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## Review

Review article

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## Modern scientific and practical approaches to the production of substrates from semiconductor compounds $A^3B^5$ . Review

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### Abstract

Modern electronic and optical engineering uses  $A^3B^5$  single-crystal semiconductor materials (GaAs, GaSb, InAs, InSb, and InP) as substrates for epitaxial growth. These materials are obtained in the form of massive single-crystal ingots. Therefore, technologies for processing of these  $A^3B^5$  wafers are developed to produce the substrates for epitaxial growth. The miniaturization of modern systems and devices demands the high quality of the substrates surface. One of the main criteria is a low surface roughness ( $R_q$ ) (of about 0.5 nm). To meet this requirement, it is necessary to elaborate the existing methods of surface treatment.

The review analyses the current approaches to the treatment of the surface of semiconductor wafers of  $A^3B^5$  single-crystal materials. It considers the specifics of wafers machining followed by their polishing. The article also presents an analysis of the polishing methods. It reveals that at the moment the chemical-mechanical polishing of  $A^3B^5$  wafers is the most commonly used method. The review presents the main parameters of this process and systematizes the existing theoretical approaches. The analysis determined the key tendencies in the development of chemical-mechanical polishing of semiconductor  $A^3B^5$  wafers aimed at increasing the quality of wafers. The article also analyses the latest studies regarding the methods of chemical polishing as an alternative to chemical-mechanical polishing. The next section focuses on surface passivation methods used upon obtaining wafers with a low roughness. Passivation is performed to reduce the reactivity of the surface and stabilize surface states of wafers.

A classification of passivation methods is suggested based on the obtained chemical composition of the surface, when the passivation layers are created using oxidation, sulfidizing, or nitriding. Another classification is based on the method of creating passivating coatings and includes wet chemical methods and physico-chemical methods.

**Keywords:** Semiconductor plates,  $A^3B^5$  materials, Machining, Polishing, Chemical mechanical polishing, Surface passivation

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## 1. Introduction

The variety of binary compounds  $A^3B^5$  includes antimonides, arsenides, nitrides, and phosphides of indium, gallium, aluminum, and boron. Many of them are of special interest for the development of electrical engineering, microwave electronics, optoelectronics, photonics, and the production of sensors. At the moment, some of the  $A^3B^5$  compounds are obtained during the production of semiconductors as single-crystal ingots, which are then divided into wafers for further production of semiconductor devices. Another way is to obtain such compounds in the form of films on substrates by means of epitaxial growth methods. Direct band gap materials with high electron mobility, including GaAs, GaSb, InAs, InSb, InP, and GaN, are most commonly used as substrate materials. Gallium nitride is grown by both epitaxial growth methods on substrates made of other materials and an expensive ammonothermal method from a Na-Ga-N melt [1]. There are also techniques for the industrial production of GaAs, GaSb, InAs, InSb, and InP single crystals, which are then divided into wafers. However, dividing single-crystal ingots into wafers results in a highly defective surface. Therefore, it is important to consider these materials due to two factors. First, they are of great interest for instrument manufacturers. Second, the industrial production of massive single-crystal ingots uses GaAs, GaSb, InAs, InSb, and InP semiconductor compounds, and the techniques for obtaining high quality wafers for the precision epitaxial growth are being developed for these materials only.

The rapid development of various fields of optics and electronics requires the miniaturization of semiconductor devices and structures. This, in turn, requires a higher quality of wafers used to produce such devices. At the moment, epi-ready wafers are in high demand [2], as they are the most technologically advanced. According to [3], epi-ready single-crystal semiconductor wafers can be used (primarily in the epitaxy processes) with no further treatment. However, there is no universal definition of the term epi-ready. Besides the specific electrophysical characteristics and low defectiveness, another important criterion for the quality of semiconductor wafers is the planarity of the surface with a maximum roughness ( $R_a$ ) of 0.5 nm.

At the moment, single-crystal  $A^3B^5$  wafers are produced following a technological scheme, which generally includes five main stages:

1. a single crystal is cut into wafers;
2. the wafers are beveled;
3. the wafers are machined and chemically purified;
4. the surface is polished and washed;
5. the surface is passivated.

The purpose of this review was to systematize and analyze the existing scientific approaches and practical recommendations on machining and polishing of semiconductor wafers obtained from single crystal ingots of GaAs, GaSb, InAs, InSb, and InP.

## 2. Machining of semiconductor wafers

After a single crystal is cut into wafers, they need to be flattened. If semiconductor single crystals are cut using dicing blades, a rough non-planar layer is formed in the near-surface region of the wafers. This is mainly caused by the large diamond points with an average size of 28–40  $\mu\text{m}$  used for dicing [4]. Therefore, further machining is required to reduce the roughness of the surface and ensure its planarization, which results in significant losses of the expensive material. Diamond wire sawing of single crystals helps to reduce the thickness of rough layers due to a smaller size of diamond grains (less than 20  $\mu\text{m}$ ) as well as due to a small degree of thermodynamic tension in the region of contact between the saw and the ingot [4, 5]. This helps to avoid material losses, but does not solve the problem of surface planarization. Therefore, today the main purpose of the machining process is to ensure high surface planarity and low roughness.

During the machining process, abrasive grains penetrate into the material and remove its fragments. As a result, the thickness of the wafer becomes more uniform, while the wafer itself becomes thinner. At the same time, a damaged area is formed [6], including a rough layer, a crack layer, and a defective layer, containing residual cracks and tensions. The thickness of this area is proportional to the size of abrasive grains [7, 8], their number, and the hardness of the abrasive (usually about three times larger than the abrasive grain).

There are two basic methods of machining of semiconductor wafers: grinding and lapping [9, 10].

There are generally three material removal mechanisms:

- chipping the material microparticles with abrasive embedded into the plate;
- cutting of the material with an abrasive;
- chipping the material after the free (loose) abrasive are indented into the material and cracks and tensions are formed.

Lapping presents a combination of all three methods. The most preferable method of material removal is to chip the material at the intersections of cracks formed as a result of indentation of loose abrasive particles. This helps to remove the material evenly. Grinding involves the first two mechanisms with machining being the main part of the process. Grinding can also be performed by means of quasi-elastic material removal [12, 13], when the required tension is obtained in the surface layer [10, 12, 14]. This seems to be a promising approach to the processing of  $A^3B^5$ . However, grinding is rarely used by the manufacturers of  $A^3B^5$  semiconductors and therefore is beyond the scope of this review.

### 2.1. Lapping of semiconductor wafers

The purpose of lapping is to ensure that the roughness  $R_a$  of  $A^3B^5$  wafers is about 0.63–1.0  $\mu\text{m}$  and their total thickness variation ( $TTV$ ) is 4–6  $\mu\text{m}$ .

Double-sided lapping is usually characterized by a smaller total thickness variation of wafers than single-sided lapping due to a more homogeneous treatment of wafers. The lapping pressure induces the indentation of abrasive grains into the surface layers of the wafer at a depth of 5–10% of their size and cutting/chipping off fragments of those layers [15]. There should be a gap between the surface of the wafer and the surface of the abrasive so that the lapping suspension could distribute evenly. For this, an inert solvent with a required viscosity is used (water or organic solvents including oils).

