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SCIENTIFIC PAPER

539.216+546.81–31+542.913:628.675

SYNTHESIS OF THIN FILMS BY THE PYROSOL PROCESS

Among many aerosol routes, the Pyrosol process, due to its simplicity, low cost and quality of obtained films, represents a promising technique for the synthesis of thin films. The pyrosol process is based on the transport and pyrolysis of an aerosol of processor solution, generated in an ultrasonic atomizer, on a heated substrate. The theoretical principles of the pyrosol process are presented in this paper, as well as the influence of some synthesis parameters on the deposition of SnO_2 thin films.

Materials in thin film form, due to their scientific, technical and economic importance, have been prepared for over a century. A very wide range of application, from microelectronic and optical devices, to protective and decorative coatings, have contributed to the development of a number of techniques in the search for the most reliable and the cheapest method for thin films production. Synthesis methods may be divided into physical methods of deposition (vacuum evaporation, sputtering), chemical methods of deposition (CVD–chemical vapor deposition, sol–gel, aerosol process) and hybrid methods [1,2].

Aerosol processes offer a variety of approaches for the deposition of oxide and non–oxide ceramic, metal, organic and composite thin films. The approaches may be divided into solution droplet deposition, vapor deposition and molten or solid particle deposition processes [3].

In the spray (aerosol) deposition process, usually called the spray pyrolysis process, a precursor solution is pulverized, so that it arrives at the substrate in the form of very fine droplets, where constituents react to form a deposit. Numerous spray atomization techniques have been developed for thin film preparation such as pneumatic (twin–fluid), ultrasonic and electrostatic atomization [4].

The pyrolysis of an ultrasonically generated aerosol or the pyrosol process is a technique halfway between CVD techniques and spray pyrolysis. Under certain conditions the process could be assimilated in to the CVD technique, removing some of its restrictions. It is sometimes called atmospheric pressure CVD (APCVD) or aerosol–assisted CVD (AACVD) [3,5]. Compared with conventional spray pyrolysis with pneumatic atomization, the pyrosol process has an advantage in comparison to ultrasonic spray formation, namely, the droplet diameter can be controlled better and the size distribution is narrower. Also, the gas flow rate is independent of the aerosol flow rate and, hence control of the substrate surface temperature becomes easier.

Some of the advantages of the pyrosol process include:

- simplicity and low cost (only an atomizer and substrate heater are required, it operates at atmospheric pressure),
- many choices for precursors,
- deposition of multicomponent films with controlled stoichiometry,
- operation at moderate temperatures (100–500°C),
- deposition on complex substrate topographies,
- high deposition rates
- deposition of oriented films.

PRINCIPLE TECHNOLOGY OF THE PYROSOL PROCESS

In the pyrosol process precursors of the material to be deposited are dissolved in an appropriate solvent, which is usually water, alcohol or ketone. The aerosol of the precursor solution, generated in an ultrasonic atomizer is conveyed by a carrier gas at atmospheric pressure through a nozzle toward a heated substrate where, through pyrolysis of the droplets, film deposition occurs.

The equipment for implementating of the pyrrosol process is simple and relatively inexpensive. Essentially, the set–up consists of an ultrasonic atomizer, a transport nozzle, a pyrolysis reactor and an exhaust system for the gases (Fig. 1). Two types of reactor geometry can be defined – a parallel and perpendicular set–up, depending on whether the aerosol flux arrives parallel or perpendicular to the substrate surface [6]. A parallel set–up gives a thickness gradient of the deposited film in the flow direction, while a perpendicular set–up leads to a circular symmetry thickness set–up.

The ultrasonic atomizer comprises a glass vessel containing the precursor solution to be sprayed, which

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Paper received: September 10, 2002
Paper accepted: September 26, 2002.

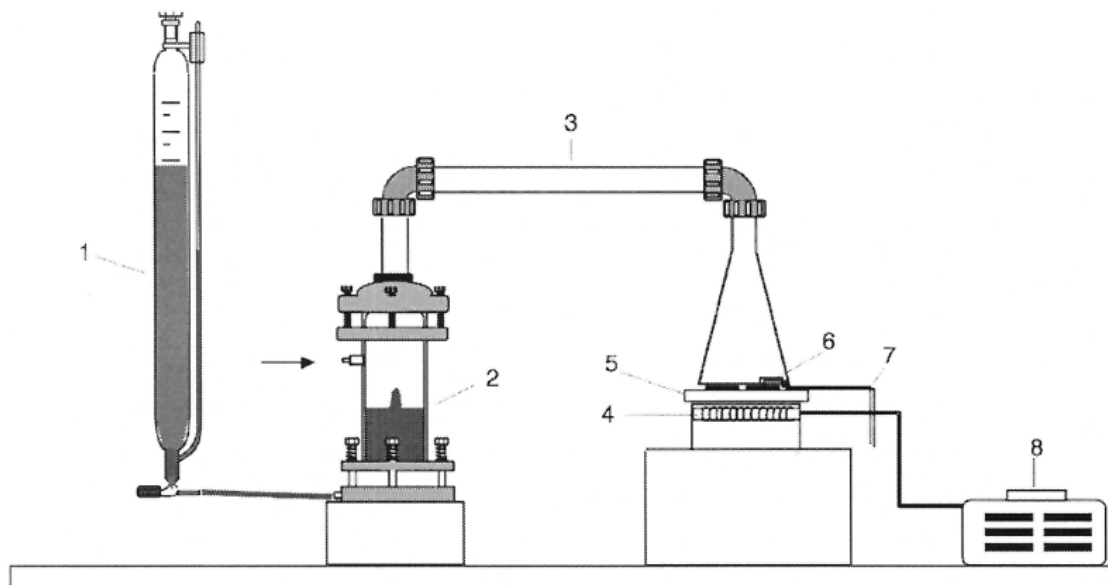

Figure 1. Pyrosol process experimental set–up (1 – constant level container, 2 – ultrasonic atomizer, 800 kHz, 3 – transport tube, 4 – heater, 5 – ceramic plate, 6 – substrate, 7 – thermocouple, 8 – tempearture controller)

