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A Study of Cd_2SnO_4 Thin Film Deposited at Low Temperature using Reactive Magnetron Sputtering

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Introduction

Transparent conductive oxide (TCO) coatings will underpin the development of the next generation of photovoltaic solar cells, flat panel displays, and optoelectronic components. All TCO have semiconducting properties with a large band gap providing spectrally selective characteristics and they all have a good transmission in the visible part of the spectrum together with high reflection in the infrared part. Indium tin oxide (ITO) is the material with the highest conductivity and luminous transmittance ($R_s = 10\ \Omega/\square$ and $T = 90$ %). However, there is much interest in the use of alternative, cheaper coating materials, such as Cd_2SnO_4 (CTO). The optical and electrical properties of CTO coatings are, though, notoriously sensitive to process parameters and depend on control of film composition, structure, crystallinity, defect density, surface roughness, and dopant concentration. Cd_2SnO_4 films have been produced by many different techniques including reactive direct current (DC) magnetron sputtering from segmented metallic targets, and radio frequency (RF) magnetron sputtering from ceramic targets.

Reactive magnetron sputtering process is complicated and depends on many parameters. Deposition of layer on relatively high temperature substrate (about 300 °C) or deposition with following annealing is used to manufacture transparent and conductive Cd_2SnO_4 layers with desirable properties [1-3], however such process is undesirable in some ways, particularly when heat-sensitive substrates are used.

Electrically conductive and optical transparent Cd_2SnO_4 film synthesis process using reactive magnetron deposition on relatively low temperature (room temperature) substrate was investigated in this work.

Experimental

The Cd_2SnO_4 films were deposited with DC magnetron MAG-5 (USSR) installed in vacuum evaporation system UVN-2M-1 (Russia). Modified power supply unit BP-196 was used as DC power supply. The cathode of magnetron (target) was made from the alloy of Cd_2Sn (66,2 % Cd and 33,8 % Sn in mass), sweated on copper base. Cd_2SnO_4 films were deposited on glass and polymer (lavsan) substrate at relatively low temperature (room temperature) by reactive DC magnetron sputtering. The equipment used to achieve this process is shown in Fig. 1.

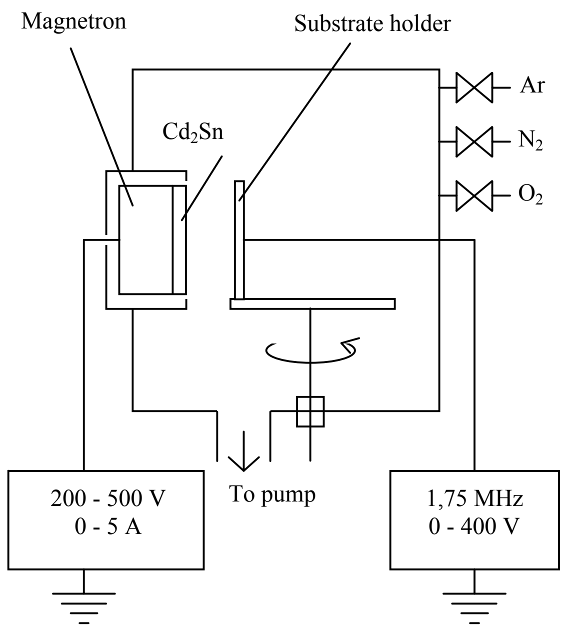

Fig. 1. The DC magnetron sputtering system

Substrates were cleaned according to the standard technology before deposition. Use a lavsan film as substrate persuaded us that the temperature did not exceed 100 °C during layer deposition, so the formation of compound took place at a relatively low temperature. The reactive deposition process conditions are summarized in Table 1.

The discharge voltage and current, partial pressure of active gas and total pressure in chamber, the layer deposition rate were measured during the process. Electrical sheet resistance R_s or specific resistivity and optical transmittance T in wide range of light wavelength were measured for deposited films.

