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Chemical-dynamic polishing of InAs, InSb, GaAs and GaSb crystals with $(NH_4)_2Cr_2O_7$–HBr-citric acid etching composition

I.V.Levchenko, V.M.Tomashyk, I.B.Stratiychuk, G.P.Malanych, A.S.Stanetska, A.A.Korchovyi

V.Ye.Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41 Nauki Ave., 03028 Kyiv, Ukraine

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The chemical dissolution of InAs, InSb, GaAs and GaSb crystals in $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$ etching solutions has been investigated. The dissolution rate of the semiconductor materials has been measured as a function of etchant composition, stirring rate and temperature. The limiting stages of dissolution process, regions of the polishing and unpolishing solutions have been established. The polishing etchant compositions and conditions for chemical-dynamic polishing of the InAs, InSb, GaAs and GaSb crystals have been proposed and optimized.
Keywords: gallium arsenide, indium arsenide, gallium antmonide, indium antimonide, chemical-dynamic polishing.

Исследован процесс химического растворения кристаллов InAs, InSb, GaAs и GaSb в травильных растворах $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$. Установлены зависимости скорости растворения полупроводниковых материалов от состава, скорости перемешивания и температуры травителя. Определена лимитирующая стадия процесса растворения, а также составы полирующих и неполирующих растворов. Предложены и оптимизированы составы полирующих травителей и условия химико-динамического полирования кристаллов InAs, InSb, GaAs и GaSb.

Хіміко-динамічне полірування кристалів InAs, InSb, GaAs та GaSb в травильних розчинах $(NH_4)_2Cr_2O_7$–HBr і цитратна кислота. *І.В.Левченко, В.М.Томашик, І.Б.Стратійчук, Г.П.Маланич, А.С.Станецька, А.А.Корчовий.*

Досліджено процес хімічного розчинення кристалів InAs, InSb, GaAs та GaSb в травильних розчинах $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$. Встановлені залежності швидкості розчинення напівпровідникових матеріалів від складу, швидкості перемішування та температури травника. Визначено лімітуючу стадію процесу розчинення. А також склади поліруючих та не поліруючих розчинів. Запропоновані та оптимізовані склади поліруючих травників та умови хіміко-динамічного полірування кристалів InAs, InSb, GaAs та GaSb.

1. Introduction

The technology of high-quality surface of semiconductor materials obtaining with perfect structure and homogeneous composition plays a main role in the semiconductor devices production. The chemical-dynamic polishing (CDP) is the one of the most effective and inexpensive liquid-phase methods of the perfect crystals surface preparation. The etching compositions with low etching rates are especially promising, because they provide the possibility to control the process and conditions of the semiconductor surface chemical modification.

The optical properties of the III–V semiconductors make them promising for appli-

cations in the optoelectronics, photonics and sensorics, particularly for making of infrared spectrum lasers, photodiodes, terahertz emitters, optical windows and solar cells.

The etching mixtures based on $Br_2{:}C_2H_4(OH)_2$ with a volume ratio of etchant components 1:100 provide the GaSb crystals mirror surface [1]. The authors [2] compared the influence of etching solutions based on HBr/Br_2 and $H_3PO_4/H_2O_2/C_6H_8O_7$ on InSb crystal surface and showed that the kinetics of dissolution in $H_3PO_4/H_2O_2/C_6H_8O_7$ mixtures is an equivalent to the kinetics of controlled and reproducible etching in HBr/Br_2 solutions. In [3] the using of $C_6H_8O_7{:}H_2O_2$ etching solutions promotes to selective etching and formation of smooth surface with the same etched profiles. The etching rate is about 12 ± 2 $nm \cdot s^{-1}$.

The bromine emerging etching compositions are more convenient for practical reasons. Such solutions are more stable in time, in comparison with bromine containing solutions because the concentration of the active component — bromine, which is formed at the interaction of initial mixture reagents, changes slowly. Also the bromides, which are formed by oxidation of the crystals surface layers, promote the transition of dissolution process into diffusion region. The introduction of the organic component helps to regulate the etching rate and improves the polishing properties of etchant.