Abrasive grains can be of various shapes: round, flattened, cylindrical, and polygonal amorphous. The shape of the grains affects the above described material removal mechanisms. Grains of various sizes (from 3 to 63  $\mu\text{m}$ ) can

be used for lapping. The most common are grains with a size of 5–20  $\mu\text{m}$  [16]. There are also various national standards used to classify abrasive powders: GOST 52381-2005 (Russia), FEPA (Europe, USA), ANSI – CAMI (USA), and JIS (Japan).

Coarse-grained powders (with grains of a large size) are usually used to remove larger asperities and make the thickness of the wafer more uniform. Then, fine powders with grains of a smaller size are used. We should note that wire cutting allows obtaining a high enough quality of wafers to perform one-stage lapping.

To ensure the effective planarization of a rough wafer, the abrasive used should be harder than the wafer material. Both hard and softer abrasive powders are studied as possible abrasives for the lapping of fragile  $A^3B^5$  materials. Thus, in [17] (100) oriented InSb wafers were flattened using a diamond suspension with a particle size of 1  $\mu\text{m}$ . In [18], an  $\text{Al}_2\text{O}_3$  abrasive with a particle size of 5  $\mu\text{m}$  was used for the lapping of GaAs. In [2], the lapping of GaAs and InSb was performed using aluminum oxide powders with grain sizes of 10–14  $\mu\text{m}$  and 5–7  $\mu\text{m}$  respectively. These lapping conditions allowed obtaining a flat surface without curling [17], while the strength of GaAs and InSb wafers slightly increased after cutting [2]. There are also a number of commercially available abrasive powders and suspensions containing, for instance,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{ZrO}_2$ . However, it is not clear, if the composition of such powders presents a mixture of the said compounds, or there is an equal amount of all the three substances in each particle of the powder [19].

Another factor affecting the lapping process is the material of the lapping plate. Prior to the lapping of semiconductor wafers, it is necessary to flatten the lapping plates. As a result, the planarity of the lapping plates should be equal to the mean size of abrasive grains. The most common are lapping plates made of pig iron and glass of various makes, which are harder than the abrasives. Therefore, abrasive grains do not penetrate into the lapping plates. This allows them to roll about the surface of a semiconductor wafer, which destroys the abrasive grains.

Besides selecting the size of abrasive grains and the lapping plates, optimization of the lapping conditions involves determining the

lapping pressure, the concentration of the abrasive particles in the lapping suspension, the suspension supply rate, and the velocity of the grinding disk. Optimization of these parameters can result in  $R_a$  of about  $0.63 \div 1 \mu\text{m}$  and  $TTV$  of about  $2 \div 4 \mu\text{m}$ .

### 3. Polishing of semiconductor wafers

Semiconductor wafer polishing follows the machining stage. The main task is to remove the damaged layer and smooth out the surface while retaining the shape obtained during lapping. Polished wafers should have no mechanical defects (cracks, scratches) and residual abrasive particles on the surface [12].

There are the following main methods of polishing:

- mechanical polishing;
- chemical polishing (chemical-dynamic polishing, electrochemical polishing, dry etching);
- chemical-mechanical polishing (CMP) with or without an abrasive.

Since GaAs, GaSb, InAs, InSb, and InP are highly fragile and soft, mechanical polishing does not meet the requirements for the epitaxy quality of the surface [20].

#### 3.1. Chemical-mechanical polishing

##### 3.1.1. CMP parameters

Chemical-mechanical polishing is most commonly used for the industrial treatment of  $A^3B^5$  semiconductor materials. This type of polishing is based on a combined effect of the chemical and mechanical treatment of materials. The process is performed on a rotary polishing pad with or without an abrasive. There are also other configurations of polishing pads. Thus, [21] studies the functioning of a roll-type linear chemical mechanical polishing system.

Various CMP techniques have been developed for particular  $A^3B^5$  materials. In [22], the polishing of InP wafers involves the interaction with an oxidizing agent, NaClO. The formed oxide layer is mechanically removed by the polishing pad without an abrasive. The GaAs CMP method presented in [23] involves formation of oxide layers on the wafer surface when interacting with  $H_2O_2$  or NaClO. The oxides then interact with alkali producing hydroxides, which are mechanically removed by an abrasive.

On the whole, chemical mechanical polishing involves changing the chemical form of the processed material, primarily to oxides or hydroxides, followed by the mechanical removal of these compounds. The specific features of these processes depend on the conditions of CMP. Optimal polishing conditions are determined for every particular system.

Generally, the key parameters of the CMP process determining the quality of the surface are the following:

1. Parameters of mechanical treatment:
    - 1.1. the material and hardness of the polishing pad, the position of grooves, the geometry of grooves, and the surface morphology of the polishing pad;
    - 1.2. the polishing pressure (load, down force) applied to the wafer;
    - 1.3. the size and concentration of abrasive particles;
    - 1.4. the temperature;
    - 1.5. the relative velocity between the wafer to the polishing pad;
    - 1.6. the viscosity of the polishing slurry.
  2. Parameters of chemical treatment:
    - 2.1. the substances constituting the polishing slurry and their concentrations: an oxidizer, a complexant, a passivating agent, an abrasive, a dispersant ensuring stable distribution of the abrasive particles in the solution, and a solvent; stability of the components during storage, pH of the slurry;
    - 2.2. the slurry supply rate.
  3. Parameters of the polished material:
    - 3.1. the total thickness variation and geometric parameters of the wafer after lapping;
    - 3.2. the type, chemical composition, and specific features of the treated material, the crystallographic orientation of the wafer.
- The parameters listed above are interconnected and can affect each other. Therefore, it is reasonable to analyze the connections between them.
- a) The optimization of CMP modes usually starts with determining the required **polishing pressure on the wafer and the relative velocity between the wafer and the polishing pad**. They contribute greatly to the rate of material removal from the surface of the wafer. Publication [24] demonstrated that when polishing GaAs 4”

wafers at a pressure lower than 90 H, the material removal rate is not uniform. At a polishing pressure over 90 H, the material removal rate becomes even and the roughness of the surface decreases.

Publication [25] shows that when polishing InSb wafers using a slurry based on a colloidal solution of silicon dioxide (0.2 vol. % of SiO<sub>2</sub> colloidal solution with a particle size of 50 nm, the content of silicon dioxide in the initial colloidal solution – 31 wt.%), hydrogen peroxide, and citric or lactic acid at pH = 4 and the velocity of the polishing pad 60 r/min, the optimal polishing pressure is 80 g/cm<sup>2</sup>. This is accounted for by the optimal thickness of the polishing slurry between the wafer and the polishing pad as well as the correspondence between the chemical reaction rate and the material removal rate. When the pressure is reduced to 40 g/cm<sup>2</sup>, the surface becomes rougher. The authors believe that this can be caused by a thicker layer of the polishing slurry between wafer and polishing pad, which results in the inhomogeneity of the chemical processes on the wafer surface. When the pressure is over 100 g/cm<sup>2</sup>, the material is mainly removed mechanically, which also results in the deterioration of the wafer properties[25].

