



## A VOLTAMMETRY INVESTIGATION OF THE EXCHANGE PROCESSES RUNNING ON THE INTERPHASE CdSb/ELECTROLYTE

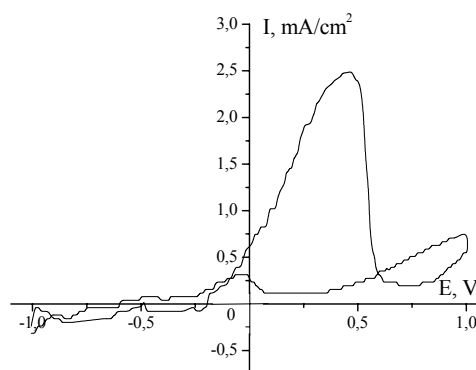
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Processes running on the interphase between the non-doped p-conductive CdSb monocrystal and a liquid medium at various pH were investigated voltammetrically and simulated through thermodynamic calculations. The boundaries between electrode passivity and activity regions were determined for different pH of the solution, types, and intensity of electrode polarization. Atom absorption spectroscopy and polarographic measurements were employed to investigate the rate and the dynamics of crystal surface dissolution and measure the contents and the qualitative composition of the components produced during this process. All the data obtained were used to compose a scheme of the chemical reactions running at different surface states of CdSb and for various pH values.



### INTRODUCTION

The state of the semiconducting monocrystal's surface is one of the key factors determining its electrophysical characteristics. It is known that the compositions "semiconductor/oxide," "semiconductor/sulfide," or "semiconductor/metal" are required to develop new electronic devices and schemes such as advanced gas analysis sensors, electrochemical appliances, ionizing radiation sensors, and others.<sup>1-5</sup> These compositions can be obtained using a number of easily controllable electrochemical methods of surface modification of metals. It should be noted that the electrochemical methods are more technology-friendly and flexible than the purely chemical analogs. For instance, cadmium telluride can be used as a component of nuclear radiation detectors. The passivation of the cadmium telluride surface

causes a decrease in unwanted noise of the detector and enhances its resolution<sup>1</sup>. An electrochemical etching of the p-type porous GaAs used as an antireflection covering for solar cells has been investigated by Bioud *et al.*<sup>2</sup> A significant decrease in cathode luminescence due to changes in the chemical composition of the covering was reported. A possibility of construction of gas detectors based on metal-oxide-semiconductor compositions was discussed in the works<sup>3-5</sup> in the context of their sensitivity, selectivity, stability, etc. and the influence of the detector's material pretreatment on these characteristics.

Cadmium antimonide is a representative of the A<sup>II</sup>B<sup>V</sup> class of semiconductors. It is a well-investigated compound; methods used for its synthesis are thoroughly elaborated, while the area of utilization of this anisotropic material in various electronic, thermoelectric, and optoelectronic

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devices is quite wide.<sup>6–10</sup> Zhou and co-authors<sup>6</sup> have identified and provided the description of the main parameters representing highly effective thermoelectric properties of the CdSb monocrystals. Another analysis of the thermoelectric properties of some materials with multicenter anisotropic bonds is given in.<sup>7</sup> It has been found that the Ag-doped CdSb can be rather effective for low-temperature energy generation. Some spectral parameters and other characteristics of CdSb-based light-sensitive elements and IR filters have been investigated by G. Vorobets *et al.*,<sup>8</sup> who have vacuum-deposited the interference-absorbing thin layers on the surface of CdSb crystals in order to filter out the IR spectral zone. Some sulfide-sensitive electrodes have been constructed in<sup>9</sup> using sulfidized semiconducting monocrystals of CdSb placed in anhydrous superbasic solutions. Then the molar ratio between Cd and Sb atoms has been determined in the surface sulfide film by atom-absorption spectrometry (AAS).

Thus, CdSb was chosen for the present investigation as a promising material that is used widely in many applications. It was planned to combine polarographic and AAS experimental data with theoretical thermodynamic calculations in order to identify the processes running on the electrode's surface during its modification. A preliminary simulation represented by the authors of<sup>10</sup> proved that either selective or stoichiometric dissolution might occur on the CdSb surface under anodic polarization. Alternatively, passivating oxide phases might also be formed on the surface. In these processes, pH is the main factor governing the realization of the above scenarios.

This work deals with the details and mechanisms of the surface modification processes running on CdSb under different pH values.

