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Deposition of the low resistive ITO-films by means of reactive magnetron sputtering of the In/Sn target on the cold substrate

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Abstract. Detailed information on the deposition technology of the low-resistive ITO-films in oxygen-containing media by magnetron reactive sputtering from the In(90%)/Sn(10%) target on the cold substrate is given. Developed technology allows deposition ITO-films with sheet resistance 2-3 Ω/□, transparency higher than 90%. Developed technology is notable for high reproducibility of results and is compatible with production technology of semiconductor devices of optoelectronics.

1. Introduction

Up-to-date electronics is substantially defined by the properties of low-dimensional semiconductor materials. At the present time a lot of research groups report about prospect researches of semiconductor transparent oxides, such as In_2O_3, ZnO, SnO_2, CdO, Ga_2O_3, TiO_2 and more complex double oxides and tertiary oxides [1-3]. Transition metal oxides in contrast with metals and semiconductors have broader spectrum of possible physical states and properties. Control of electron flow and light flux in semiconductor heterostructures, researched by J. Alferov, led to semiconductor revolution of the XX century. So, the next breakthrough in new functional materials is connected with control of electron flows and magnetism in low-dimensional heterostructures made of transition metal oxides [2].

There is no doubt that one of the most demand materials of such category is indium oxide films doped with tin (indium tin oxide, ITO), which found wide application as transparent electrodes in different devices [2, 4].

This paper is concerned with development of the technology of deposition of the low resistive ITO-films by means of reactive magnetron sputtering of the In(90%)/Sn(10%) metal target on the cold substrate with post-annealing.

2. Results and discussion

Magnetron sputtering of ITO-films was worked through and described in [6]. This technology provides value of sheet resistance as 10 Ω/□ with value of transparency 87% and implies sputtering of the metal target in the oxide-containing media, condensation of the oxidized atoms of tin and indium on the heated up to 200-250^o C substrate, with post-annealing during 30-40 minutes at the temperature of 250^o C.

There is need in industry to deposit such ITO-films with sheet resistance that is 10 Ω/□ on the cold substrate, since a lot of plants for magnetron sputtering do not have heating devices for substrate's heating. Furthermore, deposition of the low-resistive ITO-films is connected with its posterior integration to the technology of planar LED production, which implies deposition of ITO-films on the reverse mask of photoresist (explosive photolithography).

Features of ITO-films' deposition are described well in papers [6-7]. Main conclusion of these papers is that during ITO-films' deposition on the cold substrate the process of oxidation is nearly stopped on the substrate. Thus tolerance to the lack of oxygen is sufficiently smaller than the same deposition on the hot substrate. Content of oxygen in gas mixture should be sufficient for oxidation of all metal atoms to the moment of its condensation in the structural film grid. So, there is strong dependence between partial pressure of the oxygen in the chamber and film growth rate. Hence, the consequence of deposition technology of ITO-films on the cold substrate is the next.

2.1. Experiment I – "Measurement of ITO-film deposition rate"

Dependence between partial pressure of the oxygen in the chamber and film growth rate needs optimal film growth rate which is in the range of 2 – 3.5 Å/s [5-7]. Test samples were obtained by magnetron sputtering of metal target In/Sn in the gas mixture of Ar(50%)/O_2(50%) with different values of the discharge current (0.2 A; 0.3 A; 0.4 A) during the equal time (10 minutes). Distance from target to sample was 10 cm. Samples were made of glass ceramics. Thickness of the films was measured by means of interference microscope MII-4M. Results of the experiment are shown in the table 1.

Table 1. Measurement of the deposition rate of ITO-films.

Mode 1: discharge current – 0.2 A; deposition time - 10 minutes. Measured sputtering rate - 1Å/s	
• Before annealing: ρ_S =80 mΩ/□ d=0.06 μm Etching time in the cold HCl – 1.5 minutes	• After annealing in the N_2 media (450˚C, 25 minutes): ρ_S=40 kΩ/□ d=0.057 μm Etching time in the cold HCl - 3 minutes
Mode 2: discharge current – 0.3 A; deposition time - 10 minutes. Measured sputtering rate – 1.9 Å/s	
• Before annealing: ρ_S =100 mΩ/□ d=0.11 μm Etching time in the cold HCl – 1.5 minutes	• After annealing in the N_2 media (450˚C, 25 minutes): ρ_S =34 kΩ/□ d=0.09 μm Etching time in the cold HCl - 4 minutes
Mode 3: discharge current – 0.4 A; deposition time - 10 minutes. Measured sputtering rate 2.5 Å/s	
• Before annealing: ρ_S =100 mΩ/□ d=0.11 μm Etching time in the cold HCl – 3.5 minutes	• After annealing in the N_2 media (450˚C, 25 minutes): ρ_S =26 kΩ/□ d=0.1 μm Etching time in the cold HCl - 8 minutes

Conducted experiment shows that structure of films with deposition rate higher than 2 Å/s is denser. That is proved by the time of films' etching – dense film needs more time for etching. Post-annealing make the film structure even denser.