Table 1. Summary of deposition conditions

Magnetron	disk, planar
Area of cathode (target), cm^2	108
Material of the target	Cd_2Sn
Area of target erosion, cm^2	45
Discharge voltage, V	200 – 500
Discharge current, mA	100 – 1000
Magnetic field near the cathode, A/m	$2 \cdot 10^4$
Working gases	Ar + O_2
Initial pressure in chamber, Pa	$< 10^{-3}$
Partial pressure of active gas (O_2), Pa	$0 – 2 \cdot 10^{-2}$
Total pressure in chamber, Pa	$2 \cdot 10^{-2}$
Distance between the cathode and the substrate, cm	6

Results

Two modifications of cadmium stannate Cd_2SnO_4 and $CdSnO_3$ are well known. Both modifications of cadmium stannate are wide gap n-type semiconductor. Cd_2SnO_4 modification is widely investigated because the thin film of this material looks promising in fabrication of transparent electrodes for different optoelectronic devices and thermal mirrors [3]. The main parameters of layer used in fabrication of conductive electrodes are sheet resistance R_s and transmittance T in visible light range. Sometimes the figure of merit $F = T/R_s$ is used [1]. The transparent electrode requirements are not less then 80–100 % of light transparency and not more then 10–100 Ω/□ of thin layer sheet resistance.

According to the results of experimental study on Cd_2SnO_4 layer reactive magnetron deposition at room temperature the light transmittance T and sheet resistance R_s most depend on three parameters of the process: 1) magnetron discharge voltage; 2) work gas O_2/Ar composition, and 3) substrate potential (bias).

The dependence of sheet resistivity of deposited Cd_2SnO_x layer on discharge voltage at different composition of work gas O_2/Ar is shown in Fig. 2. The sharply expressed minimum in R_s=f(U) diagram can be seen. The location of minimum depends on work gas composition. Discharge voltage values at which the minimum of R_s is achieved increases with the oxygen concentration.

The dependence of light transmittance (λ_1=550 nm and λ_2=350 nm) of deposited Cd_2SnO_x layer on discharge voltage at work gas O_2/Ar composition 0,50 is shown in Fig. 3. All deposited layers characterize high light transparency in all interval of deposition parameters while the electric conductivity varies thousand times. Decrease of light transmittance is observed only at relatively large discharge voltage (especially for λ_2=350 nm). It can be supposed that non-stoichiometric layer with oxygen deficit was obtained at high discharge voltage. The dependence of main figure of the merit for electrically conductive and optically transparent layers F on magnetron discharge voltage at relative oxygen concentration 0,7 is shown in Fig. 4.

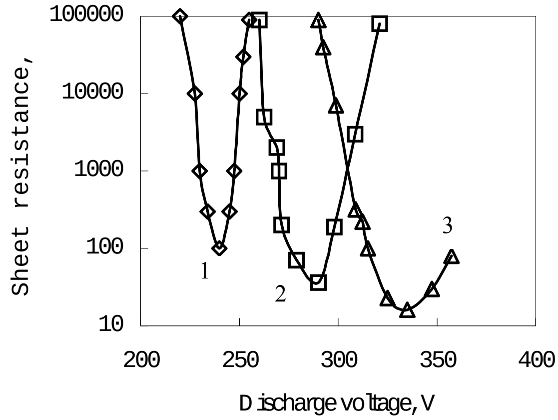

Fig. 2. Sheet resistance of reactive magnetron deposited Cd_2SnO_x film versus discharge voltage at different oxygen concentration (1 - C_{Ox} = 0,20; 2 - 0,50; 3 - 0,70) and p = 0,02 Pa, deposition time 100 s, T < 100 °C

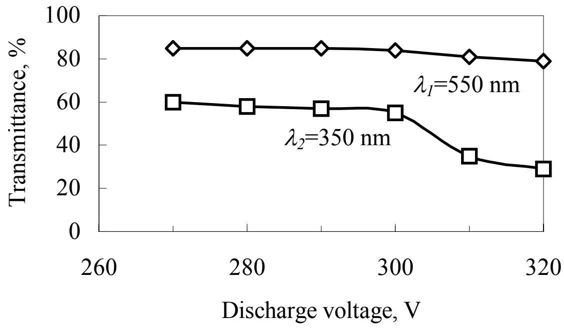

Fig. 3. Variation of optical transmittance at 550 nm and 350 nm of Cd_2SnO_x layer versus magnetron discharge voltage (relative oxygen concentration 0,5, total work gas pressure 2×10^{-2} Pa)

