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Chemical Interaction of InAs, InSb, GaAs, and GaSb with $(NH_4)_2Cr_2O_7$–HBr–$C_4H_6O_6$ Etching Solutions

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Abstract—This paper presents results on the kinetics and mechanism of the physicochemical interaction of InAs, InSb, GaAs, and GaSb semiconductor surfaces with $(NH_4)_2Cr_2O_7$–HBr– $C_4H_6O_6$ etching solutions under reproducible hydrodynamic conditions in the case of laminar etchant flow over a substrate. We have identified regions of polishing and nonpolishing solutions and evaluated the apparent activation energy of the process. The surface morphology of the crystals has been examined by microstructural analysis after chemical etching. The results demonstrate that the presence of $C_4H_6O_6$ in etchants helps to reduce the overall reaction rate and extend the region of polishing solutions.

Keywords: antimonides, arsenides, dynamic chemical polishing, etch rate, apparent activation energy

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INTRODUCTION

Wet chemical etching influences the efficiency and threshold current of lasers fabricated from III–V compound semiconductors [1]. A qualitatively new level of requirements for such light sources stimulates further investigation of the basic technological steps in the fabrication of their gain elements. Detailed knowledge of the effects of solution concentration and temperature on the semiconductor dissolution process is critical for the ability to optimize the key characteristics of etching solutions.

Solutions based on elemental bromine are among the most widely used etchants for III–V compounds [2, 3]. Br_2–CH_3OH solutions can be used in a wide range of bromine concentrations [2]. At low Br_2 concentrations, the etch rate is linearly proportional to bromine content. At a Br_2 content of 0.05 vol % in CH_3OH, the etch rate reaches 750 Å/min. Raising the bromine concentration is favorable for the polishing etching process.

$K_2Cr_2O_7$-based etching solutions are characterized by slow etch rates (1.2–2.8 μm/min) and produce polished (100) surfaces of GaAs crystals [4]. The use of an organic acid, for example, $C_4H_6O_6$, favors the formation of smoother, defect-free surfaces of InP and GaSb crystals. The formation of soluble chelate compounds between an organic acid and indium ensures effective indium removal from the substrate surface [5, 6].

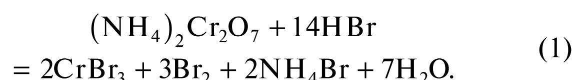
Etching with $C_4H_4KNaO_6$–H_2O–HCl–H_2O_2 solutions is favorable for the formation of smooth surfaces with roughness values in the range ±1.5 nm at an etching rate of ~75.3 ± 12.3 nm/min for InAs and ~449.5 ± 6.3 nm/min for GaSb [7].

Since a literature search has revealed no data on the use of $(NH_4)_2Cr_2O_7$-based bromine-releasing etching solutions, it is reasonable to investigate the mechanism and kinetics of chemical interaction of InAs, InSb, GaAs, and GaSb crystals with $(NH_4)_2Cr_2O_7$–HBr–$C_4H_6O_6$ solutions, evaluate the effect of the organic component on the basic physicochemical parameters of the etching process, and develop and optimize low-rate polishing etchants for the dynamic chemical polishing (DCP) process.

THEORETICAL ANALYSIS

The chemical etching of the III–V semiconductors is accompanied by redox reactions on the surface of the crystals, which ensures removal of the surface material. The choice of the components of $(NH_4)_2Cr_2O_7$ + HBr + $C_4H_6O_6$ etchant mixtures is related not only to the expected good polishing performance of the mixtures but also to the ability of these reagents to break chemical bonds in the corresponding semiconductors and form soluble compounds owing to the high acidity of the medium.