The wetting mode and thickness of the slurry between the wafer and the polishing pad are determined by the polishing pressure and its ratio with the relative velocity between wafer and pad and the viscosity of the polishing slurry ( $\eta \cdot V/P$ ).

b) **Viscosity** of the polishing slurry also affects the mass transfer of the reaction products removed from the surface and the movement of the abrasive particles. When the viscosity is too high, it hinders the movement of the abrasive particles in the polishing slurry and the removal of the CMP products from the surface of the wafer. Local accumulations of CMP products are also possible, which prevents the even flow of the polishing slurry.

When the viscosity is too low, the wafer is in direct contact with the polishing pad, which increases mechanical pressure on the material. This can result in uneven material removal and increased roughness.

The viscosity is determined by the chemical composition of the polishing slurry, its pH;

type, particle size, and the concentration of the abrasive [26]; as well as by the mechanical parameters of the CMP process. Publication [27] studies the dependence between the viscosity of the polishing slurry with colloidal particles of silicon dioxide and the shear rate calculated as a velocity of the wafer to the polishing pad (m/s) and the distance between them (m). The study demonstrates that a significant growth in the shear rate results in higher viscosity of a polishing slurry based on a colloidal solution of silicon dioxide, and the fact that polishing slurries can show non-Newtonian behavior. Additionally, the authors [27] note that at increased velocity between the wafer and the polishing pad, the slurry movement becomes turbulent.

c) Silicon dioxide is the most common commercial abrasive used for the CMP of A<sup>3</sup>B<sup>5</sup>. It is used in the form of colloidal solutions. To prevent the coagulation and sedimentation of particles, stabilization additives are used. However, the manufacturers keep the composition of such additives a secret. The function of the abrasive is to remove mechanically the material as well as to absorb the products of polishing and to take them away from the wafer surface. The existing studies [21, 28] provide different experimental results regarding the effect of the **size and concentration of abrasive particles** in the polishing slurry on the characteristics of CMP, including the material removal rate. The main requirements for abrasives are the following: they should be as hard as the polished material (or softer), inert to the components of the polishing slurry, and have a small particle size (tens and hundreds of nm, most commonly 10÷100 nm [29]). Publication [30] demonstrates that SiO<sub>2</sub> has a low reactivity with regard to GaAs. It also shows that CeO<sub>2</sub> abrasive particles tend to chemically interact with GaAs. It is still important to further investigate the effect of dispersants on the properties of abrasives [31–33].

Some researchers do not use abrasive particles when polishing A<sup>3</sup>B<sup>5</sup> materials [22, 34, 35]. This makes the polishing process different, because the oxidized forms of the material are removed by the polishing pad only.

d) Polyurethane **polishing pads** of various hardness are used for the CMP of semiconductor

materials both with and without abrasives. Article [36] shows that softer polishing pads ensure a smaller number of defects on A<sup>3</sup>B<sup>5</sup> wafers.

The surface morphology of the polishing pad should facilitate the removal of most asperities from the surface of the wafer. When modelling the CMP process in [37, 38] the authors tried to take into account the impact of polishing pad area being in contact with a wafer on the material removal rate. For this, the Greenwood-Williamson model was used (1):

$$A_T = (f_s / C) \cdot (R_p / \sigma_p)^{1/2} \cdot (P \cdot A_w / E_{pw}), \quad (1)$$

where  $A$  is the contact area between the polishing pad and the wafer,  $R_p$  is the curvature radius of the pad asperities,  $\sigma_p$  is the standard deviation of asperity heights of the polishing pad,  $P$  is the polishing pressure,  $A_w$  is the nominal surface area of the wafer,  $E_{pw}$  is the average Young's modulus of the wafer and the polishing pad (the elastic modulus of the polishing pad is usually three times smaller than that of the material [22]),  $f_s$  is the density of asperities of the polishing pad divided by grooves, and  $C$  is a constant equal  $0.3 \div 0.4$ .

This model was used to develop a methodology for assessing the polishing rate [52]. The contact area between the polishing pad and the wafer is not constant because of the glazing and mechanical wear of the polishing pad [37, 38]. To reduce the glazing effect, the surface of the polishing pad can be conditioned, for instance, with diamond tips [39, 40, 41, 42]. Therefore, the number of abrasive particles in the polishing pad may vary [43]. Additionally, larger number of pad asperities results in a higher chance of pad glazing [44].

e) The number of abrasive particles supplied to the polishing pad per unit of time depends on the **polishing slurry supply rate**. If the slurry supply rate is too fast, the abrasive particles can cover the whole surface of the polished wafer. This can reduce the rate of chemical reactions of the CMP due to preventing reagents access to the reaction region [21, 45].

If the slurry supply rate is too slow, the slurry can distribute unevenly over the polishing pad, which will result in inhomogeneous chemical interactions on the surface of the wafer and increased roughness.

Therefore, the slurry supply rate can affect the kinetics of the chemical interactions, the wetting of the surface, and the heat removal and reducing/maintaining the temperature in the reaction area.

f) **Temperature** is another important parameter of the CMP process. Publication [46] suggests using an IR sensor to control the temperature. Temperature affects the kinetics of the chemical processes, the viscosity of the polishing slurry (at higher temperatures the viscosity decreases), the zeta potential of abrasive particles, their hydrodynamic radius, the mechanism of material removal, and the pH of the polishing slurry. At higher temperatures, more oxygen from the air can dissolve in the polishing slurry, which can lead to the undesirable and uncontrollable oxidation of the polished material.

Taking into account the high reactivity of polished materials and chemical agents, the CMP of A<sup>3</sup>B<sup>5</sup> is performed at room temperature.

g) The chemical interaction between the polished material and the polishing slurry is the first stage of the CMP process. Generally, A<sup>3</sup> and B<sup>5</sup>, elements are oxidized, with the oxidized forms of each element having different compositions depending on the pH of the environment [47]. H<sub>2</sub>O<sub>2</sub> or NaClO are most commonly used as oxidizers. Along with an oxidizer, an abrasive, and an abrasive dispersant, polishing slurries can include a number of substances functioning as complexants, passivating agents, and solvents, as well as buffer solutions. The **composition of the slurry** determines its pH, the possible reactions, and the composition of the oxidized forms and complex compounds, which have various degrees of solubility and are more or less easily mechanically removed from the surface.

Various polishing slurries are used with particular materials (the examples of their compositions are given in Table 1, section 3.1.3). The existing literature on the problem does not provide any information about the exact composition of buffer solutions [48].

Article [49] demonstrates that the rate of chemical reactions between the polishing slurry and the polished material depends on the ratio of the slurry components and their concentrations.

h) Some studies focus on the effect of the polishing slurry pH on the rate of CMP for various A<sup>3</sup>B<sup>5</sup> materials. For instance, article [28] demonstrates that a strongly acidic or a highly alkaline environment increases the rate of GaAs removal, while a neutral pH leads to a lower material removal rate. The lowest roughness of GaAs was observed at pH = 10. Patent [25] demonstrates that polishing of InSb wafers in a solution with an alkaline pH results in the formation of scratches on the surface. When the pH decreases from 7 to 2, the roughness of the surface gradually increases together with an increase in the material removal rate. The patent suggests a method of polishing InP and InSb wafers at pH = 4÷6 with a polishing slurry containing a colloidal solution of silicon dioxide particles, hydrogen peroxide, and citric acid [25].

