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Growth of ITO Films by Modified Chemical Vapor Deposition Method

*I. G. Atabaev**, M. U. Hajiev and V. A. Pak.*

Physical Technical Institute, Uzbek Academy of Sciences, 100084 Tashkent, Uzbekistan.

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Abstract: Growth of ITO films on glass substrate by modified CVD method in quasi closed space with separate evaporator for formation of saturated vapor phase is investigated. The growth rate of ITO films was an order 0,5-1,0 micron/hour it is several times above than for conventional spray-pyrolysis in similar conditions. The lattice absorption spectra of fabricated ITO films shown that materials grown in temperature interval 170-500ºC have identical structure, have no inclusions of secondary phase and uniform. IR absorption band in the range of 2500-3800 cm^{-1} which amplitude has correlation with conductivity of ITO films is found out.

Keywords: growth, ITO films, vapor deposition method.

1 Introduction

Now ITO films (indium and tin oxides) are widely used as transparent electroconductive layers in such structures as thin-film solar cells on the base of amorphous silicon, CdTe films [1,2]. Organic solar cells and light-emitting diodes are made on glass substrates covered by ITO [3,4]. The patent for a solar cell with efficiency of 10 % on the base of ITO/Si structure [5] is known. ITO films are used also for development of gas sensors [6].

Electrical conductivity of ITO film at a room temperature can be provided both by doping of material by shallow donor or acceptor impurity and by formation of structural defects with small energy of ionization 30-140 meV (vacancies of oxygen) [7]. In the [8] the review of properties of films fabricated by number methods are presented. The ITO films have been fabricated by thermal deposition in vacuum, by magnetron sputtering of ITO source – target, by chemical vapor deposition using acetates and chlorides of indium and tin and other reagents.

Magnetron sputtering and various variants of chemical vapor deposition (a spray – pyrolysis, an electrical stimulated and an ultrasonic spray pyrolysis, etc) are the most widespread methods of fabrication of ITO films [9,10]. In chemical vapor deposition method (CVD) the pyrolitic decomposition of molecules of various compounds is carried out on substrate at temperatures of from 200 to 500ºC. For delivery of reagent molecules to front of crystallization the flow of gas - carrier is used (Argon, Helium etc.). As the oxide ITO material is growing the partial pressure of oxygen in a reactor must be controlled.

Growth rate of ITO films in a range of 10-50 nanometer/hour is slow. It is necessary to notice, that like thermal deposition in vacuum for the CVD technology the percent of use of raw materials is also low. As the temperature of gas – carrier is low in comparison with temperature of substrate the partial vapor pressure of reagents in the reactor and near surface of substrate is not maximal. And only small part of reagent molecules reaches to crystallization front. Basic part of components and products of reactions (not reacted to crystallization front on substrate) is carried away by a gas-carrier stream and then is besieged on surface of reactor units and communication tubes of CVD installation. This fact which does not have values at laboratory experiments becomes important for mass production of ITO structures.

2 Experimental Details

In the given article for improvement of efficiency of use of raw materials at manufacture of ITO structures, to improve of quality of films the laboratory installation is developed for fabrication of ITO films in “quasi closed” space conditions (not used the gas-carrier which take away most of reagents from crystallization front). It is supposed that in this conditions the partial pressure of vapor is higher and close to pressure of saturated vapor at given temperature.

*Corresponding author E-mail: atvi@uzsci.net

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To formation of vapor of reagents the separate evaporator in the reactor close to substrate is used whereas in conventional spray-pyrolysis method the vapor-gas mix moves directly on a substrate. The increasing of growth rate and reduction of losses of reagents and increase in percent of use of raw materials is expected.

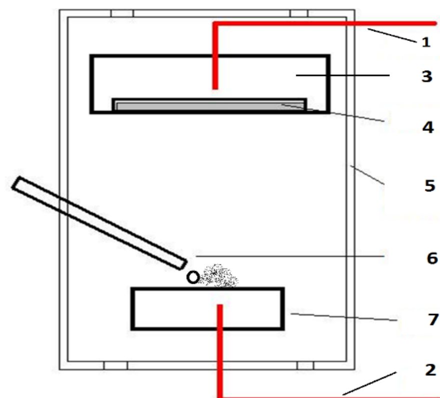

Figure 1. The scheme of installation used for fabrication of ITO films on glass substrates in a range of temperatures 170÷500^{0}C: 1,2 – thermocouples to measure of substrate (4) and evaporator (7) temperature; 3 – heater of substrate (4); 5 – "quasi-closed" CVD reactor; 6 – pipe to provide evaporator by Indium and Tin chloride solution.

