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OPTICO-ELECTRICAL PROPERTIES OF TITANIUM AND NITROGEN CO-DOPED In_2O_3 FILMS PREPARED BY SPRAY PYROLYSIS

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Titanium and nitrogen co-doped In_2O_3 films were prepared using the controlled spray pyrolysis from mixed solution of $In(NO_3)_3$ and $TiCl_4$ on heated glass substrates. Phase composition and morphology of obtained films were identified by XRD, SEM and EDX. Optico-electrical properties of the films were studied by UV-vis spectroscopy, resistance measurements and hot-probe test. By changing the deposition temperature and the concentration ratios of starting solutions, it was found that the films prepared at temperature region of 380 to 420 ^oC from solutions containing 10-40% $TiCl_4$ shown a low resistivity and remarkable photoconductivity in the visible light at room temperature. Obtained titanium and nitrogen co-doped In_2O_3 films could be promising material for the development of the high efficiency solar cell and optoelectronic devices.

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1. Introduction

In_2O_3 is one of the famous transparent conductive oxides materials. Due to íts unique optical and electrical properties In_2O_3 has been an emerging candidate for wide vareties of applications such as being used in flat panel displays, transparent thin film transistors, light emitting devices, sensor, and in thin film solar cells [1]. Although numerous applications were introduced into practice, the research on modifying In_2O_3 for the improvement of its electrical and optical properties still remains a hot topic.

It was found that ternary compound of In_2TiO_5 is a visible-light responsive photocatalyst [2,3]. In_2O_3-TiO_2 composites appeared to be a high efficiency electrode in photoelectrochemical production of hydrogen and a potential for solar cells [4, 5]. Especially titanium-doped In_2O_3 has been attracted the great attentions due to high transparency, high mobility and low resistivity [6-10] that promise significant applications in optoelectronics.

It was also reported that nitrogen doping for In_2O_3 narrowed band gap of the material from 3.6 up to 2 eV [11], which enhanced the visible light absorption. Furthermore, nitrogen-doped In_2O_3 can emit red-light in wide range and become a promising material for red-light emitting diodes and lasers productions [12].

Searching new materials for development of the high-efficiency solar cells is currently a hot issue, in which environment-friendly semiconductor compounds attract the special attentions. In_2O_3 and TiO_2 are known to be potential and were studied to use in dye-sensitized [13] or solid state solar cell [14]. It is well known that materials for the high efficiency solar cell are desired to have a high photo effect and a concomitant low resistivity. The findings that titanium-doped In_2O_3 exhibits a high conductivity and nitrogen-doped In_2O_3 can be excited by visible light led to the idea

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of combining both the dopants effects in unique In_2O_3 host for solar cell application.

Titanium-doped In_2O_3 films were deposited by sputtering [6,7], laser evaporation [10], electron beam evaporation [15], chemical vapor deposition [9] and thermal oxidation [14] methods. Nitrogen- doped In_2O_3 have been successfully prepared by sol-gel [11,16] and calcination of $In(OH)_3$ in air [12]. In this paper we for the first time used spray pyrolysis method for preparation of In_2O_3 co-doped with titanium and nitrogen films and focused on the optico-electrical properties of obtained material.

2. Experimental

The pyrolysis of $In(NO_3)_3$ is described by the equation

$$4In(NO_3)_3 = 2In_2O_3 + 12NO_2 + 3O_2$$

As a result of the reaction, In_2O_3 is formed together with NO_2 - a nitrogen doping source. Thus, from only $In(NO_3)_3$ precursor it is possible to prepare In_2O_3 and dope it with nitrogen at the same time. Furthermore, the high and stable molar ratio between NO_2 and In_2O_3 is an advantage compared to other methods using an external doping nitrogen source. Titanium dopant was produced by the pyrolysis of $TiCl_4$. 0.05M solutions of $In(NO_3)_3$ in distilled water and $TiCl_4$ in ethanol were separately prepared. Prior to spraying, the $In(NO_3)_3$ and $TiCl_4$ solutions were mixed at predetermined ratios. The spay pyrolysis system was used as presented elsewhere [17]. The frequency of spray was 40 pulses per minute and every spray pulses lasted for 0.6 s. 1.2 mm-thick microscope glass slides were used as the substrates. Depositions were carried out at different temperatures in optimum region for the both pyrolysis of $In(NO_3)_3$ and $TiCl_4$ which was determined before. At every chosen substrate temperatures, a series of solutions with $TiCl_4$ molar contents changed by the step of 10% were taken for films preparation. Because $In(NO_3)_3$ and $TiCl_4$ are pyrolyzed simultaneously, under certain conditions an In_2O_3 co-doped with titanium and nitrogen film could be formed. A low resistivity of obtained films was considered as the first sign of the doping success.