Therefore, polishing slurries of various chemical compositions are used for the CMP of specific A<sup>3</sup>B<sup>5</sup> materials.

i) The chemical composition of the polishing slurry, in turn, is chosen to the **characteristics of the polished material**, including its chemical composition and the crystallographic orientation of wafers. Elements of A<sup>3</sup>B<sup>5</sup> semiconductor compounds have different oxidation rates. The formed oxides, in turn, have different solubilities. Thus, gallium (Ga<sub>2</sub>O<sub>3</sub> [35]) and indium (In<sub>2</sub>O<sub>3</sub>) oxides are difficult to dissolve in neutral environments. Their hydroxides also have a low solubility at pH = 5÷9, for instance:  $\log C_{\text{Ga(OH)}_3} = -7.5$  at pH = 7.5;  $\log C_{\text{In(OH)}_3} = -9$  at pH = 7.0 [50]. Conversely, As and Sb oxides are easily dissolved in neutral environments [47].

As a result, atoms of different elements are removed at different rates during the polishing process, and the roughness increases [51]. Therefore, it is important to take into account the crystallographic orientation of the polished wafer. For instance, the surface of [111] oriented wafers can be comprised of atoms of the same type. Surfaces of [100] and [110] oriented wafers include atoms of III and V groups.

Therefore, multiple CMP parameters demonstrate complex interconnections, which makes the optimization of the polishing process a multifactor nonlinear problem. To solve this problem, various models of the process are

developed taking into account the key factors of CMP.

### 3.1.2. Models of the CMP process

Despite the fact that CMP is widely used, its basic mechanisms are still a matter of numerous discussions [54]. Models describing CMP are usually aimed at determining the dependence between the material removal rate and the polishing pressure or the relative velocity between the wafer and the polishing pad (the Preston model), expression 2:

$$MRR = K \cdot P \cdot V, \quad (2)$$

where *MRR* is the material removal rate, *K* is the Preston's coefficient, *P* is the polishing pressure, *V* is the relative velocity of the wafer and the polishing pad, which can be simply calculated as the distance between the centers of the wafer and the polishing pad multiplied by the relative velocity r/min [55].

However, the Preston's equation does not take into account experimentally observed nonlinear changes in the material removal rate at a higher pressure and relative velocity. To solve this problem, correction indices are used (*a*, *b*, expression (3)) to assess the actual effect of these parameters [55]:

$$MRR = K \cdot P^a \cdot V^b. \quad (3)$$

Authors [56] suggest a polynomial model of chemical mechanical planarization based on a transformed Preston's equation taking into account the dependence between the planarization rate and time.

These approaches help to take into account other CMP factors affecting the material removal rate. However, they do not detail these factors and the way they affect the process.

Publication [53] suggests a model for assessing the material removal rate by abrasive particles taking into account their number and geometry; the down pressure, relative velocity between the polishing pad and the wafer asperities; the overall pressure and the relative velocity of the wafer to the pad. However, the model does not take into account the chemical aspect of the CMP process.

Article [57] considers a model for erosion during CMP and focuses on the chemical part

of the process. According to the erosion model presented in [58], the surface of the wafer is polished due to erosion whose rate is calculated as follows:

$$v_n = f(\sigma_t(t), \sigma_n(t)), \quad (4)$$

where  $v_n$  is the erosion rate along the normal to the surface of the wafer,  $f$  is the empirical ratio of chemical and mechanical erosion, which depends on the mean down pressure on the wafer and the values of  $\sigma_n$ ,  $\sigma_t$  – normal and shear stresses at a particular point on the wafer's surface.

The material removal rate is then described by expression (5):

$$V_n = K(P) \cdot (\sigma_t + D \cdot \sigma_t^2), \quad (5)$$

where  $V_n$  is the material removal rate,  $K$  and  $D$  are constants determined by the properties of the material and the chemical processes.

Thus, the study presents an effort to take into account the chemical processes taking place during polishing. It also suggests that chemical reactions and diffusion rate impact the down pressure [57].

Article [59] presents a new theoretical approach to the description of the CMP process based on the material removal rate and taking into account both mechanical and chemical aspects (expression (6)):

$$MMR_{\text{thickness}} = C3(1 - \Phi[3 - C2 \cdot P_0^{1/3}]) \sqrt{P_0} \cdot V, \quad (6)$$

where  $C2$  is a parameter determined by the mean particle size of the abrasive, the particle size distribution, the hardness of the wafer and the polishing pad, the asperities of the polishing pad, and the Young's modulus of the polishing pad;  $C3$  is a parameter determined by the degree of dilution of the polishing slurry with water, the density and mass concentration of the slurry before dilution, the mean particle size of the abrasive, the particle size distribution, the density of the abrasive, the density of the asperities of the polishing pad, its roughness and the Young's modulus;  $\Phi$  is determined as  $(x_{\max} - x_{\text{avr}})/\sigma$  – the ratio of the difference between the maximum and mean values to the standard deviation,  $P_0$  is the down pressure;  $V$  is the relative velocity of the wafer to the polishing pad.

Publication [60] proposes another model for calculating the polishing rate (expression (7)):

$$MRR(x, y) = K \cdot P_{\text{avg}}^a(x, y) \cdot V_{\text{avg}}^a(x, y) \cdot \{\Omega(x, y)\}, \quad (7)$$

where  $MMR(x, y)$  is the material removal rate at a particular point of the wafer,  $P_{\text{avg}}$ ,  $V_{\text{avg}}$  are the mean pressure and relative velocity of the wafer to the pad, the exponent  $a$  is a constant determined as the contribution of the pressure and the relative velocity between the wafer and the pad, and  $\Omega$  is a spatial parameter showing the impact of pressure distribution along the wafer, the relative velocity, and the chemical processes.

Authors [42] consider various dependencies between the material removal rate and the down pressure for various interaction mechanisms between the polishing pad, the abrasive, and the polished surface. The study also tries to take into account chemical interaction between the active substance of the polishing slurry and the polished surface.

The proposed model takes into account the chemical aspect of polishing through the diffusion coefficient of the reagent in the polished material.

Article [52] suggests expressions for evaluating the material removal rate taking into account the properties of the material – the hardness of the initial material and the oxidized forms on the surface (the Brinell harness). The authors suggest various expressions for various depths of abrasive indentation in the surface layers.

Therefore, one of the main problems when modelling the CMP process is to detail the contribution of the chemical reaction and mechanical removal to the end result. The existing approaches to the problem can be classified as mechanical, chemical-mechanical, and chemical. The suggested models of the polishing process are mainly based on particular experimental conditions. This accounts for the limitations of such models and the need to adapt them to other conditions of polishing of semiconductor materials. At the same time, some authors point out the limitations of the suggested expressions for estimating the material removal rate [42, 52, 59].

### 3.1.3. Modes of CMP of $A^3B^5$

Table 1 provides examples of CMP conditions and compositions of polishing slurries used for



InSb, GaSb, GaAs, and InAs. The effectiveness of the polishing process is assessed based on the quality of the wafer. Generally, assessment of the quality of wafers is based on the following parameters: roughness (including  $R_a$ ,  $R_z$ ), the total thickness variation of the wafer; total indicator reading (*TIR*); the wafer's bow (*BOW*); and the wafer's warp (*WARP*). It is also important to monitor other defects on the wafer's surface, including scratches and residual particles (abrasive, dust, and material particles). The lower the values of these parameters are, the higher the quality of the wafer. Most studies assess the quality of polished wafers based on the roughness values, because the experiments are conducted on fragments, rather than on whole wafers.

