

Effect of chemical bond polarity on wafer and cleavage surface oxidation for GaAs, GaSb, InAs and InSb single crystals

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Received 16 August 2024 ♦ Accepted 30 September 2024 ♦ Published 14 October 2024

Citation: Matveyenka UM, Skryleva EA, Abramova EN, Kozlov RYu, Pavlov PV, Sidelnikov IV, Pavlova OS (2024) Effect of chemical bond polarity on wafer and cleavage surface oxidation for GaAs, GaSb, InAs and InSb single crystals. *Modern Electronic Materials* 10(3): 167–175. <https://doi.org/10.3897/j.moem.10.3.140714>

Abstract

Rapid development of III–V semiconductor device technologies and broadening of device applications are hindered by the high density of surface states produced in those materials by intrinsic complex oxides and surface contaminations. Surface oxides acting as non-radiating recombination centers produce a number of surface levels in the band gap. Oxidation mechanisms depend on the chemical composition of a specific III–V semiconductor compound because surface reactivities differ between materials. The effect of chemical bond polarity on surface oxidation processes in single crystal III–V semiconductor wafers is currently an important research topic. In this work, surface-sensitive XPS method has been used for studying oxidation regularities in GaAs, InAs, GaSb and InSb single crystals undergoing natural atmospheric oxidation and subjected chemical-mechanical polishing. A method of assessing oxidation levels based on chemical shifts of XPS spectral features has been developed. Oxidation level has been shown to depend on chemical bond ionicity degree, the latter being evaluated using the Sanderson and Phillips models. A decrease in surface oxidation level with an increase in bond ionicity degree has been observed for (110) single crystal wafer cleavage surfaces and for (100) single crystal wafer surfaces after single crystal slicing and chemical-mechanical polishing. We show that surface oxidation level increases in the InAs–GaAs–InSb–GaSb sequence, from arsenides to antimonides.

Keywords

III–V single crystals, ionicity degree, oxidation level, XPS, chemical shifts, gallium arsenide (GaAs), indium arsenide (InAs), gallium antimonide (GaSb), indium antimonide (InSb), chemical reactivity of surface

1. Introduction

Surface chemical reactivity is of interest from the viewpoint of fundamental surface chemistry and practical applications. Indium and gallium antimonide and arsenide

wafers are widely used as substrates for micro- and optoelectronic devices where the role of surface properties is critical [1–4]. Surface reactions in GaAs, InAs, GaSb and InSb, including oxidation, typically compromise the performance of devices due to degradation caused

by high density of surface and interface defects [5]. In contrast to silicon whose advantage is the formation of high-quality SiO_2 interfaces with low defect density, oxidation of III–V single crystals produces unstable oxides with complex compositions [6–7]. Those oxides impair the performance of devices and optical components based on III–V semiconductors and affect nucleation pattern at an early stage of epitaxial growth on III–V substrates and defect density in the epitaxial layers [1, 8–10]. Strong uncontrolled oxidation is typical of III–V single crystal wafer fabrication processes including mechanical and chemical-mechanical treatment. Oxide layer formation is avoided in advanced processes by using various surface passivation methods a review of which was reported [9]. The current trend of decreasing semiconductor device dimensions enhances the role of surface and the importance of surface chemical reactivity studies [11].

Indium and gallium antimonide and arsenide wafer technologies are known to suffer from uncontrolled surface oxidation. The listed materials have different chemical reactivities of surface: for the [100] crystallographic direction, the strongest oxidation of elements occurs in InSb and GaSb single crystal wafers, whereas InAs and GaAs single crystal wafers are less susceptible to oxidation [12]. Differences in the surface chemical reactivity of crystals having the same crystallographic orientation and subjected to similar treatment suggest that their origin should be sought in the parameters of III–V chemical bonds. It was assumed that the differences can be associated with A – B bond polarity [13, 14]. This assumption can be verified by determining the parameters which quantitatively describe chemical bonds and their reactivity.

One of the most widely used quantitative parameters for describing chemical bonds is their ionicity degree. There are various approaches to the evaluation of chemical bond ionicity: assessment through wave functions, the Pauling method, the Sanderson method, the Phillips method and others [15–19]. The Pauling and Sanderson methods characterize chemical bonds by electronegativity of atoms. Electronegativities have been calculated for all the elements and are used for predicting and understanding the formation and stability of various bond types between atoms, yet the best method of finding, calculating and treating this parameter remains a subject of discussion. A new approach was reported [19] in which the electronic structures of individual atoms are taken into account along with their conventional electronegativity. The above cited theoretical work shows the complexity and difficulty of predicting chemical reactivity in general.

