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L.N. VILINSKAYA, G.M. BURLAK

The Odessa State Academy of Building and Architecture 4, Didrichson str., Odessa, 65082 Ukraine, ph. 8 (048) 7-206-743

SENSORS ON THE BASIS OF ALUMINIUM METAL-OXIDE FILMS

Aluminum metal-oxide films sensitivity to water solutions of inorganic compounds, the ammonia dissolved in water and in a gas atmosphere, and also to water vapours is established. The possibility of sensors on a basis of metal-oxide films creation is shown.

The influence of hydrogen peroxide dissolved in water solutions concentration upon intensity of a luminescence of aluminium metal-oxide films dipped in these solutions is established earlier [1]. Because of the fact that aluminium metal-oxide films are structures with high catalytic activity surface it is possible the using these films as environment composition sensors.

In [2] the presence of a series of thermostimulated luminescence (TSL) maxima, thermostimulated exoelectronic emission (TSEE) are shown and also the occurrence of potential difference between electrodes of $Al\text{-}Al_2O_3\text{-}SnO_2$ structure [3] for aluminium metal-oxide films which adsorbed only water or water vapours was observed. It indicates the sensitivity of investigated structures to a level of humidity, and, obviously, is caused by surface metal-oxide states. In this connection it was interest to continue studying of influence of chemical processing upon aluminium metal-oxide films in water solutions of various compounds on intensity of an arising luminescence. With this purpose it is advisable to study TSL spectra. Besides it was of interest also to find out the influence of other substances dissolved in water solutions, on intensity of aluminium metal-oxide films luminescence dipped into these solutions.

In this work samples which were films on aluminium foil of the technical cleanliness, received by an electrochemical method in a water solution of sorrel acids [3] were investigated. Curves TSL were measured on the plant consisting of the lightproof box, the filter absorbing IR-radiation, photoelectronic multiplier, small currents measuring device, copper-constantan thermocouples, recorder. Heating speed was maintained constant and was 0,3 К/с.

It is known [2], that in the temperature interval from room up to 600 K in TSL spectra of oxide aluminium films some maxima are observed. They correspond to various forms adsorbate and adsorbent binding. We have established, that owing to processing aluminium metal-oxide in water solutions of some inorganic compounds additional TSL bands appear and thous which existed earlier quench. Chemical processing was carried out by boiling in Na_2SO_4, NaCl, NaI 0,1 N water solutions.

In fig. 1 TSL curves of Al_2O_3 films in the temperature interval from 450 up to 630 K, processed in: 1 - water, 2 - NaCl, 3 - Na_2SO_4, 4 – NaI are presented. Just those centres that are responsible for TSL in this temperature interval are not deactivated by sodium ions which were contained in all compounds we used. From fig. 1 it is seen, that the maximum at 560 K is observed in all samples, therefore it, obviously, is connected with dissociative water adsorption which also was available in all cases.

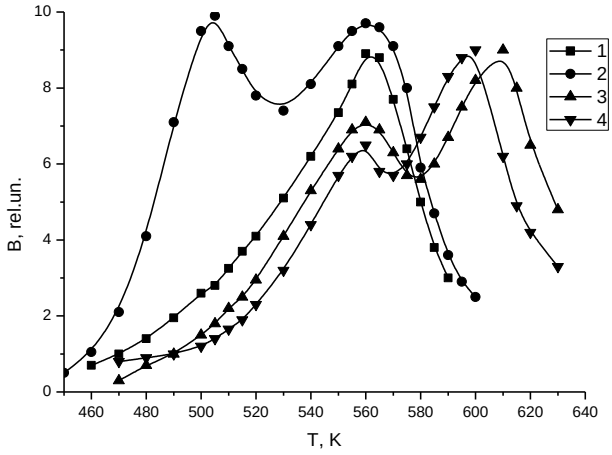

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Fig. 1. TSL curves of Al_2O_3 films processed in: 1 - water, 2 - NaCl, 3 - Na_2SO_4, 4 - NaI.