Methods of roughness measurement include atomic force microscopy and contact and non-contact optical profilometry. Optical quality control systems usually make it possible to assess the whole wafer and determine the *TTV*, *TIR*, *WARP*, and *BOW*. Defects can be monitored by means of optical (including with a 3-*d* digital optical microscope [61]) and electron microscopy. Another common method is by scanning the surface with a laser beam. To assess the surface morphologies, crystalline quality and surface defects of single-crystal wafers after CMP, other methods are also used, including white light interferometry, laser interferometry, X-ray tomography, and high-resolution X-ray diffraction [62, 63]. The need to control the chemical composition of the polished surface is determined by the chemical properties of the elements of the III and V groups. For this, X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy [34, 64], and energy dispersive X-ray spectroscopy are used.

Chemical mechanical polishing of GaAs is also performed using polishing slurries based on  $\text{Br}_2/\text{MeOH}$ ;  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ ;  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$ ;  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{O}_2$  [23].

An analysis of the CMP modes presented in Table 1 demonstrated that the following characteristics are required for a high quality polishing of  $\text{A}^3\text{B}^5$  wafers.

1) Specific chemical mechanical polishing methods and polishing slurries are developed

for each  $\text{A}^3\text{B}^5$  material.  $\text{H}_2\text{O}_2$  and  $\text{NaOCl}$  are most commonly used as oxidizers. However, the use of  $\text{NaOCl}$  may result in the formation of chlorine gas, so other oxidizers are being studied, e.g.  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ ,  $\text{NaIO}_3$ ,  $\text{NaIO}_4$ .

During the CMP of arsenides and phosphides, toxic gases  $\text{AsH}_3$  and  $\text{PH}_3$  [65–68] can be formed even in an oxidizing environment. At the same time, arsenic oxide ( $\text{As}_2\text{O}_3$ ) formed during CMP transforms into  $\text{HAsO}_2$ ,  $\text{H}_3\text{AsO}_4$ , and  $\text{AsO}_4^{3-}$  depending on the pH of the solution. When polishing In and Ga antimonides, the composition of the polishing slurry affects the oxidation of the III group elements, because antimony oxide ( $\text{Sb}_2\text{O}_3$ ) is stable practically within the whole pH range [64]. At the same time, a more homogeneous removal of material from the surface of the wafers is observed in solutions with pH below or close to 7 (the pH ranges from 4 to 7). In alkaline solutions (pH > 7), the material removal rate is significantly higher than in acidic solutions, while the surface quality decreases dramatically (the roughness increases, grooves begin to appear). Grooves can also be caused by abrasive particles in the polishing slurry. This can result from the softness of polished materials.

2) Taking into account the mentioned above, researchers are investigating the possibility of conducting polishing of the studied materials without abrasive particles or with relatively soft abrasive particles [69–72] of a nanometer size (not over a few dozen nm). The most common are polishing slurries based on  $\text{SiO}_2$ . The mechanism of the functioning of abrasive particles is still a matter of debate [73, 74]. In particular, there is no single opinion as to the participation of  $\text{SiO}_2$  in the chemical processes of CMP of  $\text{A}^3\text{B}^5$  [30, 66];

3) To remove the material more evenly and obtain surfaces of a better quality, the polishing process can also be divided into several consequent stages (from coarse to fine polishing). This is aimed at the decrease of the material removal rate during fine polishing. A decrease in the CMP rate is a general tendency for both single-stage and multistage polishing. For this, several techniques are used, including the following [75, 76]:

**Table 1.** Examples of the parameters of CMP of A<sup>3</sup>B<sup>5</sup> materials (where  $P$  – is the down pressure on the wafer,  $V_{\text{pad}}$  is the velocity of the polishing pad,  $V_{\text{wafer}}$  is the velocity of the wafer,  $V_{\text{supply}}$  is the polishing slurry supply rate,  $\tau$  is the duration of the process,  $T$  is temperature, and  $MMR$  is the material removal rate)

Material	CMP slurry composition	Polish conditions	Characterization
1	2	3	4
InSb [114]	1 step - Al <sub>2</sub> O <sub>3</sub> (3÷9 µm): H <sub>2</sub> O = 1:30; 2 step - H <sub>2</sub> O <sub>2</sub> : SiO <sub>2</sub> dispersion (25÷40 vol.%) = 1: 2÷4 (vol. ratio)	$P$ : 10÷15 g/cm <sup>2</sup> ; $V_{\text{pad}}$ : 60÷90 rpm; $V_{\text{droppng}}$ : 10÷20 drops/min; $\tau$ : ~ 20 h	Roughness < 0.1 µm
InSb <Te> (111), [87]	ZrO <sub>2</sub> (dispersion in acidic solution): 20% solution C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> (tartaric acid) in H <sub>2</sub> O <sub>2</sub> (40%) = 5:1		
InSb (112) [115]	(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (26 wt.%): HBr (42 wt.%): CH <sub>2</sub> (OH)CH <sub>2</sub> (OH) (ethylene glycol – EG) = 11: 49:40 (vol.%) dissolved in EG (0÷ 95 vol.%)	Pad: cambric tissue; $T=293$ K; $V_{\text{droppng}}$ : 2÷3 ml/min; $\tau$ : 2÷3 min	Roughness $R_a$ – 0.3 nm
InSb [34]	230 ml H <sub>2</sub> O <sub>2</sub> (30% solution), 75 ml EG, C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> , NaCl (0.08 M for rough and 0.02 M for precise polish) in 1 l CMP slurry	$P$ : 5×10 <sup>-3</sup> H/m <sup>2</sup> ; $V_{\text{pad}}$ : 35 rpm	Roughness $R_a$ 0.3÷0.5 kÅ (30÷50 nm)
InSb (100) [25]	SiO <sub>2</sub> (dispersion of 50 nm particles), C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> (C <sub>5</sub> H <sub>6</sub> O <sub>3</sub> ), H <sub>2</sub> O <sub>2</sub>	Pad: polyurethane and polyester; pH = 4÷6; $P$ : 0÷120 g/cm <sup>2</sup> ; $V_{\text{pa}}$ : 60 rpm; $V_{\text{droppng}}$ : 160 ml/min; $MMR$ : 0.2÷0.7 µm/min	Roughness $R(\text{max})$ – 3 nm
InSb [35]	NaOCl (10% solution) and C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> (50% solution)	$P$ : 0.4; 0.7 psi; $V_{\text{pad}}$ : 50; 70 rpm; $V_{\text{wafer}}$ : 30 rpm; $\tau$ : 2÷3 min	Roughness 1.5 nm. There are apparent defects
GaSb (100), GaSb <Te> (100) [86]	1 step – Br <sub>2</sub> : C <sub>2</sub> H <sub>4</sub> (OH) <sub>2</sub> = 1:100; 2, 3 steps - anodic oxidation and chemical etching	Pad: Pocerfarm 404	Roughness – 0.3÷0.4 nm
GaSb (100) [64]	NaOCl (10% solution) и C <sub>6</sub> H <sub>7</sub> O <sub>8</sub> (10% solution)	Pad: polyurethane; pH=7; $P$ : 4 kP; $V_{\text{pad}}$ : 30 rpm; $MMR$ : 10 nm/min	Roughness – 0.5 nm
GaSb [62]	SiO <sub>2</sub> (35% dispersion of 50 nm particles) and C <sub>3</sub> Cl <sub>2</sub> N <sub>3</sub> NaO <sub>3</sub> (10% solution of sodium dichloroisocyanurate): H <sub>2</sub> O = 1:20 and 2 wt.% NaHCO <sub>3</sub>	Pad: polyurethane; pore size 42÷58 µm, pore density 325/mm <sup>2</sup> , velvet length 310 µm, compressibility 15%, Shore A Hardness 42; $\tau$ : 50 min; $MMR$ : 0.216 µm/min	Roughness – 0.13 nm