The nature of the chemical interaction of the III–V semiconductor with etchant solutions HNO_3–HBr-organic component has been described in [4, 5]. The using of $C_3H_6O_3$ as complexing agent promotes the formation of the etch pits on the GaAs mirror-like surface. The introduction of the lactate acid into the etching composition promotes to formation of the "lemon peel" surface. In such conditions, the InAs and InSb crystals dissolution is limited by diffusion stage and in the case of GaSb and GaAs it is limited by the mixed kinetics. The H_2O_2–HBr-citric acid etching compositions are characterized by low etching rates (2–10 μm/min) of the GaAs, GaSb, InAs and InSb wafers [6]. The process of the InAs, InSb and GaSb crystals dissolution is limited by the diffusion stage, and in case of GaAs crystal it has mixed mechanism.

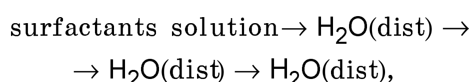
Analysis of literature data showed the prospect bromine-emerging etchants based on $(NH_4)_2Cr_2O_7$, as they are characterized by low etching rates and high polishing ability [7]. But we found no systematic researches of using such solutions for the chemical etching of InAs, InSb, GaAs, GaSb crystals and studying of processes that occur at the semiconductor/etchant interface.

The main aim of this work is to study the peculiarities of the InAs, InSb, GaAs and GaSb semiconductor wafers chemical-dynamic polishing with the $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$ etching solutions, to reveal the crystals etching rate dependencies of the etching solutions and to construct the "etchant composition—etching rate" diagrams, to define the compositions of polishing solutions and to study the kinetics of dissolution process and the effect of the citric acid introduction on the chemical etching parameters and also to optimize the chemical dynamic polishing conditions.

2. Experimental

The *n*-type InAs, InSb, GaAs and GaSb crystals have been researched in this paper. The single-crystalline ingots were cut using the string cutting. For the experimental investigations the wafers with 5×5×2 mm size were glued on the quartz substrates using chemically-resistant picein. The degreasing processes using organic solvent were carried out to remove residues of glued substance.

The mechanical grinding was the first preparatory step of the experimental research. The using of aqueous suspensions of abrasive powders (ASM 10/7, ASM 5/3 and ASM 1/0) in order of grain abrasive diameter decreasing from 10 to 1 μm ensures the removal of the damaged layer within 150 μm [8]. The removal of mechanical impurities (residues of suspensions, dust, etc.) was carried out according to the following scheme:



$$\text{surfactants solution} \rightarrow H_2O(\text{dist}) \rightarrow$$
$$\rightarrow H_2O(\text{dist}) \rightarrow H_2O(\text{dist}),$$

Purified plates were dried in a stream of dry air.

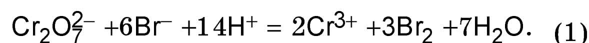
Mechanical grinding decreases the thickness of the semiconductor damaged layer but crystal surface is remained structurally imperfect after that operation. The chemical-mechanical polishing (CMP) process decreases the crystals deformation to the minimum value. The CMP operation was performed on a special etching polisher, using as a polishing solution developed in our laboratory universal bromine-emerging etchant.

CDP of the crystals decreases the surface deformation to minimum value and leads to nanosized relief obtaining. The etching compositions based on $(NH_4)_2Cr_2O_7$–HBr have good polishing properties and they are char-

acterized by low etching rates of (0.2·10.4 μm/min). In order to decrease the overall crystal etching rate and dissolution of the products which were formed after the interaction of etching mixtures with semiconductors, the organic acid was introduced into the etching solution. The citric acid is a good complexing agent that promotes to desorption of the products that were formed after the interaction of the substrates surface layers with etching solutions and a good viscosity modifier of the etching mixture.

The CDP of InAs, InSb, GaAs, GaSb substrates was performed using $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$ etching solutions. The etching mixtures were prepared using 26 mas.% $(NH_4)_2Cr_2O_7$ (reagent grade), 42 mas.% HBr (extrapure grade) and 20 mas.% $C_6H_8O_7$ (citric acid) (chemically pure) in a certain order and then they were left for 2 h to complete the reaction.