Reaction between $(NH_4)_2Cr_2O_7$ and HBr is accompanied by the formation of elemental bromine according to the scheme



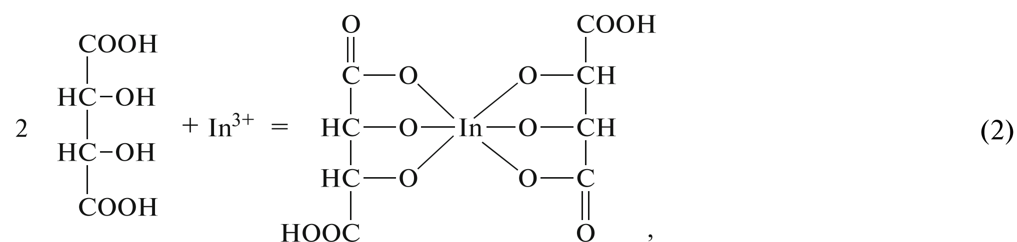
$$(NH_4)_2Cr_2O_7 + 14HBr = 2CrBr_3 + 3Br_2 + 2NH_4Br + 7H_2O. \quad (1)$$

Such reaction leads to the formation of so-called bromine-releasing solutions. Moreover, possible active components of etchant mixtures are the Br^- and $Cr_2O_7^{2-}$ anions, depending on the $[(NH_4)_2Cr_2O_7]/[HBr]$ ratio. The halogen is in a low oxidation state, which results in strong reducing properties of HBr in the composition of the etching solution. Reactions of free Br_2 with metal ions lead to the formation of water-soluble bromides. It is reasonable to assume that the formation of the bromides is due to the heterolytic bond cleavage in Br_2 molecules adsorbed on semiconductor surfaces.

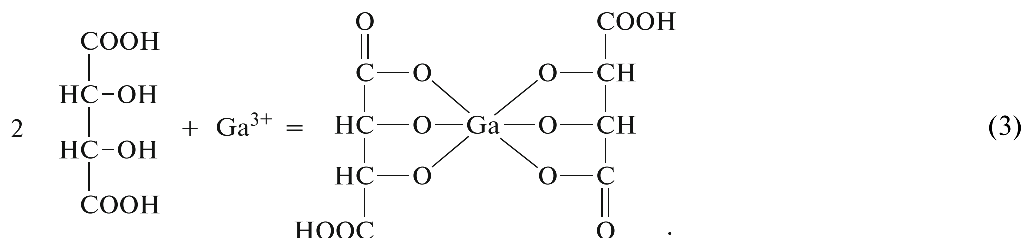
High oxidant concentration in solution is favorable for the formation of insoluble oxides: Sb_2O_3 and Sb_2O_5 [7]. The delivery of a fresh etchant prevents active antimony release on antimonide surfaces [8]. However, raising the reductant concentration leads to the formation of the soluble compound $SbBr_3$.

An important step in the dissolution process is the conversion of etchant–surface reaction products into soluble forms, which enables surface passivation to be avoided. The addition of tartaric acid as a complexing agent to an etching solution helps to control the chemical reaction between the oxidant and reductant, because it enables free Br_2 to persist throughout the reaction. Highly acidic etchant mixtures slow down the ionization of organic acids, which play a key role in converting the etchant–surface reaction products into soluble forms. Moreover, the reaction is accompanied by diffusion to or from the interface, which plays an important role in reaction kinetics. Because of this, the presence of an organic component in etching solutions is of critical importance [9].

Reactions of tartaric acid with the Ga^{3+} and In^{3+} ions are most likely accompanied by the formation of the following soluble complexes:



(2)



(3)

In addition, tartaric acid increases the viscosity of the etchant mixture, thereby reducing the overall reaction rate. Converting redox reaction products into soluble forms, $C_4H_6O_6$ improves the polishing performance of etching solutions.