**Table 1 (continued)**

1	2	3	4
GaSb [116]	1 step – Al <sub>2</sub> O <sub>3</sub> 10÷30%; grinding aid 5÷10%; dispersant 1÷10%; H <sub>2</sub> O 2 step – NaClO 1÷10%; SiO <sub>2</sub> (up to 100 nm) 10÷30%; H <sub>3</sub> PO <sub>4</sub> 0.01÷0.2%; H <sub>2</sub> O 3 step – H <sub>2</sub> O <sub>2</sub> 0.1÷10 %; PH value regulator 0.01÷5%; H <sub>2</sub> O	1 – Pad: CeO <sub>2</sub> ; P: 100÷200 g/cm <sup>2</sup> ; V <sub>pad</sub> : 10÷40 rpm; V <sub>dropping</sub> : 10÷50 ml/min. 2 – Pad: polyurethane; pH=6; P: 80÷150 g/cm <sup>2</sup> , V <sub>pad</sub> : 60÷100 rpm; V <sub>dropping</sub> : 10÷30 ml/min 3 – Pad: synthetic leather; pH = 4	Roughness R <sub>a</sub> < 0.3 nm
GaSb (100) [117]	Commercial polishing agents “BGY- 903”, “FA/OF3210”, Dongguan company “3030”, Tianjin Xi Lika “2360” : H <sub>2</sub> O: clorox = (1÷10): (50÷100): (1÷10) (vol. ratio)	T = 15÷60 °C; P: 2÷25 psi; V <sub>dropping</sub> : 10÷150 ml/min; τ: 10÷60 min	Roughness R <sub>a</sub> – 0.1÷0.2 μm; WARP – 20 μm; TTV – 5 μm
InAs [118]	NH <sub>2</sub> SO <sub>2</sub> OH (sulphamic acid): C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> : H <sub>2</sub> O <sub>2</sub> : H <sub>2</sub> O = 3:1:10:86 (%)	Pad: Synthetic buckskin; pH = 1÷2; P: 0.08÷0.12 Pa; V <sub>pad</sub> : 55÷65 rpm; V <sub>dropping</sub> : 10 ml/min	
InAs (001) [86]	(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (26 wt.%): HBr (42 mas.%): CH <sub>2</sub> (OH)CH <sub>2</sub> (OH) = 11: 49:40 (vol.%) dissolved in EG (0÷ 95 vol.%)	Pad: cambric tissue; T = 293 K; V <sub>dropping</sub> : 2÷3 ml/min; τ: 2÷3 min	Roughness R <sub>a</sub> – 0.2 nm
InAs [64]	NaOCl (10% solution) and C <sub>6</sub> H <sub>7</sub> O <sub>8</sub> (50% solution)	Pad: polyurethane; pH=7; P: 4 kPa; V <sub>pad</sub> : 30 rpm; MMR: 10 nm/min	Roughness – 0.4 nm
GaAs [65]	Commercial SiO <sub>2</sub> (30 wt.% aq. dispersion 35 nm particles): H <sub>2</sub> O <sub>2</sub> (30 wt.% aq. solution) (or NaIO <sub>3</sub> , NaIO <sub>4</sub> ): H <sub>2</sub> O = 3: 1: 96 (wt.%). Additionally HNO <sub>3</sub> or KOH.	pH = 2÷3; P: 3.5 psi; V <sub>pad</sub> : 80 rpm; V <sub>wafer</sub> : 72 rpm; V <sub>dropping</sub> : 200 ml/min; τ: 1 min	Roughness – 0.7; 0.5 nm. (Increase from primary value of 0.2 nm)
GaAs [24]	NaCl, C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> SNa (sodium benzenesulfonate), Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> , Na <sub>2</sub> CO <sub>3</sub> , SiO <sub>2</sub> dispersion	T=16°C; P: ≥ 90 H/81 cm <sup>2</sup> ; V <sub>pad</sub> : 40 rpm; V <sub>wafer</sub> : 30÷40 rpm; V <sub>dropping</sub> : 500 ml/min; τ: 10 min	Roughness R <sub>a</sub> ~ 15 nm; TTV < 5 μm
GaAs [64]	a) NaOCl: H <sub>2</sub> O= 1:10; b) NaOCl (10% aq. solution) and C <sub>6</sub> H <sub>7</sub> O <sub>8</sub> (10% aq. solution)	Pad: polyurethane; a) pH=11; b) pH=7; P: 4 kPa; V <sub>pad</sub> : 30 rpm; MMR: 10 nm/min	Roughness – a) 0.5 nm; b) 0.4 nm;