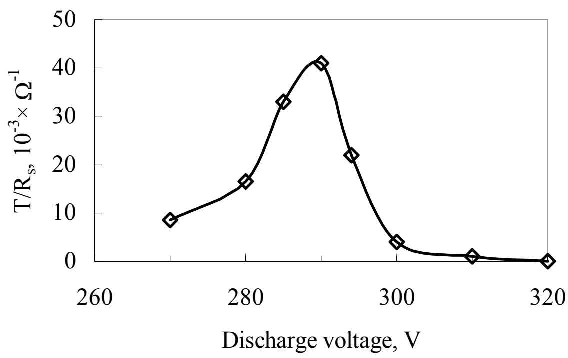

Fig. 4. Variations of the figure of merit F with voltage for Cd_2SnO_4 deposited by reactive magnetron sputtering of metallic targets at relative oxygen concentration 0,7; p_2=$2 \cdot 10^{-2}$ Pa

The figure of merit is $F \approx 40{\cdot}10^{-3}\ \Omega^{-1}$ ($R_s = 20\ \Omega/\square$ and $T = 85$ %) at the 380 V discharge voltage and 70% oxygen in argon. Analyzing $R_s = f(U,C_{O2})$, $T = f(U,C_{O2})$ and $T = f(U,C_{O2})$ dependences we can see that exist area of process parameters limited by discharge voltage U and oxygen concentration C_{O2} values in which quality layers with proper characteristics for conductive electrodes can be formed (see Fig. 5).

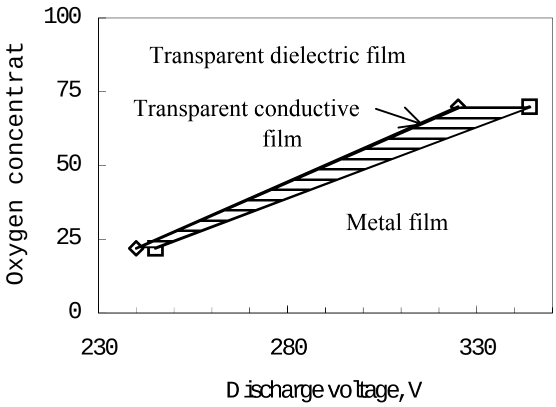

Fig. 5. Area of coating of transparent conductive CTO layer versus deposition parameters at $p = 2{\times}10^{-2}$ Pa, $T < 100$ °C

Dependence of optical transmittance of Cd_2SnO_4 layer with optimal parameters on light wavelength is shown in Fig. 6.

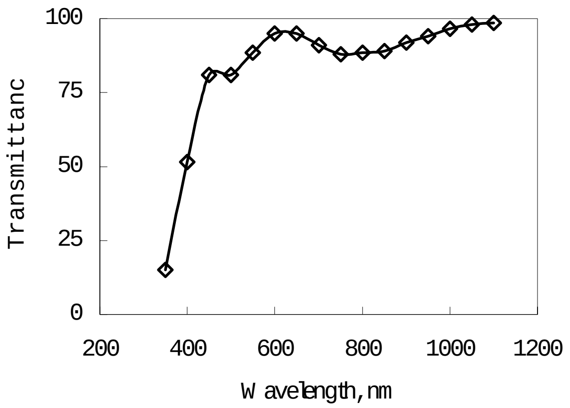

Fig. 6. Optical transmission spectra of CTO film

It can be seen that these layers (sheet resistance R_s=20 $\Omega/\square$) are enough transparent (transparency T≥50 %) for wavelength λ>400 nm. Interference minimums and maximums are observed in diagram. Registration of interference phenomenon in spectral transmittance dependence gives possibility to obtain refraction index, absorption coefficient and layer thickness. It is known that from measurement of T=f(λ) the refractive index can be expressed from formula [4]

