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Application of DC Magnetron Sputtering for Creation of Gas-Sensitive Indium Oxide Thin Films and Their Properties

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In this paper the technology of gas sensitive semiconductor structures based on indium oxide thin films by DC magnetron sputtering of indium with the subsequent thermal oxidation is developed. Structure, surface morphology and chemical composition of the obtained films have been investigated by electron diffraction, scanning electron microscopy, Auger electron spectroscopy, and X-ray photoelectron spectroscopy. Conditions of In_2O_3 films formation with high selectivity and sensitivity to NO_2, and NH_3 are established.

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1. Introduction

At present time thin indium oxide films are widely applied to formation of transparent coverings, heterogeneous catalysts, IR-reflectors, monochromators, solar cells, photoelectrochemical electrodes, MOS-structures, heterojunctions, etc.

The use of indium oxide as a gas-sensitive material is restrained by high "quasimetallic" conductivity and low selectivity. In view of an opportunity of sensitivity and selectivity increase by modification of chemical composition and structure, the interest in In_2O_3 films has recently increased.

2. Experimental details and results

Thin In_2O_3 films have been obtained by thermal oxidation of thin indium films, formed by the DC magnetron sputtering method. Deposition of indium films was carried out in the vacuum universal system VUP-5M. As an etchant gas there was used argon, with a pressure of ≈ 0.1–1 Pa in the process of sputtering. The analytical grade indium metal target was used as the cathode. The target sputtering was carried out at an accelerating voltage of 0.5 kV; the discharge current was 0.15 A. The indium films were deposited on single-crystal silicon wafers coated with dielectric layer SiO_2, Al_2O_3, or muscovite mica $KNa_3Al_3Si_3O_{12}$. After the deposition of metallic indium the films were oxidized in a muffle electric furnace in the non-isothermal regime: heating to a temperature of 500–600 °C for 40–60 min and annealing in isothermal mode at 500 °C and 600 °C for 60 min (temperature and oxidation time were chosen experimentally).

The film technology based on the method of thermal oxidation of a metal layer allows forming oxide layers with thickness from several nanometers to several hundred nanometers. A gas-sensitive layer thickness is the important factor determining metrological characteristics of sensors as with the decrease of a film thickness sensitivity and speed response of a sensor element increase. In this work the In_2O_3 films, 30–50 nm thick were investigated. The use of various conditions and temperature modes of oxidation allows to change structure, stoichiometry and composition of films and, as a consequence, its electrophysical and sensor properties.

Oxidation of metallic indium films was investigated by measuring the change in resistivity of the films in the process of their oxidation during heating in an oven at a temperature from 25 to 500 °C and annealing at 500 °C for 60 min. The resistance of the film was measured using a two-probe method with direct current. Electrical contact with the film was made by means of thin film platinum electrodes and clamping of electrodes made of titanium coated with platinum. The film resistance was measured with the reference voltage of 0.1 V. The current in the circuit was measured by the microammeter. The temperature value in the furnace was controlled by a chromel-alumel thermocouple, the working junction of which was placed in close proximity to the oxidized film.

The kinetic dependences of the temperature changes and resistivity of indium films in the process of oxidation are shown in Fig. 1. For heating there was used an electric resistance furnace of industrial production with automatic temperature regulation; one of the standard rates was chosen to achieve the desired temperature. As shown in Fig. 1, there is a gradual resistivity decrease from 0.0037 Ω cm (for the metallic indium film) to 0.00018 Ω cm at temperatures up to 310 °C. On heating the film in the temperature range 310–400 °C there is a slight increase in resistivity. Above $t = 400$ °C the resistivity increases faster with the dependence of resistance on temperature close to quadratic. After reaching a temperature of 500 °C and the transition to the isothermal regime resistivity increase is almost linear for 10–15 min, after which the growth rate of resistance begins to decrease. Exposure at 500 °C for 50–60 min leads to stabilization of film electrical resistance (Fig. 1). This fact gives an indirect indication of the completion of the film

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oxidation process at a given temperature. As the operating temperature of the sensitive layers of semiconductor sensors based on adsorption-type indium oxide does not exceed 500 °C (mostly 200–400 °C), we can assume the thermal stability of the films in the subsequent operation.