The reaction between oxidizing and reducing agents is occurred almost completely when the concentration of $(NH_4)_2Cr_2O_7$ in the etching mixture is about 30 vol.%. The elementary bromine is released as the result of the component interaction, and it forming so-called bromine emerging solutions:



$$Cr_2O_7^{2-} + 6Br^- + 14H^+ = 2Cr^{3+} + 3Br_2 + 7H_2O. \quad (1)$$

Depending on the $[(NH_4)_2Cr_2O_7]/[HBr]$ ratio in the etching mixture, the active components can be the Br^- and $Cr_2O_7^{2-}$ ions. The citric acid in the etchants composition dissolves the interaction products forming on the crystals surface, and to some extent regulates the process of free bromine formation that is produced as the result of the oxidant interaction with the reducing agent in the initial solution.

The research of CDP of InAs, InSb, GaAs and GaSb plates was performed in the reproducible hydrodynamic conditions at T = 292–294 K and disc speed rotation of γ = 78 rpm for 5–10 min. At the same time the dependences of crystals dissolution rate on the initial components concentration in the etchant composition, stirring speed and solution temperature were studied.

The kinetics of crystals surface layers dissolution process was studied on the device for the CDP using the method of disk rotating. This method allows to define the kinetic regularities of the semiconductors dissolution, including the limiting stage of the overall etching process and helps to exclude the influence of such side effects as passivation and catalysis on the nature of dissolution.

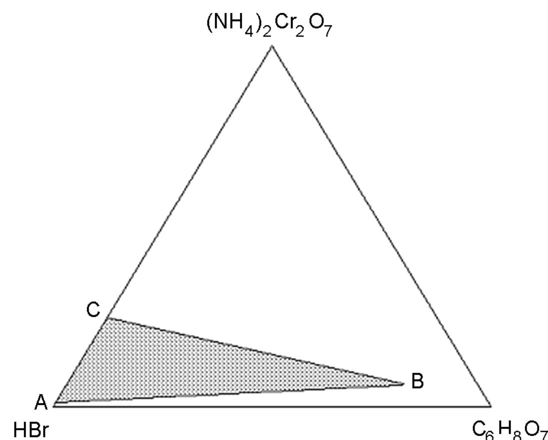


Fig. 1. The concentration interval with the ratio of initial components (in vol.%): (2–22)$(NH_4)_2Cr_2O_7$:(10–98)HBr:(0–80)$C_6H_8O_7$.

The rate of removing the damaged layer was defined using the electronic indicator TESA DIGICO 400 with an accuracy of 0.02 μm. The measurement of thickness was carried out before and after CDP at several points of 4 samples crystal surface simultaneously.

Geometric parameters of semiconductor polished surfaces were conducted on scanning probe microscope NanoScope III a Dimension 3000 TM (Digital Instruments, USA) using atomic force microscopy AFM in periodic contact mode (tapping mode) on air.

The surface morphology after etching was investigated in the white light by metallographic analysis using the MIM-7 microscope with eTREK DCM800 digital camera with an increase from 25× to 1600×.

Geometric parameters of polished surfaces were studied on scanning probe microscope NanoScope III a Dimension 3000 TM (Digital Instruments, USA) using atomic force microscopy (AFM) in periodic contact mode (tapping mode) on air.

In-process washing helps to clean the surface wafers from the remnants of etching solution and products that formed at the interaction of the etchant components with the crystals. During the researches it was found that using of $Na_2S_2O_3$ solution and distilled water is insufficient procedure for the complete crystal cleaning after etching process, because the white film is formed on the surface. That is why to the washing process we included the additional stage of washing in the 15 % NaOH solution which promotes to its dissolution. The operation was carried out during 1 min in the each solution immediately after chemical-dynamic polishing.