## EXPERIMENTAL

All investigations were carried out with monocrystalline non-doped CdSb plates exhibiting p-type conductivity. The plates were synthesized through the Czochralski method ensuring a working surface area of 0.25 cm<sup>2</sup>, which was established within the (100) crystallographic plane of CdSb. The specific electric conductivity of the plate was 0.35 Ohm<sup>-1</sup>×cm<sup>-1</sup>, and the main charge carrier concentration was 3×10<sup>15</sup> cm<sup>-3</sup>.

A thin gold film was deposited on the back side of the plates in order to solder-in a copper wire required to maintain an electric contact with outer devices. Then the contact spot and inactive surfaces were insulated by a chemically passive lacquer. A follow-up reactivation of the working surface was realized using a polishing/etching composition of HNO<sub>3</sub> (ω=68 %, ρ=1.405 g/cm<sup>3</sup>) and HF (ω=40 %, ρ=1.128 g/cm<sup>3</sup>) with volumetric ratio 1:12. It should be noted that the duration of such reactivation had to last under a few seconds since the

process ran very fast. Finally, the sample was rinsed with distilled water several times.

A metalloscope microscope MIM-6 was used for visual examination of the surface conditions, while a computerized potentiostats CheapState and PI-50.1 were employed for recording all voltammetry curves. A potential scan rate of 10 mV/s was kept throughout the entire experimental series, and all potentials were measured against a silver chloride electrode and then recalculated into the standard hydrogen electrode potential scale. pH values were measured by a pH-301 series pH-meter.

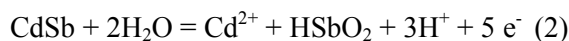
The contents of Cd and Sb in anolyte solutions were measured both polarographically and using AAS. In the course of polarographic measurements, the concentration of Sb(III) ions was determined by the half-wave potential -0.51 V using the standard three electrode cell with the saturated calomel, platinum, and mercury drop electrodes acting as a reference; auxiliary and working electrodes and the background electrolyte consisting a buffer mixture of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (pH=3÷4). Polarographic curves were visualized by a 03-series oscilloscope.

A C-115-M1 series spectrophotometer equipped with a hollow cathode lamp was used for the AAS measurements with the following characteristic wavelengths: 228.8 nm (Cd) and 217.6 (Sb).

## RESULTS AND DISCUSSION

It was found that the CdSb electrode can switch either into active or passive state after polarization by a certain potential when pH ranges between 1 and 11. However, the character and the pattern of the voltammograms recorded at various pH values are quite different. As pH increases, the maximum current, passivation current values, and the curve slope for the raising anodic current parts of the voltammograms are decreasing.

As seen in Figure 1 (a), the active state of anodic dissolution of CdSb embraces the range of potentials between -0.211 to +0.456 V for pH = 1.0. According to a thermodynamic simulation, both stoichiometric (1) and cadmium-selective (2) dissolution processes are allowed for the CdSb electrode:



As pH increases to 3, the pattern of the voltammograms changes (see Fig. 1 (b)). The maximal value of the critical passivation current ( $i_{max}$ ) decreases because of the deceleration of the anodic dissolution of CdSb.

Besides, some expansion of the passive state range (from 0.129 V at pH = 1 to 0.192 V at pH = 3) can be noted. Moreover, new passivation area appears on the polarization curve between 0.637 and 0.807 V. This is an evidence of the fading influence of stoichiometric dissolution of the electrode and the increasing effect of its passivation.

