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Inorganic Chemistry

Crystalline Perfection and Microhardness in the {111} Surfaces of InAs, InP and InAsP Alloys

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Abstract. InAs and InP compounds, along with InAsP ternary alloys, are of great technological interest as crucial materials for radiation-resistant device applications. They have the ZnS crystal structure, which contains a polar axis. Due to the polarity along the [111] direction, the {111} surfaces are the most interesting. Therefore, the effects of this polarity on the chemical bond structure of InAsP alloys have been studied by oxidation processes and microhardness measurements on the (111) and ($\bar{1}\,\bar{1}\,\bar{1}$) surfaces. The polarity results in differences in the microhardness and microstructure on the (111) and ($\bar{1}\,\bar{1}\,\bar{1}$) surfaces. The polarity effect persists even after heat treatment of experimental samples at 500°C. Increasing P concentration in InAsP alloys, both before and after annealing, relates to increased chemical bond stiffness of a material, which in turn increases its microhardness. The microhardness testing results can be accurately described as the cubic polynomial function of InAsP alloy composition. © *2025 Bull. Natl. Acad. Sci. Georg.*

Keywords: chemical bond, etching pits, thermal annealing, crystal structure

Introduction

InAs and InP form a continuous series of ternary InAsP alloys with gradually varying properties. The possibility to regulate the properties of InAsP by varying the amounts of As and P makes these alloys highly valuable for creating radiation-resistant devices for specific optical and electronic functionalities. With the introduction of InAs and InP compounds and their alloys to science and technology, their surface studies have become of great interest and are necessary as an important step in device technology. Key aspects of surface study include chemical etching (Lu et al., 2022) and microhardness measurements (Navamathavan et al., 2006). Understanding the crystalline perfection made from the studies by the morphology and internal deformation behavior of surfaces at the nanoscale level is necessary for the application of InAs, InP, and InAsP alloys in devices. Study of the surfaces of InAs, InP and InAsP alloys is of particular interest for devices operating under a large range of stresses, radiation conditions and

high temperatures. Although surface studies date back to the last century, information on the etching and microhardness of bulk III-V semiconductors remains limited, particularly compared to the extensive research on Si and Ge. There are no microstrain data on heat-treated InAs, InP and InAsP alloys crystals. Taking this into account the etch pit morphology and microhardness on {111} surfaces of bulk crystals of InAs, InP and their ternary alloys are extensively studied in the present paper.

Materials and Methods

The surfaces of InAs, InP and InAsP alloys reveal unusual properties as a result of the crystallographic polarity along the [111] direction**.** In the ZnS crystal structure, three principal planes can be identified: {111}, {110} and {100}. All other planes can be expressed as a combination of them. The {111} surfaces are of special interest due to their stability from an energetic point of view and polarity along the [111] direction.

Chemical etching. Etching of semiconductors to obtain pits on the surface is one of the most common methods for controlling and studying dislocations (Sangwal, 2012). Dislocations are revealed by etching pits and their morphology enables distinguishing the types of dislocations. In the case of ZnS, due to the presence of two types of atoms in the unit cell, two forms of 60° "edge" dislocations are formed on the {111} planes: α – when the excess half-plane terminates with the row of In atoms and β – when the excess half-plane terminates with the row of As and P atoms (Holt, 1962).

Microhardness. The principle of microhardness measurement coincides with the principle of the bulk hardness study. Measurements of microhardness were made with an optical microscope PMT-3 at applied a 100g load. The microhardness values (H) (in kg/mm^2) were calculated using the formula H=1854 p/d^2, where p is the applied load (g) and d (μm) is the diameter of the indenter imprint.

Results and Discussion

Chemical etching on {111} surfaces of InP. Each {111} plane contains one (111) layer of In atoms and ($\bar{1}\ \bar{1}\ \bar{1}$) layer of P atoms, spaced by one-quarter of the distance between the lattice planes. Strong covalent bonds are fixed between the atoms of these two layers. Such a bilayer structure determines the different properties of the two opposing {111} planes. The commonly used etching reagents for InP surfaces are reagents such as HNO_3, HF, HCI, and Br_2. These reagents reveal dislocations on the (111) plane. A typical example of chemical etching is the reaction of InP with concentrated HCl solution, which produces $InCl_3$ and PH_3 as the final products:

$$InP+3HCl \rightarrow InCl_3 +PH_3. \qquad (1)$$

Figures 1*a*) and 1*b*) show microstructure of (111) and ($\bar{1}\ \bar{1}\ \bar{1}$) planes of InP developed by etching in 0.4 M $FeCl_3 \cdot 6H_2O$ in HCl.