**Table 1 (end)**

1	2	3	4
n-GaAs (100) [82]	TiO <sub>2</sub> (anatase) (5÷10 nm): 7.4 wt.% in H <sub>2</sub> O <sub>2</sub> (15% aq. solution)	Pad: suede; P: 9.8 kPa; V <sub>pad</sub> : 80 rpm; V <sub>wafer</sub> : 60 rpm; V <sub>dropping</sub> : 30 ml/min; UV light: λ = 250 nm (380 nm)	Roughness R <sub>a</sub> – 0.4÷0.5 nm
GaAs (2 inch) [119]	H <sub>2</sub> O <sub>2</sub> 7.0÷70.0 vol.%; C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> (30% solution) 7.0÷60.0; EG 5.0÷15.0; H <sub>2</sub> O	Pad: cambric; P: 4.3÷7.5 kPa; V <sub>pad</sub> : 20 rpm; V <sub>dropping</sub> : 15÷20 ml/min; MMR: 0.4÷1.2 μm/min	TIR – 2÷3 μm
GaAs (100 mm) [120]	1 step) dichloroisocyanuric acid (C <sub>3</sub> O <sub>3</sub> N <sub>3</sub> CL <sub>2</sub> NA) 23 wt.%; sodium triphosphosphate (Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> ) 20÷31 wt.%; Na <sub>2</sub> SO <sub>4</sub> 8 wt.%; Na <sub>2</sub> CO <sub>3</sub> 3 mas.%; H <sub>2</sub> O SiO <sub>2</sub> (50 wt.% dispersion). 2 step) dichloroisocyanuric acid 23 wt.%; sodium triphosphosphate 13÷19 wt.%; Na <sub>2</sub> SO <sub>4</sub> 8 mas.%; Na <sub>2</sub> CO <sub>3</sub> 3 wt.%; H <sub>2</sub> O SiO <sub>2</sub> (50 mas.% dispersion).	Pad: polyurethane; Two side polish: P: 50 g/cm <sup>2</sup> ; V <sub>pad</sub> : up – 7.7 rpm, bottom – 23.2 rpm; V <sub>dropping</sub> : 800 ml/min; τ: 1 step) 30 min, 2 step) 15 min; MMR: 1 step) 0.6÷1.2 μm/min; 2 step) 0.2÷0.4 μm/min	
InP [36]	Commercial SiO <sub>2</sub> (dispersion of 100 nm particles in acidic media)	Pad: shore hardness D13	Roughness – 0.4÷0.5 nm
InP (001) (4 inch) [22]	a) NaOCl: H <sub>2</sub> O = 1:20; b) C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> : H <sub>2</sub> O = 1:4;	Pad: polyurethane; P: 4 kPa; V <sub>pad</sub> : 30 rpm; MMR: 5 nm/min. τ: 150÷210 min	Roughness < 1 nm
InP [121]	Commercial SiO <sub>2</sub> (30 wt.% aq. dispersion 35 nm particles): H <sub>2</sub> O <sub>2</sub> (wt.% aq. solution): C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> (or C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> , C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> ) = 3: 1: 0.72 (wt.%) in H <sub>2</sub> O. HNO <sub>3</sub> or KOH added	a) pH = 6 (C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> ); b) pH = 8 (C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> ); P: 24.1 kPa; V <sub>pad</sub> : 72 rpm; V <sub>wafer</sub> : 80 rpm; V <sub>dropping</sub> : 200 ml/min	Roughness – a) 0.1 nm; b) 0.7 nm
InP <S> (100) (2 inch) [25]	SiO <sub>2</sub> (dispersion 50 nm particles), C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> (C <sub>5</sub> H <sub>6</sub> O <sub>3</sub> ), H <sub>2</sub> O <sub>2</sub>	Pad: polyurethane and polyester; pH=4÷6; P: 0÷100 g/cm <sup>2</sup> ; V <sub>pad</sub> : 60 rpm; V <sub>dropping</sub> : 160 ml/min; MMR: 0.2÷0.7 μm/min	Roughness R(max) – 1.5 nm
InP<S> (100) (2 inch) [122,123]	a) NaOCl (50 vol.%) и C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> ; b) NaOCl (50 vol.%), C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> , SiO <sub>2</sub> (5 wt.% dispersion)	Pad: polyurethane and polyester; pH = 5÷6; P: 100 g/cm <sup>2</sup> ; V <sub>pad</sub> : 40 rpm; V <sub>dropping</sub> : 30 ml/min; MMR: a) 0.05 ml/min, b) 0.78 ml/min	Roughness – a) R <sub>a</sub> – 0.1 nm, R(max) – 0.8 nm; б) R <sub>a</sub> – 0.4 nm, R(max) – 3 nm

- reducing the down pressure on the polished wafer to optimal values;
- adapting the pH of the polishing slurry (as discussed earlier in the article);
- optimizing, including reducing the concentration of reagents in the polishing slurry [22, 34].

Today, the industrial processing of wafers obtained from single-crystal ingots of GaAs, GaSb, InAs, InSb, and InP involves CMP [77]. However, the theoretical basis of CMP has not been developed enough yet. This concerns primarily the chemical aspects: kinetics and thermodynamics of the material interaction with various oxidizers and the impact of the properties of the material (its crystallographic orientation, defects); the effect of the mechanical polishing on the chemical processes; the interaction of the oxidation products with complexants; and the effect of the presence of buffer solutions in the polishing slurry on the kinetics of the processes. Authors [65] note that pH is maintained by adding KOH, HNO<sub>3</sub>, and NaHCO<sub>3</sub>. It is assumed that they do not interact with the polished materials. However, most studies do not mention these additives.

Besides the conditions and polishing slurries used in traditional CMP, new approaches to the technology are also studied based on various semiconductor materials. For instance, publication [78] suggests using the chemical etching of silicon wafers followed by polishing with Double Disk Magnetic Abrasive Finishing. Magnetic field-assisted polishing is also studied in [79, 80]. CMP of GaAs was also performed with an abrasive ice disc [81], and a TiO<sub>2</sub> abrasive and an ultraviolet ray [82]. A new method of surface planarization of 4H-SiC is investigated in [83], where silicon is oxidized by means of plasma electrolytic processing followed by the removal of the oxide with an abrasive slurry. This method involves moving the polished wafer from the electrolytic cell to the polishing pad, which makes it difficult to upscale the technology. Article [84] suggests a way to modernize CMP of gallium nitride by putting gold nanoparticles onto the polishing pad. The authors assume that gold nanoparticles interact with the polished surface under UV light, which

results in the formation of charge carriers (holes) in the valence band of the polished material. This, in turn, facilitates the oxidation process. This approach allowed obtaining a roughness  $R_a$  of about 1.3 nm. However, the use of gold nanoparticles makes the process significantly more difficult and expensive.

Authors [85] propose modernizing the slurry supply system by the slurry ionization, when a cathode and anode are put into the slurry tank. The ionized slurry is atomized with oxygen or nitrogen gas using a spray slurry nozzle.

### **3.2. Chemical polishing of semiconductor wafers: new approaches**

Non-contact chemical polishing of semiconductor wafers is performed under hydrodynamic conditions in a rotary barrel polishing pad [17] or while stirring the solution close to the polished surface in order to ensure the homogeneity of chemical reaction with the etchant. Solutions based on etchants including HF, HCl, Br<sub>2</sub>, and NH<sub>3</sub>·H<sub>2</sub>O [86] and oxidizers, like HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> [87], are used for chemical polishing of A<sup>3</sup>B<sup>5</sup>. Publications [88, 89] report the effect of bromine on chemical etching of InSb, InAs, and GaAs wafers. The studies demonstrate that such solutions are the most suitable for etching of InAs. However, a drawback of bromine is its high reactivity and toxicity.

Publication [90] suggests a method which combines the electrogeneration of the etchant Br<sub>2</sub> and chemical etching of a GaAs wafer.

Article [86] studies the electrochemical anodizing of wafers in a mixture of C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>/C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub> at the voltage of 50÷100 V followed by the chemical removal of the resulting oxides with a HCl solution.

Authors [91] investigate a method based on polishing the SiC surface with a KOH melt. This method is also applicable to A<sup>3</sup>B<sup>5</sup> materials. A promising field of study seems a research of reagents to treat GaAs, GaSb, InAs, InSb, and InP materials with their melts.

Publication [92] suggests using hydride vapor-phase epitaxy for the planarization of (100) GaAs. However, the authors note that the method is rather expensive. The literature on the problem also suggests polishing GaSb by means of etching

of the surface in argon and reactive ion etching in  $\text{CCl}_2\text{F}_2$  or  $\text{CCl}_4$  plasma [86].

Therefore, the approaches to the chemical polishing include polishing with melts, as well as wet chemical, gas-phase, and electrochemical treatment. The most developed is wet chemical polishing. The main drawback of the wet and electrochemical polishing is that it is difficult to ensure homogeneous interaction of the etchant with the surface of the wafer.

New methods of chemical polishing of semiconductor wafers are indeed of a great scientific interest. Their application requires non-trivial engineering solutions as well as ensuring economic feasibility.

