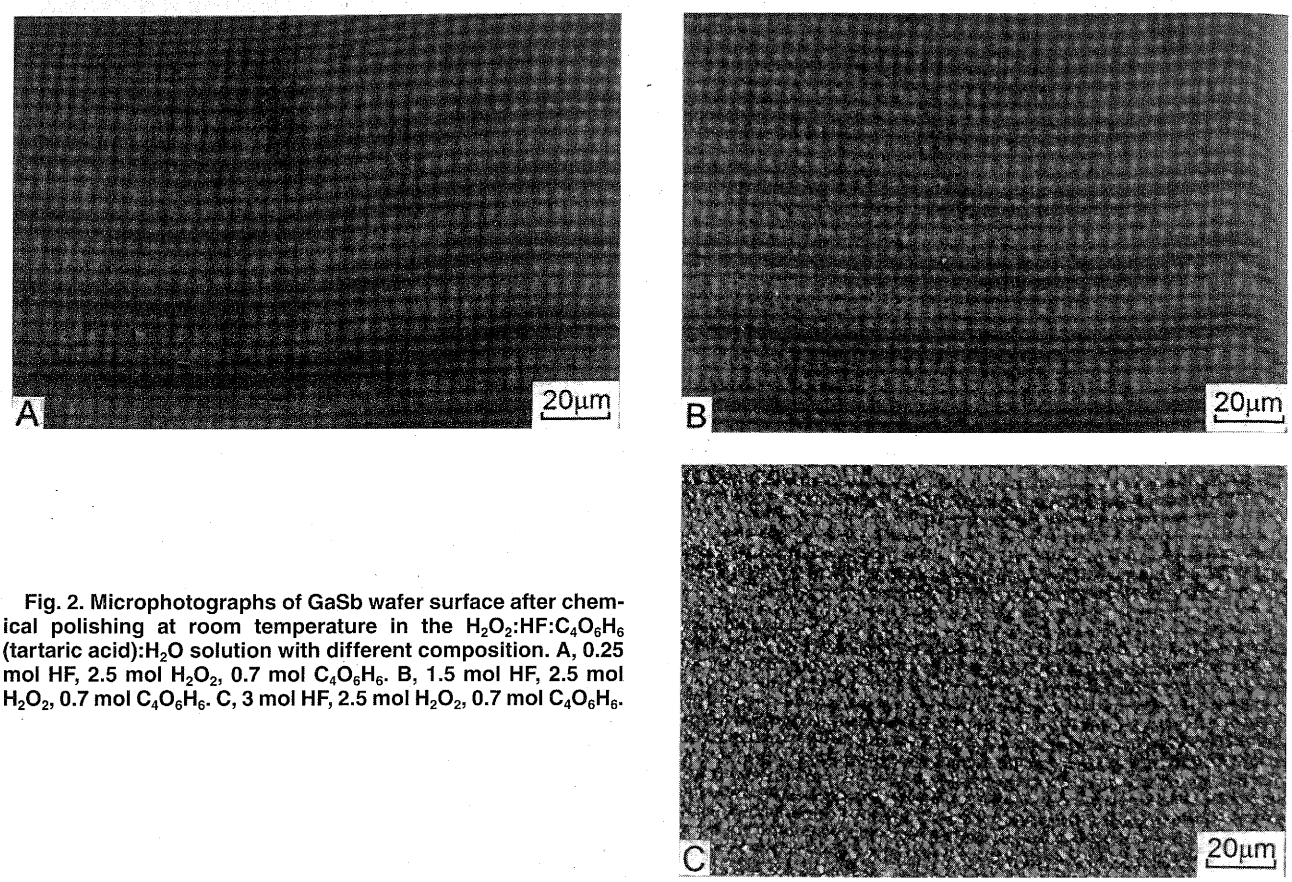

**Fig. 2. Microphotographs of GaSb wafer surface after chemical polishing at room temperature in the $H_2O_2$:HF:$C_4O_6H_6$ (tartaric acid):$H_2O$ solution with different composition. A, 0.25 mol HF, 2.5 mol $H_2O_2$, 0.7 mol $C_4O_6H_6$. B, 1.5 mol HF, 2.5 mol $H_2O_2$, 0.7 mol $C_4O_6H_6$. C, 3 mol HF, 2.5 mol $H_2O_2$, 0.7 mol $C_4O_6H_6$.**

slower than the rate of formation of insoluble oxide islands on the surface. The resulting surface morphology in this area is rough.

The temperature dependence of $V_{ETCH}$ is shown in Fig. 4 for a solution of 0.6 mol HF, 3 mol $H_2O_2$, and 0.7 mol $C_4O_6H_6$ (tartaric acid) which corresponds to the area of compositions with good polishing properties. The activation energy of the chemical reaction was found to be around 5.2 kcal/mol indicating a diffusion-controlled dissolution mechanism.