EXPERIMENTAL

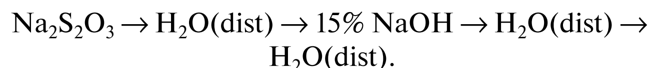
In our experiments, we used *n*-type InAs, InSb, GaAs, and GaSb crystals 5 × 5 × 2 mm in dimensions, which were cut from single-crystalline ingots by a diamond wire saw lubricated with distilled water during the cutting process. Characteristically, the III–V semiconductors have a very low plastic deformation boundary, which causes brittle fracture, leading to the formation of cleaves and cracks on the surface of crystals as a result of cutting. To reduce the thickness of the surface deformation layer, all of the samples were first abrasively ground. The next step was chemical–mechanical polishing and the final polished surface preparation step was DCP. In mechanical grinding, we used aqueous suspensions of the ASM 10/7, ASM 5/3, and ASM 1/0 abrasive powders, with the abrasive grain size gradually reduced from 10 to 1 μm. In chemical–mechanical polishing, we used a universal etchant proposed in our laboratory.

DCP as the final wafer processing step allows the geometric parameters of the wafers to remain unchanged and ensures the preparation of smooth crystal surfaces. In DCP, we used $(NH_4)_2Cr_2O_7$–HBr–$C_4H_6O_6$ etching solutions, which were prepared by mixing the following starting reagents: 26% $(NH_4)_2Cr_2O_7$ (analytical grade), 42% HBr (extrapure grade), and 40% $C_4H_6O_6$ (analytical grade).

The DCP of InAs, InSb, GaAs, and GaSb crystals was studied at T = 294–296 K and a disk rotation rate γ = 78 rpm over a period of 5–10 min under identical and reproducible hydrodynamic conditions using the rotating-disk method and an appropriate experimental setup [10]. This technique ensures a stable delivery

of a fresh etchant to crystals and the removal of reaction products. Using this technique, we measured the dissolution rate of the semiconductors as a function of disk rotation rate, and the results were represented as plots of v^{-1} against $\gamma^{-1/2}$, which allowed us to assess the nature of the dissolution process [10].

Immediately after each chemical etching step, the samples were rinsed according to a procedure proposed by us using the reagents indicated below (for 1 min in each solution):



$$Na_2S_2O_3 \rightarrow H_2O(\text{dist}) \rightarrow 15\%\ NaOH \rightarrow H_2O(\text{dist}) \rightarrow H_2O(\text{dist}).$$

The dissolution rate of the InAs, InSb, GaAs, and GaSb crystals was evaluated from the decrease in wafer thickness as a result of etching, using a TESA Digico 400 electronic indicator with an accuracy of ±0.02 μm. The measurements were made at several points on the crystal surface.

The surface microstructure of the semiconductors was studied by optical microscopy. Surfaces were examined in white light at magnifications from 25× to 1600× on an MIM-7 microscope fitted with an eTREK DCM800 digital video camera.

RESULTS AND DISCUSSION

The concentration dependences of the etch rate for InAs, InSb, GaAs, and GaSb crystals at various solution compositions were studied using mathematical design of experiments on a simplex. The use of a fourth-order equation for a ternary system makes it possible to reduce the number of experiments, performing them at particular points of a simplex lattice [11].

A search for $(NH_4)_2Cr_2O_7$ + HBr polishing etchants for the samples under investigation allowed us to identify the following range: 2–22 vol % $(NH_4)_2Cr_2O_7$ in HBr. These compositions were used as a working range for optimizing the tartaric acid concentration. To minimize passivation and two-phase solution regions, we chose a composition region of mixtures bounded by a triangle *ABC* with an $(NH_4)_2Cr_2O_7$: HBr : $C_4H_6O_6$ volume ratio of 2 : 98 : 0 at corner *A*, 10 : 10 : 80 at corner *B*, and 22 : 78 : 0 at corner *C*.

Composition dependences of the etch rate for InAs, InSb, GaAs, and GaSb crystals in $(NH_4)_2Cr_2O_7$–HBr–$C_4H_6O_6$ solutions were represented as plots of the etch rate against etchant composition using Scheffe's method of simplex lattices. The composition dependences thus obtained are presented in Fig. 1.