Melting temperature of In/Sn alloy is relatively small, so optimal mode for ITO-films deposition was chosen to avoid target's melting: discharge current – 0.3 A; deposition time – 12 minutes. Approximate film thickness was 130 nm.

2.2. Experiment II "Determination of the optimal Ar/O_2 ratio in the operating media"

Range of oxygen percentage in the gas mixture is 10-50% [5-6]. It should be noted that optimal Ar/O_2 ratio in the gas mixture can vary from plant to plant due to different vacuum pumping systems and discharge power of the magnetrons sputtering system.

Determination of the optimal ratio of the partial pressures was made as follows. Series of experiments with optimal operating mode (discharge current 0.3 A; deposition time – 12 minutes) was made. Oxygen content was gradually reduced in series from 50 % by 3-5 % from deposition to deposition, until unoxidized atoms of Sn and In appeared in the growing film, i.e. transparent samples became brown colored. Conductivity and transparency of such films can be improved by annealing in the oxygen-containing media. In such annealing the structural grid of ITO-film is rebuild and not fully oxidized oxides become fully oxidized with simultaneous generation of oxygen vacancies.

Conductivity of the fully oxidized ITO-films can be improved by annealing in the vacuum or in the nitrogen media. This process is caused by diffusion of oxygen atoms, embedded in the crystal lattice or grain boundary from the volume of film during high-temperature annealing. Generated oxygen vacancies act like donor for electrons thus increasing electron concentration. So, annealing decrease sheet resistance both by increase in the concentration of electrons and by growth of their mobility.

Results of the conducted experiment of determination of the optimal Ar/O_2 ratio in the gas mixture are shown in the table 2.

Table 2. Determination of the optimal Ar/O_2 ratio in the gas mixture.

Mode 1: discharge current 0.3 A; deposition time - 12 minutes. Oxygen content - 16%. Films are not fully oxidized (black color).	
• Annealing in the N_2 (450˚C; minutes): ρ_S =2.8 Ω/□ black colored films	• Annealing in the air (450˚C; 25 minutes): ρ_S =7 Ω/□ brown colored films
Mode 2: discharge current 0.3 A; deposition time - 12 minutes. Oxygen content - 25%. Films are not fully oxidized (brown color).	
• Annealing in the N_2 (450˚C; minutes): ρ_S =14 Ω/□ brown colored films	• Annealing in the air (450˚C; 25 minutes): ρ_S =3 Ω/□ transparent films
Mode 3: discharge current 0.3 A; deposition time - 12 minutes. Oxygen content - 29%. Films are fully oxidized (transparent).	
• Annealing in the N_2 (450˚C; minutes): ρ_S =24 Ω/□ transparent films	• Annealing in the air (450˚C; 25 minutes): $\rho_S \to \infty$ transparent films
Mode 4: discharge current 0.3 A; deposition time - 12 minutes. Oxygen content - 33%. Films are fully oxidized (transparent).	
• Annealing in the N_2 (450˚C; minutes): ρ_S =33 Ω/□ transparent films	• Annealing in the air (450˚C; 25 minutes): $\rho_S \to \infty$ transparent films
Mode 5: discharge current 0.3 A; deposition time - 12 minutes. Oxygen content - 50%. Films are fully oxidized (transparent).	
• Annealing in the N_2 (450˚C; minutes): ρ_S =98 Ω/□ transparent films	• Annealing in the air (450˚C; 25 minutes): $\rho_S \to \infty$ transparent films

Conducted studies proved our theory of conductivity in films of transparent metal oxides, based on generation of oxygen vacancies that behave as donor centers after high-temperature annealing [8].

Optimal Ar/O_2 ratio for the gas mixture are the follows:

1) 25% O_2 + 75% Ar with post annealing in the air;
2) 29% O_2 + 71% Ar with post annealing in the nitrogen media.

After determination of the optimal Ar/O_2 ratio for the gas mixture correction of the deposition time was made to provide the deposited film with thickness 130 nm. It was necessary because deposition rate in the Ar/O_2 gas mixture depends on percentage of Ar. Deposition time was reduced to 10 minutes.