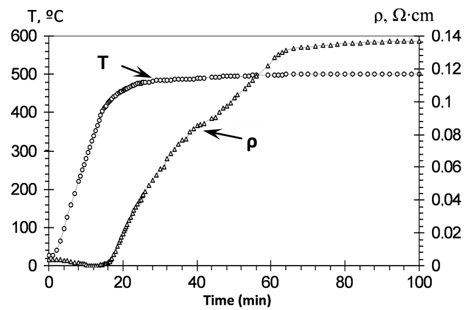
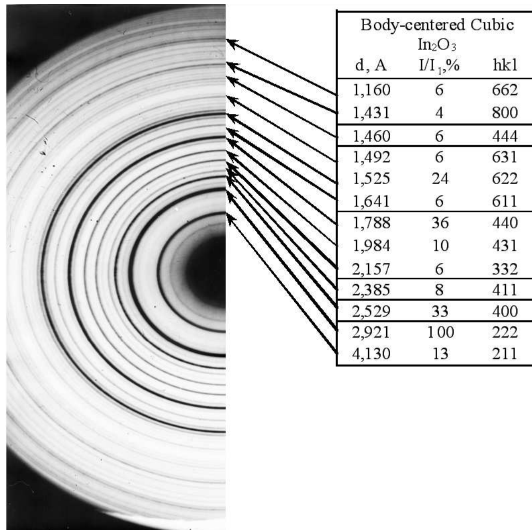


Fig. 1. Temperature and resistivity changes of a thin indium film during its thermal oxidation.

The phase structure and morphology of surface have been investigated by the electron diffraction methods using TEM H-800 (Hitachi) and SEM S-806. Analysis of electron diffraction patterns shows that the only identifiable crystal phase in the process of oxidation and in the oxide films is a cubic phase with a polycrystalline structure of In_2O_3 (Fig. 2).



Body-centered Cubic In_2O_3		
d, A	I/I$_1$,%	hkl
1,160	6	662
1,431	4	800
1,460	6	444
1,492	6	631
1,525	24	622
1,641	6	611
1,788	36	440
1,984	10	431
2,157	6	332
2,385	8	411
2,529	33	400
2,921	100	222
4,130	13	211

Fig. 2. Electron diffractogram of In_2O_3 films.

The indium films deposited on silicon are characterized by the pronounced grain structure (Fig. 3) with a particle size ranging from 10 to 70 nm, the bulk (80%) accounting for the interval from 15 to 50 nm (Fig. 4a). Formation of oxide film on the silicon substrate is accompanied by a decrease in the amount of fine particles and the increased content of particles of larger size, the bulk of which (≈ 80%) is in the range of 20–55 nm, with the maximum in the range of 30–35 nm (Fig. 4b).

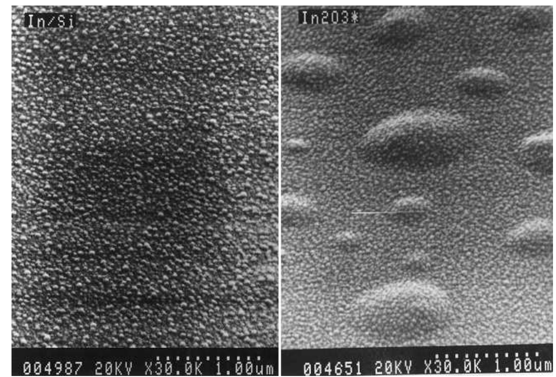


Fig. 3. SEM images of indium and indium oxide films (magnification is 30,000).

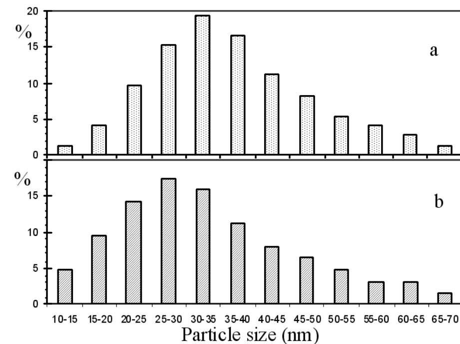


Fig. 4. Particle size distribution in indium (a) and indium oxide (b) films.

The elemental composition of In_2O_3 films surface has been studied by the Auger electron spectroscopy using the AES spectrometer PHI-660 (Perkin Elmer). Electron shells of atoms were excited by the primary electron beam with the 2000 eV energy. Locality in the depth analysis is ≈ 3 nm, scan area ≈ 1 mm^2. The depth distribution of the film composition is investigated by 3.5 keV Ar-ions sputtering with the registration of the Auger electrons $KL_{23}L_{23}$ — transition for oxygen and $M_4N_{45}N_{45}$ — transition for indium. The quantitative analysis is performed by the pure standards method, by which the Auger electron current intensity is adjusted by a factor related to the Auger spectrometer sensitivity.

The elemental composition profiles of the In_2O_3 film thickness on the Si substrate are presented in Fig. 5. The indium and oxygen distribution in the film thickness is uneven. The stoichiometry coefficient in the surface layer defined by the escape depth of the Auger electrons ≈ 5 nm is 1.41. With the surface sputtering to a depth of 5–10 nm the stoichiometric ratio is 1.31.

The chemical composition and state of the In_2O_3 film surface elements are investigated by X-ray photoelectron spectroscopy (XPS). XPS spectra were recorded with a multipurpose electron spectrometer PHI 5700 (Perkin Elmer). Chemical status of indium and oxygen was determined by the binding energies of the photoelectron lines of In $3d_{5/2}$, In $3d_{3/2}$ and O $1s$ (Fig. 6).