This work is an attempt to reveal the regularities of oxidation for a limited number of III–V compounds by experimental study of the effect of chemical bond polarity between III and V group atoms in InSb, GaSb, InAs and GaAs single crystal semiconductors on their surface oxidation processes. The oxidation resistance of the materials was studied as a function of chemical bond ionicity

degree on the basis of the Sanderson and Phillips concepts. Surface oxidation processes were studied using X-ray photoelectron spectroscopy (XPS). Natural air oxidation was studied for single crystal wafer cleavage surfaces, and oxidation resulting from chemical-mechanical polishing, for original wafer surfaces. The chemical reactivity of surfaces was evaluated using a new parameter, i.e., oxidation level. The latter parameter was characterized using a newly developed method on the basis of chemical shifts in X-ray photoelectron spectra.

2. Experimental

The test materials were polished 50.8 mm diam. 600 μm thick n type GaAs, GaSb, InAs and InSb (100) single crystal wafers. The InSb, GaSb and GaAs specimens were tellurium doped and the InAs ones, sulfur doped. The wafers were manufactured by Giredmet JSC using a process route which includes chemical-mechanical wafer polishing. Before loading into the XPS spectrometer the as-manufactured wafers were stored in air at 22 °C and RH 40 to 60% (without condensation) during 4 months for GaSb, InAs and InSb and 6 months for GaAs. Before the measurements, the wafers were cut into smaller chips to suit the spectrometer chamber size.

Untreated crystal specimens were made by cleaving the wafers in air along the (110) cleavage plane immediately before loading into spectrometer, i.e., the atmospheric exposure time was less than 2 min. Natural oxidation occurred in the lab atmosphere at 22 °C and RH 50%.

The wafers were studied using XPS on a PHI5000 VersaProbeII spectrometer. Photoemission was excited with monochromatic AlK_α radiation ($h\nu = 1486.6$ eV) at a 25 or 50 W power. The emission angle θ (between the analyzer axis and the normal to the specimen surface) was 45 deg, the residual gas pressure in the chamber was within the order of $3 \cdot 10^{-8}$ Pa and the probing area diameter was 100 or 200 μm . The binding energy E_b scale was calibrated by the Au $4f_{7/2}$ (83.96 eV) and Cu $2p_{3/2}$ (932.63 eV) peaks.

The element atomic concentrations were calculated using integral peak intensities in the survey spectra and the element relative sensitivity factors (RSF) borrowed from the PHI database and corrected for the III–V cleaved specimens, the A and B atomic concentration ratio being taken equal to unity. The survey spectra were recorded at an analyzer pass energy of 117.4 eV with a 1 eV/step. The Ga $3d$, In $3d$, Sb $3d$ and As $3d$ high-resolution spectra were recorded at an analyzer pass energy of 23.5 eV with a 0.2 eV step.

The high-resolution spectra were processed using nonlinear least squares approximation with the Gauss–Lorentz function. The As $3d$ photoelectron spectrum is a doublet of the $3d_{5/2}$ and $3d_{3/2}$ peaks produced by the spin-orbit splitting of the $3d$ level (jj bond). Doublet fitting of the spectrum was carried out by fixing the integral intensity ratio of the $3d_{3/2}$ and $3d_{5/2}$ peaks, which

was 0.67, and the energy spacing of the peaks, which was 0.69 eV.

2.1. III–V single crystal surface oxidation level evaluation method

The definition of oxidation level was introduced for single crystal surface oxidation evaluation. The oxidation level is a parameter describing the total share of the A and B atoms bound with oxygen in an III–V crystal in one of the configurations illustrated in Fig. 1 for the example of GaAs.

The Ga[O, 3As], Ga[2O, 2As] and Ga[3O, As] configurations indicate partial oxidation of trivalent Ga (III), and the Ga[3O] configuration corresponds to Ga₂O₃. For the As and Sb elements forming III- and V-valence oxides, the As[5O] and Sb[5O] configurations indicate As₂O₅ and Sb₂O₅ oxides. The oxidation level ω_{ox} takes into account the bond configurations and A and B atomic concentrations and is calculated as follows:

$$\omega_{ox} = \frac{C(A)}{C(A)+C(B)} \sum_i (k_{ox_i} I(A_{ox})_i) + \frac{C(B)}{C(A)+C(B)} \sum_j (k_{ox_j} I(B_{ox})_j), \quad (3)$$

where $C(A)$ and $C(B)$ are the A and B element concentrations (at.%); i and j are the configuration indices as determined from the high-resolution A and B element spectra; $I(A_{ox})$ and $I(B_{ox})$ are the relative intensities (%) of spectral features pertaining to specific configurations; k_{ox} is the coefficient taking into account bond configuration and valence.

