

VILNIUS UNIVERSITY

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CHEMICAL VAPOUR DEPOSITION AND INVESTIGATION OF OXIDE  
MATERIALS FOR ELECTRO- AND PHOTO-CATALYTICAL  
APPLICATIONS

Summary of doctoral dissertation  
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VILNIAUS UNIVERSITETAS

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OKSIDINIŲ MEDŹIAGŲ, TAIKOMŲ ELEKTROKATALIZĖJE IR  
FOTOKATALIZĖJE, PLONŲ SLUOKSNIŲ NUSODINIMAS IŠ CHEMINIŲ  
GARŲ FAZĖS IR TYRIMAS

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## INTRODUCTION

### Relevance of the work

This dissertation content involves two topical issues of materials science: one of them related with application of functional metal oxide thin films in electro- and bioelectrocatalysis, and another with their application in photocatalysis. The main regard was allowed to the synthesis technologies of such thin films and film properties, such as composition, structure, morphology and functional properties.

Very fast denaturation of protein on electrodes is a crucial problem in protein redox transformations. Electrocatalytically active electrodes such as platinum, palladium, gold and other start a rapid denaturation of protein in contact with protein solution due to a strong interaction with sulphur atom of aminoacids. This process causes loss of very expensive proteins. Futhermore, during denaturation the electrode becomes electrochemically inactivated (in literature this phenomenon is refering as “protein fouling”).

It is known that metaloxide surfaces are more “friendly” in point of protein molecules. Such electrodes can be for a long time in contact with protein solutions without noticeable protein denaturation. But electron transfer on these surfaces is slow. Metaloxide electrodes with high electron transfer rapidity would solve a lot of important fundamental and applied bioelectrochemistry problems, such as standart formal redox potentials determination by direct voltamperometric measurements or artificial bioreactors, where electrodes could substitute portion of expensive biochemical reagents (proteins, cofactors, redox mediators).

So, creation of thin film metaloxide electrodes with high electrocatalytic activity, good electrical conductivity, optical transparent, which will be suitable for using in processes with protein solutions is one of topical task in bioelectrocatalysis. One of perspective candidate for such applications is cadmium-tin oxide  $Cd_2SnO_4$  thin films, exhibiting rapid electron transfer in protein redox systems [1, 2]. Unfortunately, sol-gel synthesized thin films showed large dispersion of parameters and poor reproducibility. It was expected, that alternative methods for the synthesis of such films, for example, deposition from chemical vapour, would eliminate these demerits.

Photocatalytical decomposition of water using solar energy and oxide semiconductors to generate clean-energy hydrogen has been a dream of humankind for several decades. The key factor is to develop highly efficient photocatalysts that are active under visible light irradiation. Since the first experiment of H<sub>2</sub> formation via photocatalysis with TiO<sub>2</sub> several decades ago [3], most of the photocatalysts developed up to now have such wide band gaps that they only respond to the ultraviolet light, which occupies only about 4% of the solar spectrum and thus renders overall process impractical. For this reason, considerable efforts have been invested in developing photocatalysts capable of using the less energetic but more abundant visible light, which accounts for about 43% of the incoming solar energy.

A decade ago, first studies on novel series of water splitting photocatalysts InMO<sub>4</sub> (M = Ta, Nb, V) [4, 5] have been reported. It was found, that these photocatalysts can evolve H<sub>2</sub> from pure water under visible light irradiation. Moreover, with Ni doping to the matrix structure, the compounds can split water into H<sub>2</sub> and O<sub>2</sub> in a 2:1 stoichiometric ratio, under visible light irradiation.

Oxide photocatalysts may also be applied in thin films form. Thin film photocatalyst active under visible light irradiation and coated on particular surface can be applied not only for water splitting, it may also be efficient in other redox reactions with materials situated in water or air. This enables potential using of photocatalyst-coated surfaces (for example, glass of windows, dishes,...) for self-cleaning or modification of hydrophility, for decontamination and purification of used water (or air), etc. Visible light active thin films of novel InTaO<sub>4</sub>, InNbO<sub>4</sub> and InVO<sub>4</sub> photocatalysts would be particularly suitable for such purposes. However, technologies of their depositions are just in initial stage, there are just few studies concerned with InTaO<sub>4</sub> and InVO<sub>4</sub> thin films deposition by employing physical methods or chemical sol-gel method. Thin films deposition from chemical vapor phase, as perspective chemical method to deposit such materials, have not been applied yet.

### **Main aims and tasks of the work**

Goals of the work were two considering two research directions:

1. Synthesize by chemical vapor deposition technique thin  $\text{Cd}_2\text{SnO}_4$  films exhibiting high electron transfer rate in redox processes, good electrical conductivity, optical transparency, suitable for applications as electrodes for electro- and bioelectrocatalysis.
2. Synthesize by chemical vapour deposition techniques thin films of  $\text{InTaO}_4$ ,  $\text{InNbO}_4$ ,  $\text{InVO}_4$  and their Ni-doped analogues, suitable for photocatalytical applications.

Tasks to be solved for achieving of main goals:

- Selection and/or synthesis of suitable volatile metalorganic (MO) compounds (precursors) for films deposition from chemical vapour phase.
- Investigation of the influence of various deposition conditions on films growth rate, elemental and phase composition, crystallinity, surface morphology, electric and optical properties, selection of optimal conditions for the films growth.
- Investigation and evaluation of electrocatalytical and photocatalytical activity of synthesized thin films in redox reactions.

### **Novelty of the accomplished research work**

1. Possibilities of deposition by simple aerosol pyrolysis method of thin  $\text{Cd}_2\text{SnO}_4$  films for electrocatalysis applications were investigated for the first time. Crystalline  $\text{Cd}_2\text{SnO}_4$  films with good properties were obtained in-situ at low deposition temperature. Low temperature films formation methods allows using substrates with low melting-point temperature.
2. Possibilities of deposition by low pressure pulsed liquid injection MOCVD method of perspective photocatalysts  $\text{InTaO}_4$  and Ni-doped  $\text{InTaO}_4$  thin films were investigated for the first time.
3. Possibilities of deposition of  $\text{InMO}_4$  ( $M = \text{V}, \text{Nb}, \text{Ta}$ ) films by aerosol pyrolysis method were investigated for the first time and films containing pure crystalline phase were obtained.
4. Possibilities of deposition of Ni-doped  $\text{InMO}_4$  ( $M = \text{V}, \text{Nb}, \text{Ta}$ ) thin films were investigated the first time. Crystalline films with pure  $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$  and  $\text{In}_{1-x}\text{Ni}_x\text{VO}_4$  phases were obtained by aerosol pyrolysis. Photocatalytic activity of synthesized  $\text{In}_{1-x}\text{Ni}_x\text{VO}_4$  thin films was demonstrated for the first time.

**Practical importance of the work:** Deposition of practically important electro- and photocatalyst films were investigated, technological conditions for the synthesis of good crystalline quality films were found.

## 1. LITERATURE REVIEW

In this chapter the literature and existing state-of-art are reviewed in the research field related with the subject of the actual dissertation: transparent conducting oxides and semiconductor oxide photo-catalysts, most important representatives, their structure, properties, synthesis in the bulk and thin film forms, applications for electro- and photocatalysis, related problems.

## 2. EXPERIMENTAL

### *2.1. Volatile metalloorganic compounds and their solutions, substrates*

Complex oxides films have been grown from one vapour source, i.e. from solution where a mixture of metalloorganic components was dissolved in suitable solvent. Selection of suitable commercial metalloorganic (MO) precursors was a big problem. Some of known commercial MO precursors were not suitable for our purposes because of instability of their solutions in organic solvents. That is why some of MO compounds were synthesized in our laboratory.

Selected MO precursors:

#### **For Cd<sub>2</sub>SnO<sub>4</sub> thin films:**

Synthesized Cd(thd)<sub>2</sub>(TMEDA) (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate, TMEDA = N,N,N',N'-tetramethylethylenediamine).

Commercial Sn(Bu)<sub>2</sub>(acac)<sub>2</sub> (acac = (CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>2</sub> or acetylacetonate).

#### **For InTaO<sub>4</sub> thin films:**

Synthesized In(thd)<sub>3</sub> (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate).

Commercial Ta(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub> = Ta(OEt)<sub>5</sub> (by MOCVD method),

Commercial Ta(OEt)<sub>4</sub>(acac) = Ta(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>(CH<sub>3</sub>COCHCOCH<sub>3</sub>) (by aerosol pyrolysis method).



**For InNbO<sub>4</sub> thin films:**

Synthesized In(thd)<sub>3</sub> (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate).

Commercial Nb(thd)<sub>4</sub> (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate).

**For InVO<sub>4</sub> thin films:**

Synthesized In(thd)<sub>3</sub> (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate).

Commercial V(acac)<sub>3</sub> = V(CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>3</sub>.

Synthesized Ni(thd)<sub>2</sub> (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) was used for film doping with nickel.