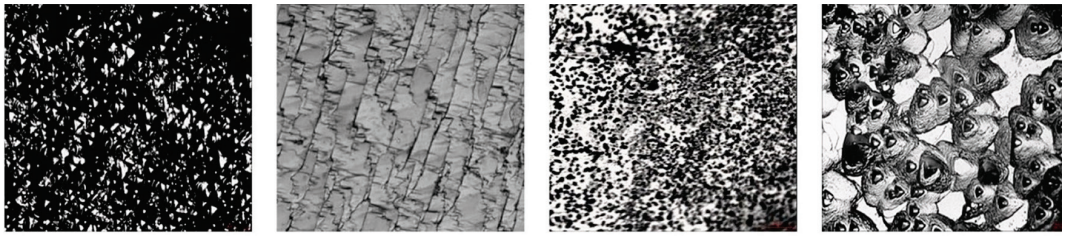
As expected, the (111) and ($\bar{1}\ \bar{1}\ \bar{1}$) planes have shown different chemical behavior: ($\bar{1}\ \bar{1}\ \bar{1}$) plane is more active (dissolving faster) than the (111) plane. The crystallographic polarity leads to a difference in the dissolution rates of the {111} opposite planes in the solution and the formation of α-dislocation pits only on (111) plane (Holt, 1962).

Chemical etching on {111} surfaces of InAs. The process of etching of InAs surfaces is similar to one of InP. Figures 1*c*) and 1*d*) show microstructure of (111) and ($\bar{1}\ \bar{1}\ \bar{1}$) planes of InAs developed by etching in solution of HNO_3 and HCl according to the following reaction:

$$HNO_3 + 3HCl = NOCl + 2H_2O + Cl_2\,. \qquad (2)$$

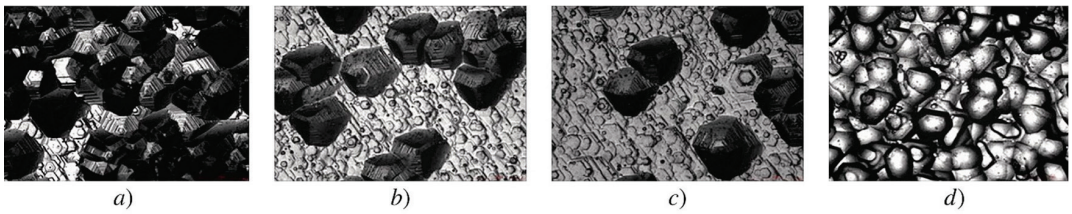
For InAs, as for InP, the effect of crystallographic plane is observed: the (111) In plane is the least active, while the ($\bar{1}\ \bar{1}\ \bar{1}$) As plane is characterized by higher reactivity. Figure 1*d*) shows α- dislocation pits only on (111) plane.

Chemical etching on {111} surfaces of InAsP alloys. Figure 2 shows the typical microstructure on (111) and ($\bar{1}\ \bar{1}\ \bar{1}$) surfaces obtained after etching in different parts of $InAs_{1-x}P_x$ alloys system.



a) *b)* *c)* *d)*

Fig. 1. Pits developed by etching with (*a* and *b*) 0.4 M $FeCl_3 \cdot 6H_2O$ in HCl on InP and (*c* and *d*) with HNO_3: HCI= 1:1 on InAs surfaces. Surfaces: *a*)-($\bar{1}\,\bar{1}\,\bar{1}$)P; *b*)- (111) In; *c*)-($\bar{1}\,\bar{1}\,\bar{1}$) As; *d*)-(111)In. Magnification:x 250.



a) *b)* *c)* *d)*

Fig. 2. Microstructure obtained by etching with 0.4 M $FeCl_3 \cdot 6H_2O$ in HCl solution on InAsP alloys surfaces. Surfaces (111): *a*) InAs- rich InAsP alloy and *b*) InP-rich $InAs_{1-x}P_x$ alloy. Middle of InAsP alloys system: *c*) (111) and *d*) ($\bar{1}\,\bar{1}\,\bar{1}$). Magnification: x 250.