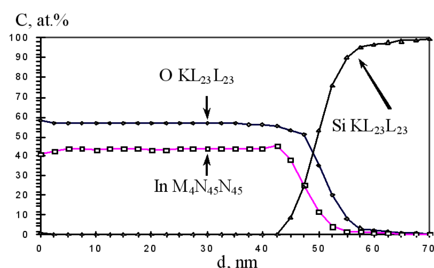


Fig. 5. AES profile of elements distribution in In_2O_3 films deposited on silicon.

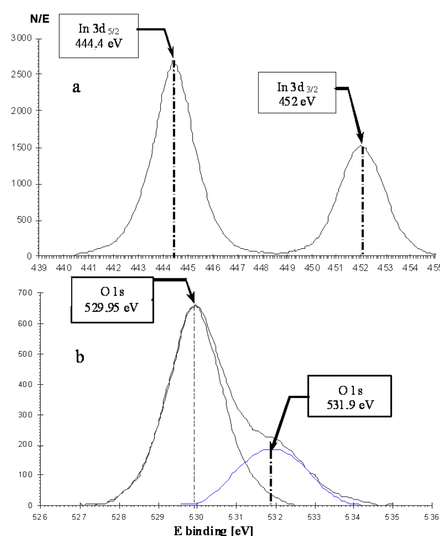


Fig. 6. XPS spectra of indium (a) and oxygen (b) on the surface of In_2O_3 films.

XPS spectrum of indium is characterized by the presence of two spectral lines with the binding energies of 444.4 and 452 eV (Fig. 6a), due to multiplet splitting of the 3d level. The chemical shift of the line In $3d_{5/2}$ in the oxide film relative to the In^0 (reference data for the average binding energy of 443.5 eV) is 0.9 eV, which can be attributed to the state of In^{3+} (change in the binding energy of the oxidation of In, In_2O_3, based on the reference data, is +0.8–1.2 eV).

The oxygen photoelectron line is shown in Fig. 6b. Oxygen peak has a pronounced asymmetry, indicating the presence of overlapping components that differ in energy, shape and intensity, with the binding energies of 529.95 eV and 531.9 eV. The photoelectron line with $E_{\mathrm{b}} = 529.95$ eV has higher intensity and corresponds to the oxygen lattice state (reference data for the average O^{2-} binding energy in the In_2O_3 compound is 530 eV, and varies from 529.1 to 530.9 eV). The broad envelope of the photoelectron O 1s lines in the range 531–534.5 eV is associated with a sufficiently large number of oxygen and its compounds adsorbed on the surface. The photoelectron line with a binding energy of 531.9 eV may correspond to the surface adsorbed oxygen in various forms, as well as to the oxygen incorporated in a hydroxyl group. In addition, the surface of the In_2O_3 film contained a small amount of chemisorbed water, which may indicate a small plateau of the total XPS-peak, protruding above the background of the binding energies of 533–534 eV, but the concentration is negligible.

Calculation of the indium–oxygen stoichiometric ratio depending on the intensities of photoelectron lines and the relative photoionization cross-sections (S(In $3d_{5/2}$) = 13.2; S(O 1s) = 2.85) shows that the stoichiometric ratio of elements is 1.13. The stoichiometric ratio, calculated from the total intensity of the two photoelectron lines of oxygen ($\sum I\mathrm{O}1s = 840$) is 1.45, which agrees with the value obtained by the AES. The ratio of the intensity of the O 1s binding energy 531.9 eV to the total intensity of the two oxygen photoelectron lines, shows that $\approx 22\%$ oxygen in the surface layer of the In_2O_3 film is in the adsorbed state, or incorporated into the hydroxyl groups.

Gas sensitive properties of indium oxide sensor element have been investigated with respect to ammonia and nitrogen dioxide. The In_2O_3 films obtained by oxidation at 500 °C for 1 h, showed a high sensitivity of the thermo-EMF in the detection of low concentrations of ammonia. The impact on the sensor with air mixture containing ammonia, results in the increasing thermoelectric power value at a constant temperature difference between the contacts. Studies of sensor properties of these films in the detection of low concentrations of NO_2 showed no significant sensitivity of the thermo-EMF to the content of NO_2 in air. As shown by the electrophysical properties of the In_2O_3 films, obtained by different modes of oxidation, the increase in temperature oxidation of the In films from 500 to 600 °C leads to an increase in films resistivity, the Seebeck coefficient and sensitivity to NO_2 [1, 2].

3. Conclusion

The process of indium oxide films formation was studied by measuring the resistivity of indium films in the process of oxidation. The structure and chemical composition of the obtained films were investigated using the methods of electron diffraction, scanning electron microscopy, Auger electron and X-ray photoelectron spectroscopy. The vacuum technology of thin indium oxide films formation with thermoelectric parameters, sensitive to the composition of the environment, by magnetron sputtering metal source, followed by thermal oxidation is developed. The obtained results can be used in microelectronic sensor analyzers.

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