The most suitable solvents are monoglyme and toluene. Due to higher aerosol generation rate the monoglyme was preferred over toluene. Toluene was used for InTaO<sub>4</sub> deposition by MOCVD method.

Films were mainly grown on silicon (100) substrates, but for comparison and for spectrophotometrical measurements some of films have been grown on glass or sapphire (R-plane) substrates.

**2.2. Deposition methods and equipment**

Two deposition techniques were used for films growth from chemical vapour phase:

1) low pressure MOCVD method, employing pulsed liquid injection MOCVD modification (PI-MOCVD), using a home-build vertical hot-wall PI-MOCVD reactor and solution of volatile MO precursors (for InTaO<sub>4</sub> and In<sub>1-x</sub>Ni<sub>x</sub>TaO<sub>4</sub> films);

2) simple aerosol pyrolysis deposition method at the atmospheric pressure employing home-build deposition equipment and solution of volatile MO precursors (for Cd<sub>2</sub>SnO<sub>4</sub>, InTaO<sub>4</sub> and In<sub>1-x</sub>Ni<sub>x</sub>TaO<sub>4</sub>, InVO<sub>4</sub>, In<sub>1-x</sub>Ni<sub>x</sub>VO<sub>4</sub>, InNbO<sub>4</sub>, In<sub>1-x</sub>Ni<sub>x</sub>NbO<sub>4</sub> films).

Schemes of deposition equipment are shown in Fig.1. Spray pyrolysis method becomes simplified modification of MOCVD, if solutions of volatile MO compounds are used. Solvent and MO precursors of aerosol evaporates near the substrate, so, the film is growing from vapour phase. In contrast to the low pressure MOCVD, in the aerosol pyrolysis process the film grows under atmospheric pressure and expensive vacuum equipment is unnecessary. So, aerosol pyrolysis is simpler and cheaper method than MOCVD.

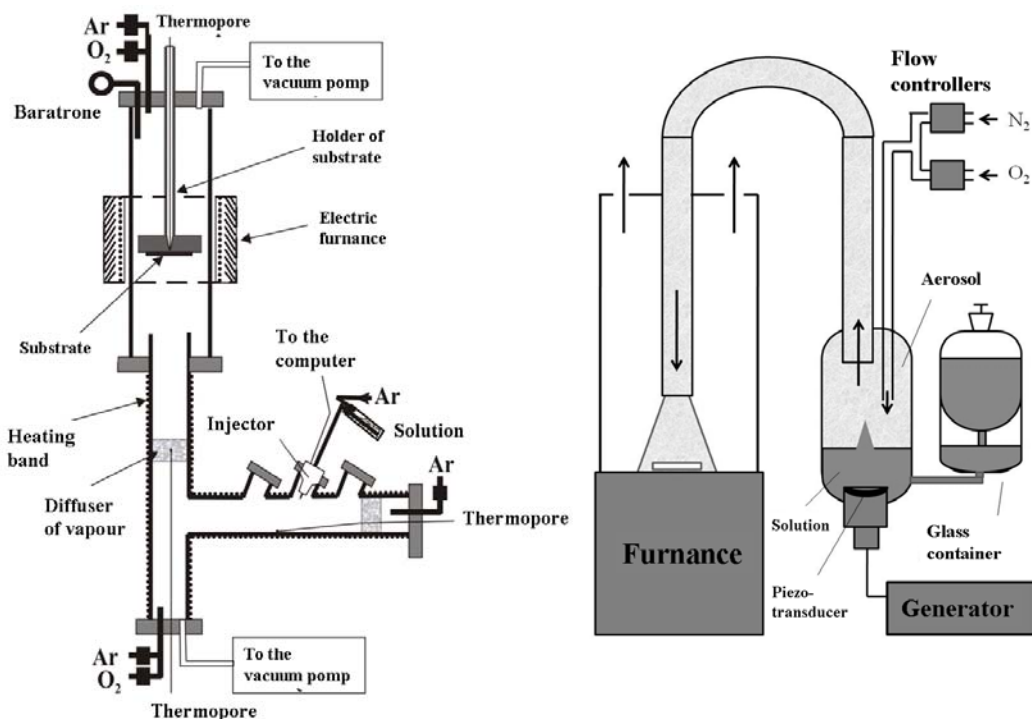


Fig. 1 Schemes of deposition equipment: on the left – PI-MOCVD reactor, on the right – aerosol pyrolysis equipment.

### 2.3. Methods and equipment for films characterisations.

Various methods and equipment were used for investigation of deposited films :

- X-ray diffraction (XRD) (Bruker D8, Philips diffractometers) – to study films crystallinity and microstructure.
- Optical microscopy (LEITZ microscope) – for preliminary study of film surface morphology.
- Atomic force microscopy (AFM) (Digital Instruments Multimode Scanning Probe Microscope) – for study of surface morphology and roughness.
- Profilometry (Taylor-Hobson profilometer) – for determination of film thickness.
- Scanning electron microscopy (SEM), wavelength dispersive X-ray spectroscopy (WDS) and energy dispersive X-ray spectroscopy (EDS) (PEM-100 or XL-30ESEM microscopes with analyzers) – for study of films surface morphology and composition.
- X-ray photoelectron spectroscopy (XPS) (Riber LAS200 instrument) – for study of films composition and atoms oxidation states.

- Spectrophotometry (Perkin Elmer UV/VIS Lambda 35) – for measuring of transmittance/absorbance spectra of films and precursors solutions.
- Electrochemical impedance spectroscopy (EIS) (PGSTAT 302 with FRA 2 module, Autolab, Utrecht, Netherlands) – for capacitance measurements of Cd<sub>2</sub>SnO<sub>4</sub> electrodes.
- Cyclic voltamperometry (μAutolab Type III, Utrecht, Netherlands) – for evaluation of electrocatalytic activity of Cd<sub>2</sub>SnO<sub>4</sub> films in redox reactions.
- Water contact angle measurements (using 125 W Xe lamp, CERMAX PE175BUV from CVI) and photodegradation method were used for evaluation of photocatalytic activity of grown films.
- Four-probe technique – for resistivity measurements of Cd<sub>2</sub>SnO<sub>4</sub> films.

### 3. RESULTS

#### 3.1. Cd<sub>2</sub>SnO<sub>4</sub> deposition by aerosol pyrolysis.

Cd<sub>2</sub>SnO<sub>4</sub> thin films were deposited by aerosol pyrolysis using solution of Cd(thd)<sub>2</sub>(TMEDA) and Sn(Bu)<sub>2</sub>(acac)<sub>2</sub> in monoglyme. At first, the possibilities of deposition of individual CdO and SnO<sub>2</sub> thin films were investigated before depositions of Cd<sub>2</sub>SnO<sub>4</sub> thin films. Then, a series of depositions of Cd-Sn-O films was carried under similarly deposition conditions, at 400°C, by changing only molar ratio of Cd and Sn MO precursors in solution in the range 0,8 – 4. Deposition conditions of individual and complex oxides are summarised in Table 1.

Table 1. General deposition conditions of CdO, SnO<sub>2</sub> and Cd<sub>2</sub>SnO<sub>4</sub> films by aerosol pyrolysis.

Condition	CdO	SnO <sub>2</sub>	Cd – Sn – O
MO precursors	Cd(thd) <sub>2</sub> TMEDA	Sn(Bu) <sub>2</sub> (AcAc) <sub>2</sub>	Cd(thd) <sub>2</sub> TMEDA, Sn(Bu) <sub>2</sub> (AcAc) <sub>2</sub>
Solvent	Monoglyme	Monoglyme	Monoglyme
Concentration, M	0,01	0,01	Cd + Sn = 0,02
Deposition temperature, °C	300 - 450	300 - 450	400
Nitrogen flow, l/min	4,5	4,5	4,5
Distance*, cm	3	3	3
Oxygen flow, l/min	0,5	0,5	0,5
Cd/Sn ratio in solution	-	-	variable
Substrate	Si (100)	Si (100)	Si (100), sapphire (R-plane), glass
Growth rate, nm/min	8,5 – 10,5	6 – 11.5	10 - 20

The ratio Cd/Sn in films was determined by EDS analysis. Fig. 2 shows the relationship between atomic Cd/Sn ratio in solution and in film together with the change of films resistivity. Near linear relation between Cd/Sn ratios in film and in solution was found, however, films containing stoichiometric ratio Cd/Sn = 2 are obtained from solutions, in which the

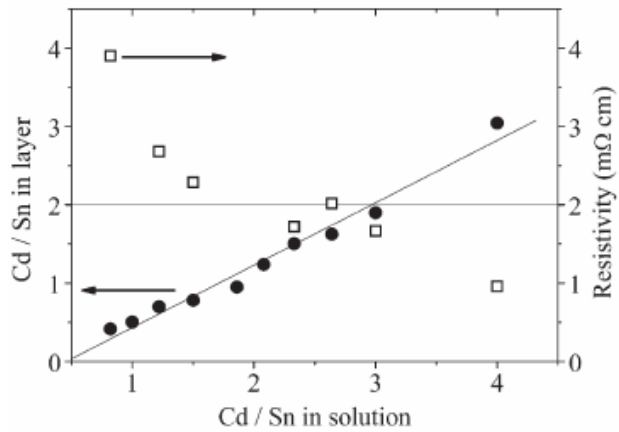


Fig. 2. Cd/Sn ratio in Cd-Sn-O film on silicon (●) and film resistivity (□) vs. Cd/Sn ratio in solution  $T_{dep} = 400$  °C.