Note that, in the composition region under consideration, there is a well-defined trend of the variation in the etch rate of the semiconductors. The etch rate increases from a minimum value of 0.05 μm/min at point *B* to a maximum level on the *AC* side. It is also worth noting that the etch rates of the InAs and GaAs crystals vary in a similar way, as well as those of InSb and GaSb. The highest etch rates of the InAs and GaAs wafers were observed at point *C* (the highest $(NH_4)_2Cr_2O_7$ concentration): 7.5 and 5.6 μm/min, respectively. The observed decrease in etch rate to 0.9–1.1 μm/min with decreasing oxidant concentration indicates that $(NH_4)_2Cr_2O_7$ has a significant effect on the rate of the redox reaction and the release of the corresponding amount of Br_2.

In the case of InSb and GaSb, the etch rate varies in a somewhat different manner. The etch rate of the antimonides increases to 7.9–8.4 μm/min at an $(NH_4)_2Cr_2O_7$ concentration in solution of 17 vol % and decreases slightly at higher oxidant concentrations. This may be associated with the formation of a film on the surface of the crystals, which prevents structural layers of the material from being removed.

In the case of solution saturation with tartaric acid (corner *B*), the dissolution rate of all the crystals under consideration drops precipitously to 0.05–0.1 μm/min. It is therefore clear that $C_4H_6O_6$ indeed reduces the etch rate in the solutions under investigation.

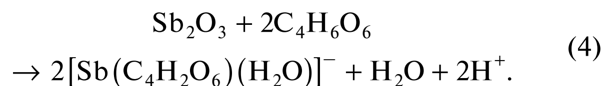
Thus, the dissolution rate of the InAs and GaAs semiconductors in $(NH_4)_2Cr_2O_7$ + HBr + $C_4H_6O_6$ etchant mixtures reaches a maximum level in the range from 5.6 to 7.5 μm/min at an $(NH_4)_2Cr_2O_7$ concentration in HBr of 22 vol % (corner *C*) and a minimum level at the highest $C_4H_6O_6$ concentration in solution (corner *B*) and at reduced $(NH_4)_2Cr_2O_7$ concentrations (side *AC*). The dissolution rate of the InSb and GaSb samples reaches a maximum level (7.9 to 8.4 μm/min) at 17 vol % $(NH_4)_2Cr_2O_7$ in HBr. The tendency for the etch rate of the antimonides to decrease is similar to the tendency for the arsenides. Given that all of the materials under consideration have similar etch rate contour plots, we believe that their dissolution follows similar mechanisms.

In the composition range under consideration, we observed two types of surface morphology. In the case of the InAs and GaAs crystals, all of the compositions studied ensured a polishing effect (region I). The polishing region of the arsenides contains 2–22 vol % $(NH_4)_2Cr_2O_7$, 10–98 vol % HBr, and 0–80 vol % $C_4H_6O_6$. The region of polishing solutions for the InSb and GaSb crystals contains 2–19 vol % $(NH_4)_2Cr_2O_7$, 10–98 vol % HBr, and 0–80 vol % tartaric acid.

At the maximum $(NH_4)_2Cr_2O_7$ concentration in HBr (corner *C*), a white film was formed on the surface of the InSb and GaSb crystals (region II). This region had a very rough morphology. After the film was removed by filter paper, the surface of the crystals was dull and lusterless. The presence of the white film was, most likely, due to the formation of the insoluble oxides Sb_2O_3 or Sb_2O_5. In this region, the removal rate of the reaction products formed is slower than the formation rate of insoluble compounds. The binding of

Fig. 1. Etch rate (μm/min) vs. etchant composition diagrams (T = 294–296 K, γ = 78 rpm) for the (a) InAs, (b) InSb, (c) GaAs, and (d) GaSb crystals in $(NH_4)_2Cr_2O_7$–HBr–$C_4H_6O_6$ solutions; the $(NH_4)_2Cr_2O_7$: HBr : $C_4H_6O_6$ volume ratio in corners A, B, and C is 2 : 98 : 0, 10 : 10 : 80, and 22 : 78 : 0, respectively; (I) polishing and (II) nonpolishing solutions.

