Mechanochemical activation and gallium and indiaarsenides surface catalycity

I A Kirovskaya, E V Mironova, I V Umansky, O Yu Brueva, A O Murashova and A V Yureva

Omsk State Technical University, 11, Mira ave., Omsk, 644050, Russia
e-mail: kirovskaya@omgtu.ru

Abstract. The present work has been carried out in terms of determining the possibilities for a clearer identification of the active sites nature, intermediate surface compounds nature, functional groups during adsorption and catalysis, activation of the diamond-like semiconductors surface (in particular, the A IIIBV type) based on mechanochemical studies of the “reaction medium (H_2O, iso-C_3H_7OH) – dispersible semiconductor (GaAs, InAs)” systems. As a result, according to the read kinetic curves of dispersion in water, both acidification and alkalinization of the medium have been established and explained; increased activity of the newly formed surface has been noted; intermediate surface compounds, functional groups appearing on the real surface and under H_2O adsorption conditions, adsorption and catalytic decomposition of iso-C_3H_7OH have been found (with explanation of the origin). The unconcealed role of coordinatively unsaturated atoms as active sites of these processes has been shown; the relative catalytic activity of the semiconductors studied has been evaluated. Practical recommendations on the preferred use of gallium arsenide in semiconductor gas analysis and semiconductor catalysis have been given.

Keywords: semiconductors, newly formed surface, active sites, relative catalytic activity, semiconductor gas analysis.

1. Introduction
Analyzing the possibilities of using the results of physical and chemical studies of diamond-like semiconductors surfaces in nano- and sensor technology, it is reasonable to consider the preparation and investigation of newly formed surfaces in various reaction media. In a logical way, one expects a clearer identification of the nature of the active sites, nature of the intermediate compounds, mechanochemical activation of the surface [1].

The objects of the present work are semiconductors of A IIIBV type, isanoionic analogues – GaAs, InAs, water and isopropyl alcohol (propanol-2) act as reaction media.

2. Problem statement
To conduct mechanochemical studies of the newly formed surface of A IIIBV type (GaAs, InAs) semiconductors in various reaction media (H_2O, iso-C_3H_7OH). As a result to reveal more clearly the nature of active sites, nature of the intermediate compounds, functional groups arising on the real, partially hydrated surface of semiconductors and under the adsorption conditions of water, adsorption and catalytic decomposition of isopropyl alcohol on the newly formed surface; expected surface
activation; to estimate the relative catalytic activity of the semiconductors under examination in the dehydration reaction of iso-C$_3$H$_7$OH; to assess the possibility of their use in semiconductor gas analysis and semiconductor catalysis.

3. Experimental part

The work was carried out according to a specially developed procedure [2]: polycrystals of semiconductors had been dispersed in the chosen medium (water, isopropyl alcohol) until the constant pH value was established. IR spectroscopic studies of suspensions of medium-dispersible semiconductor systems were conducted simultaneously [2]: IR spectra of multiple frustrated total internal reflection (IRS MFTIR) were recorded on the Fourier spectrometer Infralum FT-02 in wave numbers 800–8000 cm$^{-1}$ area at a room temperature.

Based on the results obtained, the kinetic isotherms of the medium pH changes were made during the dispersal of GaAs and InAs semiconductors, according to which the state of the newly formed surface and the IRS MFTIR were previously evaluated, allowing to describe in details the behavior of the newly formed surface (compared to exposed in the air), reveal its mechanism. Comparing quantitatively intensities of the IR bands 1383, 3200–3500 and 1650, 3600 cm$^{-1}$ corresponding to the deformation and valence vibrations of OH groups of isopropyl alcohol and water formed by the isopropyl alcohol decomposition, one can judge the catalytic conversion of iso-C$_3$H$_7$OH and relative catalytic activity investigated with the semiconductors. At the same time, the mechanism of catalytic decomposition of isopropyl alcohol on diamond-like semiconductors at room temperature described in [2], including the stages of dehydrogenation and dehydration (with water removal) was the key for that. So the following is expected: in the IR spectra of the «iso-C$_3$H$_7$OH-dispersible semiconductor» systems, in comparison with the IR spectrum of isopropyl alcohol, the decrease in the intensity of the 1383, 3200-3500 cm$^{-1}$ bands corresponding to the deformation and valence vibrations of the iso-C$_3$H$_7$OH OH groups and the appearance along with the increased (with growth of dispersion time)1650, 3600 cm$^{-1}$ bands intensity corresponding to the deformation and valence vibrations of the OH groups of the water formed and adsorbing on the surface in accordance with the donor-acceptor mechanism.

4. Results and discussion

Dispersing semiconductors GaAs, InA in water, one notes: a decrease in pH (acidification of the medium) in the first case and an increase in pH (alkalinization of the medium) – in the second (fig.1).
Figure 1. Kinetic isotherms of dispersing semiconductors GaAs (1) and InAs (2) in water.

Taking into account IR spectra containing bands of coordinately bound water (1650, 3600 cm\(^{-1}\)) and acid residues of AsO\(_4^{3-}\) (825, 850 cm\(^{-1}\)) (fig. 2, 3) and earlier made points (for example, in [3, 4]), the acidification of the medium can be explained by the formation of H\(_3\)AsO\(_4\) acid — the result of the interaction of the particles H\(^+\) and O\(^-\), appearing during the dissociative desorption of chemically adsorbed H\(_2\)O molecules (fig. 2, [2, 3]), with coordinatively unsaturated As atoms, most efficiently seen on a newly formed surface. In the process of mechanochemical action, H\(_3\)AsO\(_4\) acid passes into the medium, eliminating AsO\(_4^{3-}\).