ratio Cd/Sn = 3. XRD study demonstrated (Fig.3) that Cd-Sn-O (CTO) films grown at 400 °C from solutions with Cd/Sn = 3 contained pure cubic  $Cd_2SnO_4$  phase. Films on silicon and glass were polycrystalline (Fig. 3a), while those grown on sapphire had a strong (100) texture (the full width at half maximum of rocking curves was 1,5-1,7 °) (Fig. 3b). XRD  $\phi$ -scan for  $Cd_2SnO_4$  (220) reflection presented in Fig. 3c shows that  $Cd_2SnO_4$  crystallites are in-plane oriented (the full width at half maximum was 1,8-2,0 °) on sapphire, so the films can be considered as biaxially textured.  $Cd_2SnO_4$  thin films obtained by aerosol pyrolysis exhibit > 80 % transparency in the spectral range from 500 to 1000 nm.

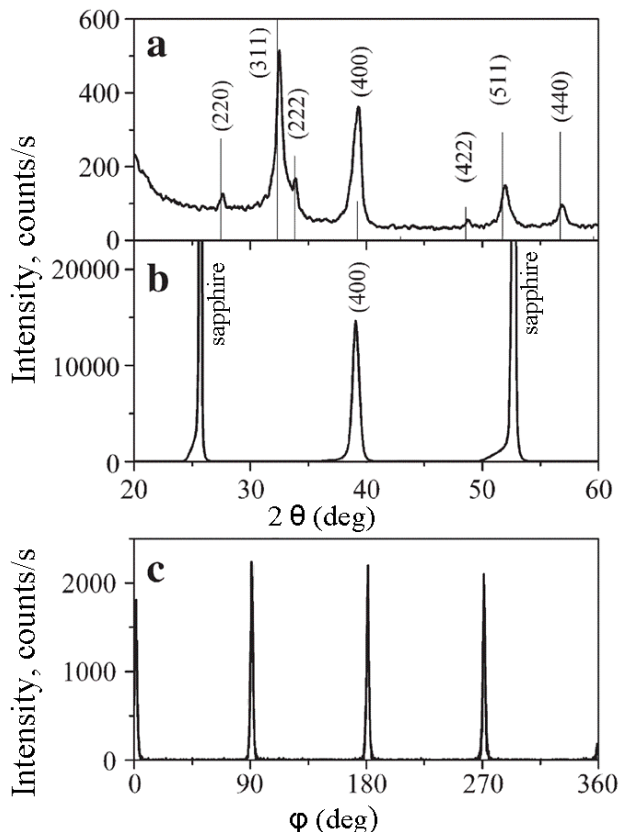


Fig. 3. XRD  $\theta/2\theta$  scans for  $Cd_2SnO_4$  films on silicon (a) and sapphire (b) grown at 400 °C from solutions with Cd/Sn=3. Vertical lines show peak positions from powder XRD data file of cubic  $Cd_2SnO_4$ . (c) XRD  $\phi$ -scan of  $Cd_2SnO_4$  (220) reflection for film on sapphire.

Capacitance of double electric layer of  $\text{Cd}_2\text{SnO}_4$  electrodes was determined by electrochemical impedance spectroscopy (EIS) by measuring EIS at different electrode potential. Frequency varied in the range from 7 to 30 kHz. Buffer solution of 0,1 M NaCl, 0,01M  $\text{NaH}_2\text{PO}_4$  and NaOH was used as electrolyte (pH = 7). Silver-silver chloride electrode filled with saturated KCl solution was used as a reference. Coiled Pt wire served as an auxiliary electrode.

In Fig. 4, Mott–Schottky plot is indicating linear dependence of  $C^{-2}$  vs. E (C is the differential electrode capacitance, and E is the potential) in the potential range 0,4-1,1 V. In this potential range, the slope that is inversely proportional to the charge carrier concentration in the semiconductor was found to be  $6,72 \cdot 10^8 \text{ F}^{-1}\text{V}^{-1}\text{cm}^2$ , which is by a factor of  $\sim 2,5$  smaller than the one reported for the CTO sol–gel films ( $1,72 \cdot 10^9 \text{ F}^{-1}\text{V}^{-1}\text{cm}^2$ , [1]) annealed at  $750 \text{ }^\circ\text{C}$ . The Mott–Schottky slope of  $6,72 \cdot 10^8 \text{ F}^{-1}\text{V}^{-1}\text{cm}^2$  suggests charge carrier concentrations as high as  $N > 10^{21} \text{ cm}^{-3}$ , thus, attesting for the electronic degeneration in these films.

Electrochemical activity of the grown  $\text{Cd}_2\text{SnO}_4$  films was tested using three redox systems: hexacyano ferro/ferricyanide (FC), safranin T (ST) and redox protein cytochrome C. Background subtracted cyclic voltammograms, recorded using

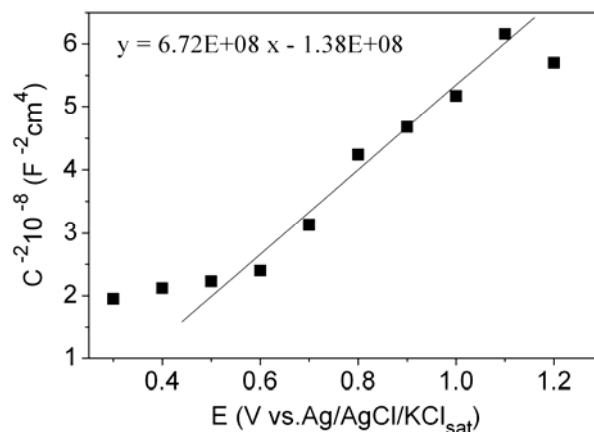


Fig. 4. Capacitances in Mott–Schottky plot, linear equation approximating experimental line is displayed on the plot. Data are normalized with respect to the geometric surface area. Substrate – silicon..

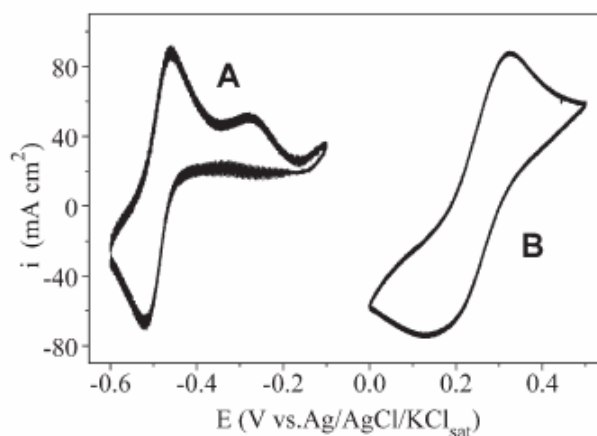


Fig.5. Background-subtracted cyclic voltammetry curves of: A — safranin T, and B— hexacyano ferricyanide on  $\text{Cd}_2\text{SnO}_4$  film deposited on glass substrate. Solution: 0.1 M NaCl, 0.01 M  $\text{NaH}_2\text{PO}_4$  adjusted with NaOH to pH 7.2. Concentration of the redox species is 0.001 M. Sweep rate—20 mV/s. Current normalized with respect to the geometric surface area.

spray-pyrolysis  $\text{Cd}_2\text{SnO}_4$  electrodes on glass substrates are shown in Fig. 5. The cyclic voltammetry response exhibits typical features of a quasi-reversible electron transfer process. The midpoint potentials of the FC and ST redox systems,  $E^\circ(\text{FC}) = 0,230 \text{ V}$  and  $E^\circ(\text{ST}) = -0,495 \text{ V}$  match well with the ones reported in Ref. [1]. As seen from the data in Table 2, the spray-pyrolysis cadmium stannate films exhibit electron transfer (ET) rates one or two orders of magnitude higher compared to the sol-gel films annealed at  $600 \text{ }^\circ\text{C}$ . Compared to the sol-gel films annealed at  $750 \text{ }^\circ\text{C}$  (these are the most electrochemically active films obtained via sol-gel route) ET transfer rate is  $\sim 3$  times higher for the ST system and about the same for the FC system (Table 2).

These results suggest that, for the low-melting point substrates (for example, glass), the spray-pyrolysis technique has an advantage over the sol-gel technique because it allows using much lower film formation temperature, and at the same time renders noticeably higher electrochemical activity  $\text{Cd}_2\text{SnO}_4$  electrodes compared to films obtained via sol-gel route.