The k_{ox} coefficient was determined from the quantity of oxygen atoms bound with A or B elements and accepted to be 1 for the A [3O] and B [3O] configurations and 5/3 for the B [5O] configuration. For partial oxidation configurations k_{ox} was 1/3 (one oxygen atom) or 2/3 (two oxygen atoms).

It should be noted that the oxidation level has limitations imposed by its evaluation method. This parameter takes into account the number of oxygen bonds in the surface layer the thickness of which depends on the photoelectron free path. The oxidation level is 100% if all the bonds in the surface layer are occupied. This means

that the oxide layer thickness is more than 5 nm since it is three times the inelastic mean free path (IMFP) of electrons emitted from the Ga 3d (1.7 nm), Sb 3d3 (1.3 nm), In 3d5 (1.3 nm) and As 3d (1.9 nm) levels (calculated for Ga₂O₃, Sb₂O₃, In₂O₃ and As₂O₃ oxides for a $\theta = 45$ deg angle) [20]. The method is not applicable beyond this depth.

2.2. Chemical bond ionicity evaluation

The ionicity of chemical bonds was evaluated using the Sanderson and Phillips models on the basis of the calculation formulas and earlier data [15–17].

The Sanderson model is based on electronegativity interpretation as a chemical potential that is to some extent equalized upon molecule formation. This approach allows evaluating the ionicity degree of a chemical bond from the partial anion charge generated as a result of electronegativity equalization. In turn, the partial charge is calculated as

$$\delta = \frac{\Delta S}{\Delta S_c}, \quad (2)$$

where ΔS is the difference between the electronegativities of the element S and the intermediate electronegativity S_b ; ΔS_c is the change in electronegativity required for the element to acquire unit positive or negative charge.

The S and ΔS parameters of all the elements are available in Sanderson's tables [16]. The intermediate electronegativity S_b is given by the geometric mean of the individual electronegativities of the component atoms. For the III–V compounds in question the intermediate electronegativity was evaluated using the formula

$$\Delta S_b = \sqrt{S_{III} S_V}, \quad (3)$$

For the Phillips approach the ionicity degree of a chemical bond is evaluated from the optical absorption spectra.

The ionicity degrees of the GaAs, InAs, GaS band InSb bonds were calculated as per the Sanderson model using Eqs. (2) and (3) and the chemical bond ionicity degrees calculated using the Phillips model were borrowed directly from available tabulated data [17]. The ionicity degrees of the A – B bonds calculated using both models are summarized in Table 1.

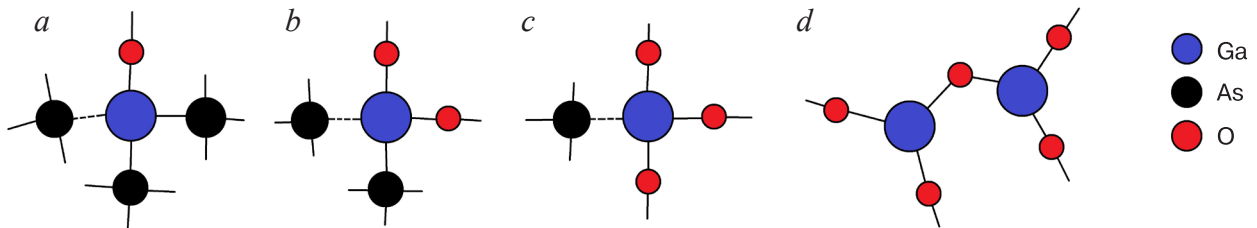


Figure 1. Schematic of four Ga and As bonds with oxygen in single crystal GaAs: (a) Ga[O, 3As]; (b) Ga[2O, 2As]; (c) Ga[3O, As]; (d) Ga[3O]. Dashed line shows bond between unshared pair of Ga atom valence electrons

Table 1. Ionicity degrees of $A-B$ bonds in III–V semiconductor compounds

Compound	Chemical bond ionicity degree (%)	
	Sanderson model	Phillips model
GaSb	1	26
InSb	7	32
GaAs	8	31
InAs	14	36

The ionicity degree estimates made using the above two models differ significantly. The Phillips ionicity degrees of the GaAs, InAs, GaSb and InSb compounds are close and range from 26 to 36%. The Sanderson ionicity degrees differ tangibly: it is 1% for GaSb and 14% for InAs. Moreover, the Sanderson ionicity degrees are far lower than the Phillips ones. The difference originates from a discrepancy between the different ionicity degree evaluation methods and the choice of ionicity degree scale limits. Sanderson takes into account the chemical bond ionicity degrees of all possible compounds [16] whereas the range of compounds considered by Phillips is limited [17].

