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

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Abstract—We have studied the nature and kinetics of the chemical interaction of InAs, InSb, GaAs, and GaSb crystals with aqueous $(NH_4)_2Cr_2O_7$–HBr solutions. The dissolution rate of the crystals has been measured as a function of etchant composition, solution stirring rate, and temperature. The results demonstrate that the dissolution rate of the semiconductors is diffusion-limited. We have determined the composition ranges of polishing solutions, optimized their compositions, and found conditions for the dynamic chemical polishing of the semiconductors. Ultrasmooth polished semiconductor surfaces have been obtained, with $R_a \approx 1$ nm.

Keywords: chemical etching, gallium arsenide, indium arsenide, gallium antimonide, indium antimonide, dissolution rate, dynamic chemical polishing

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INTRODUCTION

III–V compounds occupy a leading place among known compound semiconductors because they are used in the fabrication of a variety of electronic and optoelectronic devices. InAs, InSb, GaAs, and GaSb crystals are promising materials for microwave devices, integrated circuits, IR light-emitting diodes, photodetectors, cascade solar cells, and thermophotoelectric generators [1–3].

One problem with III–V semiconductors is that processing their surfaces in device fabrication presents serious difficulties, because they readily oxidize and require surface passivation.

The lack of a universal, technologically viable process capable of meeting requirements of all manufacturers of semiconductor products stimulates the development of new techniques for the chemical treatment of such materials and control over the condition of substrates based on them. Chemical polishing is favorable for highly efficient cleaning of semiconductor surfaces and preparation of a nanoscale surface profile. To avoid technical problems in optimizing the composition of etchant mixtures, additional research into the mechanism and kinetics of chemical dissolution of semiconductors is needed [4].

Chemical treatment of III–V compound semiconductors, including InAs, InSb, GaAs, and GaSb, has yet to be studied in sufficient detail. Use is typically made of solutions based on elemental bromine, which offer good polishing performance and ensure high etch rates. Raising the Br_2 concentration in solutions increases the dissolution rate of crystals and improves the quality of their surface [5–7]. However, the toxicity and instability of bromine-containing solutions, associated with the high bromine volatility, prevent such etchants from being widely used.

Bromine-releasing etchants have attracted great interest, because they are safer and technologically attractive. In particular, as shown by Chu et al. [8], solutions based on HNO_3–HBr can be utilized for structural etching of InP. The chemical etching of InAs, InSb, GaAs, and GaSb crystals in aqueous H_2O_2–HBr solutions has been the subject of detailed studies [9, 10]. The dissolution rate of doped and undoped III–V semiconductors was determined as a function of the H_2O_2 concentration in etchant mixtures [9], and solutions containing 10–15 vol % H_2O_2 in HBr and ensuring dissolution rates of up to 20 μm/min were proposed as etchants for dynamic chemical polishing (DCP). Shelyuk et al. [10] investigated etchants with low H_2O_2 concentrations in HBr (2–20 vol %). The dissolution of the anion sublattice of the antimonides and arsenides was shown to have a significant effect on the nature of the chemical etching process. Raising the H_2O_2 concentration in etchant mixtures from 2 to 20 vol % increases the dissolution rate of GaAs and InAs in the range 1.2 to 11.8 μm/min. In the case of InSb and GaSb crystals, the etch rate increases from 1.5 to 12.7 μm/min in the range 2–10 vol % H_2O_2 in HBr, whereas further increase in oxidant concentration is accompanied by a sharp drop in the dissolution rate of crystals.

Previous work by Chukhnenko et al. [11] demonstrated considerable potential of $(NH_4)_2Cr_2O_7$-based bromine-releasing etchants. Such solutions offer high polishing performance in combination with slow, well-controlled etch rates.