Sb^{3+} ions into complexes with the use of tartaric acid reduces the release of antimony on the surface of the crystals:



$$Sb_2O_3 + 2C_4H_6O_6 \rightarrow 2[Sb(C_4H_2O_6)(H_2O)]^- + H_2O + 2H^+. \quad (4)$$

As to As_2O_3, it readily dissolves in water:

$$As_2O_3 + H_2O = As(OH)_3. \quad (5)$$

In acid solutions, the following reaction is also possible:

$$As(OH)_3 + H^+ = As(OH)_2^+ + H_2O. \quad (6)$$

These assumptions can be supported by the arrangement of polishing and nonpolishing regions of the solutions under investigation.

The region of nonpolishing solutions for the antimonides is bounded by the compositions 19–22 vol % $(NH_4)_2Cr_2O_7$, 69–81 vol % HBr, and 0–11 vol % $C_4H_6O_6$.

Since the dissolution process in these etchants has slow rates, a uniform layer is removed by etching. This is favorable for the formation of an essentially plane-parallel surface.

In the case of a diffusion-limited etching process, the dissolution of the material depends on the transfer

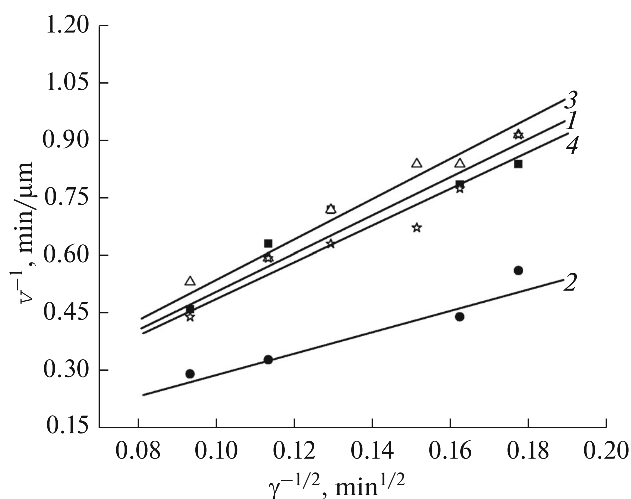


Fig. 2. Dissolution rate as a function of solution stirring rate ($T = 293$ K) for the (*1*) InAs, (*2*) InSb, (*3*) GaAs, and (*4*) GaSb wafers in an etchant mixture with the composition 9 vol % $(NH_4)_2Cr_2O_7$ + 71 vol % HBr + 20 vol % $C_4H_6O_6$.

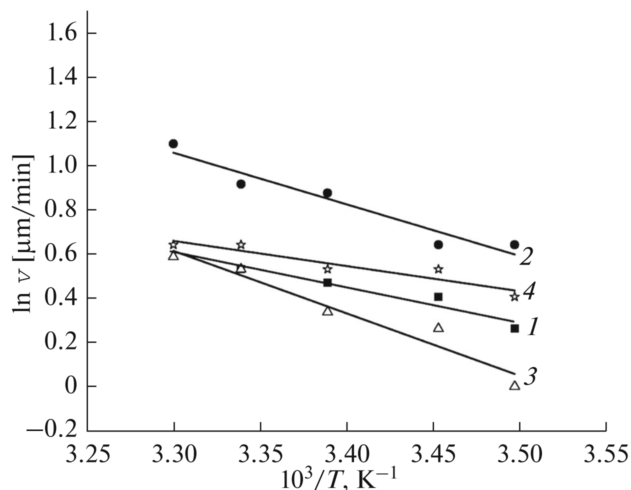


Fig. 3. Dissolution rate as a function of etchant mixture temperature ($\gamma = 78$ rpm) for the (*1*) InAs, (*2*) InSb, (*3*) GaAs, and (*4*) GaSb wafers in a solution with the composition 9 vol % $(NH_4)_2Cr_2O_7$ + 71 vol % HBr + 20 vol % $C_4H_6O_6$.