3. Results and discussion

3.1. Natural oxidation

Direct effect of ionicity degree on the surface chemical reactivity of the crystals was assessed for natural air oxidation under similar conditions (temperature, humidity and atmospheric exposure time). The wafers were cleaved along their cleavage planes (110), and the cleaved specimens were clamped in the spectrometer holder which was then loaded in the spectrometer preparation chamber evacuated to a less than $2 \cdot 10^{-6}$ Pa residual gas pressure. The atmospheric exposure time was 2 min for this procedure. The cleavage surface survey spectra taken in the spectrometer analytical chamber exhibited carbon and oxygen photoelectron bands indicating adsorption of those elements by the atomically pure cleavage surface

Table 2. Atomic concentrations of elements on (110) cleavage surfaces of GaAs, GaSb, InAs and InSb single crystals

Cleaved specimen	Atomic concentrations (at.%)					
	C (± 1.5)	O (± 1.0)	Ga (± 0.7)	In (± 0.7)	As (± 0.7)	Sb (± 0.7)
GaAs	3.8	17.5	39.2	–	39.5	–
GaSb	12.0	35.7	26.2	–	–	26.1
InAs	18.5	7.9	–	36.9	36.7	–
InSb	21.8	35.3	–	21.5	–	21.4

during the short air exposure time. The element atomic concentrations are summarized in Table 2.

The carbon concentrations on the cleavage surfaces are within 22 at.%, the lowest one being that on the GaAs cleavage. As regards oxygen, its concentration on the gallium and indium antimonide cleavages is far higher than that of carbon, and on the arsenide cleavages it is far lower than that on the antimonide cleavages. There are no clear regularities in the carbon and oxygen atomic concentration ratios. However, direct comparison between the oxygen concentrations calculated for the surfaces of the test materials from the survey spectra does not allow one to draw any definitive conclusion as to the chemical reactivity of the surfaces. The XPS-measured oxygen concentration is an integral parameter since it includes both chemically bound oxygen and adsorbed species. Selective analysis of chemically bound oxygen can be done from the high-resolution spectra of A and B as shown in Fig. 2. The presence of single peaks or doublets shifted to the left-hand side of the E_b energy scale (i.e., to higher energies) relative to the main state peaks in the Ga $3d$, In $3d5$, As $3d$ and Sb $3d5$ spectra indicates oxygen bonds. The greater the shift (the chemical shift of ΔE_b in XPS terms), the greater the number of oxygen bonds, i.e., different configurations shown in Fig. 1 produce different shifts.

Correct interpretation of the chemical shifts was achieved using literary available reference data [6, 21–26] and the Authors' own experimental results for III–V polished commercial wafer specimens with thick stoichiometric oxide layers on the surface. The chemical shifts ΔE_b of the oxide peaks from the main element state peaks (hereinafter the latter is the chemical state of the elements A and B in the III–V lattice) were as follows:

- +1.4 eV for Ga $3d$ (Ga_2O_3 – GaAs);
- +3.2 eV for As $3d$ (As_2O_3 – GaAs);
- +2.8 eV for Sb $3d$ (Sb_2O_3 – InSb);
- +0.9 eV for In $3d$ (In_2O_3 – InSb).

Partial oxidation configurations were identified by introducing the definition of unit chemical shift Δ_{+1} which is the magnitude of chemical shift caused by attachment of one oxygen atom to the element A or B . The unit shift was accepted to be one third of the chemical shift for a trivalent oxide in the assumption that the chemical shift is linearly dependent on the number of oxygen bonds.

Figure 2 illustrates the differences (between compounds) in the intensities of spectral features pertaining to A and B atoms bound with oxygen atoms (green-filled areas). It can be seen that the area under those spectral features is the greatest for the GaSb and InSb cleavages. The quantitative data (including standard deviation of repeatability) obtained by approximation of high-resolution cleavage spectra are summarized in Table 3. The oxidation level ω_{ox} was calculated using Eq. (1).

The data in Table 3 suggest a general regularity for all the four test III–V compositions, i.e., preferential oxidation of the A elements: the shares of oxide peaks are 31 and 41% in the Ga $3d$ and In $3d5$ spectra, respectively,