3 Results

In figure 1 the scheme of installation used for fabrication of ITO films on glass substrates in a range of temperatures 170-500ºC is presented for various parities between In_2O_3 and SnO_2 content. Fabrication was carried out by thermal pyrolysis of vapor of water or ethanol solution of indium and tin chlorides. ITO film growth modes were set by following parameters: Ts - substrate temperature, Te - evaporator temperature, R-rate of delivery of a solution on the evaporator (g/min), C – content of indium and tin chlorides in solution.

CVD fabrication of ITO films was made for various parities of components (chlorides of indium and tin) in solution. The solvents were deionized water and ethanol. Preliminary experiments have shown that more effective solvent is ethanol. In water solution colloids particles was formed and then were allocated in a deposit.

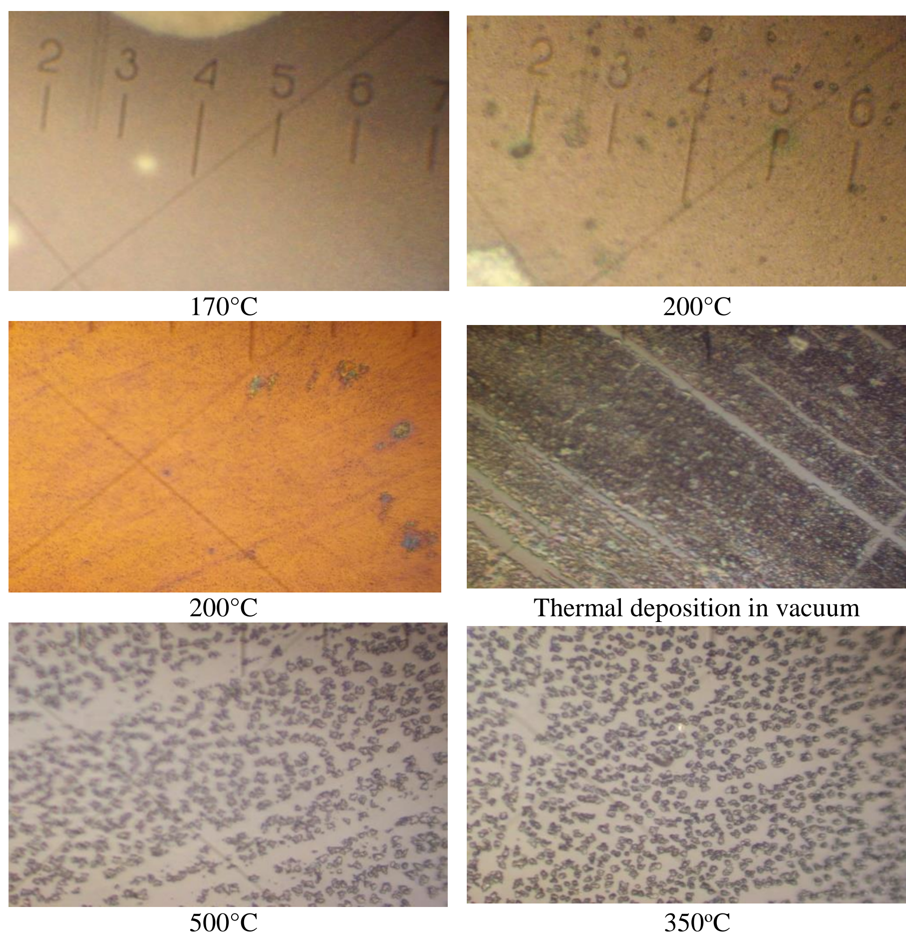

Figure 2. The microphotos of a surface of ITO films grown on glass substrates at various temperatures and parities of reagents.

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The optimum temperature of the evaporator depends on growth rate and it should be less temperature of thermal disintegration of Indium and Tin chlorides. As the evaporator temperature is set irrespective of a substrate, preliminary experiments have been made and it is established that the optimum temperature of the evaporator is in an interval 80-120ºC.

As it expected the growth rate of ITO films in our experiments was an order 0,5-1,0 micron/hour it is several times above than for conventional spray-pyrolysis in similar conditions. In figure 2 the microphotos of a surface of ITO films grown on glass substrates at various temperatures and parities of reagents are resulted.

Apparently from figures in our experiments at substrate temperature below 350ºC the continuous ITO film was grew and at substrate temperature of 350-500ºC on a surface of glass substrates the island growth was observed. It is known disintegration of Indium and Tin chlorides starting at temperature above 150-160^{0}C and then on the surface of substrate molecules of Indium and Tin oxides are formed. At temperatures up to 300-350ºC the surface diffusion constant is small and therefore the thin continuous film grows as oxide molecules are formed on all surface of a substrate homogeneously.