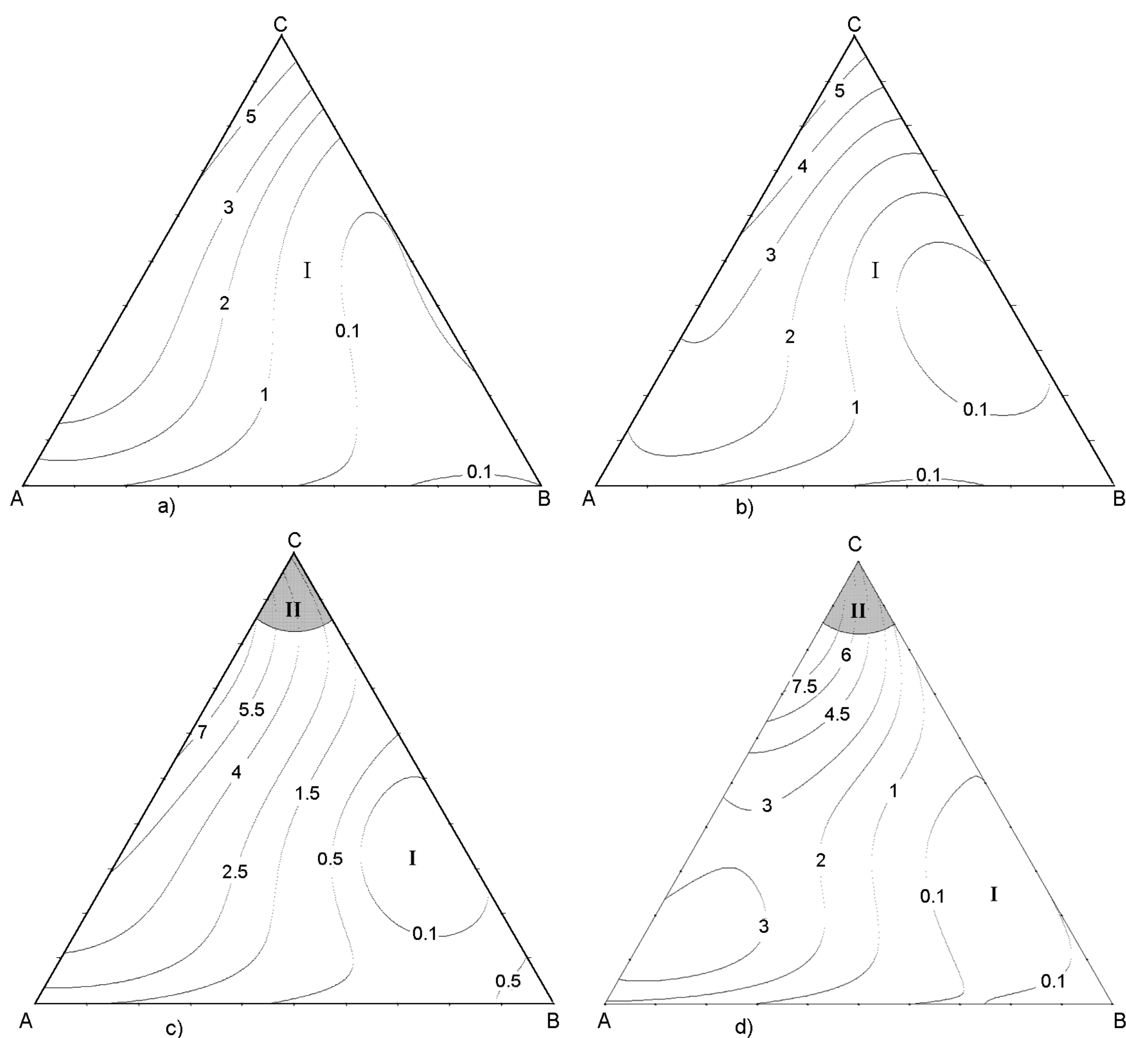


Fig. 2. The concentration dependences of etching rate (μm/min) of InAs — (*1*), GaAs — (*2*), InSb — (*3*), GaSb — (*4*) in the $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$ aqueous solitions I — polishing region, II — unpolishing region (T = 292–294 K, γ = 78 rpm).

3. Results and discussion

In studying of CDP process of InAs, InSb, GaAs and GaSb semiconductors in $(NH_4)_2Cr_2O_7$–HBr etching solution, the polishing solutions compositions were established in the interval (in vol.%): (2–22) $(NH_4)_2Cr_2O_7$ in 42 mas.% HBr with etching rates 0.9–8.4 μm/min. Therefore such interval was working for the selection of the organic component — citric acid. For experimental researches the concentration interval with the ratio of initial components concentrations (in vol. %): (2–22) $(NH_4)_2Cr_2O_7$:(10–98)HBr: (0–80) $C_6H_8O_7$ was chosen (Fig. 1).