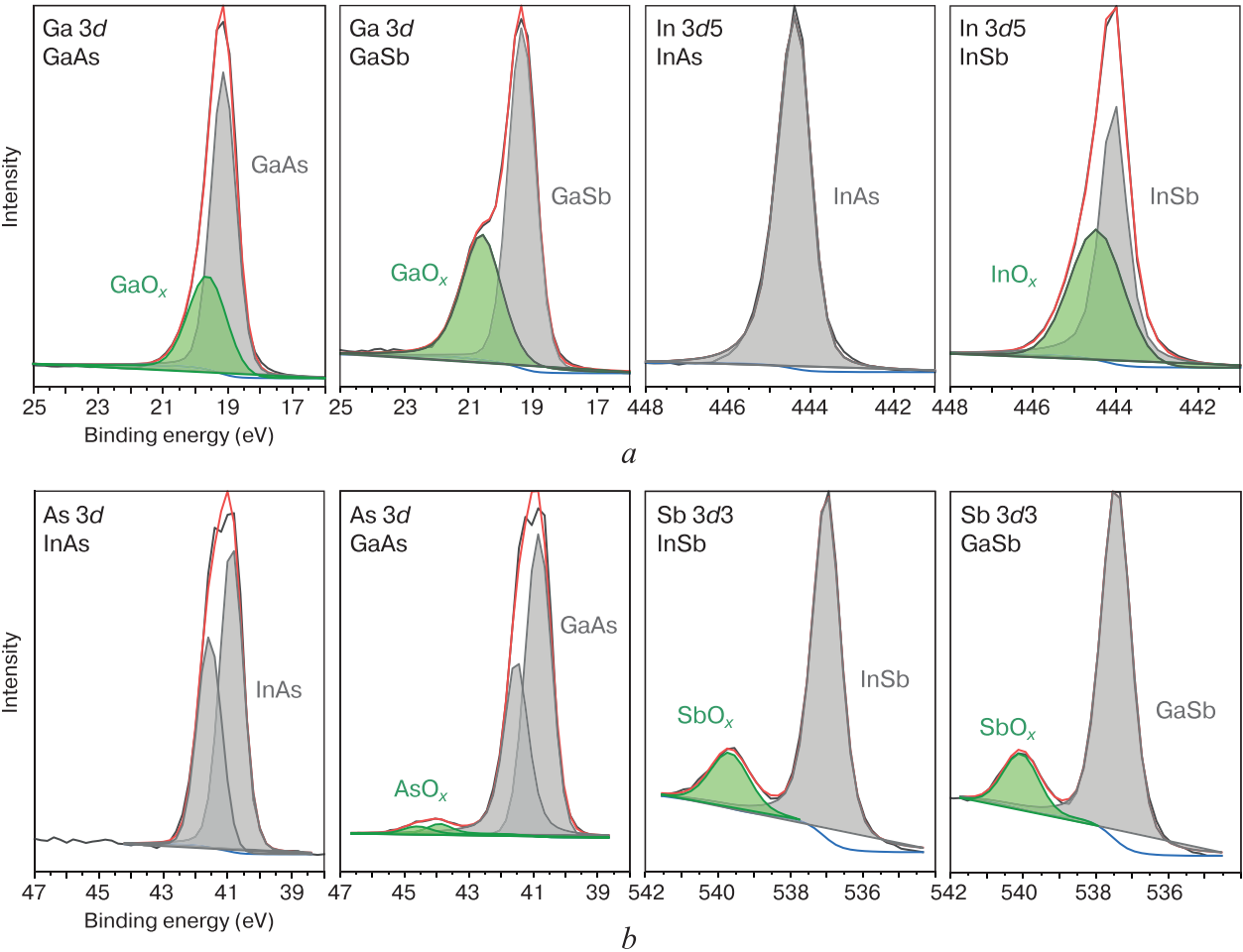


Figure 2. High-resolution photoelectron spectra of (a) *A* and (b) *B* elements for (110) cleavages of III–V compounds (GaAs, GaSb, InAs and InSb). Peaks of oxidized element states are green-filled

and only 3 and 14% in the As 3*d* and Sb 3*d*3 spectra. However, the overall oxidation level ω_{ox} suggests a tangible difference in the reactivities of the above compounds. The oxidation level of cleavages increases in the InAs–GaAs–InSb–GaSb sequence, from arsenides to antimonides. The Sanderson *A–B* chemical bond ionicity degree (see Table 1) decreases in the same sequence. The InAs

spectra of the test compositions with the greatest ionicity degree did not contain oxidation-related peaks, hence $\omega_{ox} = 0$, with the highest ω_{ox} being that for the GaSb surface where the ionicity contribution is the lowest.

Figure 3 shows oxidation level of (110) cleavage as a function of chemical bond ionicity degree. The curves demonstrate a clear decrease in the oxidation level of

Table 3. Approximation parameters of Ga 3*d*, As 3*d*, Sb 3*d*3 and In 3*d*5 high-resolution photoelectron spectral bands for (110) cleavages of GaAs, GaSb, InAs and InSb single crystals and their surface oxidation levels