The phase and the morphology of as-prepared films were characterized by XRD, SEM, and EDX. The films were also subjected to UV-vis spectroscopy and thermo-electric test to determine the type of conductivity. For the investigation on resistivity and photoconductivity, the films were deposited in a shape of photoresistor with active area of $5x10mm^2$. The ohmic contacts to active materials were made from 15 Ω/sq SnO_2:F films. The photoresistors of identical configuration prepared at different temperatures and various components ratios were subjected to measuring the electric resistance in the dark (R_D) and under visible light (R_L) of 50w halogen lamp at distance of 12 cm in room condition. The measured resistances were presented in the surface resistivity unit (ohm/sq).

3. Results and discussion

3.1 Material characterization

Electrical measurement revealed that films prepared at 380 to 420^0C from solutions contained 10-40% $TiCl_4$ shown a low resistivity, which is a specific characteristic of the In_2O_3 doped with titanium. XRD characterizations of the films prepared at 380 ^{0}C from starting solutions comprised 10, 20 and 30% $TiCl_4$ are presented in fig. 1. As seen in the figure, all the diffraction peaks can be indexed to In_2O_3 with cubic crystals. Obtained diffraction patterns is similar to that of pure In_2O_3 [18], nitrogen-doped In_2O_3 [11,12,16] and titanium-doped In_2O_3 [6,7] prepared from different methods. No clear peaks from other possible compounds such as InN, TiN, TiO_2 and In_2TiO_5 were detected. Only crystallinity of films prepared from mixed solutions appears to be slightly lower than that from 100% $In(NO_3)_3$ solution. The average size of In_2O_3 crystals estimated using Scherrer equation was about 15 nm.

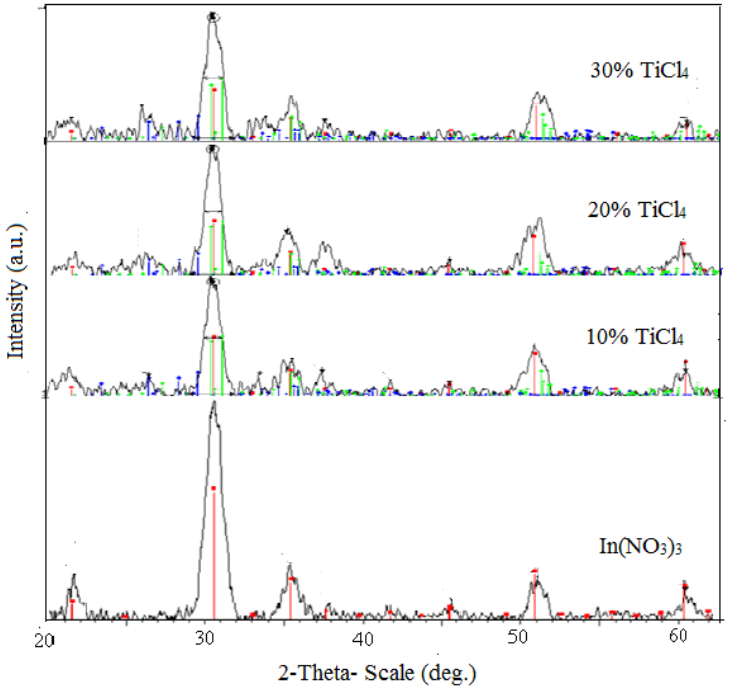

Fig. 1: XRD patterns of films prepared at 380 °C from $In(NO_3)_3$ solution and mixed solutions consisted of *10, 20, 30 $TiCl_4$*

The morphology of the films examined by SEM was shown to be homogeneous as presented in fig. 2. The elements consisted in the films were estimated by EDX analysis. Tab. 1 and 2 show the representative EDX of the films prepared at 380 °C and 420 °C from solution containing 30% $TiCl_4$.