Figure 2. MFTIR IR spectra of GaAs (1) and InAs (2) semiconductors initial surfaces.
An increase in the pH of the medium (when dispersing InAs) can be related to AsO$_4^{3-}$ ions hydrolysis. The role of coordinatively unsaturated atoms, which is most effective on a newly formed surface, should also be mentioned when dispersing GaAs and InAs semiconductors in isopropyl alcohol: iso-C$_3$H$_7$OH$^+$ – As$^8$ surface compounds are formed, fragments of which (AsO$_4^{3-}$) are found in IR-spectra (fig. 3).

It is logical to assume that the formation of the marked surface compounds of chemically adsorbed by the donor-acceptor mechanism of iso-C$_3$H$_7$OH precedes the multistage reaction of its decomposition. In this case, the activation and subsequent rupture of certain bonds in the parent molecules will cause appropriate selectivity [2].

To confirm such considerations, let us consider the results of a comparative analysis of the pure isopropyl alcohol IR spectra 15 minutes later its contact with polycrystals of semiconductors and after dispersion of these polycrystals in it, taking into account their composition and dispersion time (fig. 4). Here comes under notice the absence of AsO$_4^{3-}$, MeOH, Ga$^{3+}$, In$^{3+}$ bands in the second case, which indicates a very low solubility of the semiconductors samples in isopropyl alcohol, and appearance of new absorption bands when they are dispersed in the same medium. Specifically, absorption bands with maxima at 1650 and 3600 cm$^{-1}$ appear in the IR spectra of the «isopropyl alcohol-dispersible semiconductor» systems, corresponding to the deformation and valence vibrations of OH groups resulting from the dehydration of iso-C$_3$H$_7$OH water ($\delta_{\text{OH}}$) [3] and at the same time the intensities of the absorption bands in areas 1393 and 3200–3500 cm$^{-1}$ corresponding to the deformation and valence vibrations of OH groups of isopropyl alcohol [5].
Figure 4. MFTIR IR spectra of pure iso-C₃H₇OH (1) 15 minutes later its contact with polycrystals of GaAs (2a), InAs (2b), and suspensions of «iso-C₃H₇OH-dispersible GaAs» (a) and «iso-C₃H₇OH – Dispersible InAs» (b) systems for different dispersing times: 3 – 15, 4 – 30, 5 – 60, 6 – 75 min.

Different intensity in IR spectra of the examined semiconductors of the deformation and valence vibrations absorption bands of the OH groups of water (1650, 3600 cm⁻¹), formed as a result of the dehydration of iso-C₃H₇OH, (fig. 5, table 1) should also be noted.
Figure 5. MFTIR IR spectra of pure iso-C₃H₇OH (1), suspensions of the systems «iso-C₃H₇OH – dispersible GaAs» (2) and «iso-C₃H₇OH – dispersible InAs» (3) at the same dispersion time (75 min)

It allows to estimate the unequal relative catalytic activity and accordingly, the unequal strength and concentration of acid sites [2], responsible for the catalytic reaction proceeding in this case by the acid-base mechanism [1,2]. The intensities of the bands 1650, 3600 cm⁻¹ and, accordingly, relative to the catalytic activity, gallium arsenide is noticeably leading (Table 1, Fig. 4). It is proposed as a material for microimpurities of isopropyl alcohol vapor and as an active, selective catalyst for its dehydration.

Table 1. Dependence of ir-absorbing band intensity changing on the composition of semiconductors dispersatable in iso-C₃H₇OH at the same time of dispersion (75 min).

| Dispersible semiconductor | ∆I, % | (1650 cm⁻¹) | (3600 cm⁻¹) | (1393 cm⁻¹) | (3400 cm⁻¹) |
|---------------------------|-------|-------------|-------------|-------------|-------------|
| InAs                      | 20    | 20          | 25          | 22          |
| GaAs                      | 40    | 40          | 43          | 45          |

5. Conclusions
- The kinetic isotherms of gallium and indium arsenides dispersion in water indicating both acidification (decrease in pH) and alkalinization (increase in pH) of the medium. The reasons are:
- intermediate compounds, functional groups have been found appearing on the real, partially hydrated surface of semiconductors and under water adsorption conditions, adsorption and catalytic decomposition of isopropyl alcohol on the newly formed surface;
- increased activity of newly formed surface;
– enrichment of the newly formed surface with coordination-unsaturated atoms, more clearly acting on such surface as active sites during the adsorption of H₂O, iso-C₃H₇OH type molecules and their decomposition has been established;
– the relative catalytic activity of the examined semiconductors (GaAs, InAs) in the dehydration reaction of iso-C₃H₇OH has been estimated;
– practical recommendations on the preferential use of GaAs in semiconductor gas analysis (for measuring cells production) and in semiconductor catalysis (especially for dehydration reactions) have been given.

References
[1] Kirovskaya I A 2015 Physico-chemical properties of binary and multicomponent diamond-like semiconductors (Novosibirsk, SB RAS Publ) p 367
[2] Kirovskaya I A 2010 Solid solutions of binary and multicomponent semiconductor systems (Omsk: Omsk State Technical University) p 400
[3] Kirovskaya I A 2001 Surface phenomena (Omsk: Omsk State Technical University) p 176
[4] Borovikova E Yu, Kurazhkovskaya V S, Boldyrev K N, Sukhanov M V, Petrkov V I and Kokarev S A 2014 Vibrational spectra and factor-group analysis of double arsenates of zirconium and alkali metal MZr₂(AsO₄)₃ (M = Li – Cs) Vibrational Spectroscopy Vol 73 pp 158–163
[5] Kiselev A V and Lygin V I 1972 Infrared spectra of surface compounds (Moscow: Nauka) p 459