The concentration interval of solutions was selected taking into account the necessity to avoid the passivation areas and two-phase solutions. The experimental researches range was determined using method of mathematical simulation of the experiment on the simplex [9].

Using the results of the experimental measurements, the concentration dependences of the InAs, InSb, GaAs, GaSb substrates dissolution rate were built, and limits of the polishing (region I) and unpolishing solutions (region II) were established (Fig. 2). The crystals dissolution rate reaches a maximum value near AC side of the triangle. The etching rate of InAs and GaAs substrates increases from 0.9 μm/min to 5.6 and 7.5 μm/min respectively in the concentration interval with (2–22) vol.% $(NH_4)_2Cr_2O_7$ in the etching mixture. InSb and GaSb crystals etching rate increases from 1.5 to 8.4 mμ/min at the increasing the oxidant concentration in the solution.

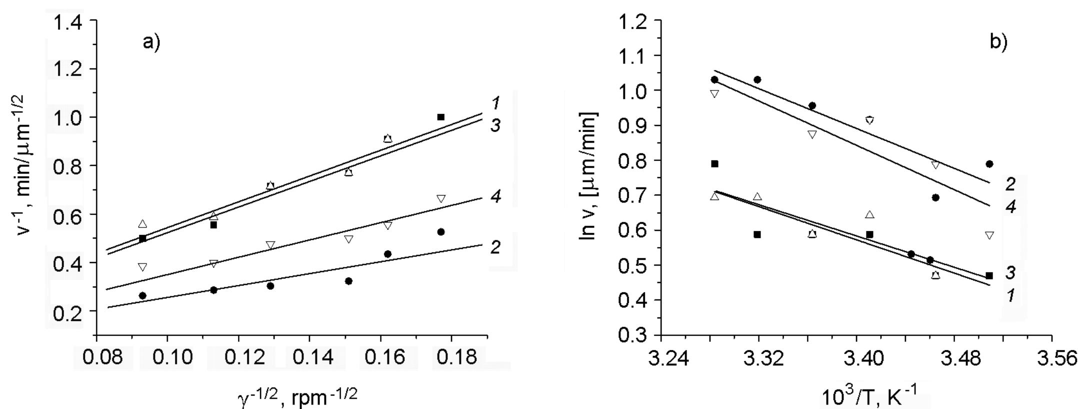


Fig. 3. The dependence of dissolution rate versus (a) solution stirring rate (T = 293 K) and (b) temperature (γ = 78 rpm) in the solution with composition (in vol.%): $9(NH_4)_2Cr_2O_7$–71HBr–$20C_6H_8O_7$ for InAs — (*1*), InSb — (*2*), GaAs — (*3*), GaSb — (*4*).

The saturation of etching solution by organic component has a different effect on the crystals etching character. So, for the InAs and GaAs crystal etching rate sharply decreases to 0.05–0.1 µm/min at the saturation by citric acid and for InSb and GaSb crystals etching rate decreases to 0.1–0.3 µm/min.

Summarizing the obtained experimental results, it is possible to argue that there are the analogy between antimonides and arsenides behavior. The GaAs and InAs crystals dissolution rates are increasing to maximum values of 5.6–7.5 µm/min in the *C* triangles vertex with 22 vol. % $(NH_4)_2Cr_2O_7$ in the etching solutions and minimum values of 0.05 µm/min in the *B* corner. For the InSb and GaSb crystals, maximum etching rate is displaced, in comparison with arsenides and is achieved in the point with 17 % vol. oxidant in the solution. The increasing of citric acid concentration in the etchant decreases the dissolution rate of InSb and GaSb substrate to a lesser extent, in comparison with InAs and GaAs crystals.