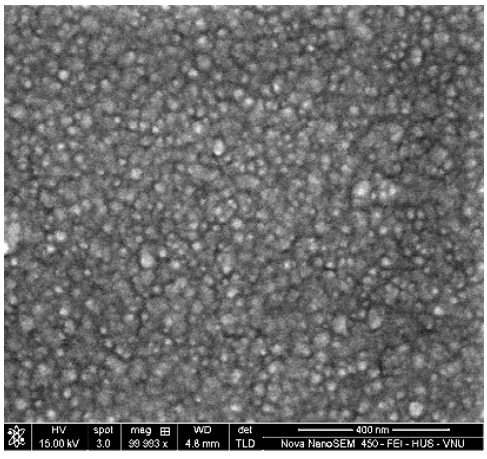

Fig. 2: SEM photography of film prepared at 380 °C from solution containing 30% $TiCl_4$ and 70% $In(NO_3)_3$

As the results from XRD and EDX, deposited films are In_2O_3 doped with Ti. Due to the limitation of EDX methodology, nitrogen element is invisible in the analysis. However, the fact that In_2O_3 was formed in a high nitrogen concentration media and visible light photoeffect of the films presented below allowed conclusion that deposited films were the In_2O_3 co-doped with titanium and nitrogen (denoted as ITiNO). It was also revealed that the ratios of Ti to In were almost unchanged from starting solutions to formed films. Furthermore, from the same starting

solution the ratios were constant at different substrates temperatures. Obtained result allowed characterizing the films according to the compositional ratios of the precursor solutions.

Tab. 1. EDX of film prepared at 380 °C from solution consisted of 30% $TiCl_4$

Element	Weight %	Atomic %
O K	49.27	82.28
Si K	3.89	3.70
Cl K	1.21	0.92
Ti K	7.64	4.26
In L	37.98	8.84
Total	100.00	100.00

Tab. 2. EDX of film prepared at 420 °C from solution consisted of 30% $TiCl_4$

Element	Weight %	Atomic %
O K	46.97	80.09
Si K	5.45	5.29
Cl K	1.43	1.10
Ti K	7.69	4.38
In L	38.46	9.14
Total	100.00	100.00

3.2 Optico-electrical characterization

Fig. 3 show the UV-vis absorption spectrum of ITiNO film prepared at 380 °C and 20% $TiCl_4$. From the absorption spectrum it is possible to estimate the optical band gaps using the Tauc's equation described as $\alpha h\nu = A (h\nu - E_g)^m$.

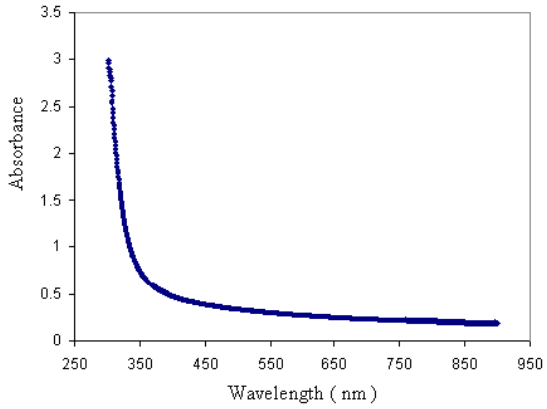

Fig. 3: UV-vis absorption spectrum of film prepared at 380 °C from solution containing 20% $TiCl_4$