#### 4. Cleaning and passivation of the surface of $\text{A}^3\text{B}^5$ materials

The high reactivity of  $\text{A}^3\text{B}^5$  materials results in the formation of nonstoichiometric oxides of the elements of III and V groups on the surface of wafers in the air. The chemical composition and the thickness of oxide layers depend on the environment and change over time [93]. The presence of natural oxides results in the inhomogeneity of the properties of the material both on the surface and in the bulk. The most significant are the increased density of surface states and the appearance of new levels in the band gap in near-surface layers. All this affects the electronic, chemical, and optical properties of wafers [86,94]. The presence of oxides also affects the nucleation process during the initial stage of epitaxial growth on substrates and the density of defects in the epitaxial layers [93].

In this regard, various methods are developed for the cleaning [40] and passivation of the surface of  $\text{A}^3\text{B}^5$ . Passivation can either be a separate stage of processing of semiconductor substrates, or be combined with polishing without any significant gaps in the process. (Passivation techniques for semiconductor structures are out of scope of our review.) The purpose of the passivation of substrates is to significantly reduce the reactivity of the semiconductor surface and stabilize surface states of the wafer.

Wafer cleaning can involve washing in solutions of acids, for instance  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{HF}$  or bromine [95–97], as well as atomic hydrogen cleaning [98]. Thermal annealing can be used to

remove natural oxide layers from the surface of only some of the  $\text{A}^3\text{B}^5$  materials. For instance, for InSb material oxides of In are removed at a temperature of about 325 °C, while oxides of Sb are removed at a temperature close to the melting point of the material.

There are various classifications of passivation methods [99]. One such classification is based on the resulting chemical composition of the surface, when the passivation layers are created using oxidation, sulfidizing, nitriding, etc. [100].

There is also a classification based on the methods of passivation, which are generally divided into wet-chemical techniques and physico-chemical techniques.

At the moment, plasma and anodic oxidation methods are being developed for wafers from single-crystal materials. Thus, electrochemical oxidation of GaSb, InSb, and InAs is performed in electrolytes based on  $\text{KMnO}_4$ ,  $\text{KOH}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{H}_3\text{AsO}_4$  [86]. However, a significant drawback of the electrochemical treatment is the inhomogeneity of the anodizing process in various regions of the wafer's surface [101]. Publication [88] focuses on chemical oxidation of (111) InSb wafers in  $\text{HBr}-\text{Br}_2$  solutions:  $\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4-\text{H}_2\text{O}_2$ :  $\text{H}_2\text{O}$ . The study demonstrates that oxidation in phosphoric acid results in thicker and more loose layers enriched with In. At the same time, oxidation in  $\text{Br}_2$  based solutions results in thinner oxide layers on the surface.

Article [102] considers the methods of sulfidizing InAs surface in solutions of thiols, cystamine, thioacetamide,  $(\text{NH}_4)_2\text{S}_x$ , as well as amino acids and peptides. It is assumed that thiols formed by carbon chain and the SH- group tend to self-assemble and form a passivating monolayer on the  $\text{A}^3\text{B}^5$  surface, which prevents oxidation [95, 103].

Publications [93,84] suggest a method for sulfidizing the InSb surface in a sodium sulfide at a temperature of 45°C. According to [105], unlike most  $\text{A}^3\text{B}^5$  compounds, annealing of InSb wafers after treatment with sulfur-containing solutions results in the braking of the In-S and Sb-S bonds at temperatures of 310 and 400 °C respectively. Authors [106] propose a method for the passivation of InSb in a  $\text{Na}_2\text{S}$  based electrolyte. At the same time, in [107] anodic sulfidizing of InSb in a sulfuric acid based electrolyte resulted in

the enrichment of the surface with Sb. Generally, sulfidizing of the surface of  $A^3B^5$  wafers helps to significantly reduce the density of surface states and electroactive centers and prevent interaction with atmospheric oxygen by creating chemical bonds with sulfur [106,108]. However, when exposed to atmosphere for a long time,  $A^3B^5$  wafers with sulfidized surface can still be oxidized [109].

Publication [109] suggests a different approach to GaAs surface passivation – deposition of silicon nitride on a sulfidized GaAs surface by means of low-frequency plasma enhanced chemical deposition. This approach is based on the passivation method of finished semiconductor structures.

GaAs nitriding methods are also being developed in hydrazine solutions [96, 110] and in nitrogen plasma [111].

Therefore, effective passivation of single-crystal wafers of  $A^3B^5$  materials is an important technological and scientific problem [112,113]. The applicability and feasibility of the existing solutions depend on the application area of a particular material. Instrument engineering usually requires both the chemical purity of the substrate surface and high planarity. Removing passivating heteroatoms when preparing substrates for epitaxial growth can significantly undermine the surface planarity. This accounts for the need of further studies and development of new passivation methods.

## 5. Conclusions

In our study, we reviewed the current approaches to the machining, polishing, and passivation of the surface of GaAs, GaSb, InAs, InSb, and InP semiconductor wafers. Unique characteristics of these materials, including fragility, various degrees of reactivity of Ga, In, Sb, As, P and anisotropy of properties in different crystallographic directions, make it necessary to determine special polishing techniques and the compositions of polishing slurries. The review systematizes the existing approaches to wafer polishing: mechanical polishing, chemical-mechanical polishing, and chemical polishing.

Since mechanical polishing does not provide the required quality of GaAs, GaSb, InAs, InSb,

and InP wafers, it was not considered in the article.

The chemical-mechanical polishing of  $A^3B^5$  includes single-stage and multistage approaches with or without abrasives. CMP is the main method of GaAs, GaSb, InAs, InSb and InP surface treatment, since it has the highest productive capacity and ensures the required surface quality. However, the theoretical aspects of the chemical processes and the impact of the mechanical polishing are developed incompletely. The suggested models for chemical mechanical polishing are mainly based on specific experimental conditions (polished materials, compositions of the polishing slurries, and abrasives). This accounts for the limitations of such models and the need to adapt them to other conditions of polishing. Besides theoretical issues, the main practical problem of CMP of arsenides and phosphides is the formation of toxic gases  $AsH_3$  and  $PH_3$ . This problem is not observed for antimonides. This makes CMP the most practical and promising method for InSb and GaSb. CMP also appears to be the most used method of surface treatment of arsenides and phosphides. However, to optimize the technology for the treatment of these materials, it is necessary to reduce and prevent the formation of toxic gases during the process.

Chemical polishing includes polishing with melts, as well as wet chemical, gas-phase, electrochemical polishing. Wet-chemical polishing is performed in two ways: in a rotary barrel polishing pad or while stirring the solution close to the polished surface. It is the most developed theoretically and practically method. The main drawback of wet chemical and electrochemical polishing is that it is difficult to ensure homogeneous polishing of the whole surface of the wafer. A promising research area with regard to polishing of antimonides, arsenides, and phosphides of indium and gallium can be surface treatment with melts of etching agents.

The review also systematized the existing methods of surface passivation. The classification approaches are based on the following principles: the resulting chemical composition of the surface (oxidation, sulfidizing, nitriding) and the method

of creation of passivating coatings (wet-chemical methods and physico-chemical methods).

### Contribution of the authors

The authors contributed equally to this article.

### Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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