For InSb and GaSb crystals the polishing solutions (region I) are formed in the most part of the investigated concentration interval and unpolishing solutions (region II) take less than 10 % of the studied interval. At the concentration of about 22 vol. % $(NH_4)_2Cr_2O_7$ in HBr the white film is formed on the InSb and GaSb samples surface. In the case of GaAs and InAs crystals, all researched etching compositions are polishing. The polishing solutions regions of InAs, GaAs crystals is limited by the interval (in vol. %): (2–19)$(NH_4)_2Cr_2O_7$:(10–98)HBr:(0–80)$C_6H_8O_7$. The InSb and GaSb polishing solutions are limited by the interval (in vol. %): (2–22)$(NH_4)_2Cr_2O_7$:(10–98)HBr:(0–80)$C_6H_8O_7$. The regions of unpolishing solutions for the InSb and GaSb crystals are limited by compositions (in vol. %): (19–22)$(NH_4)_2Cr_2O_7$:(69–81)HBr:(0–11)$C_6H_8O_7$. Analyzing the Gibbs diagrams, it can be argued about the similarity of InAs and GaAs, InSb and GaSb crystals dissolution mechanisms.

The dependence of InAs, InSb, GaAs and GaSb crystals dissolution rate on the solution mixing speed was studied in the etching composition (in vol. %): $9(NH_4)_2Cr_2O_7$–71HBr–$20C_6H_8O7$. With the increasing of disk rotation speed from 32 to 116 rpm, the GaAs Vd InAs crystals etching rate is growing faster than in the case of d2InSb and GaSb crystals. From the resulting dependencies (1–4), constructed in the coordinates of υ^{-1}–$\gamma^{-1/2}$, it is possible to extrapolate into the coordinate's origin (Fig. 3a).

It indicates on the diffusion-limited nature of the investigated semiconductors dissolution in the appropriate solution.

The temperature dependence of the etching rate was investigated to confirm the obtained in the previous experiment data about the nature of the limiting processes of studied crystals dissolution in $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$ solution. The experiment was carried out at T = 285–305 K and speed of the disk rotation γ = 78 rpm. The obtained dependencies were constructed in the coordinates of $\ln\upsilon - 10^3/T$ and are presented at Fig. 3b. It should be noted that with temperature increasing the crystals dissolution rate is also increasing. Such dependency for InAs crystal almost coincides dependency for GaAs depending, and in the case of InSb and GaSb crystals they are the

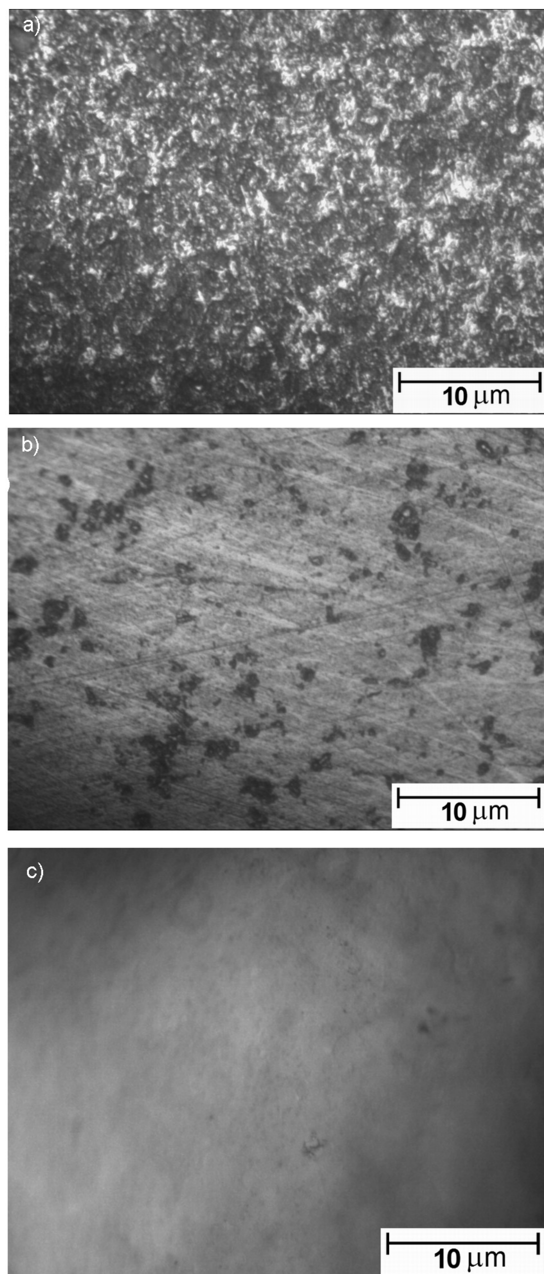


Fig. 4. The surface morphology of InAs after 1) — cutting, 2) — grinding, 3) CDP in the $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$ solution.

