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Changing the properties of indium tin oxide by introducing aluminum cations

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ABSTRACT

The properties of the semiconductor material indium tin oxide (ITO) have been studied. A technique allowing the properties of ITO to be changed by introducing aluminum cations into the structure during cyclic voltammetry has been developed. Changes in transparency, conductivity, and band gap were measured during the course of the experiment. It was shown that these ITO properties can be significantly improved by changes in chemical composition.

1. Introduction

There is much research interest in complex thin-film oxides based on indium and tin (ITO) due to their applications in optoelectronics, photovoltaic devices, solar cells and biological systems. They are also used in flat panel displays, for thermal protection, and in electrodes.

Indium tin oxide is a highly degenerate n-type semiconductor with a large band-gap of around 4 eV [1]. Under certain conditions, it can exhibit p-type conductivity [2]. ITO is a solid solution of indium oxide and tin oxide, typically 90% In_2O_3 and 10% SnO_2 by weight. Indium tin oxide is one of the most common transparent conductive oxides, with high electrical conductivity and optical transparency. It also has low resistivity ($<10^{-4}$ Ω/cm), mechanical hardness and chemical inertness [3]. The drawback of indium tin oxide is its cost. Another transparent conductive oxide is zinc oxide (ZnO); this is less expensive and, therefore, more widely used [4].

Methods for improving the properties of ITO films and multicomponent ITO have been studied [5–7]. There are a number of articles dedicated to changing ITO properties by doping with different metals: Ga, Zr, V, Fe, and Zn [8–12]. It has been found that ITO films doped with a small amount of foreign metal not only maintain the basic properties of ITO films but that some of these properties can be improved. Thus the objective of this research is to study the possibility of changing the properties of indium tin oxide by introducing aluminum cations into its structure, and searching for the optimal experimental parameters which allow improvement of the electrical conductivity and reduction in band gap, while maintaining the initial properties of the ITO.

2. Experimental

2.1. Cyclic voltammetry

Cyclic voltammetry was carried out using electrochemical workstation CHI660C in a three-electrode cell. The process was conducted in a potentiodynamic mode with anodic polarization using a platinum wire counter electrode and saturated calomel reference. Indium tin oxide (ITO-coated two surfaces silicon dioxide) with a resistance 9.5 Ω/sq was used as a working electrode. The area of 0.5 × 2 cm^2 was exposed to the electrolyte. The scan rate was 0.05 V/s and sensitivity 0.001 A/V.

Before cyclic voltammetry, ITO samples were cleaned ultrasonically in acetone, ethanol and ethan, and then rinsed in distilled water. Crystalline aluminum chloride solution ($AlCl_3 \cdot 6H_2O$) was used as electrolyte; it contains 0.005 mol/L $AlCl_3$ and 0.1 mol/L KCl. Potassium chloride was in solution as a supporting electrolyte in order to reduce solution ohmic resistance [13]. Afterwards, the samples were immediately removed from the solution, washed thoroughly with distilled water and blow-dried with N_2 flow.

2.2. X-ray photoelectron spectroscopy

Sample analysis was carried out using an XPS spectrometer "AXIS Ultra DLD XPS" from Kratos Analytical Company, Japan. Depth profiling

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was conducted to obtain information about the depth of aluminum cations introduced into ITO thin films. Measurements were carried out for each sample: without removing the top layer (without etching) and with a consecutive etching of 2, 4, 6, 8, 10, 20, and 30 nm.

2.3. X-ray powder diffraction

The X-ray powder diffractometer X'pert Pro (PANalytical Ltd.) was used. The measuring range of 10–80° (2θ) using CuKa radiation was chosen since according to [14] a number of peaks for In_2O_3 are located in the region of 70°.

2.4. Surface morphology study (Scanning electron microscopy, Atomic force microscopy)

Analysis of the samples morphology was carried out using Scanning electron microscope — JIB-4500 Multibeam (Jeol, Japan) and Atomic force microscope — Solver P24H (NT-MDT, Russian Federation).

2.5. Ultraviolet/visible Fourier spectroscopy

Samples analysis was carried out using Fourier spectrometer UV/VIS/NIR Lambda 900 (Perkin Elmer) with Fourier quartz cell. During the research, absorption and transmission spectra in the wavelength range of 200–1000 nm were taken. Five measurements were conducted for each spectrum: initial sample of ITO, initial sample of ITO in KCl solution, and ITO samples after 5, 10, and 30 cycles.

2.6. Electroconductivity changing

Measurements were carried out by means of the Hall Effect measurement system (HL5500PC) at room temperature. Resistance measurements were conducted by Van der Pauw method [14].