Table 2. Comparison of the electron transfer rate constants ( $k_s$ ) for two redox systems on spray pyrolysis  $\text{Cd}_2\text{SnO}_4$  electrodes and the ones reported earlier [1] for the sol-gel  $\text{Cd}_2\text{SnO}_4$  films.

Redox System	$k_s, \text{ cm s}^{-1}$		
	spray-pyrolysis films, $400 \text{ }^\circ\text{C}$	sol-gel films annealed at $600 \text{ }^\circ\text{C}$ [1]	sol-gel films annealed at $750 \text{ }^\circ\text{C}$ [1]
Hexacyano ferro/ferricyanide	$7,08 \cdot 10^{-4}$	$7,90 \cdot 10^{-6}$	$6,70 \cdot 10^{-4}$
Safranine T	$1,70 \cdot 10^{-3}$	$1,69 \cdot 10^{-5}$	$4,49 \cdot 10^{-4}$

Redox protein cytochrome C was also examined by cyclic voltammetry, but there was not observed any clear current of a redox process, maybe because the commercial “Sigma” protein was not purified additionally.

### 3.2. *InTaO<sub>4</sub> deposition by low pressure MOCVD.*

Low-pressure MOCVD method is more complicated than spray pyrolysis because process goes under vacuum, though not very deep. A modification of MOCVD - pulsed liquid injection MOCVD (PI-MOCVD) was used for  $\text{InTaO}_4$  films deposition.

Preliminary, the possibilities to grow single oxide layers of  $\text{In}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  on Si (100) substrates were studied using  $\text{In}(\text{thd})_3$  and  $\text{Ta}(\text{OC}_2\text{H}_5)_5$  MO precursors. Crystalline phase of cubic  $\text{In}_2\text{O}_3$  forms in thin films at  $\geq 500$  °C and monoclinic  $\text{Ta}_2\text{O}_5$  forms only at 700 °C temperature. When temperature of substrate was lower, amorphous layers of  $\text{Ta}_2\text{O}_5$  were obtaining.

Depositions of  $\text{InTaO}_4$  was carried out on silicon (100) substrates using solution of

Table 3. Deposition conditions of  $\text{InTaO}_4$  films by MOCVD

Parameter	
MO compounds	$\text{In}(\text{thd})_3$ , $\text{Ta}(\text{OC}_2\text{H}_5)_5$
Temperature of evaporator	280 °C
Argon flow	420 sccm
Oxygen flow	250 sccm
Pressure	5 Torr
Impulse time	2,5 ms
Frequency	2 Hz

$\text{In}(\text{thd})_3$  and  $\text{Ta}(\text{OC}_2\text{H}_5)_5$  in toluene (total concentration 0,05 M). Fixed preliminary deposition conditions are shown in Table 3. The influence of solution composition and of substrate temperature on elemental and phase composition and crystallinity of In-Ta-O films were estimated. XRD analysis showed that the films deposited at 700 °C were composed from a mixture of cubic  $\text{In}_2\text{O}_3$  and monoclinic  $\text{Ta}_2\text{O}_5$  (Fig. 6 a). However, films deposited at 850 °C already contained monoclinic  $\text{InTaO}_4$  phase together with  $\text{In}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  phases (Fig. 6b). The attempts to obtain pure  $\text{InTaO}_4$  phase in films by changing solution composition was unsuccessful, there were always more or less intermixtures of  $\text{In}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$ .

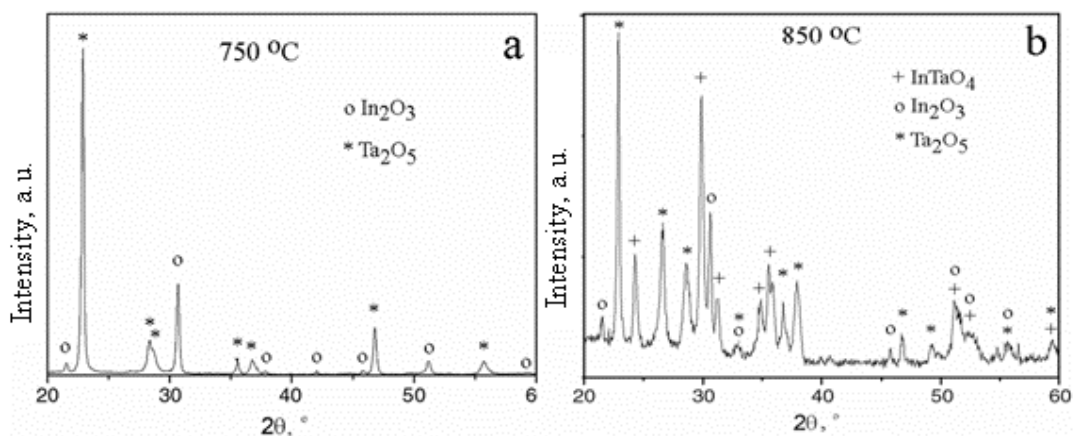


Fig. 6. XRD  $\theta/2\theta$  scans for In-Ta-O films grown at 750°C (a) and at 850 °C (b). In:Ta ratio in solution is 1:1.

According to literary review of works in the research field, nickel doping into position of indium has a big influence on photocatalytic activity of indium tantalate. So, we also tested the possibility to grow Ni-doped indium tantalate films by MOCVD. Our

best  $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$  thin films were grown at 850 °C using adjusted composition of solution and gas flows: 0,027 M  $\text{In}(\text{thd})_3$ ; 0,02 M  $\text{Ta}(\text{OC}_2\text{H}_5)_5$ ; 0,003 M  $\text{Ni}(\text{thd})_2$ , 570 sccm Ar + 100 sccm  $\text{O}_2$ . XRD analysis showed that monoclinic  $\text{InTaO}_4$  phase was predominant, but films still had some amount of indium and tantalum oxides.

Even though a pure phase in undoped and Ni doped  $\text{InTaO}_4$  thin films was not obtained, their photocatalytic activity was evaluated from changes of film hydrophilic properties under light irradiation. Reduction of water contact angle demonstrates the increase of hydrophilic behavior of film surface, this indirectly demonstrates photocatalytic activity of material. The evolution of the contact angle for an In-Ni-Ta-O thin films illuminated with visible and UV+visible light is shown in Fig.7. The decrease in contact angle from 85 ° to around 60 ° was observed under visible light illumination, a proof that visible photons are able to induce surface photochemical processes. Thereafter, the UV filter was removed and the film was exposed to UV + visible spectrum illumination and the surface becomes fully hydrophilic with a contact angle near 0 ° (i.e., super-hydrophilic state). The contact angle of undoped  $\text{InTaO}_4$  exposed to visible light irradiation changes from 90° to only 83°. However, this sample became fully hydrophilic when illuminated with the full spectrum of the lamp (curve not shown). This shows that both undoped and Ni-doped indium tantalate films exhibit certain photocatalytic activity, but first of them is more active under visible light.

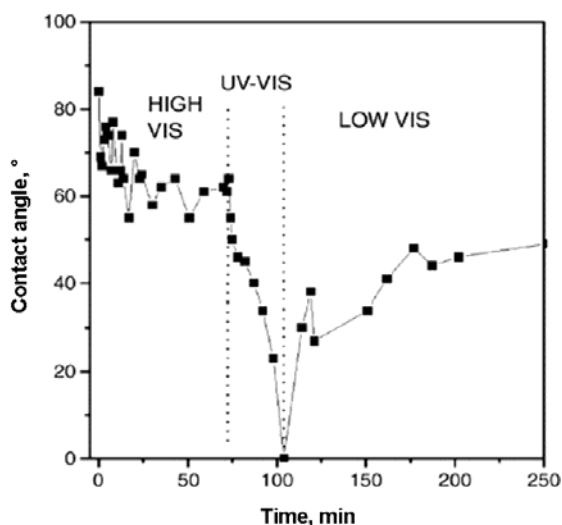


Fig.7. Evolution of the water contact angle of Ni doped indium tantalate thin film deposited at 850 °C, subjected to sequential illumination with visible, UV+visible, and visible photons.

### 3.3. Deposition of $\text{InMO}_4$ ( $M = \text{Ta}, \text{Nb}, \text{V}$ ) films by aerosol pyrolysis.

At first, the possibilities to grow individual oxides  $\text{In}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  by aerosol pyrolysis, using above-mentioned (section 2.1.) selected MO precursors were investigated. This let us to evaluate growth rates of oxide films at different substrate temperatures and crystallization temperatures of oxides. Deposition of complex



oxides  $\text{InTaO}_4$ ,  $\text{InNbO}_4$  and  $\text{InVO}_4$  by spray pyrolysis further were investigated considering the determined conditions of the growth and crystallization of single oxides.