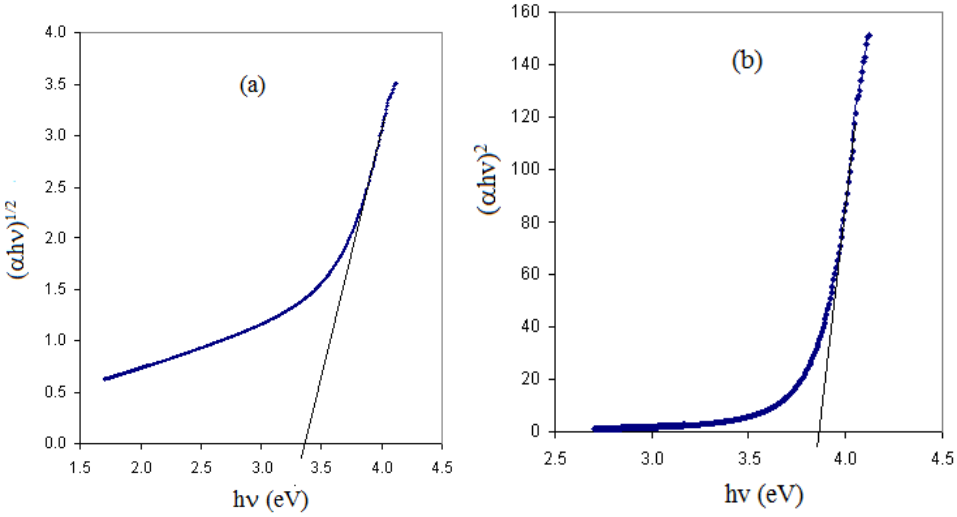

Fig. 4: Graphical determination of the band gap energy (a): indirect transition, (b): direct transition

Fig. 4 (a,b) show the results of graphical band gap determination of the film. It was estimated that the optical band gap of the film is 3.3 eV for indirect transition (with m=2) and 3.84 eV for direct transition (with m=1/2). The value higher than 3.6 eV is explained by the quantum confinement effect [18].

Electrical characterizations of ITiNO were started with the examination of the interface characteristic between SnO_2:F and the deposited ITiNO films. Using current-voltage (I-V) measurement it was found that SnO_2:F provided the ohmic contact to ITiNO films as presented in fig. 5. Obtained interface characteristic enables to investigate the resistivity of the films as a function of deposited conditions.

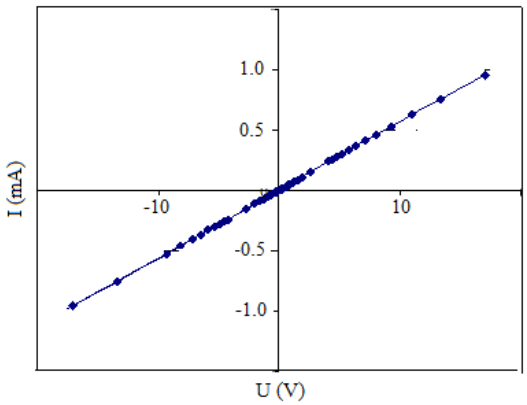

Fig. 5: I-V characteristic of SnO_2:F and ITiNO interface.

Fig. 6 presents the dark resistances of ITiNO films obtained by pyrolysis from solutions contained 10-40% $TiCl_4$ at temperature of 380 and 420 ^oC. As seen in fig. 6, the resistivities of the films depend on $TiCl_4$ concentrations and deposition temperature. Because Ti contents in the films are equivalent to those in starting solutions, the decrease of film resistivity can be explained by the increase in Ti impurity concentration that produces more conductive electrons. At high $TiCl_4$ contents, the structural destruction and the formation of high resistivity phases (such as TiO_2) can be appeared that resulted in the raising resistivity of the films. The optimum concentration of $TiCl_4$ corresponds to the minimum resistivity of the ITiNO films was estimated to be from 20 to 30%. The role of substrate temperature is to motivate chemical reactions and improve structure that positively influence on conductivity of the films. So resistivity of films prepared at 420 ^oC was shown to be lower than that of films prepared at 380 ^oC. And a minimum resistivity of 7 kohm/sq. was reached at 420 ^oC.

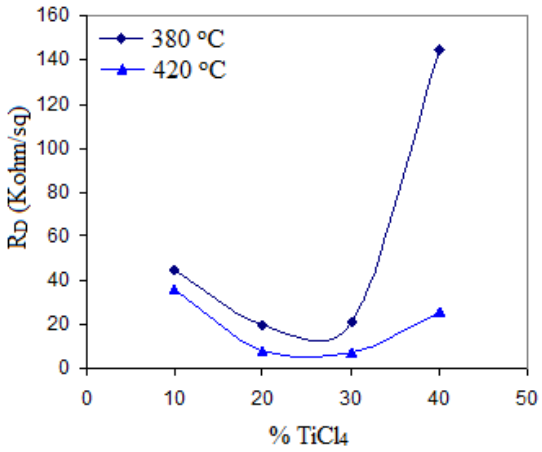

Fig. 6: Dark resistivity of ITiNO films as a function of deposition temperatures and percentages of $TiCl_4$ in starting solutions.