In conclusion, the etching solution $H_2O_2$:HF:$C_4O_6H_6$ (tartaric acid):$H_2O$ has been studied for GaSb chemical polishing in a wide range of HF concentrations. It was found, that two kinds of surface can be obtained. Excellent polishing properties were observed in the area of etchant composition with HF concentration lower than 1.5 mol. The resulting polished surface was mirror-like. Observations by optical microscope with Nomarski interference did not reveal any inhomogeneities on surface morphology. Increasing the HF concentration in the solution resulted in the appearance of an insoluble dark layer on the GaSb surface, in which case the surface morphology was very rough.

Our results suggest that $H_2O_2$:HF:$C_4O_6H_6$ (tartaric acid):$H_2O$ etching solution can be successfully used to prepare GaSb substrates for epitaxial growth.

## Acknowledgments

The authors wish to thank Dr. A. Garcia for his comments and useful discussion, Dr. Alfonso Lastras Martinez and Dr. Hugo Navarro for their interest and attention.

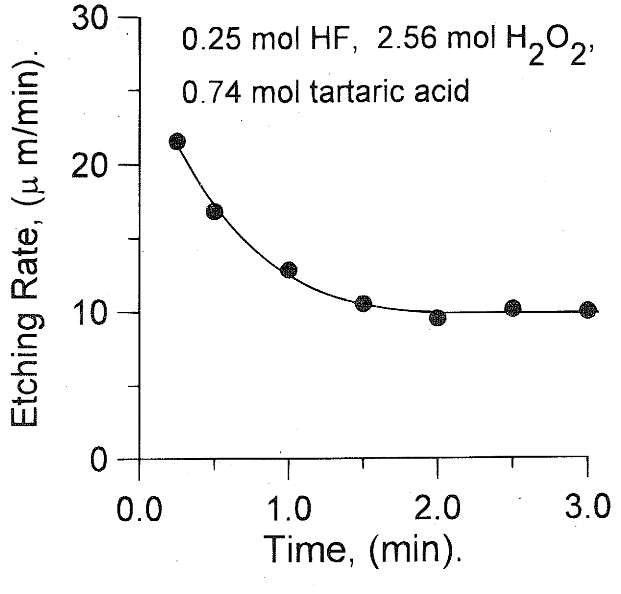

**Fig. 3. Etching rate at room temperature as a function of process time for chemical polishing of GaSb in the solution with shown composition.**

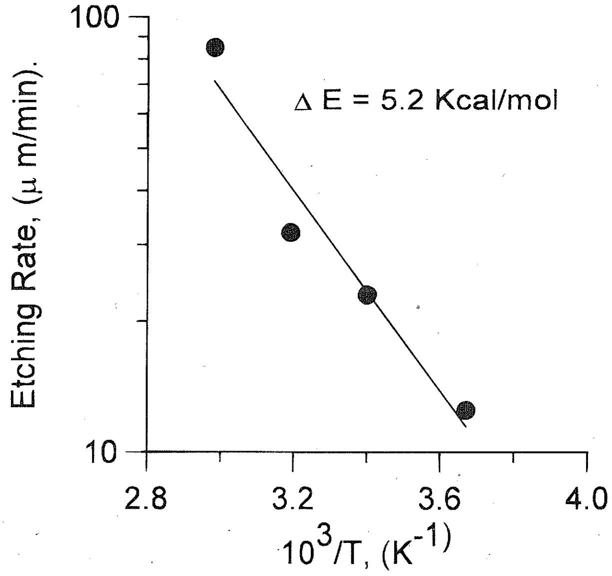

**Fig. 4. Temperature dependence of GaSb etching rate for a solution of 0.6 mol HF, 3 mol $H_2O_2$, and 0.7 mol $C_4O_6H_6$.**

This work was supported by CONACYT and FAI at UASLP.

Manuscript submitted April 7, 1995; revised manuscript received June 21, 1995.

*The Universidad Autonoma de San Luis Potosi assisted in meeting the publication costs of this article.*

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# Lithium Intercalation in Vanadium Pentoxide Aerogels

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ABSTRACT

Vanadium pentoxide ($V_2O_5$) aerogels were prepared by supercritical drying of a vanadyl alkoxide precursor. Thin films prepared from the aerogel were found to intercalate up to 1.9 mols of Li per mol of aerogel with good cycling reversibility.