Cleaved specimen	Parameter	Ga 3 <i>d</i>		In 3 <i>d</i> 5		As 3 <i>d</i>		Sb 3 <i>d</i> 3		ω_{ox} (%)
		III–V	GaO _x	III–V	InO _x	III–V	AsO _x	III–V	SbO _x	
GaAs	<i>E_b</i> (eV)	19.0	19.5	–	–	40.8	43.9	–	–	7
	<i>I_{rel}</i> (%)	69	31	–	–	97	3	–	–	
GaSb	<i>E_b</i> (eV)	19.3	20.6	–	–	–	–	537.4	540.0	21
	<i>I_{rel}</i> (%)	59	41	–	–	–	–	86	14	
InAs	<i>E_b</i> (eV)	–	–	444.4	–	40.9	–	–	–	0
	<i>I_{rel}</i> (%)	–	–	100	–	100	–	–	–	
InSb	<i>E_b</i> (eV)	–	–	444.0	444.4	–	–	537.0	539.6	13
	<i>I_{rel}</i> (%)	–	–	64	36	–	–	87	13	

I_{rel} is relative peak intensity. Standard deviation of repeatability is ±0,2 eV for *E_b*, ±5% for *I_{rel}* and ±3% for ω_{ox}

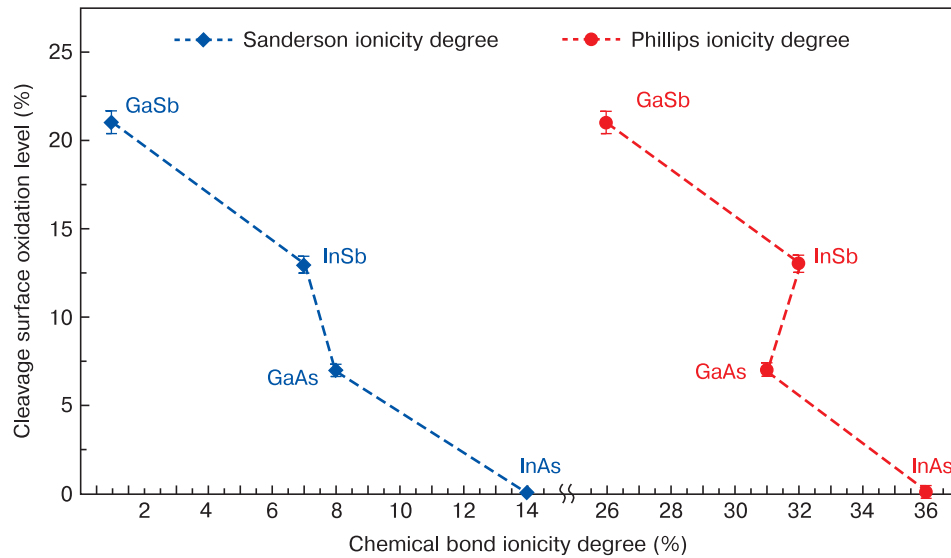


Figure 3. GaAs, GaSb, InAs and InSb single crystal (110) cleavage surface oxidation level as a function of $A-B$ chemical bond ionicity degree

GaAs, GaSb, InAs and InSb single crystal surfaces with an increase in the chemical bond ionicity degree. Interestingly, the pattern of the curves is similar regardless of whether Sanderson or Phillips ionicity degree calculation method was used (different order values).

Thus, the effect of chemical bond ionicity degree on natural chemical reactivity was revealed. One more question to be solved is whether this regularity is valid for oxidation resulting from III–V crystal wafer surface treatment during industrial processes.

3.2. Oxidation due to chemical-mechanical polishing

Surface oxidation of treated GaAs, GaSb, InAs and InSb wafers was studied for chemically-mechanically polished specimens. In general, wafer fabrication route includes the following operations:

- slicing of Cz-grown single crystals;

- wafer grinding and chemical-mechanical polishing in chemical reactant solutions;

- multistage rinsing.

The as-treated wafers were stored in open cassettes for 4 months except for GaAs which were stored for 6 months.

Table 4. Atomic concentrations of elements on (100) GaAs, GaSb, InAs and InSb single crystal wafer surfaces after chemical-mechanical polishing

Wafer specimen	Atomic concentrations (at.%)						
	C (± 1.5)	O (± 1.0)	Ga (± 0.7)	In (± 0.7)	As (± 0.7)	P (± 0.7)	Sb (± 0.7)
GaAs	29.7	42.7	16.1	–	11.5	–	–
GaSb	23.7	39.3	31.1	–	–	1.0	4.9
InAs	35.4	36.4	–	13.8	14.4	–	–
InSb	30.8	30.9	–	21.7	–	14.3	2.2

Table 5. Approximation parameters of Ga 3d, As 3d, Sb 3d3 and In 3d5 high-resolution photoelectron spectral bands for (100) GaAs, GaSb, InAs and InSb single crystal wafers and their oxidation levels