The photoconductivity was estimated via the decrease in the resistance of ITiNO films under illumination. At the first exposition moment, the reduction of resistance was rapid then slow similar to results of In_2O_3 doped with sulfur [19]. After time delay (around 10 minute), stationary resistances were taken as the light resistances for evaluation of photoconductivity using formula $K = (R_D-R_L)/R_D$. Fig. 7 presents the calculated K for the films prepared at conditions of low resistivity. As seen in the fig. 7, the photoconductivity of these films is fairly high. Furthermore, the dependence of photoconductivity is similar to that of resistivity. Based on obtained results, it is reasonable to suggest that nitrogen doping regime were stable for all ITiNO films.

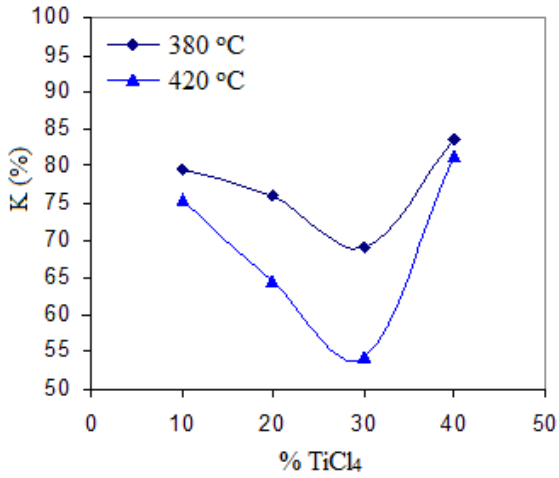

Fig. 7: Photoconductivity of films depended on deposition temperatures and $TiCl_4$ percentages in starting solutions.

Thermoelectrical test was also carried out in order to estimate the type of conductivity. Based on positive sign of thermo electromotive force at the hot end it was concluded that all the ITiNO films were n-type semiconductors.

Titanium was considered as a substitutional dopant in In_2O_3 that could compensate carriers scattering effect originated from interstitial oxygen [7]. Furthermore, titanium belongs to IV group so the substitution causes an increase of carrier concentration compared to that of indium. Both the effects of titanium dopant resulted in an enhancement of electrical conductivity. Regarding nitrogen dopant, it was shown [11, 12, 16, 20] that nitrogen atoms can be incorporated into In_2O_3 by partially substitution of oxygen or interstitial doping with NO_x^- species, which create the nitrogen levels in the In_2O_3 band gaps. These levels cause absorption and electron generation in the visible region of light spectrum. The mechanisms of titanium and nitrogen doping for In_2O_3 are different. So, the co-doping with titanium and nitrogen could result in the combination of the two doping effect at a certain condition. Consequently obtained ITiNO films simultaneously exhibited a low resistivity together with a visible light photoconductivity. Together with wide band gap, visible light transparency and linear interface with SnO_2:F, titanium and nitrogen co-doped In_2O_3 films show an promising potential to enhance the efficiency of photoanode in dye sensitized and window layer in solid state solar cells.

4. Conclusion

Titanium and nitrogen co-doped In_2O_3 films have been successfully deposited onto glass slides by spay pyrolysis from solutions consisted of $In(NO_3)_3$ and $TiCl_4$. Obtained films exhibited specific characteristics of both titanium and nitrogen dopants: the films were conductive and visible light photoconductive.

The films prepared at temperature region of 380-420 ^oC from solutions consisted of 20-30% $TiCl_4$ shown the minimums of resistivity and photoconductivity under visible light at room temperature.

The dependences of the resistivity and photoconductivity on the deposition temperature and $TiCl_4$ concentration allow tailoring the characteristics of titanium and nitrogen doped In_2O_3 for the application aim.

With concomitant collection of high photoeffect, low resistivity, high band gap, transparency and linear contact to SnO_2:F, titanium and nitrogen co-doped In_2O_3 films prepared using simple spray pyrolysis method are shown to be a valuable candidate for the development of the high efficiency solar cells and other optoelectronic devices.

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