rate of reactive etchant components diffusing to the crystal surface or on the rate of removal of reaction products from the surface. DeSalvo et al. [12] reported some characteristics determining the diffusion-limited etching mechanism for the III–V semiconductors:

(1) the etch rate is proportional to the square root of the etching time;

(2) the etch rate increases with an increase in the stirring rate of the etching solution;

(3) the etch rate is relatively insensitive to changes in temperature;

(4) stirring increases the activation energy for the process, which usually does not exceed 35 kJ/mol; and

(5) etching is isotropic relative to the crystal orientation.

These characteristics are supported by the present results on the influence of solution temperature and stirring (disk rotation) rate on the etch rate in $(NH_4)_2Cr_2O_7$–HBr–$C_4H_6O_6$ mixtures. Figure 2 shows the crystal dissolution rate as a function of solution stirring rate in the range $\gamma = 32$–116 rpm. It is seen that increasing the delivery rate of a fresh etchant helps to increase the reaction rate. The observed reduction in reaction rate with decreasing solution stirring rate indicates that the reaction reduces the amount of the reactive component and leads to the formation of stable final and intermediate reaction products. The fact that lines *1*–*4* extrapolate to the origin suggests that the dissolution of the semiconductor wafers is a diffusion-limited process [10].

The apparent activation energy (E_a) of the process was determined graphically, from the slope of plots of ln v vs. $1/T$ (Fig. 3). Using the plots thus obtained, we evaluated tan φ. According to Stromberg and Semenchenko [13], the apparent activation energy as a function of tan φ can be represented as follows:

$$E_a = R\tan\varphi.$$

The calculated apparent activation energy was found to be no higher than 35 kJ/mol (Table 1), which is characteristic of diffusion-limited dissolution processes.

The observed difference in activation energy can be accounted for in terms of the effect of passivating processes, which reduce the etch rate with increasing temperature. It is also worth noting that raising the solution temperature helps to increase the dissolution rate of the surface layer of the crystals under consideration.

Thus, the present results demonstrate that the temperature dependence of the rate of reaction between the semiconductors under study and the etching solutions follows the Arrhenius law and that the observed apparent activation energy confirms the diffusion-limited nature of the heterogeneous processes in question.

Table 1. Apparent activation energy (E_a) and logarithm of the pre-exponential factor (ln C_E) for the dissolution of InAs, InSb, GaAs, and GaSb in a 9 vol % $(NH_4)_2Cr_2O_7$ + 71 vol % HBr + 20 vol % $C_4H_6O_6$ mixture

Semiconductor	E_a, kJ/mol	ln C_E
InAs	13.2	5.9
InSb	19.5	8.8
GaAs	23.5	10.0
GaSb	9.4	4.4

CONCLUSIONS

The present results on the nature of reactions of InAs, InSb, GaAs, and GaSb crystals with $(NH_4)_2Cr_2O_7$–HBr–$C_4H_6O_6$ solutions under reproducible hydrodynamic conditions have been used to plot the etch rate against etchant composition and find the composition boundaries of polishing solutions: 2–22 vol % $(NH_4)_2Cr_2O_7$, 10–98 vol % HBr, and 0–80 vol % $C_4H_6O_6$ for the InAs and GaAs crystals and 2–19 vol % $(NH_4)_2Cr_2O_7$, 10–98 vol % HBr, and 0–80 vol % $C_4H_6O_6$ for the InSb and GaSb semiconductors.

The dissolution rate of the crystals has been shown to be diffusion-limited. We have optimized the composition of low-rate polishing solutions and found conditions for the DCP process. The addition of tartaric acid to etchant mixtures helps to reduce the overall dissolution rate of the InAs, InSb, GaAs, and GaSb crystals to 0.05–0.1 μm/min.

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