Analyzing the literature, we have found no systematic research into the use of bromine-releasing etchants based on ammonium dichromate and hydrobromic acid for chemical treatment of III–V semiconductors. It is, therefore, reasonable to investigate in greater detail the chemical etching behavior of InAs, InSb, GaAs, and GaSb crystals in etchant mixtures based on aqueous $(NH_4)_2Cr_2O_7$–HBr solutions.

The objectives of this work were to study the characteristic features of the DCP of the surface of III–V compound semiconductor crystals with $(NH_4)_2Cr_2O_7$–HBr etchant solutions; determine the dissolution rate of these materials as a function of etchant solution composition, stirring rate, and temperature; find polishing solution compositions; and assess the surface quality after chemical etching with optimized polishing etchants.

EXPERIMENTAL

Our experiments comprised several steps: slicing of single-crystalline ingots into wafers, abrasive lapping, removal of the surface deformation layer by chemical–mechanical polishing (CMP), DCP of the crystals, and rinsing between the steps.

We used *n*-type InAs, InSb, GaAs, and GaSb samples. Wafers 5 × 5 × 2 mm in dimensions were cut from single-crystalline ingots by a diamond wire saw, which was lubricated with distilled water during the cutting process. The cutting of the crystals was accompanied by a strong mechanical effect on the surface. The surface deformation layer was up to 150 μm deep.

For subsequent investigation, the unprocessed side of the crystals was glued to quartz substrates with picein. The residual picein was removed by an organic solvent, in particular by acetone. The cutting-induced surface deformation layer was removed by mechanical grinding with aqueous suspensions of appropriate abrasive powders (ASM 10/7, ASM 5/3, and ASM 1/0), with the abrasive grain size gradually reduced from 10 to 1 μm. To remove the surface contamination produced on the wafer surface in the cutting and grinding steps, the wafers were rinsed in warm distilled water containing surfactants, rinsed with a large amount of distilled water, and then dried in flowing dry air.

Since the abrasive grinding process reduced the thickness of the surface deformation layer to 10–35 μm, DCP was preceded by CMP, which removed the disturbed surface layer and reduced the strain in the crystal. In CMP, we used a universal etchant proposed by us.

The final step in preparing high-quality polished surfaces was DCP, which ensured that geometric parameters remained intact and allowed smooth substrate surfaces to be prepared. The DCP process was run at $T = 293$ K and a disk rotation rate $\gamma = 78$ rpm for 5 min using a system for kinetic studies of the dissolution process by the rotating-disk method [4]. This technique allows one to control the hydrodynamic conditions of crystal–etchant interaction and ensures a stable delivery of a fresh etchant to crystals and the removal of interaction products.

The components of the etchant used were an aqueous 42% HBr (extrapure grade) solution and an aqueous 26% $(NH_4)_2Cr_2O_7$ (analytical grade) solution. The reactants were mixed in small portions in a certain order. The amounts of the components corresponded to their volume ratio in the etchant mixture. The solutions were held at room temperature for 120 min, to ensure completion of the reaction

$$\begin{aligned}(NH_4)_2Cr_2O_7 + 14HBr = 3Br_2\\ + 2CrBr_3 + 2NH_4Br + 7H_2O.\end{aligned} \tag{1}$$

To remove the residual etchant and etchant–crystal reaction products, the samples were rinsed between the processing steps according to the procedure proposed by us, for 1 min in each solution:

$$\begin{aligned}Na_2S_2O_3 \to H_2O(\text{dist}) \to 15\%\,NaOH\\ \to H_2O(\text{dist}) \to H_2O(\text{dist}).\end{aligned} \tag{2}$$

The dissolution rate of the crystals was evaluated from the decrease in wafer thickness using a TESA Digico 400 electronic indicator with an accuracy of ±0.02 μm.

The surface microstructure of the InAs, InSb, GaAs, and GaSb wafers was studied by optical microscopy. Surfaces were examined in white light on an MIM-7 metallurgical microscope fitted with an eTREK DCM800 digital video camera (8 Mpix) at magnifications from 25× to 1600×. The quality of polished surfaces was assessed by atomic force microscopy (AFM) using intermittent contact mode imaging on a NanoScope IIIa Dimension 3000TM scanning probe microscope (Digital Instruments, USA).