The observed catalytic activity increase develop in the fact that after processing in sodium chloride for effective lightsum storage it is necessary for a sample not hours, and minutes. It can be explained by the fact that chlorine ions in a small amount increase catalytic activity of aluminium metal-oxide surface. Chlorine strongly binds with valency and coordinated nonsaturated aluminium atoms. While samples are in the air the dissociative adsorption of water and its vapour appear with creation of doped charged OH^- complexes which carry out a role of adsorptive nature traps. This

process occurs quickly enough. As the power distance between the levels created by hydroxyl and chlorine ions on a surface is very little approximately 0,06 eV [3] a part of carriers already at room temperature pass to chlorine levels and then are thermally release in the conduction bend. As to others anions which were used they do not change surface catalytic activity, therefore enough quantity charged hydroxyl groups have no time to be created.

The influence of ammonia concentration dissolved in water solutions (in particular, sea water) on the intensity of aluminium metal-oxide films luminescence, dipped in these solutions has been studied. Intensity of a luminescence was weak. Thus the alternating voltage of about 1,3 V, were applied providing electrolyte ions to the semiconductor surface but insufficient for electroluminescence excitation. Preliminary the intensity aluminium metal-oxide films luminescence in NaCl 3 % solution was determined. After that concentration of ammonia in this electrolyte was created. Luminescence intensity changes were measured. The addition of the few doses of ammonia increased aluminium metal-oxide films emission intensity (Fig.2). The sensors sensitivity depends on technology metal-oxide films preparation and temperature. The sensors were investigated in a temperature interval 278-354 K. The threshold of detecting is maximal in temperature interval 288-302 K. These results allow us to create sensors for measurement ammonia concentration in water solutions operating in temperature range 278-353 K.

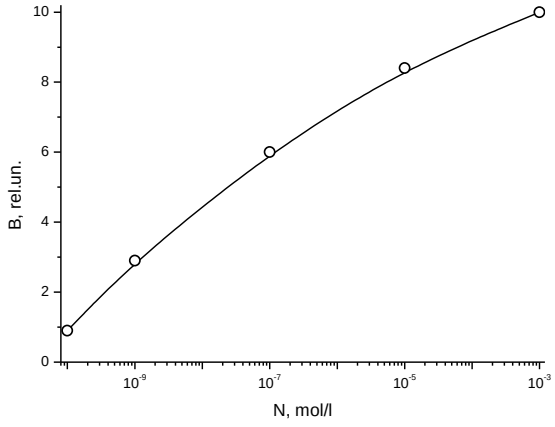

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Fig. 2. Dependence aluminium metal-oxide films luminescence intensity on concentration of ammonia dissolved in water.

The influence water vapour and ammonia concentration in a gas atmosphere on value EMF generated by structures $Al\text{-}Al_2O_3\text{-}SnO_2$ was studied. Such structures so are created by electrochemical oxiding of aluminium foil in water solution of sorrel acid with the following deposit SnO_2 layer on oxide film by pyrolysis method of $SnCl_4$. It is established, that the appearance of EMF occurs in following way. Since SnO_2 layers are porous penetration of adsorbed molecules of water or ammonia from a gas atmosphere in micropores of oxide film is possible. The aluminium metal-oxide surface is catalytically active and consequently adsorbed molecules dissociation takes place. Dissociation products (positive and negative charged ions and electrons) get space separation along the film thickness because the difference in their diffusion coefficients. The space separation continues until an internal electric field will arise and balance the diffusion products flow of dissociation products. As a result potential difference between aluminium and SnO_2 electrode arises. The value of this potential difference depends on ammonia concentration in a gas atmosphere. Detection threshold of these sensors is 0,1 g/m^3 .

Thus, aluminium metal-oxide films can be used for creation of ammonia sensors in a gas atmosphere, in water ammonia solutions and some inorganic substances.

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Л.Н. ВИЛИНСКАЯ, Г.М. БУРЛАК

СЕНСОРЫ НА ОСНОВЕ ПЛЕНОК ОКСИДА АЛЮМИНИЯ

Установлена чувствительность оксидных пленок алюминия к водным растворам неорганических соединений, аммиака, растворенного в воде и в газовой атмосфере, а также к парам воды. Показана возможность создания сенсоров на основе оксидных пленок.

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СЕНСОРИ НА ОСНОВІ ПЛІВОК ОКСИДУ АЛЮМІНІЮ

Встановлено чутливість оксидних плівок алюмінію до водяних розчинів неорганічних сполук, аміаку, розчиненого у воді та у газовій атмосфері, а також до водяної пари . Показано можливість створення сенсорів на основі оксидних плівок.

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