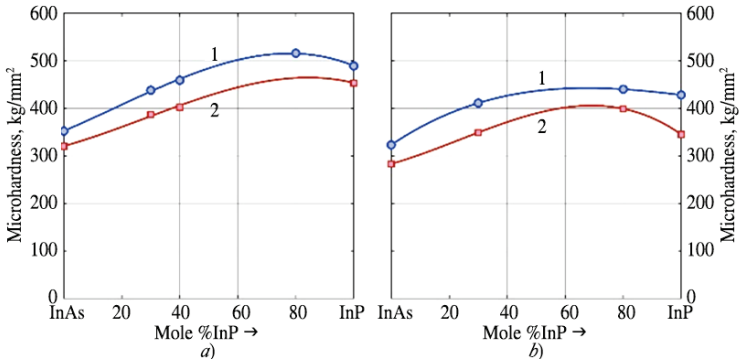


Fig. 3. Microhardness of InAs, InP and InAsP alloys versus the concentration of P at a load of 100g: *a*) before and *b*) after thermal annealing. Solid curves: 1-surface (111) (In atoms layer); 2- surface ($\bar{1}\,\bar{1}\,\bar{1}$) (P and As atoms layer).

Figure 2 shows that the formation of dislocation etch pits takes place only on the (111) surfaces of InAsP alloys terminated with In atoms. This phenomenon may be related to the fact that on the two surfaces – (111) and ($\bar{1}\,\bar{1}\,\bar{1}$) – the In, As and P atoms are bonded differently to the crystal lattice. Investigations have also revealed that on the InAs-rich side of the InAsP alloy system, the structure of the InAs sublattice dominates, whereas on the InP-rich side the structure of InP sublattice prevails. This phenomenon confirms the phenomenological criterion of the "two-mode" behavior of the InAsP system, as theoretically assumed (Chang & Mitra, 1968).

Polarity of microardness. The experimental values of the microhardness of InAs, InP and InAsP alloys at 100 g load, against the concentration of P before and after thermal annealing at 500°C are presented in Fig. 3.

The increase in microhardness of InAsP alloys with increasing phosphorus concentration, before and after annealing at 500°C, reflects the phenomenon that increased bond stiffness raises the material's resistance to volume strain, which in turn increases its microhardness (Pathak et al., 2021). It should be noted that the chemical bonds between atoms of InAs, InP and InAsP alloys is a mixture of covalent and ionic ones. The covalent nature of the

bond contributes to the material's strength, while the ionic component weakens the bond (Pathak et al.,2017). Thus, the unequal and independent contributions of covalency and ionicity to the total bond strength are reflected in the increased microhardness with higher phosphorus concentration in InAsP alloys.

Comparison of curves 1 and 2 in Fig. 3 a) shows that the crystallographic polarity leads to markedly different microhardness values for (111) and ($\bar{1}\,\bar{1}\,\bar{1}$) surfaces. The polarity effect persists even after heat treatment – see Fig. 3 b). Analytical relationships between microhardness (H) and composition (x) in InAsP alloys were obtained using polynomial approximation via the least squares method (Fig. 3 a):

curve 1(111) surface:

$$H(x) = -0.0001x^3 - 0.0061x^2 + 3.1033x + 350.6294 \quad (3)$$

and

curve 2 ($\bar{1}\,\bar{1}\,\bar{1}$) surface:

$$H(x) = -0.0002x^3 + 0.0122x^2 + 2.4986x + 302.6224. \quad (4)$$

Figure 3(*b)* shows the results of microhardness measurements of InAs, InP, and InAsP alloys after annealing at 500°C for 1 h. The temperature of 500°C is high enough to allow atoms to move and rearrange. The main effect of annealing is to soften the material, reduce its strength, and increase its plasticity, making it more ductile and less rigid. This is achieved by reducing internal stresses, improving the uniformity of the structure, and reducing of existing defects, allowing for rearrangement. Annealing allows the material to return to a more stable, less stressed state. Annealing in semiconductors differs significantly from that in metals, as it does not cause major changes in the microstructure of the material. Figure 3 (*b*) shows the best-fit functions for microhardness for heat-treated samples by the following polynomials:

curve 1(111) surface:

$$H(x) = -0.0000x^3 - 0.0098x^2 + 2.2551x + 339.9301 \quad (5)$$

and

curve 2($\bar{1}\,\bar{1}\,\bar{1}$) surface:

$$H(x) = -0.0003x^3 + 0.0271x^2 + 1.2434x + 283.566. \quad (6)$$

Conclusions

The active components of surface analysis, such as chemical etching and microhardness measurements, were used to investigate the morphology and internal deformation behavior of surfaces of InAs, InP compounds and their ternary InAsP alloys at the nanoscale level. A particular type of dislocation etch pits was observed on the {111} surfaces terminated with In atoms in InAs, InP and their alloys. No dislocation etch pits were detected on the ($\bar{1}\,\bar{1}\,\bar{1}$) crystallographic planes terminated with As and P atoms. The different microstructures on opposite (111) and ($\bar{1}\,\bar{1}\,\bar{1}$) crystallographic planes were found in InAs, InP and their alloys, which are affected by the polarity of the zinc- blende structure. Microstructural investigations also revealed that in the InAs rich- side of the InAsP alloy system, the crystallographic structure of the InAs sublattice dominates, whereas in InP rich- side the crystallographic structure of InP sublattice prevails. The effects of polarity on the bond structure of InAsP alloys was also observed by investigations of microhardness. Microindentations were carried out under a 100 g load. Microindentations show that the microhardness values of InAsP on both the (111) and ($\bar{1}\,\bar{1}\,\bar{1}$) crystallographic planes increase with P concentration. A mixture of covalent and ionic chemical bond between atoms of InAsP alloys defines the type of microhardness dependence on composition. The heat treatment process at 500^0C affects the microhardness of InAs, InP and their alloys by softening the material and making it more ductile and less rigid. The microhardness data can be excellently approximated as by a cubic polynomial function of alloy composition.

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არაორგანული ქიმია

კრისტალური სტრუქტურა და მიკროსისალე InAs, InP და InAsP შენადნობების {111} ზედაპირებზე

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InAs და InP ნაერთები და InAsP სამმაგი შენადნობები დიდ ტექნოლოგიურ ინტერესს წარმოადგენს, როგორც რადიაციისადმი მდგრადი მოწყობილობების გამოყენებისთვის აუცილებელი მასალები. მათ აქვს ZnS კრისტალური სტრუქტურა, რომელიც შეიცავს პოლარულ ღერძს. {111} ზედაპირები ყველაზე საინტერესოა პოლარულობის [111] მიმართულებით. ამიტომ, ამ პოლარულობის გავლენა InAsP შენადნობების ქიმიური ბმის სტრუქტურაზე შესწავლილი იყო დაჟანგვის პროცესებისა და მიკროსისალის გაზომვებით ინდიუმისა და დარიშხანის ატომების ზედაპირებზე. პოლარულობა იწვევს მიკროსტრუქტურისა და მიკროსისალის განსხვავებებს აღნიშნულ ზედაპირებზე. პოლარულობის ეფექტი ნარჩუნდება ექსპერიმენტული ნიმუშების თერმული დამუშავების შემდეგაც კი 500°C ტემპერატურაზე. InAsP შენადნობებში P კონცენტრაციის ზრდა როგორც გამოწვამდე, ასევე მის შემდეგ, დაკავშირებულია მასალის ქიმიური ბმის სიმტკიცის ზრდასთან, რაც თავის მხრივ, ზრდის მის მიკროსისალეს. მიკროსისისალის ტესტირების შედეგები ზუსტად შეიძლება აღიწეროს, როგორც InAsP შენადნობის შემადგენლობის პოლინომიალური კუბური ფუნქცია.

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