RESULTS AND DISCUSSION

One of the main factors governing the crystal dissolution process is the etchant composition. To study the effect of solution concentration on the dissolution rate, we examined the composition range 1–80 vol % $(NH_4)_2Cr_2O_7$ in HBr. This concentration range was studied because, beyond it, the quality of polished semiconductor wafer surfaces was markedly lower and the etch rate dropped to a minimum level. Our experiments were carried out at $T = 292$–294 K and $\gamma = 78$ rpm.

It is worth noting that the variation of the dissolution rate with the $(NH_4)_2Cr_2O_7$ concentration in the

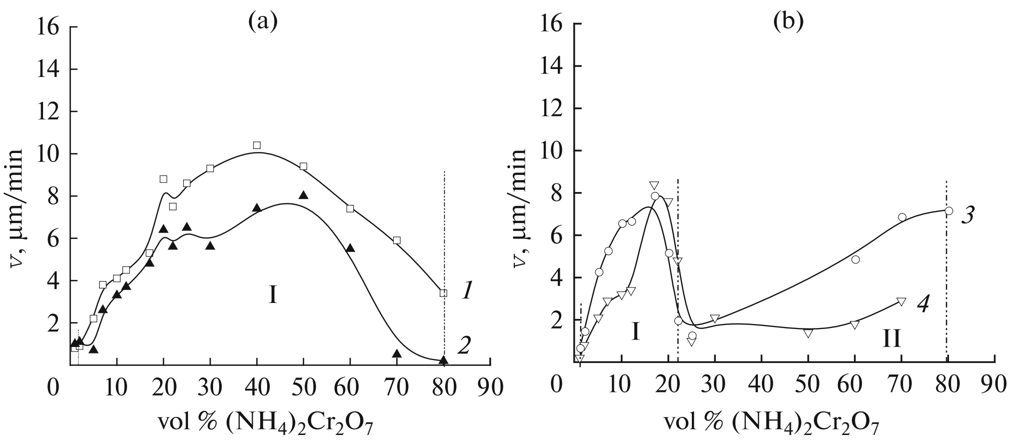

Fig. 1. Concentration dependences of the dissolution rate for (*1*) InAs, (*2*) GaAs, (*3*) InSb, and (*4*) GaSb crystals in $(NH_4)_2Cr_2O_7$–HBr solutions: (I) polishing and (II) nonpolishing regions (T = 292–294 K, γ = 78 rpm).

etchant mixtures for the arsenides differs from that for the antimonides (Fig. 1). In the case of the InAs and GaAs crystals, increasing the oxidant content from 1 to 50 vol % increases the etch rate from 0.8 to 10.4 μm/min. Further increasing the $(NH_4)_2Cr_2O_7$ concentration in HBr (from 50 to 80 vol %) leads to a reduction in the dissolution rate of the InAs and GaAs crystals. At oxidant concentrations in the etchant mixture from 2 to 80 vol %, the substrates have a polished surface, with characteristic metallic luster.

In contrast to the dissolution rate of the arsenides, that of InSb and GaSb rises from 0.2 to 8.4 μm/min as the $(NH_4)_2Cr_2O_7$ content of the etchant mixture increases from 1 to 17 vol %. At oxidant concentrations in HBr from 2 to 22 vol %, the antimonides also have mirror-smooth surfaces with metallic luster. Raising the $(NH_4)_2Cr_2O_7$ content of the solution from 17 to 22 vol % leads to a decrease in the etch rate of the crystals, and the surface quality degrades in the range 22–80 vol %, with the formation of a dense white layer on the crystals.