Wafer specimen	Parameter	Ga 3d		In 3d5		As 3d			Sb 3d3			ω_{ox} (%)
		III–V	Ga ₂ O ₃	III–V	In ₂ O ₃	III–V	As ₂ O ₃	As ₂ O ₅	III–V	Sb ₂ O ₃	Sb ₂ O ₅	
GaAs	E_b (eV)	18.9	20.2	–	–	40.5	43.6	45.1	–	–	–	73
	I_{rel} (%)	29	71	–	–	38	38	23	–	–	–	
GaSb	E_b (eV)	–	21.0	–	–	–	–	–	–	–	540.8	100
	I_{rel} (%)	–	100	–	–	–	–	–	–	–	100	
InAs	E_b (eV)	–	–	444.4	445.4	40.9	44.2	45.7	–	–	–	66
	I_{rel} (%)	–	–	28	72	54	25	21	–	–	–	
InSb	E_b (eV)	–	–	444.3	445.2	–	–	–	537.3	540.1	–	70
	I_{rel} (%)	–	–	13	87	–	–	–	55	45	–	

Standard deviation of repeatability is ± 0.2 eV for E_b , $\pm 5\%$ for I_{rel} and $\pm 10\%$ for ω_{ox}

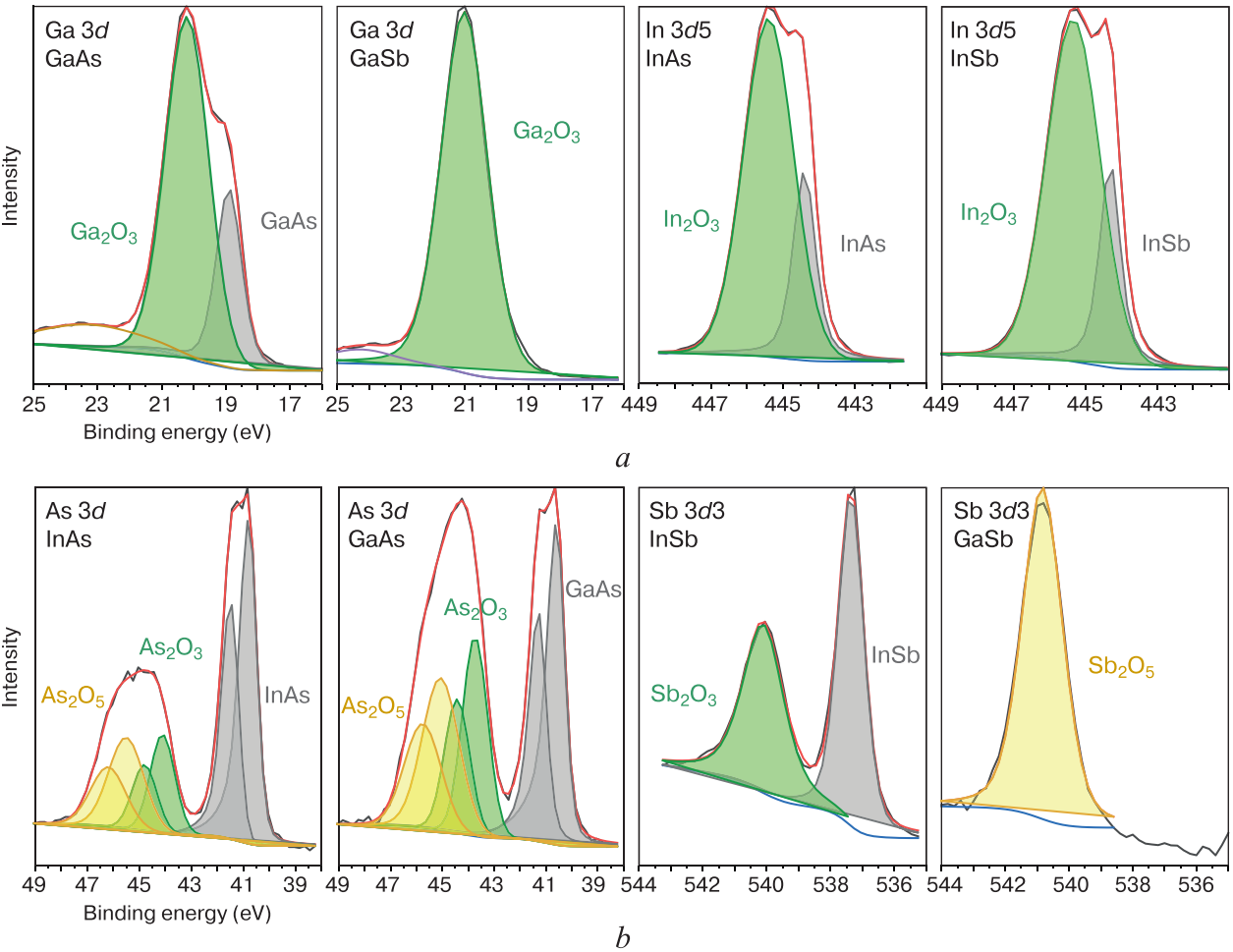


Figure 4. High-resolution photoelectron spectra of (a) *A* and (b) *B* elements for III–V (100) wafers (GaAs, GaSb, InAs, InSb). Peaks of trivalent oxides are green-filled and peaks of pentavalent oxides are yellow-filled