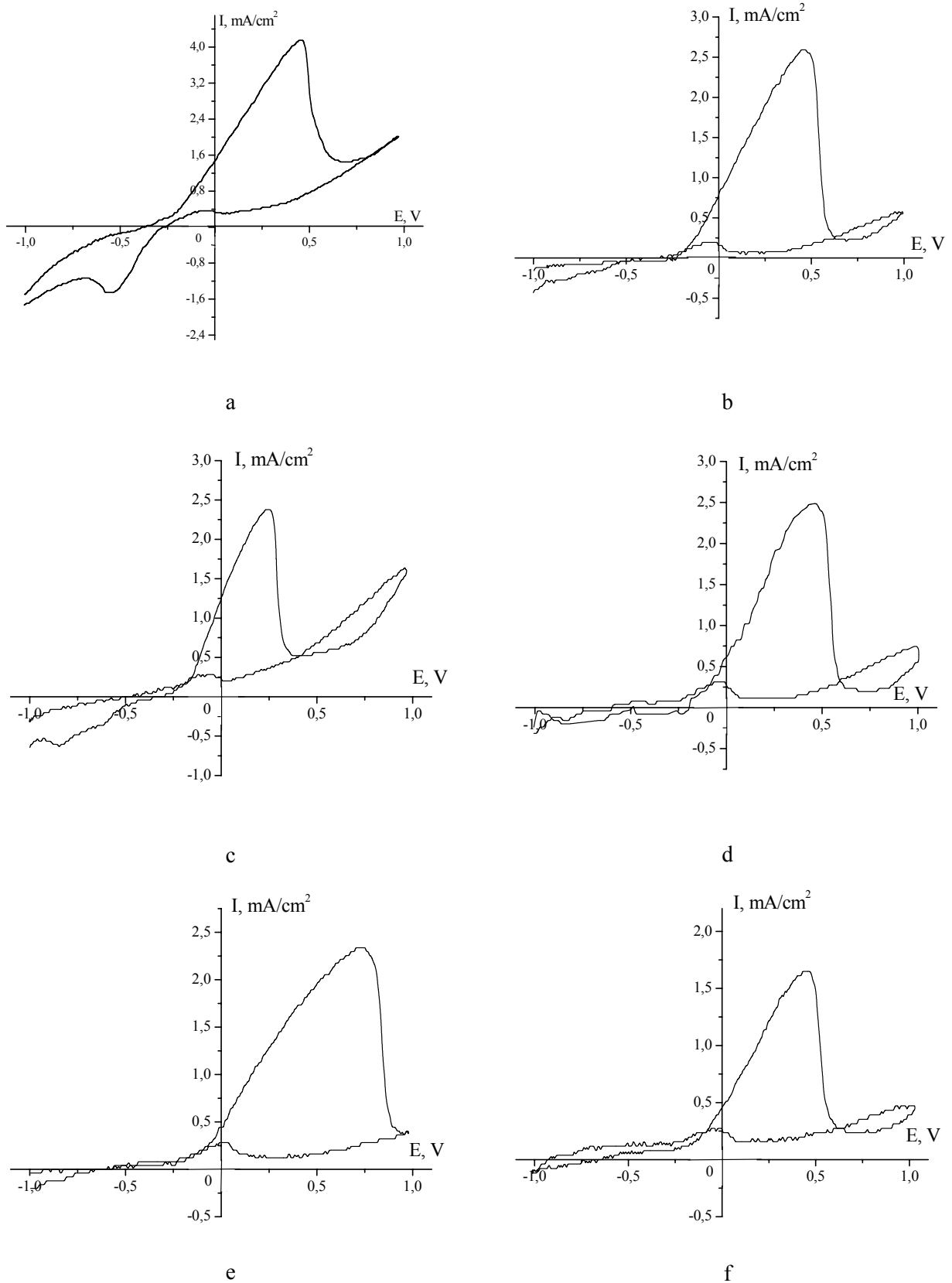
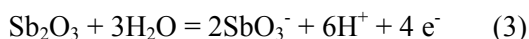


Fig. 1 – Voltammograms of CdSb-electrode in the HCl-NaCl-NaOH electrolytes at pH: 1(a), 3(b), 5(c), 7(d), 9(e) and 11(f).

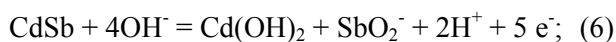
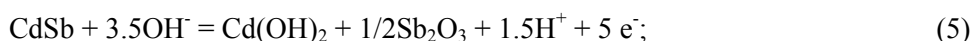
The peak passivation current ( $i_{max}$ ) is further decreasing if the reaction runs in a slightly acidic electrolyte (pH=5), while ionization of CdSb occurs within the potential range  $-0.154 \div 0.245$  V (see Fig. 1 (b)). The reaction of CdSb dissolution (see Eq. (2) above) is allowed thermodynamically under such conditions: the process of the electrode surface passivation starts to substitute the anodic dissolution of CdSb for the potentials ranging between 0.245 and 0.369. There is a 0.105 V wide fragment of the polarization curve lying between 0.369 and 0.474 V, which corresponds to this passive state of the CdSb electrode.

Therefore, based on the polarization experiment results and comparing them with the thermodynamic calculations, one can suppose that the preceding deposition of  $Sb_2O_3$  on the electrode surface can be referred to as the process responsible for its further passivation, while the dissolution of this compound (Eq. (3)) causes a strong raise of the electric current within the repassivation part of the curve:



If the electrolyte is neutral, the process of the electrochemical dissolution of CdSb switches on and manifests itself through a distinctive raise in the passivation current  $i_{max}$  (see Fig. 1 (d)). It can be seen that the area of the active electrode state widened while the passivation ranges became narrower.