Using the present results, we identified the composition boundaries between regions of polishing (region I) and nonpolishing (region II) solutions: region I is located between 2 and 80 vol % $(NH_4)_2Cr_2O_7$ in HBr for InAs and GaAs and between 2 and 22 vol % for InSb and GaSb. It should be noted that the solutions with relatively low $(NH_4)_2Cr_2O_7$ concentrations (2–22 vol %) are the most attractive for the DCP of III–V semiconductor surfaces.

To optimize DCP process conditions, we examined the dissolution kinetics of the InAs, InSb, GaAs, and GaSb crystals in $(NH_4)_2Cr_2O_7$–HBr polishing etchants and examined the dependences of the dissolution rate (v) on the disk rotation rate (γ) in the form of plots of v^{-1} against $\gamma^{-1/2}$ in the range γ = 32–116 rpm and the dependences on the etchant temperature in the form of plots of ln v against $1/T$ in the range T = 286–306 K. Plotting the etch rate against solution stirring rate enables the nature of the crystal dissolution process to be identified (Fig. 2a). Since the straight lines thus obtained extrapolate to the origin, the rate of the dissolution process is diffusion-limited. This assumption is supported by the temperature dependences of the etch rate of the InAs, InSb, GaAs, and GaSb crystals in the same solution (Fig. 2b). The apparent activation energy E_a evaluated from these data does not exceed 35 kJ/mol (table). According to the present results and a commonly accepted classification of the rate-limiting steps in chemical etching processes [12], the dissolution rate of our samples in $(NH_4)_2Cr_2O_7$–HBr is indeed diffusion-limited.

Figure 3 illustrates the surface microstructure of the semiconductor wafers after each processing step (cutting, grinding, CMP, and DCP). Analysis of surface microstructures after chemical polishing in the $(NH_4)_2Cr_2O_7$–HBr solutions suggests that these mixtures are potentially attractive for the DCP of InAs, InSb, GaAs, and GaSb surfaces. Using AFM (Fig. 4), we examined the surface structure of our samples after DCP on a nanoscale. For example, the average arith-

Apparent activation energy (E_a) and logarithm of the preexponential factor (ln C_E) for the dissolution of InAs, InSb, GaAs, and GaSb in a 12 vol % $(NH_4)_2Cr_2O_7$ + 88 vol % HBr solution

Semiconductor	E_a, kJ/mol	ln C_E
InAs	12	1
InSb	14	2
GaAs	17	2
GaSb	9	1

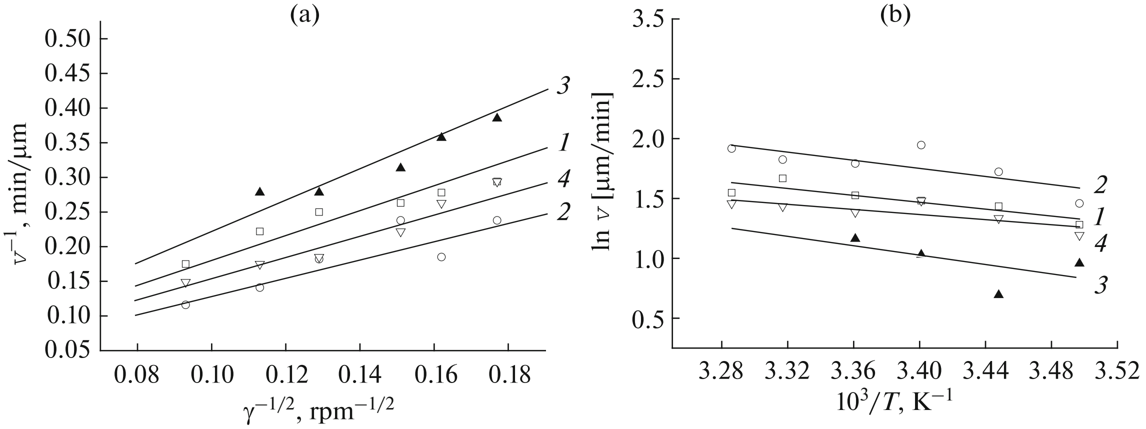

Fig. 2. Dissolution rate as a function of (a) disk rotation rate ($T = 294$ K) and (b) solution temperature ($\gamma = 78$ rpm) for (*1*) InAs, (*2*) InSb, (*3*) GaAs, and (*4*) GaSb crystals in a solution with the composition (vol %) $12(NH_4)_2Cr_2O_7 + 88HBr$.