2.3. Experiment III "Testing of annealing mode of ITO-films"

Series of samples that were obtained during the experiment II with optimal gas mixture were annealed at different temperatures (400˚C, 500˚C and 600˚C) within 15 and 25 minutes for determination of optimal high-temperature annealing mode of ITO-films.

Results of the conducted studies are shown in table 3. Transmission spectrums of samples obtained in gas mixtures with oxygen percentage of 25 % and 29 % before annealing and with minimal resistance after annealing are shown on the fig. 1 and fig. 2 respectively.

Table 3. Testing of annealing mode of ITO-films.

Mode 1 (cartridge A): discharge current 0.3 A; deposition time - 10 minutes; oxygen content - 25%; annealing in the air.	
Sample A6: without annealing ρ_S=26 Ω	Sample A1: 400˚C, 25 minutes. ρ_S=1.7 Ω
Sample A2: 500˚C, 15 minutes. ρ_S=6.6 Ω	Sample A3: 500˚C, 25 minutes. ρ_S=6.3 Ω
Sample A4: 600˚C, 15 minutes. ρ_S=2.6 Ω	Sample A5: 600˚C, 25 minutes. ρ_S=2.3 Ω
Mode 2 (cartridge B): discharge current 0.3 A; deposition time - 10 minutes; oxygen content - 29%; annealing in the N_2.	
Sample B6: without annealing $\rho_S \to \infty$	Sample B1: 400˚C, 25 minutes. ρ_S=24 mΩ
Sample B2: 500˚C, 15 minutes. ρ_S=35 Ω	Sample B3: 500˚C, 25 minutes. ρ_S=16 Ω
Sample B4: 600˚C, 15 minutes. ρ_S=13 Ω	Sample B5: 600˚C, 25 minutes. ρ_S=13 Ω

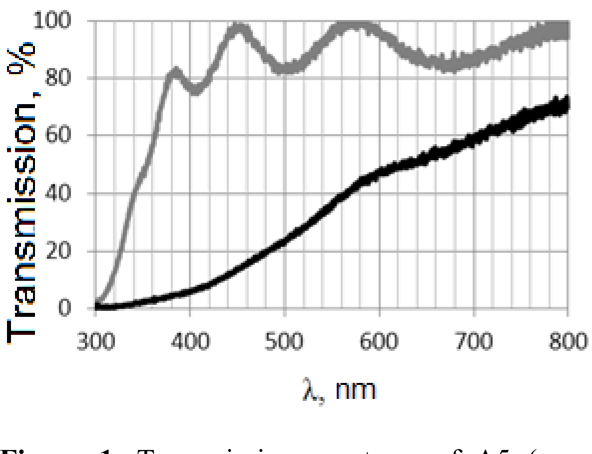

Figure 1. Transmission spectrum of A5 (grey curve) and A6 (black curve) samples

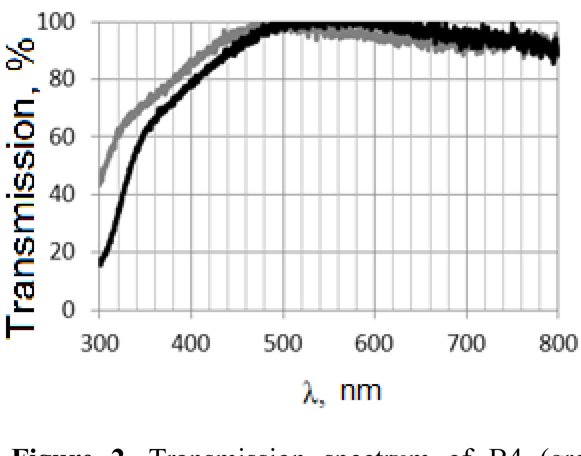

Figure 2. Transmission spectrum of B4 (grey curve) and B6 (black curve) samples

Thus, the best results in sheet resistance and transmittance in the range of blue spectral color (wavelength 440-485 nm) are obtained in the follows modes of deposition and annealing:

- deposition: discharge current – 0.3 A; deposition time - 10 минут; oxygen percentage in the gas mixture - 25%;

- annealing: in the air at the temperature 600˚C; annealing time - 25 minutes.

3. Conclusion

Developed technology of the deposition of the low-resistive ITO-films in by magnetron reactive sputtering from the In(90%)/Sn(10%) metal target with post-annealing provide low-resistive ITO-films with sheet resistance from 2 to 3 Ω/□ on the cold substrate. Such technology provides temporal and temperature stability of ITO-properties after annealing as well as high electrical and optical properties. Densification of ITO-films after annealing leads to higher chemical stability.

References

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