Vanadium oxides have been studied for over a century; however, in recent years there has been renewed interest in these materials because of their interesting electrical and optical properties.[1] Several different vanadium oxide compositions are of interest as insertion electrodes for secondary lithium batteries because of their reversible lithium intercalation properties.[2] Vanadium pentoxide ($V_2O_5$) is one of these compositions, and the electrochemical properties of vanadium pentoxide xerogels ($V_2O_5 \cdot nH_2O$) have shown considerable promise.[2,3] An attractive feature of these materials is that they are readily prepared as films or powders by sol-gel methods through the protonation of an ion exchanged sodium metavanadate solution.[1] Recently, researchers have shown that up to 3 mols of lithium can be intercalated per mole of $V_2O_5 \cdot 0.5H_2O$.[4]

Xerogels are formed when the liquid phase filling the pores of a wet gel evaporates causing the partial collapse of the gel network and some densification.[5] It is common for xerogels to possess porosities in the range of 50%. An alternative method for removing the pore liquid is to use supercritical extraction. In this case the gel network remains essentially intact, there is very little pore collapse, and a highly porous material, termed an aerogel, is produced. Aerogels are characterized by a porosity in excess of 90% and extremely high surface areas (several hundred $m^2/g$ to over 1000 $m^2/g$).[5] They have been used in the catalyst field because of their elaborate pore structure and high surface areas.[6] Much of the prior work with aerogels has been devoted to silica-based systems and other electrically insulating oxides. With the exception of carbon aerogels, the electrochemical properties of aerogels have not yet been explored.[7]

Previous work on the synthesis of vanadium pentoxide aerogels (VAG) suggested that the fine colloid size, high surface area (300-400 $m^2/g$), and controllable porosity makes these materials excellent candidates for lithium insertion electrodes.[8] This paper presents results on the lithium intercalation properties of VAG films prepared from an alkoxide precursor and supercritically dried using $CO_2$.

## Experimental

Monolithic VAG samples were prepared by supercritical drying with liquid $CO_2$. The alkoxide precursor, vanadyl triisopropoxide, $VO(OC_3H_7)_3$ (Gelest, Inc.), was hydrolyzed in acetone-water solutions and condensed to form a "wet gel." The molar ratio of the sol components was 1/30/15 [$VO(OC_3H_7)_3$/water/acetone]. The wet gels were aged for 3 days and then washed in anhydrous acetone to ensure complete replacement of the initial acetone mixture. The acetone-exchanged gels were then transferred to an autoclave (Polaron E3000 critical point dryer) for supercritical extraction by $CO_2$. The samples were cast as gels and dried in the form of rods, 1 cm in diam by 4 cm in length. The synthesis conditions for the gels used in this study produced an aerogel with a density of 0.07 $g/cm^3$ which corresponds to a solid fraction of ≈2%. The chemical and structural properties of VAG monoliths were reported previously.[8] The aerogel materials are electronically conducting with room temperature values $\approx 1 \times 10^{-4}$ S/cm for the composition $V_2O_5 \cdot 0.5H_2O$.

The vanadium oxide aerogels were ground into fine powders and mixed with cyclopentanone (Aldrich Chemical Co.). This mixture was stirred rigorously for 12 h after which the VAG particles became suspended in the cyclopentanone. The VAG-cyclopentanone mixture was spun onto molybdenum-coated glass slides to obtain thin films which were heat-treated at 125°C for 12 h. The films were then exposed to laboratory air and allowed to hydrate under ambient conditions.

A 1 *M* solution of $LiClO_4$ (Aldrich Chemical Co.) in anhydrous propylene carbonate (Aldrich Chemical Co.) was prepared in an argon atmosphere glove box and used as the electrolyte. Elemental lithium served as both the counter and reference electrode, and the VAG film was used as the working electrode. Cyclic voltammetry (CV) was carried out on six thin film samples. Film thicknesses were determined from scanning electron microscopy and found to vary from 1 to 4 μm. The film weight was determined using a Cahn C-31 microbalance, and the charge measurements were calculated by integration of the cathodic and anodic sweeps in the experiments.

## Results and Discussion

The open-circuit potential ($V_{oc}$) of the cells was approximately 3.7 V. The CV scans started at 3.6 V, decreased to 1.6 V, and then returned to 3.6 V at a sweep rate of 1 mV/s. After the first sweep, the $V_{oc}$ decreased to approximately 3.4 V. The reduction in the $V_{oc}$ from 3.7 to 3.4 V after the first sweep suggests that some Li was inserted irreversibly into the VAG. This amount was determined from the current-time response at a constant voltage of 3.7 V and was found to be less than 10% of the total lithium intercalated. The amount of intercalated Li ($x$ in $Li_xV_2O_5$) was calculated by integrating the anodic and cathodic sweeps and measuring the weight of aerogel in the film. The weight of the VAG included the adsorbed water; previous experiments with aerogels found that $n$ in $V_2O_5 \cdot nH_2O$ was between 2.0 and 2.2.[8] It should also be noted that the value of $x$ assumes that all the charge is associated with lithium intercalation.

A representative CV plot for the six films is shown in Fig. 1. The sample was scanned five consecutive times, and only the first and fifth sweeps are plotted. Two distinct intercalation peaks were present at approximately 2.85 and 2.35 V, followed by a large deintercalation peak at 3.3 V. It appears that there were two peaks (2.95 and 3.3 V) superimposed on the large deintercalation wave.

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