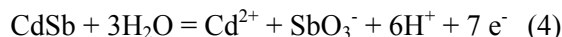
Besides, one can note an increase of the potentials corresponding to the electrode passivation. Therefore, it can be concluded that stoichiomet-



Therefore, the quantitative analysis of the voltammograms (Table 1) proves that the electrochemical behavior of the CdSb electrode is seriously dependent on pH.

The values of the maximal and the passivation current of the polarization curves are decreasing as pH rises, and so does the anodic current hysteresis. The slopes of the voltammetric curves corresponding to the rate of the electrochemical dissolution of CdSb within the active state ranges tend to decrease as pH shifts from acidic to alkaline. At the same time, the dependence of the energy parameters of the voltammetry curves (such

ric dissolution becomes a more influential part of the ionization of CdSb running according to (4):



This assumption can also be confirmed by a decrease of the repassivation currents related to the dissolution of the passivating phase  $Sb_2O_3$  (see above).

The pattern and the quantitative parameters of voltammograms recorded in the alkaline solutions (pH=9) are significantly different (Fig. 1 (e)). First, the active state region becomes wider (it extends between  $-0.065$  and  $0.742$  V). This can be caused by the formation of the surface hydroxo-oxide layer on the CdSb electrode (chemical passivation), occurring at the onset of the CdSb equilibrium potential. Further, the dissolution of this layer runs as a part of the anodic process.

Additional peculiarities can be noted for electrochemical behavior of CdSb electrode in strongly alkaline solutions (pH=11): the maximum of the critical passivation current decreases significantly, the transition state areas become significantly narrower, well notable passive state areas appear on the polarization curve, and the repassivation current values become significantly lower (Fig. 1(f)).

These changes prove a deeper passivation state of the electrode at pH=11. According to thermodynamic calculations, this state can be caused by the following processes resulting in the formation of some poorly soluble compounds on the electrode surface:

as critical passivation potential, passivation, and repassivation potentials) on pH is more complex. All these values are decreasing as pH increases up to pH=5. Then they switch to increasing for the pH range between 5 and 9 and, finally, switch back to decreasing after pH exceeds 9.

A more detailed investigation of the processes running on the interphase semiconductor/electrolyte has been performed through applying anodic polarization of CdSb electrodes dipped in electrolytes with different pH. The applied polarization potentials corresponded to the maximal currents. Then the contents of  $Cd^{2+}$  and  $Sb^{2-}$  ions were determined by AAS in the analytes obtained after such polarization. The results of this determination are given in Table 2.

Table 1

Some quantitative parameters of the voltammograms for the system CdSb electrode/electrolyte (see Fig. 1 (a) to identify the voltammogram's parts: A – peak current corresponding to the beginning of the passivation; B – electrode switches into the state of passivity; BC – passivity area of the electrode)

pH	Voltammogram parameter				
	A		B		BC
	$i_{max}$ , mA	$E_{min}$ , V	$i_{pass}$ , mA	$E_{pass}$ , V	$\Delta E$ , V
1	4.18	0.46	1.52	0.61	0.18
3	2.60	0.46	0.24	0.63	0.14
5	2.38	0.25	0.53	0.37	0.11
7	2.47	0.47	0.23	0.62	0.23
9	2.34	0.74	0.36	0.96	0
11	1.65	0.46	0.28	0.88	0.30

$i_{max}$  – critical passivation current;  $E_{min}$  – critical passivation potential;  $i_{pass}$  – current value for the passive state of the electrode;  $E_{pass}$  – the potential for switching the electrode into passive state;  $\Delta E$  – passive state potentials range.

Table 2

AAS contents of Cd and Sb in the analytes (the volume of all samples was 50 mL)

pH	1	3	5	7	9	11
Cd content, mg	0.856± 0.0075	0.820± 0.0062	0.195± 0.0047	0.178± 0.0051	0.121± 0.0042	0.062± 0.0037
Sb content, mg	0.824± 0.0045	0.398± 0.0051	0.119± 0.0037	0.198± 0.0042	0.140± 0.0047	0.084± 0.0037

Table 3

Results of the polarographic determination of Sb in the analytes at different pH

pH	1	3	5	7	9	11
Sb(III) content, mg	0.203± 0.0096	0.109± 0.0081	0.117± 0.0048	0.141± 0.0064	0.129± 0.0088	0.053± 0.0036
Percentage of Sb(III) in the total Sb content, %	24.6± 1.16	27.5± 2.04	98.3± 4.03	71.2± 3.23	92.1± 6.28	62.5± 4.25

As seen from Table 2, the amounts of Cd and Sb dissolved in the analytes are decreasing as pH rises. Besides, the ratio between both dissolved species is also changing with pH. These data were obtained polarographically and they are shown in Table 3. It should be noted that antimony can be present in the solutions either as Sb(III) or as Sb(V).