$$n = \left[N + \left(N^2 - n_1^{\,2}\right)^{1/2} \right]^{1/2}, \tag{1}$$

where

$$N = \frac{1 + n_1^{\,2}}{2} + 2n_1 \frac{T_{\max} - T_{\min}}{T_{\max} T_{\min}} \tag{2}$$

and layer thickness

$$d = \frac{M \lambda_1 \lambda_2}{2n(\lambda_2 - \lambda_1)}, \tag{3}$$

where n is the refractive index of layer, M – the number of oscillations between the first and the second interference maximum, d – layer thickness, λ_1 and λ_2 – wave lengths at which the interference maximums are observed, T_{max} and T_{min} – the largest and the lowest value of light transparency in the region of oscillations.

Analysis of measurement results gives average refractive index $n \approx 2$ and thickness $d \approx 300$ nm for the deposited layers. Measured refractive index is in good accordance with other author results (n = 1,9) [5].

The plot of $(\alpha h\nu)^2$ versus $h\nu$, where α is the optical absorption coefficient and $h\nu$ is the energy of the incident photon is shown in Fig. 7. If we consider that Cd_2SnO_4 is a direct transition semiconductor, α is related the optical energy band gap E_g by [5]

$$(h\upsilon\alpha)^2 = \beta\left(h\upsilon - E_g\right), \tag{4}$$

where β is a parameter, E_g is determined by extrapolating the straight line portion $(\alpha h\nu)^2 = 0$.

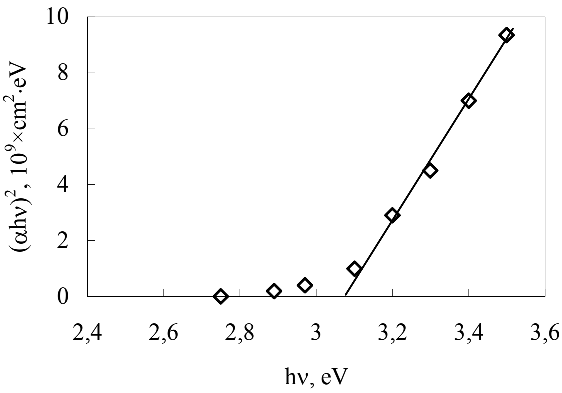

Fig. 7. Variation of $(\alpha h\nu)^2$ versus $h\nu$

It is determined that band gap $E_g = 3{,}07$ eV for deposited Cd_2SnO_4 layers (Fig. 7). In literature reported values are 2,1 - 2,9 eV [5]. Obtained forbidden gap is wider and this can be explained by Moss-Burstein effect.

Conclusions

Optically transparent and electrically conductive thin Cd_2SnO_4 (CTO) layers were deposited by reactive magnetron sputtering on room temperature substrate.

Properties of deposited layers (light transmittance and electrical conductivity) depends on reactive magnetron deposition process parameters to a very large degree.

Optically transparent and electrically conductive thin Cd_2SnO_4 layers with the sheet resistivity R_s≈20 $\Omega/\square$ and optical transmittance $T = 85$ % in visible light range (400-800 nm) were formed at optimal process parameters and relatively low temperature (room temperature).

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J. Dudonis, A. Jotautis, R. Naujokaitis. Žematemperatūrio plonų Cd_2SnO_4 plėvių nusodinimo reaktyviojo magnetroninio dulkinimo būdu tyrimas // Elektronika ir elektrotechnika. - Kaunas: Technologija, 2003. - Nr. 5(47). – P. 48-51.