analogical character. From the temperature dependencies of the etching rate the values of apparent activation energy (E_a) were calculated for all crystals using the Arrhenius equation ($v = C_E e^{-}E_a/RT$) (Table).

The value of E_a is located within 9.3–13.2 kJ/mol and it is less than 35 kJ/mol, which is considered a typical for the diffusion limited dissolution process [10]. The obtained results confirm the previous conclusion about diffusion limitation of the InAs, InSb, GaAs and GaSb crystals dissolution in $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$ solutions.

Table. Apparent activation energy (E_a) and logarithm of the pre-exponential multiplier ($\ln C_E$) of InAs, InSb, GaAs and GaSb crystals dissolution in the solution (in vol. %): $9(NH_4)_2Cr_2O_7$–71HBr–$20C_6H_8O_7$.

Semiconductor	E_a, kJ/mol	$\ln C_E$
InAs	9.9	4.61
InSb	11.8	5.73
GaAs	9.3	4.38
GaSb	13.2	6.23

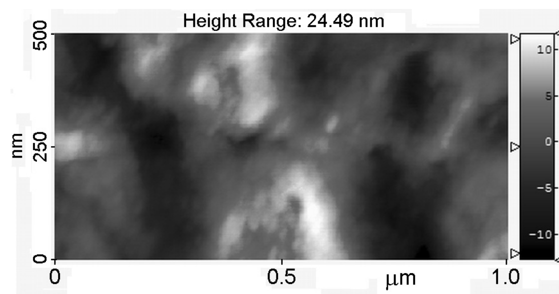


Fig. 5. The InAs surface structure after CDP in the $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$ solution.

The metallographic analysis of the semiconductor crystals surface after cutting, grinding and chemical-dynamic polishing are presented in Fig. 4.

The surface of all mention above crystals is smooth with a mirror shine after chemical treatment in such etchant. Fig. 5 shows the the semiconductor surface after CDP.

The value of the InAs roughness parameter is R_a = 3.6 nm. According to the data of [11], the semiconductor substrates have the super-smooth polished surfaces.

Summarizing the metallography results of the InAs, InSb, GaAs and GaSb crystals morphology, it possible to assert about the possibilities of using etching solutions $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$ for obtaining the quality polished surface of researched semiconductors using chemical-dynamic polishing. It is necessary to note also such advantages of bromine emerging etching solutions like low etching rate, controlled thinning of substrates and solutions adaptability.

4. Conclusions

In the reproducible hydrodynamic conditions the peculiarities of InAs, InSb, GaAs and GaSb crystal dissolution in $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$ etching solution were investigated. Using experimental data

of etching rate dependencies on the etchant composition the Gibbs diagrams were constructed and the boundaries of polishing solutions (region I) were allocated, which contain (in vol.%): (2–22) $(NH_4)_2Cr_2O_7$, (10–98) HBr and (0–80) citrate acid for InAs and GaAs crystals, and in the case InSb and GaSb crystals (in vol. %): (2–19) $(NH_4)_2Cr_2O_7$, (10–98) HBr and (0–80) $C_6H_8O_7$. The unpolishing solutions boundaries (region II) were allocated also. The kinetics of the dissolution process was investigated and it was determined that the etching has diffusion character. It was established that the addition of citric acid to the etching mixture decreases the crystals dissolution rate and enhances the polishing properties of the etching solutions. The conditions of InAs, InSb, GaAs and GaSb semiconductors chemical-dynamic polishing by etching solutions $(NH_4)_2Cr_2O_7$–HBr–$C_6H_8O_7$ for controlled removal of thin layers material which provides the obtaining high-quality polished surface were optimized.

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