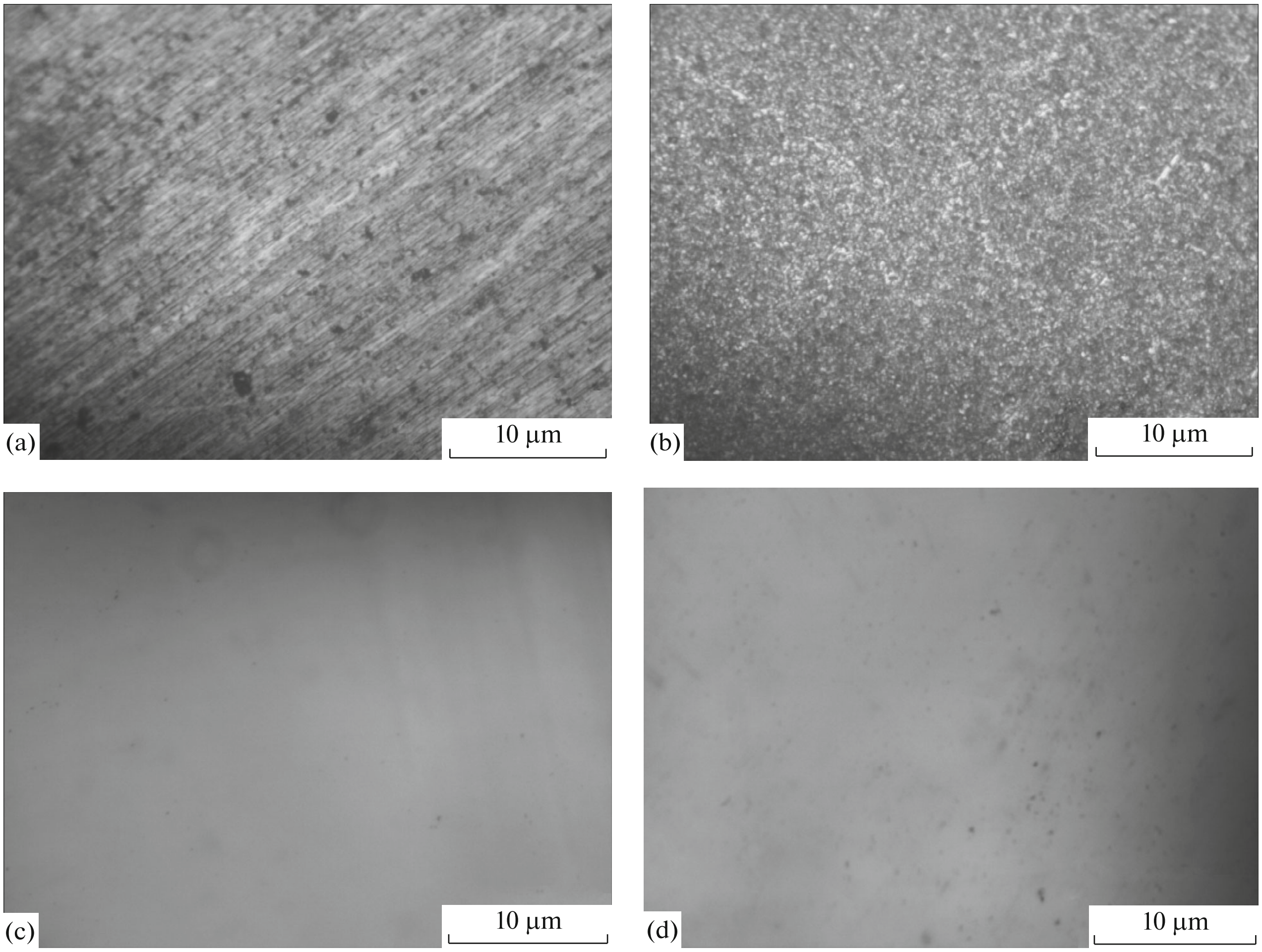

Fig. 3. Surface microstructures of InSb after (a) cutting, (b) abrasive grinding with ASM 5/3, (c) CMP, and (d) DCP in a solution with the composition (vol %) $7(NH_4)_2Cr_2O_7 + 93HBr$.

metic surface roughness of the InSb substrate after DCP is $R_a = 1.1$ nm. It is worth noting that, according to requirements for ultrasmooth polished semiconductor surfaces [13], R_a should be no greater than 10 nm.

It follows from the above that such etching solutions ensure controlled thinning of crystalline wafers to a predetermined thickness and high-quality surface finish.

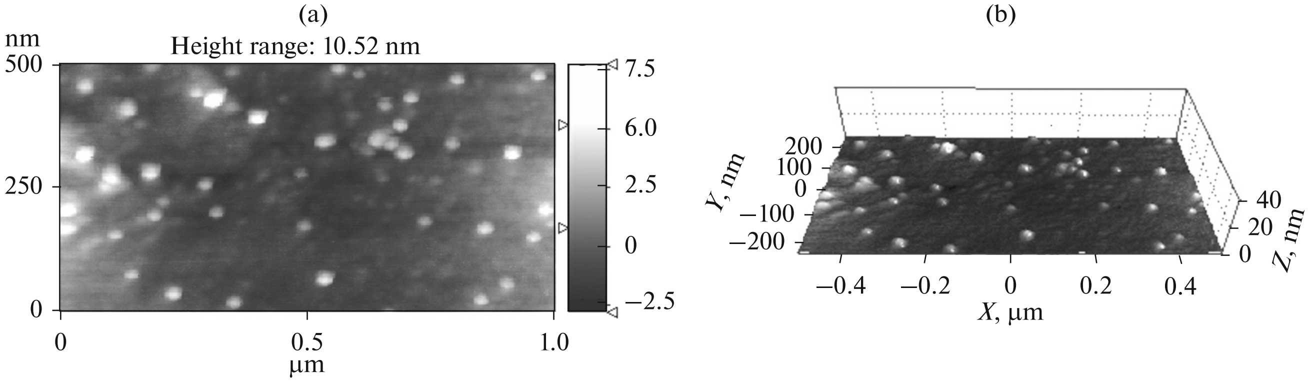

Fig. 4. AFM images of the surface of InSb crystals after DCP in a solution with the composition (vol %) 7$(NH_4)_2Cr_2O_7$ + 93HBr.

CONCLUSIONS

The present results on the chemical interaction of InAs, InSb, GaAs, and GaSb crystals with $(NH_4)_2Cr_2O_7$ + HBr etchant mixtures demonstrate that raising the $(NH_4)_2Cr_2O_7$ concentration in HBr from 1 to 50 vol % for InAs and GaAs and from 1 to 20 vol % for InSb and GaSb increases the etch rate, whereas further increase in oxidant concentration leads to a decrease in etch rate. The composition range of polishing solutions is 2–80 vol % $(NH_4)_2Cr_2O_7$ in HBr for InAs and GaAs and 2–22 vol % for InSb and GaSb.

The rate of chemical dissolution in the polishing solutions is diffusion-limited ($E_a \le 35$ kJ/mol). The proposed $(NH_4)_2Cr_2O_7$ + HBr etchant mixtures with a relatively low oxidant concentration (2–22 vol %) are the most attractive for the DCP of III–V semiconductors, because they produce ultrasmooth polished surfaces ($R_a \approx 1$ nm).

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