### 3.3.1. Deposition of $\text{InTaO}_4$ films.

Solutions of  $\text{In}(\text{thd})_3$  and  $\text{Ta}(\text{OEt})_4(\text{acac})$  in monoglyme (total concentration 0,02 M) were used for  $\text{InTaO}_4$  deposition. The main problem was that  $\text{InTaO}_4$  in crystallizes only at high temperature ( $> 800\text{ }^\circ\text{C}$ ). However, high deposition temperature ( $\geq 700\text{ }^\circ\text{C}$ ) is dangerous in aerosol pyrolysis technique due to possible inflammation of aerosol in presence of oxygen, so the studied deposition temperature was limited to  $650\text{ }^\circ\text{C}$ . The in-situ growth of  $\text{InTaO}_4$  films was unsuccessful in the temperature range  $500\text{-}650\text{ }^\circ\text{C}$ . Only crystalline cubic  $\text{In}_2\text{O}_3$  phase was observed in films by XRD even when elemental composition of the films was near stoichiometric ( $\text{In}/\text{Ta} \approx 1$ ). This suggests that indium oxide is probably distributed in the matrix of amorphous tantalum oxide in these films. So, a two-steps ex-situ approach was investigated for the preparation of  $\text{InTaO}_4$  films. It consisted of deposition of complex film at  $500\text{ }^\circ\text{C}$  in the first step and film annealing in air or Ar atmosphere at  $800\text{-}900\text{ }^\circ\text{C}$  in the second step.

It consisted of deposition of complex film at  $500\text{ }^\circ\text{C}$  in the first step and film annealing in air or Ar atmosphere at  $800\text{-}900\text{ }^\circ\text{C}$  in the second step.

In order to get stoichiometric  $\text{In}/\text{Ta}$  ratio in film, it was important to select the suitable  $\text{In}/\text{Ta}$  ratio in solution. A series of  $\text{In-Ta-O}$  films was grown at  $500\text{ }^\circ\text{C}$ , using solutions with different  $\text{In}/\text{Ta}$  ratio. Films were annealed at  $800\text{ }^\circ\text{C}$  in air or argon atmospheres. EDS analysis showed the linear dependence between compositions of films and solution, but  $\text{In}/\text{Ta}$  ratio in film always was smaller than in solution. XRD study (Fig.8) showed that after annealing in Ar, pure monoclinic  $\text{InTaO}_4$  phase in film can be

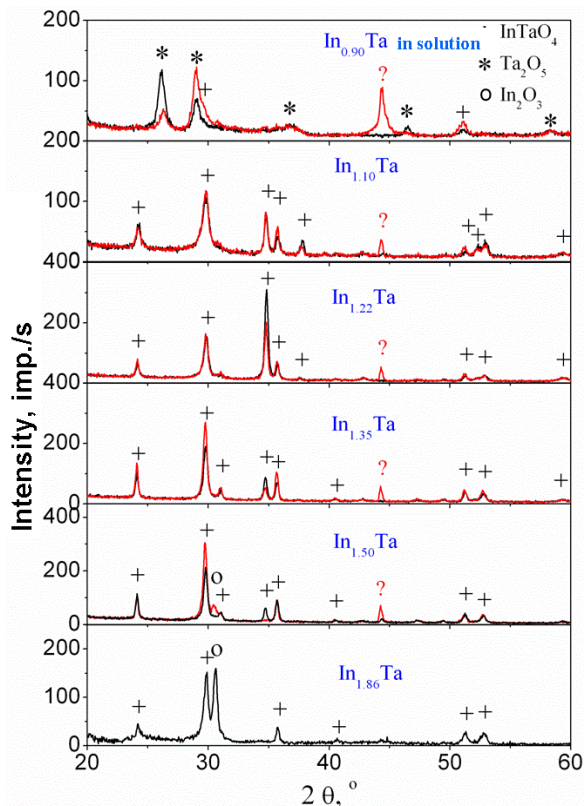


Fig.8. XRD patterns of  $\text{InTaO}_4$  films deposited in two-step (ex-situ, deposition at  $500\text{ }^\circ\text{C}$  + annealing at  $800\text{ }^\circ\text{C}$ ) processes using solutions with different  $\text{In}/\text{Ta}$  ratio. Black curves – annealed in the Ar atmosphere, red curves – in the air.

obtained when In/Ta ratio in solution is in the range 1,1-1,35. Outside this range, additional monoclinic Ta<sub>2</sub>O<sub>5</sub> or cubic In<sub>2</sub>O<sub>3</sub> phases were found in films. In accordance with EDS analysis, annealed films with pure InTaO<sub>4</sub> phase have In/Ta ratio 0,88-1,04, i.e. they are deficient in In. This suggests that the crystal structure of InTaO<sub>4</sub> films tolerate some deficiency of In. Main difference between films annealed in air and Ar is that the first films contain additional unidentified phase (peak at 2θ = 44,3 °, Fig. 8), probably corresponding to some product of interaction between film and substrate.

Results presented in this chapter show that films containing high crystallinity pure InTaO<sub>4</sub> phase may be obtained by aerosol pyrolysis.

### 3.3.1. Deposition of InNbO<sub>4</sub> films.

Solutions of In(thd)<sub>3</sub> and Nb(thd)<sub>4</sub> in monoglyme (total concentration 0,02 M) were used for InNbO<sub>4</sub> deposition by aerosol pyrolysis. InNbO<sub>4</sub> films may be obtained by both ex-situ and in-situ processes. Films grown at 400 °C were amorphous. Annealing (800 °C, 1h, Ar) of amorphous films grown from solutions with proper In/Nb ratio (~ 1,1) results in crystallisation of monoclinic InNbO<sub>4</sub> phase (Fig.9).

At higher temperature (500 and 600 °C), pure monoclinic InNbO<sub>4</sub> phase in film may be obtained in as-grown films (Fig.9) when In/Nb ratio in solution is ~0,85 and ~0,7, respectively.

### 3.3.3. Deposition of InVO<sub>4</sub> films.

Solutions of In(thd)<sub>3</sub> and V(acac)<sub>3</sub> in monoglyme (total concentration 0,02 M) were used for InVO<sub>4</sub> deposition by aerosol pyrolysis. Films of InVO<sub>4</sub> may also be obtained using ex-situ and in-situ approaches like to InNbO<sub>4</sub> films. The relation between

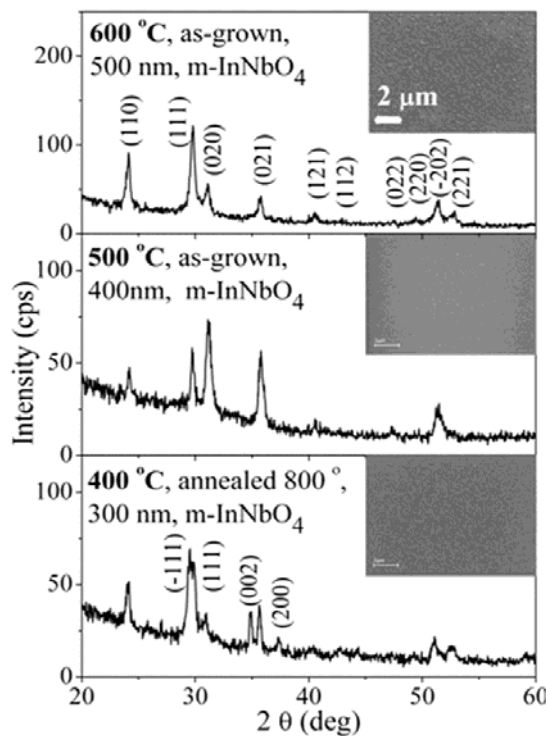


Fig.9. XRD patterns and SEM pictures of InNbO<sub>4</sub> films prepared by aerosol pyrolysis on silicon, in single or two-step processes.

In/V ratio in film and solution is given in Fig. 10. Figure shows, that in case of different deposition temperatures, different In/V ratio in solution has to be used in order to get stoichiometric In/Va ratio in films. Near stoichiometric films may be obtained when In/V ratio in solution is  $\sim 0,8$  (400 °C),  $\sim 1,2$  (500 °C) and  $\sim 1,5$  (600 °C)

Films grown at 400 °C were amorphous, similarly to InNbO<sub>4</sub> films. Annealing of stoichiometric amorphous films at 800 °C in Ar results in formation of pure orthorhombic phase (Fig. 11). Films grown in-situ at higher temperature exhibit different crystallization behavior depending on deposition temperature: monoclinic InVO<sub>4</sub> forms at 500 °C and orthorhombic at 600 °C (Fig. 11) in stoichiometric films.

Near stoichiometric films are obtained when In/V ratio in solution is around 0,8 (400 °C), 1,2 (500 °C) and 1,5 (600 °C) (Fig. 10).