Skaidrios ir laidžios elektros srovei oksidų dangos labai svarbios kuriant naujos kartos saulės baterijas, skystųjų kristalų monitorius ir kitus optoelektronikos elementus. Alternatyva plačiai naudojamam indžio oksidui gali būti pigesnės medžiagos, pavyzdžiui, Cd_2SnO_4. Tačiau šios dangos optinės ir elektrinės savybės labai priklauso nuo technologinių parametrų, plėvelės sudėties, struktūros, defektų tankio, paviršiaus nelygumo ir priemaišų koncentracijos. Šiame darbe eksperimentiškai ištirtas reaktyviojo magnetroninio nusodinimo procesas ir gauta, kad suformuotų plėvių skaidrumas ir elektrinis laidumas labiausiai priklauso nuo magnetrono išlydžio įtampos, darbinių O_2 + Ar dujų sudėties ir padėklo potencialo (priešįtampio). Esant tam tikroms išlydžio įtampoms, gaunama mažiausia plėvelės paviršinė varža, o šios įtampos priklauso nuo darbinių dujų sudėties. Skaidrumas mažiau priklauso nuo išlydžio įtampos ir tik esant didesnėms išlydžio įtampoms sumažėja trumpesniųjų bangų srityje. Analizuojant tyrimų rezultatus, nustatyta optimalių technologinių parametrų sritis, kai gaunamų plėvelių charakteristikos atitinka reikalavimus, keliamus skaidriems laidiems elektrodams. Il. 7, bibl. 5 (anglų kalba; santraukos lietuvių, anglų ir rusų k.).

J. Dudonis, A. Jotautis, R. Naujokaitis. A Study of Cd_2SnO_4 Thin Film Deposited at Low Temperature using Reactive Magnetron Sputtering // Electronics and Electrical Engineering. - Kaunas: Technologija, 2003. - No. 5(47). – P. 48-51.

Transparent conductive oxide coatings will underpin the development of the next generation of photovoltaic solar cells, flat panel displays, and optoelectronic components. As alternative, the cheaper coating material Cd_2SnO_4 (TCO) can be used instead of indium tin oxide. The optical and electrical properties of CTO coatings are, though, notoriously sensitive to process parameters and depend on control of film composition, structure, crystallinity, defect density, surface roughness, and dopant concentration. The paper presents results of experimental study of magnetron deposition process. Transparency and electrical conductivity of deposited films most depends on magnetron discharge voltage, work gas O_2 + Ar composition and substrate potential (bias). The minimum of sheet resistance was obtained at particular voltage, and this voltage depends on work gas composition. Transparency depends on discharge voltage to a lesser degree and drops only in short wave edge at larger discharge voltage. The area of optimal technological parameters where quality layers with proper characteristics for conductive electrodes can be formed was determined by analysis of experimental results. Ill. 7, bibl. 5 (in English; summaries in Lithuanian, English and Russian).

Ю. Дудонис, А. Йотаутис, Р. Науйокайтис. Исследование процесса осаждения тонких пленок Cd_2SnO_4 методом реактивного магнетронного распыления при низкой температуре // Электроника и электротехника. - Каунас: Технология, 2003. - № 5(47). – С. 48-51.

Прозрачные и электропроводящие оксидные покрытия очень важны при создании солнечных батарей нового поколения, жидкокристальных дисплеев и других элементов оптоэлектроники. Альтернативой широко применяемому оксиду индия могут стать более дешевые материалы, например, Cd_2SnO_4. Однако, оптические и электрические свойства этого материала сильно зависят от технологических параметров, состава и структуры пленки, плотности дефектов, неровности поверхности и концентрации примесей. В данной работе экспериментально исследован процесс реактивного магнетронного осаждения и определено, что прозрачность и электропроводность осаждаемых пленок наиболее зависит от напряжения магнетронного разряда, состава рабочего газа O_2 + Ar и потенциала подложки (смещения). Наименьшее поверхностное сопротивление пленки получается при определенных напряжениях разряда, которые в свою очередь зависят от состава рабочего газа. Прозрачность зависит от напряжения разряда в меньшей степени, и лишь в коротковолновом участке уменьшается при больших напряжениях. Анализ результатов исследования позволил определить область оптимальных технологических параметров, при которых формируемые пленки отвечают требованиям, предъявляемым к прозрачным проводящим электродам. Ил. 7, библ. 5 (на английском языке; рефераты на литовском, английском и русском яз.)