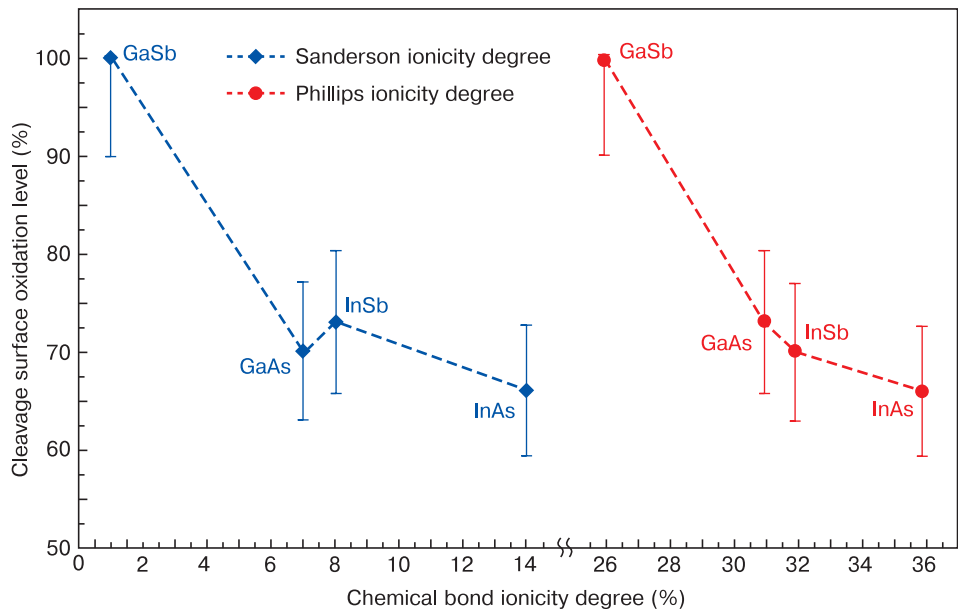


Figure 5. GaAs, GaSb, InAs and InSb single crystal (100) wafer surface oxidation level as a function of *A*–*B* chemical bond ionicity degree

The atomic concentrations of elements on the wafer surfaces after storage are summarized in Table 4. The adsorbed carbon and oxygen concentrations prove to be far higher than those for cleavages. Furthermore, there was a disproportional change in the A and B element concentrations, most expressed for GaSb. The C_A/C_B concentration ratio was > 1 (except for InAs) indicating preferential oxidation of the A elements.

The high-resolution spectra for the wafers (Fig. 4) exhibit significantly larger areas of the oxide peaks. The Ga $3d$ and Sb $3d$ spectra of the GaSb specimen do not show peaks relating to the main states of gallium and antimony. Quantitative data obtained by high-resolution peak approximation are presented in Table 5.

One can see higher oxygen bond peak intensities and greater chemical shift ΔE_b . For example, ΔE_b of the Ga $3d$ band was 0.5 eV for the GaAs cleavage and 1.3 eV for the GaAs wafer indicating partial gallium oxidation on the cleavage surface and Ga₂O₃ oxide formation on the wafer surface. The As $3d$ and Sb $3d$ spectra contain peaks indicating the presence of pentavalent arsenic and antimony oxides As₂O₅ and Sb₂O₅. As a result, the oxidation levels of the wafers were several times those of the cleavages for the same specimens (see Tables 4 and 5). Despite the limitations of the oxidation level assessment method used, the oxidation patterns for all the four test compositions were the same for the wafers and for the cleavages.

Figure 5 shows chemically-mechanically polished wafer surface oxidation level as a function of chemical bond ionicity degree. It can be seen that the oxidation level decreases with an increase in the chemical bond ionicity degree, both for natural oxidation and chemical-mechanical polishing stimulated oxidation.

4. Conclusion

The difference in the chemical reactivities GaAs, GaSb, InAs and InSb single crystal surfaces was shown to originate from differences in the polarity of chemical bonds that can be evaluated from the oxidation level and the ionicity degree. With a decrease in the A – B bond ionicity degree the oxidation level of cleavage and wafer surfaces increases in the InAs–GaAs–InSb–GaSb sequence.

Acknowledgements

This work was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation under State Assignment (Fundamental Studies, Project No. 0718-2020-0031). Experiments were conducted on equipment of Materials Science and Metallurgy Collective Use Center.

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