Detailed XRD analysis showed that pure orthorhombic InVO<sub>4</sub> phase forms in films deposited at 600 °C may be obtained from solutions with In/V ratio in the range of 1-1,5. At 500 °C, the pure monoclinic phase crystallizes in film when using solutions with In/V  $\approx 1-1,2$ . These films are deficient in In, what shows that InVO<sub>4</sub> structure

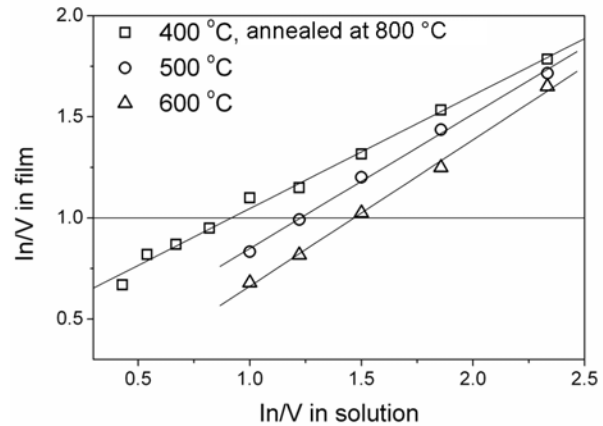


Fig.10. In/V ratio in films in relation with In/V ratio in solution, at different deposition temperatures. Films grown at 400 °C were annealed at 800 °C, 1h in argon.

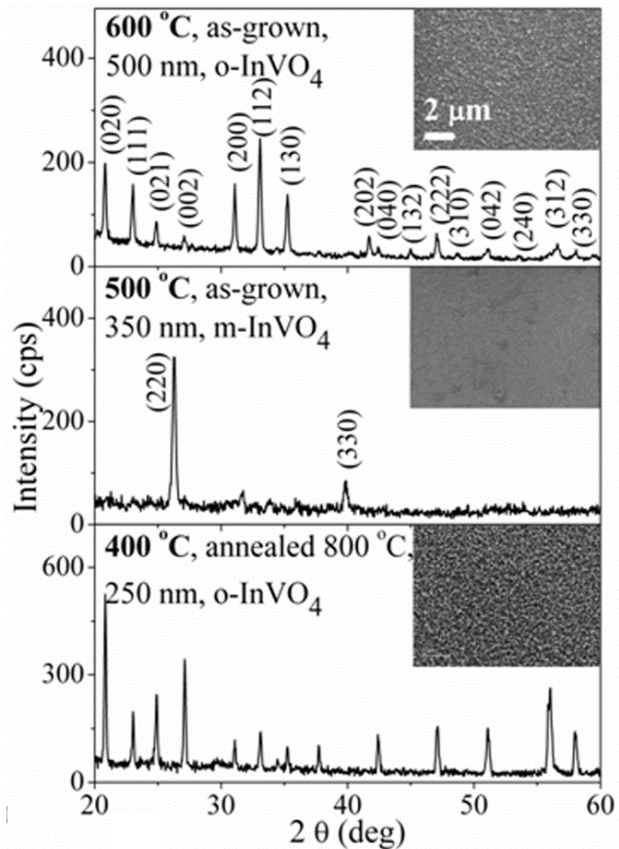


Fig.11. XRD patterns and SEM pictures of InVO<sub>4</sub> films prepared on silicon at different temperature in a single or two-step processes (in-situ or ex-situ deposition).

tolerate some deficit of In, moreover, it was found that such In deficit may be bigger than in case of  $\text{InTaO}_4$  structure.

### 3.3.4. Deposition of Ni-doped $\text{InVO}_4$ and $\text{InTaO}_4$ films.

Ni-doped  $\text{InVO}_4$  films were grown in-situ at 600 °C. Solutions of  $\text{In}(\text{thd})_3$ ,  $\text{V}(\text{acac})_3$  and  $\text{Ni}(\text{thd})_2$  in monoglyme were used for  $\text{In}_{1-x}\text{Ni}_x\text{VO}_4$  deposition.  $\text{In}(\text{thd})_3$  and  $\text{V}(\text{acac})_3$  concentration in solution were fixed at values (0,012 M and 0,008 M, respectively) which resulted obtaining pure orthorhombic  $\text{InVO}_4$  phase in films.

Concentration of  $\text{Ni}(\text{thd})_2$  was varied in the range 0-0,0075 M. Fig.12 shows the changes of film composition (at. %) in relation to nickel content added to solution. The increase of Ni content in solution resulted in the increase of Ni quantity and decrease of In quantity in films, while V content in films remained almost the same. (In+Ni)/V ratio in film remains near 1 in all range of Ni additions. Such change of films composition suggests that In is changed by Ni in vanadate structure.

XRD study of films of this series confirms that indium is exchanged by nickel in the structure (Fig.13). All films of the series have pure orthorhombic  $\text{In}_{1-x}\text{Ni}_x\text{VO}_4$  phase. Some shift of diffraction

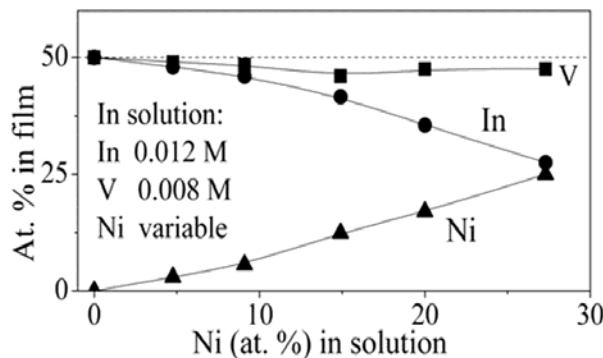


Fig.12. Composition of Ni-doped  $\text{InVO}_4$  films grown at 600 °C in relation with Ni quantity in solution.

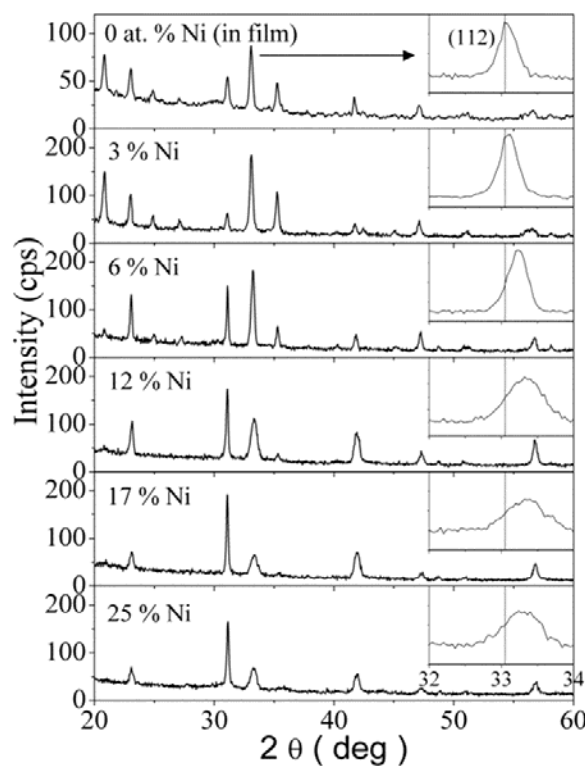


Fig.13. XRD patterns of Ni-doped films. Atomic % was calculated as element quantity ratio to the total Ni, In, V quantity. Insets correspond to enlarged parts of XRD patterns ( $2\theta = 32-34^\circ$ ) demonstrating the shift of (112) reflection position.

peaks to higher angles may be observed when Ni content in films increases (insets in Fig.13). This may be attributed to the decrease of the cell volume due to substitution of bigger  $\text{In}^{3+}$  (0,092 nm) by smaller  $\text{Ni}^{2+}$  (0,078 nm).  $\text{In}_{1-x}\text{Ni}_x\text{VO}_4$  structure remains stable when doped by Ni up to 25 at. % (or up to  $x \approx 0,5$ ). The further increase of Ni quantity in solution (and in film) resulted in apparition of admixture of NiO in films.

Preliminary study of the photocatalytic activity of Ni-doped  $\text{InVO}_4$  films was made observing the photodegradation process of organic dye methylene blue in presence of film, under UV light ( $\lambda \sim 365$  nm) irradiation. Activity of undoped indium vanadate film was also investigated for comparison. Photodegradation curves of methylene blue in presence of  $\text{InVO}_4$  film doped with different Ni quantity are shown in Fig.14. Undoped  $\text{InVO}_4$  films and films doped by Ni up to  $\sim 12$  at. % did not exhibited any photocatalytic activity. However, the film doped by  $\sim 25$  % of Ni already demonstrated photocatalytic activity which may be considered as interesting, taking into account very small quantity/surface area ( $\sim 1$  cm<sup>2</sup>) of photocatalyst.