As seen from Table 3, there are two maximums for the content of Sb(III) at pH = 5 and pH = 9. Taking into account an experimental error, it can be considered that the entire antimony obtained at the dissolution of CdSb is present at these pH values in the anolyte as Sb(III). However, both Sb(III) and the ions of antimony with a higher oxidation degree can be found in the anolyte at other pH values.

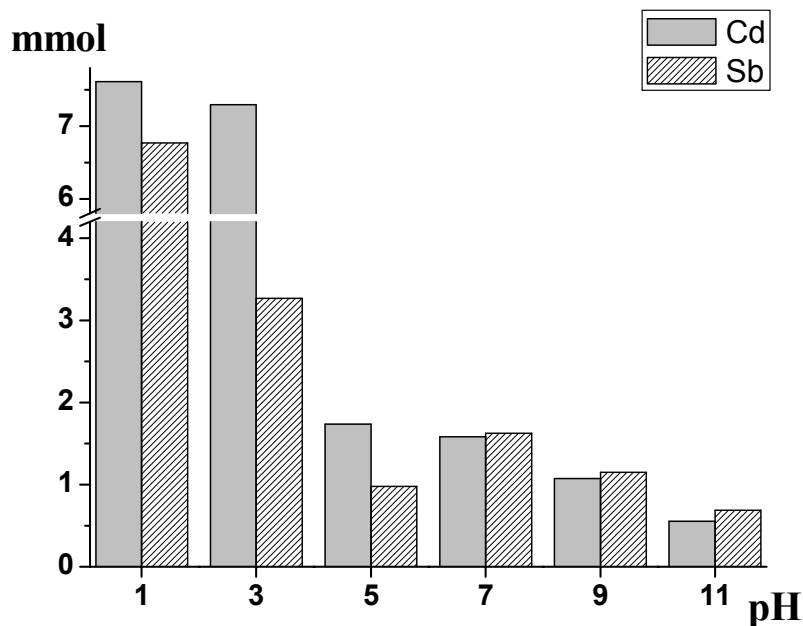
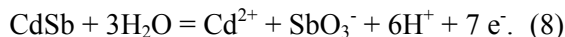


Fig. 2 – Molar contents of Cd and Sb vs pH for the analytes obtained at CdSb dissolution.

The molar contents of Cd and Sb in the analytes vs pH are given in Fig. 2. As seen from that figure, a close-to-stoichiometric ratio between both species can be obtained for the anodic dissolution running either in a neutral or a slightly alkaline solution. Comparing the data of Table 2 and Fig. 1 with the thermodynamic calculations given in<sup>10</sup>, it can be assumed that the process of dissolution runs according to the scheme (8):



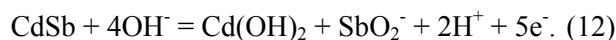
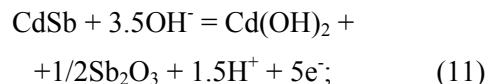
The most active electrochemical dissolution runs at pH=1, and this process forms an amount of Cd ions that is slightly greater than that of Sb. According to the Pourbaix diagram, this reaction should correspond to the scheme (9):



A more preferential (Cd-selective) dissolution of Cd takes place in a weakly acidic solution. This process is controlled by the formation of poorly soluble Sb compounds according to the process (10):



The selectivity coefficients Cd/Sb are, for example, 2.23 and 1.78 for pH=3 and 5 correspondingly. Finally, if the medium is strongly alkaline (pH=11), only a weak anodic dissolution can be registered, and its Sb/Cd selectivity coefficient is 1.25. The corresponding reactions are:



## CONCLUSIONS

It can be concluded that the character of the interphase exchange processes and the semiconductor surface state can be investigated and described using a thermodynamic calculation, voltammetry, and a complex investigation of the interphase boundary. The conditions of the stoichiometric and selective dissolution, and surface passivation of the semiconducting crystals can be outlined, and the detailed mechanism of the processes running during these interactions can be understood using the above approach.

The most intense and almost stoichiometric dissolution of the semiconductor takes place under the anodic polarization in strongly acidic solutions (pH=1; E=0.46 V). As pH increases to pH=3 at stable polarization, the rate of dissolution of Sb decreases almost twice, while the rate of dissolution of Cd stays almost unchanged. Further increase of pH results in a significant deceleration of the dissolution of both components due to the formation of some poorly soluble compounds on the semiconductor surface.

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