3. Results and discussion

The influence of chlorides of the following metals (Al, Li, Na, Cs, Rb, Ga and Zn) on various ITO properties during cyclic voltammetry was studied. It was found that using the chlorides of aluminum, lithium, rubidium, cesium, and zinc, the ITO samples start slightly changing their color and high anodic peaks corresponding to −0.3 V potential on the voltammetric curves were observed (Fig. 1A). It was revealed that cations of these metals can incorporate into the lattice structure of indium tin oxide, partially substituting indium and tin at the galvanic potential from −0.1 to −0.9 V. This effect is most pronounced if crystalline aluminum chloride ($AlCl_3 \cdot 6H_2O$) is used as electrolytic solution.

Table 1
Initial sample of ITO.

Etch time, nm	Atomic concentration, %					
	O	Sn	In	K	Cl	Al
0	34.08	4.53	18.04	0	0.11	0
2	52.05	4.63	43.26	0.07	0	0
4	50.92	4.3	43.27	0.18	0	0
6	51.96	4.35	42.91	0	0.08	0
8	52.63	3.9	43.03	0.03	0	0
10	51.65	3.75	42.66	0	0	0
20	52.47	3.06	44.29	0	0.08	0
30	51.59	2.73	43.59	0.11	0	0

To confirm that, within the limits of the specified potential, substitution of indium and tin by aluminum take place rather than other side processes, additional experiments using a platinum working electrode instead of an indium-tin oxide one were conducted. The electrode of "CH Instruments, Inc." with "CHI 102" product number was used. The diameter of the working electrode surface was 2 mm. No peaks were detected during cyclic voltammetry (Fig. 1B).

The analysis of the results shows that during cyclic voltammetry the process of cathodic introduction of aluminum cations into ITO structure occurs. Among the main reactions occurring in the electrochemical cell, we can define the following:

$$In_2O_3 + 2Al^{3+} + 6e \rightarrow Al_2O_3 + In^0 \quad (1)$$

$$3SnO_2 + 4Al^{3+} + 12e \rightarrow 2Al_2O_3 + Sn^0. \quad (2)$$

Indium and tin formed by reactions (1) and (2) are probably deposited on the working electrode surface. As indium and tin are less electronegative than aluminum and potassium, their chemical dissolution in the electrolyte is unlikely.

To determine the quantity of aluminum moving into the indium tin oxide structure, samples were analyzed by X-ray photoelectron spectroscopy (XPS). The measurement results show that the atomic concentration of indium and tin decreases, while the atomic concentration of aluminum increases. In the initial sample of ITO aluminum was lacking. It was found that the amount of aluminum passing into the indium tin oxide depends on the duration of the electrochemical reaction, i.e. the number of voltammetry cycles.

Tables 1 and 2 give the atomic concentration of elements in the initial sample of ITO and the in ITO sample after 30 cycles.

It was revealed that aluminum cations penetrate into almost the entire depth of the indium tin oxide. The thickness of thin film is 200 nm but the depth where aluminum disappears is 180 nm.

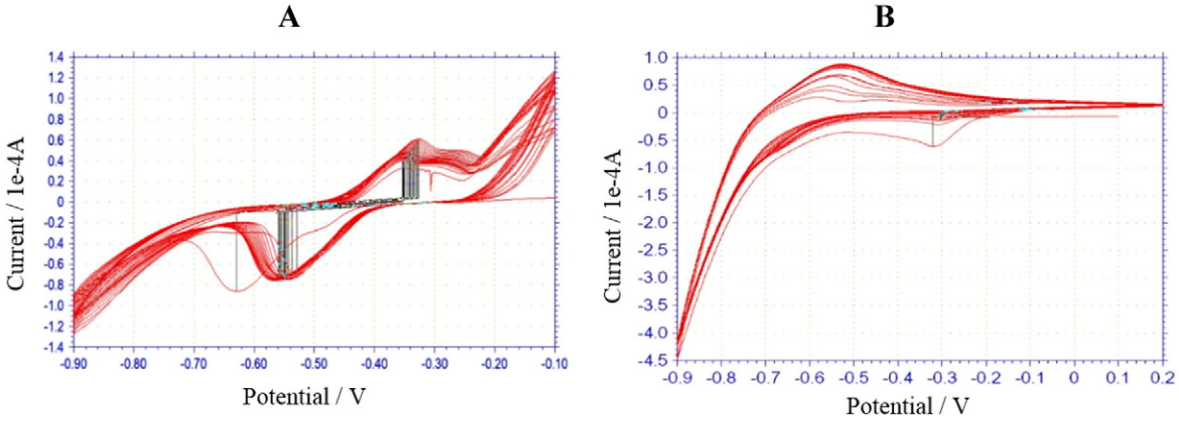

Fig. 1. Voltammetric curves obtained in a solution containing 0.005 mol/L $AlCl_3$ and 0.1 mol/L KCl (A — on ITO electrode; B — on platinum electrode).