Like to  $\text{InTaO}_4$  films, Ni-doped  $\text{InTaO}_4$  films were prepared by ex-situ process, i.e. deposition at 500 °C and annealing at 800 °C (1 h in Ar). Preparation of Ni doped  $\text{InTaO}_4$  films by ex-situ process is more complicated than in-situ growth of Ni-doped  $\text{InVO}_4$

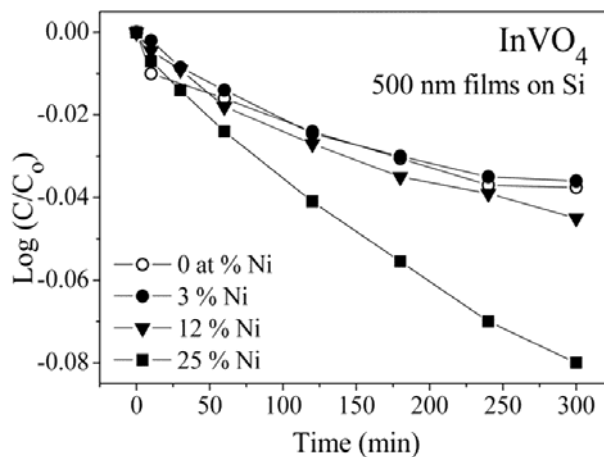


Fig.14. Photodegradation curves of methylene blue under light ( $\lambda \sim 365$  nm) in the presence of  $\text{InVO}_4$  film on silicon doped with different quantity of Ni. Films thickness is 500 nm.  $C/C_0$  is the ratio of actual and initial dye concentrations in solution.

investigated for comparison. Photodegradation curves of methylene blue in presence of  $\text{InVO}_4$  film doped with different Ni quantity are shown in Fig.14. Undoped  $\text{InVO}_4$  films and films doped by Ni up to  $\sim 12$  at. % did not exhibited any photocatalytic activity. However, the film doped by  $\sim 25$  % of Ni already demonstrated photocatalytic activity

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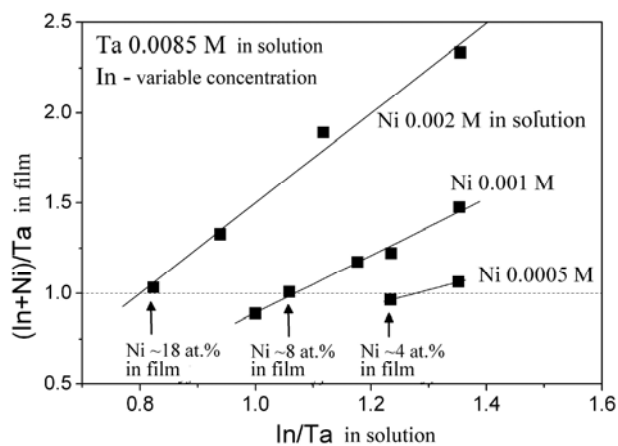


Fig. 15.  $(\text{In}+\text{Ni})/\text{Ta}$  ratio in film in relation with  $\text{In}/\text{Ta}$  ratio in solution in case of different Ni-doping levels in film. Films are grown at 500°C and annealed at 800 °C in Ar.

films. In case of Ni-doped  $\text{InTaO}_4$  films, the adding of Ni precursor to solution with optimum (for  $\text{InTaO}_4$ ) In/Ta ratio resulted in large deviation of film composition from stoichiometric (In+Ni)/Ta ratio and in formation of mixtures of various phases after annealing. The implication is that only accurate adjusting of In/Ta ratio in solutions for each Ni quantity allows obtaining the near stoichiometric (In+Ni)/Ta ratio (Fig. 15) and monoclinic  $\text{InTaO}_4$  phase in films.

As can be seen from Fig.16, pure monoclinic  $\text{InTaO}_4$  phase may be obtained in films doped by  $\sim 4$  at.% ( $x \sim 0,08$ ) and  $\sim 8$  at.% ( $x \sim 0,16$ ). Attempts to introduce higher Ni quantity (18 at.% or  $x \sim 0,36$ ) into film resulted in apparition of a small  $\text{NiTa}_2\text{O}_6$  (or  $\text{NiO}$ ?) peak in XRD pattern. Formation of admixture of  $\text{NiTa}_2\text{O}_6$  phase in  $\text{In}_{1-x}\text{N}_x\text{TaO}_4$  powder with  $x > 0,2$  was observed by other researches also, what shows the reduced stability of  $\text{In}_{1-x}\text{N}_x\text{TaO}_4$  structure when  $x > 0,2$ .

Unfortunately, no any clear photocatalytic activity has been found for Ni-doped  $\text{InTaO}_4$  films in photodegradation reaction of methylene blue. This probably shows not sufficient

optimization of Ni-doped  $\text{InTaO}_4$  films for their photocatalytic applications. There may be many other important factors for photocatalytic activity of films such as film morphology, thickness, influence of co-catalysts and etc.

In case of  $\text{InNbO}_4$  films, we did not succeed in obtaining pure Ni-doped monoclinic  $\text{InNbO}_4$  phase using both ex-situ and in-situ preparation approaches. The addition of even small quantity of Ni precursor into solution resulted in formation of mixtures of different phases in films.

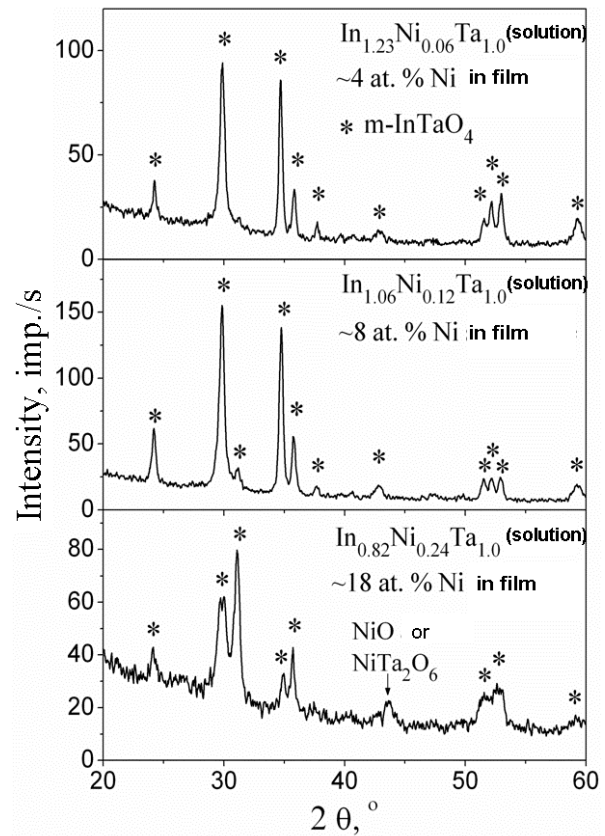


Fig. 16. XRD patterns of  $\text{InTaO}_4$  films doped with different Ni quantity. Peaks of monoclinic  $\text{InTaO}_4$  phase are marked by asterisk.

In summary, the obtained results show that aerosol pyrolysis is better method for the deposition of  $\text{InMO}_4$  ( $M = \text{V, Ta, Nb}$ ) layers than low pressure MOCVD. It may be noted, that crystalline films, consisting of pure  $\text{InTaO}_4$ ,  $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$  and  $\text{In}_{1-x}\text{Ni}_x\text{VO}_4$  phases, were deposited first time overall.  $\text{InNbO}_4$  and  $\text{InVO}_4$  thin films were deposited for the first time from vapour phase by spray pyrolysis method. Up to now,  $\text{InNbO}_4$  and  $\text{InVO}_4$  films were only prepared ex-situ by sol-gel method. Besides, we demonstrated photocatalytic activity of  $\text{In}_{1-x}\text{Ni}_x\text{VO}_4$  films for the first time.

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## CONCLUSIONS

1. Possibilities to grow  $\text{Cd}_2\text{SnO}_4$  thin films by simple aerosol pyrolysis method were investigated for the first time. Aerosol pyrolysis allows obtaining conducting and light transparent  $\text{Cd}_2\text{SnO}_4$  films.
2. Electrochemical properties of  $\text{Cd}_2\text{SnO}_4$  thin films were determined by electrochemical impedance spectroscopy and cyclic voltammetry. Higher charge carrier concentration and higher electron transfer rate in simple redox systems were obtained for aerosol pyrolysis films, compared to  $\text{Cd}_2\text{SnO}_4$  films prepared by sol-gel technique. Unfortunately, there was no any clear currents of redox processes in protein cytochrome C system, what may occur due to possible presence of impurities in tested protein.
3. Compared to sol-gel technique, aerosol pyrolysis allows obtaining of  $\text{Cd}_2\text{SnO}_4$  films with better electrochemical properties *in-situ* at low temperature (400 °C). Low

deposition temperature allows film growth on substrates with low melting-point.

4. Possibilities to grow films of potential photocatalysts  $\text{InTaO}_4$  and Ni-doped  $\text{InTaO}_4$  by low pressure MOCVD were investigated for the first time. However, admixtures of other phases were present in crystalline undoped and Ni-doped films. Using water contact angle method, it was demonstrated significant increase of films hydrophilicity after surface irradiation by visible and UV light. This indirectly shows possible photocatalytic activity of deposited films.

5. Possibilities to grow films of potential photocatalysts  $\text{InMO}_4$  ( $M = \text{V}, \text{Ta}, \text{Nb}$ ) and Ni-doped analogues were investigated systematically using aerosol pyrolysis method. Influence of various deposition conditions to crystallinity, elemental and phase composition of simple and complex oxide films was investigated.