4 Discussion

At substrate temperature above 300-350ºC factor of surface diffusion is enough high, molecules of oxides become mobile and there is a formation of thermodynamically equilibrium germs (the growth centers, microcrystals) occurs. Function of distribution of the sizes of islets has one maximum. Considering that process temperature is enough low it is possible to assume that ITO oxide growth occurs as follows: the germs forms on defects of a substrate and then growth of germs occurs because of diffusion of the molecules and atoms adsorbed on a surface. So the mechanism of diffusion coalescence [11] is realized.

In figures 3,4 the IR absorption spectra of ITO films measured using IR Fourier -spectrometer SPECTRUM BX II (Perkin Elmer) are presented.

As apparent from Figure 3 the lattice absorption spectra of ITO films grown at different temperatures are identical, so near order of atoms in a lattice does not vary. The change of phase structure of films with increase in temperature of growth is not observed.

Interesting feature of IR spectra of samples is the existence absorption band at 2500-3800 sm^{-1}. This absorption band was not observed by other authors. Estimation shows that this band corresponds to absorption of defects with deep levels with energy of ionization of an order 0,34 -0,47 eV. The amplitude of absorption band has correlation with conductivity of films - it directly proportional to conductivity. The greatest absorption in this area was observed for the dark sample fabricated by thermal deposition in vacuum of ITO-source with high electrical conductivity (~0,01 Ohm·cm). Usually the electrical conductivity of materials at a room temperature is connected with defects with low energy of activation. Possibly the given absorption band can be connected with dot defect of the structure having both deep and shallow levels, type of vacancies or divacancies, or their complexes with impurity atoms.

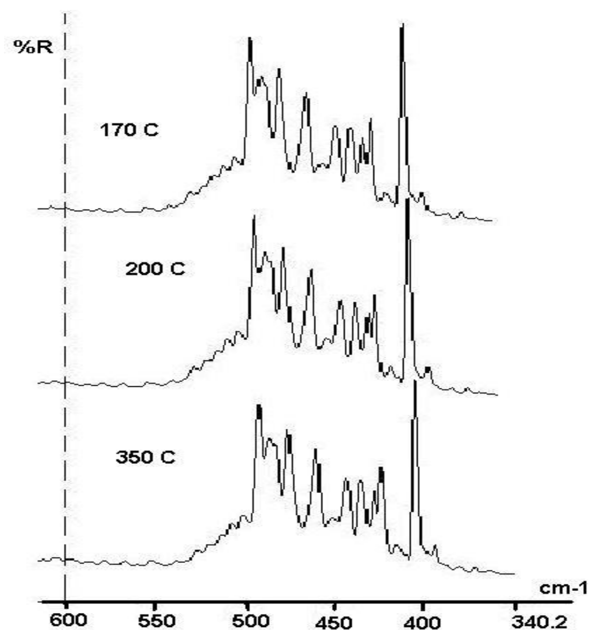

Figure 3. IR lattice absorption spectra of ITO films grown at different temperatures.

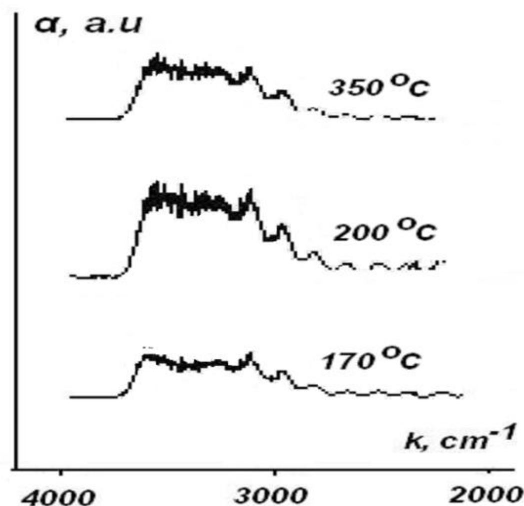

Figure 4. IR absorption of ITO films grown at different temperatures at 2500÷3800 cm^{-1}.

5 Conclusion

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formation of saturated vapor phase is investigated. The growth rate of ITO films was an order 0,5-1,0 micron/hour it is several times above than for conventional spray-pyrolysis in similar conditions. The lattice absorption spectra of fabricated ITO films show that materials grown in temperature interval 170-500ºC have identical structure, have no inclusions of secondary phase and uniform. IR absorption band in the range of 2500-3800 sm^{-1} which amplitude has correlation with conductivity of the grown films is found out.

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