6.  $\text{InTaO}_4$  thin films can not be obtained *in-situ* by spray pyrolysis. However,  $\text{InTaO}_4$  films may be obtained in two-way process: deposition at  $500\text{ }^\circ\text{C}$  and annealing at  $800\text{ }^\circ\text{C}$  (1h in argon). Crystalline pure monoclinic  $\text{InTaO}_4$  films can be obtained only in case if the composition of initial solutions is well selected. Films containing pure  $\text{InTaO}_4$  phase were obtained for the first time.

7.  $\text{InNbO}_4$  thin films may be obtained by both *ex-situ* and *in-situ* approaches, if solution composition is well selected. Amorphous films grown at low temperature ( $400\text{ }^\circ\text{C}$ ) crystallizes into pure monoclinic  $\text{InNbO}_4$  phase after annealing at  $800\text{ }^\circ\text{C}$  (1h in argon). At higher temperature ( $500\text{-}600\text{ }^\circ\text{C}$ ) crystalline monoclinic  $\text{InNbO}_4$  may be formed *in-situ*.  $\text{InNbO}_4$  films from chemical vapour phase were obtained for the first time.

8.  $\text{InVO}_4$  films, like to  $\text{InNbO}_4$  films, may be obtained by both *ex-situ* and *in-situ* approaches, if solution composition is well selected. In the first case, pure orthorombic  $\text{InVO}_4$  phase in films may be obtained after annealing at  $800\text{ }^\circ\text{C}$  of films grown at  $400\text{ }^\circ\text{C}$ . At higher deposition temperature, crystalline films may be obtained without additional annealing step. However, films growing at  $500\text{ }^\circ\text{C}$  crystallises into pure monoclinic  $\text{InVO}_4$  phase, while at  $600\text{ }^\circ\text{C}$  grows pure orthorombic phase.  $\text{InVO}_4$  films from chemical vapour phase were obtained for the first time.

9. Ni-doped  $\text{InVO}_4$  films containing pure orthorombic  $\text{In}_{1-x}\text{Ni}_x\text{VO}_4$  phase may be deposited by aerosol pyrolysis at  $600\text{ }^\circ\text{C}$ , if solution composition is well selected.  $\text{In}_{1-x}\text{Ni}_x\text{VO}_4$  structure remains stable up to Ni doping level  $x \approx 0.5$ . Synthesis of Ni-doped  $\text{InTaO}_4$  films is more complicated mainly because the *ex-situ* process has to be used



(deposition at 400 °C and annealing at 800 °C in argon). For each Ni doping level into InTaO<sub>4</sub>, suitable In/Ta ratio in solution has to be used. Stable In<sub>1-x</sub>Ni<sub>x</sub>TaO<sub>4</sub> structure was obtained in case of Ni doping  $x \sim 0.08$  and  $0.16$ . Attempts to increase Ni doping level up to  $x \sim 0,36$  resulted in apparition of admixture of NiTa<sub>2</sub>O<sub>6</sub> phase in films. Obtaining of Ni-doped InNbO<sub>4</sub> thin films by spray pyrolysis was not successful. Films consisting of pure Ni-doped InVO<sub>4</sub> and InTaO<sub>4</sub> phases were obtained for the first time.

10. Among all aerosol pyrolysis deposited undoped and Ni-doped InMO<sub>4</sub> (M = Ta, V, Nb) films, considerable photocatalytic activity under light irradiation was determined only for In<sub>1-x</sub>Ni<sub>x</sub>VO<sub>4</sub> films with  $x \sim 0.5$ . This suggests that it is not sufficient to obtain crystalline pure phase in film, probably other factors are also important (morphology, thickness, cocatalyst, etc.).

### ***List of publications by the author of the dissertation***

1. A. Abrutis, G. Valincius, G. Baltrunas, L. Parafianovic, A. Valiuniene, Z. Saltyte. Spray-pyrolysis Cd<sub>2</sub>SnO<sub>4</sub> films for electrochemical applications, Thin Solid Films 515 (2007) 6817–6823.

2. N. McSparran, V. Rico, A. Borrás, A.R. González-Elipé, G. Sauthier, E. György, J. Santiso, G. Garcia, A. Figueras, L. Parafianovic, A. Abrutis. Synthesis of undoped and Ni doped InTaO<sub>4</sub> photoactive thin films by metal organic chemical vapor deposition. Surface and Coatings Technology 201 (2007) 9365-9368.

The results of the thesis were also reported at EUROCVT-16 conference (poster): 16th European Conference on Chemical Vapor Deposition, SEP 16-21, 2007 Hague, NETHERLANDS.

Note: Third paper is submitted to Surface and Coatings Technology (A. Abrutis, L.Parafianovic, V. Kazlauskienė, V.Kubilius, G. Sautier, A. Figueras. Atmospheric pressure chemical vapour deposition of InTaO<sub>4</sub>, InNbO<sub>4</sub> and InVO<sub>4</sub> coatings for photocatalytic applications, still under review process).

## ***Curriculum Vitae***

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### ***Oksidinių medžiagų, taikomų elektrokatalizėje ir fotokatalizėje, plonų sluoksnių nusodinimas iš cheminių garų fazės ir tyrimas***

#### ***Santrauka***

Darbe ištirtos perspektyvių elektrokataliziniams ir fotokataliziniams taikymams oksidinių medžiagų plonų sluoksnių nusodinimo iš cheminių garų fazės galimybės bei gautų sluoksnių savybės.

Ištirtos  $\text{Cd}_2\text{SnO}_4$  sluoksnių nusodinimo galimybės, panaudojant paprastą aerosolių pirolizės metodą, nustatyta įvairių nusodinimo sąlygų įtaka plėvelių savybėms. Aerosolių pirolizės metodas leidžia gauti elektros srovei laidžias ir šviesai pralaidžias kristalines  $\text{Cd}_2\text{SnO}_4$  plėveles *in-situ*, jas auginant esant žemai 400 °C temperatūrai. Kristaliniai grynafaziai  $\text{Cd}_2\text{SnO}_4$  sluoksniai aerosolių pirolizės metodu gauti pirmą kartą. Elektrocheminio impedanso spektroskopijos ir ciklinės voltamperometrijos metodais ištirtos sluoksnių elektrocheminės savybės. Nustatyta, kad aerosolių pirolizės būdu nusodintiems sluoksniams būdinga panaši ar net didesnė krūvininkų koncentracija bei didesni elektronų pernašos greičiai redokso sistemose, lyginant su zolių-gelių metodu gautais  $\text{Cd}_2\text{SnO}_4$  sluoksniais. Galimybė užauginti  $\text{Cd}_2\text{SnO}_4$  sluoksnius esant žemai temperatūrai leidžia panaudoti žemos lydymosi temperatūros padėklus.

Ištirtos potencialių fotokatalizatorių  $\text{InTaO}_4$  ir nikelio legiruotų  $\text{InTaO}_4$  sluoksnių nusodinimo galimybės, panaudojant žemo slėgio MOCVD metodą. Nepaisant to, kad gauti sluoksniai nebuvo grynafaziai, vandens kontaktinius kampo matavimo metodu

sluoksniams nustatytas žymus hidrofiliškumo padidėjimas apšvietus matoma ir UV šviesa, o tai netiesiogiai rodo galimą šių sluoksnių fotokatalitinę aktyvumą.

Naudojant paprastą aerozolių pirolizės metodą, buvo ištirtos potencialių fotokatalizatorių  $\text{InMO}_4$  ( $M = \text{V}, \text{Nb}, \text{Ta}$ ) ir jų nikeliu legiruočių darinių sluoksnių nusodinimo galimybės. Ištirta įvairių nusodinimo sąlygų įtaka oksidų sluoksnių kristališkumui, elementinei ir fazinei sudėčiai. Nustatyta, kad  $\text{InTaO}_4$  bei  $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$  sluoksniai gali būti susintetinti tik naudojant dviejų etapų sintezės būdą, nusodinant sluoksnį esant  $500\text{ }^\circ\text{C}$  temperatūrai ir po to jį atkaitinant esant  $800\text{ }^\circ\text{C}$  temperatūrai.  $\text{InNbO}_4$ ,  $\text{InVO}_4$  ir  $\text{In}_{1-x}\text{Ni}_x\text{VO}_4$  sluoksniai gali būti gauti *in-situ*, nusodinant esant  $500\text{--}600\text{ }^\circ\text{C}$ , arba dviem etapais (nusodinimas esant  $400\text{ }^\circ\text{C}$ , atkaitinant esant  $800\text{ }^\circ\text{C}$ ). Sluoksnių faziniam grynumui didelę reikšmę turi pradinio tirpalo sudėtis.  $\text{In}_{1-x}\text{Ni}_x\text{VO}_4$  sluoksniams, kuriuose  $x \sim 0,5$ , buvo nustatytas žymus fotokatalitinis aktyvumas.