is fitted at the bottom with a piezoelectric transducer, excited by a high frequency power generator. A piezoelectric transducer is usually made of barium–titanate or lead zirconate–titanate. Depending on the transducer thickness and power supply, the operating resonant frequency ranges from 0.7–2.5 MHz.

The transport nozzle directs the aerosol into the pyrolysis zone. It consists of pipe that has a sufficiently large diameter to avoid coalescence of the droplets. The aerosol flow rate is measured by rotameters.

The pyrolysis reaction is carried out in hot–wall or cold–wall reactor systems. The advantage of hot–wall systems is that they are simple to operate, but the deposition may also occurr on the reactor walls [7]. The most common hot–wall reactors are pyrolysis furnaces, that may be cylindrical (carousel type) or linear (conveyer type) [5]. A tin bath is usually used as a cold–wall reactor, because it provides excellent thermal contact with the substrate, while the substrate is heated by floating in molten tin. Other types of reactors are substrate–carrying resistors, epiradiator systems and induction heating reactors [6]. The most important problem is control of the substrate temperature, which is provided by thermocouples, placed on the substrate surface.

The choice of precursor solution must satisfy some conditions: solvent–solution compatibility and stability at room temperature; a decomposition temperature higher than its evaporation or sublimation temperature. Usually, organ–metallic (alcoholates, acetylacetonates) and mineral compounds (nitrates, chlorides, acetates) are used as a precursor source and organic solvents (butanol, acetyl acetone, ethanol, methanol) or water as precursor solvents. The solute concentration in the solvent ranges from 10^{-2}–10^{-1} mol/dm^3. Below this range the deposition rate is too slow.

The carrier gas is chosen by its compatibility with the chemical reaction. If oxygen is needed for the reaction, compressed air or pure oxygen are used. For neutral atmosphere, nitrogen or argon is usually used.

The substrate should be chemically, thermally and mechanically stable at the operating temperatures. It may be amorphous, mono–crystalline or polycrystalline.

FUNDAMENTAL ASPECTS

When a high–frequency ultrasonic beam is directed at a gas–liquid interface, a "geyser" is formed at the liquid surface. The effects of cavitations within the liquid surface and the vibrations produced on its surface result in the formation of an aerosol. The quantity of produced aerosol is a function of the acoustic frequency and power intensity, as well as some physical properties of the precursor.

There is a correlation between the capillary wavelength at the liquid surface, λ, and the mean diameter of the atomized droplets, D:

$$D = \alpha \lambda \tag{1}$$

where α is a constant.

The wavelength λ may be expressed in terms of Kelvin's formula [6]:

$$\lambda = \left(\frac{8 \pi \sigma}{\rho f^2} \right)^{\frac{1}{3}} \tag{2}$$

where f is the ultrasonic excitation frequency, σ – the surface tension of the liquid and ρ – density.

Lang [8] has established the relationship:

$$D = 0.34 \left(\frac{8 \pi \sigma}{\rho f^2} \right)^{\frac{1}{3}} \tag{3}$$

For water, the mean diameter of the droplets varies from 2 to 30 microns for the frequency range 3 MHz – 70 kHz.

This frequency dependence shows a very narrow size distribution, which, in addition to the small droplet diameter, is the main advantage of ultrasonic spraying over conventional pneumatic spraying (Figs. 2 and 3).

Equation (3) shows that the mean droplet diameter is also a function of the physical properties of the liquid, as well as the quantity of produced spray, which is presented by relation [6]:

$$r = \frac{p}{\sigma \eta} \tag{4}$$

where p is the vapor pressure of the liquid, σ its surface tension and η its dynamic viscosity.

MECHANISM OF THE DEPOSITION PROCESS

Vigue and Spitz proposed a classification of deposition processes, based on the surface deposition temperature [9], which is presented by the following reaction schemes (Fig. 4):

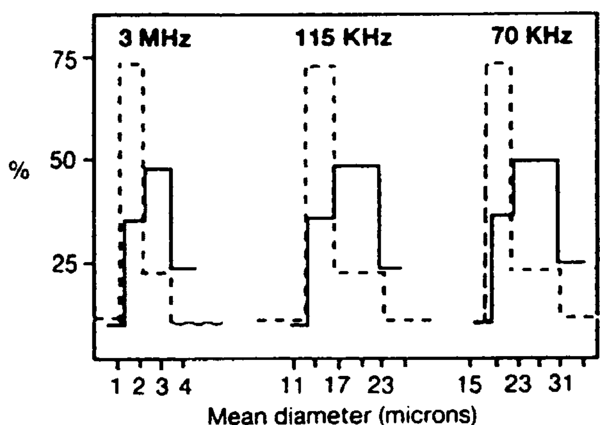

Figure 2. Mass (- - -) and volume (—) distribution of water droplets obtained by ultrasonic atomization [6]

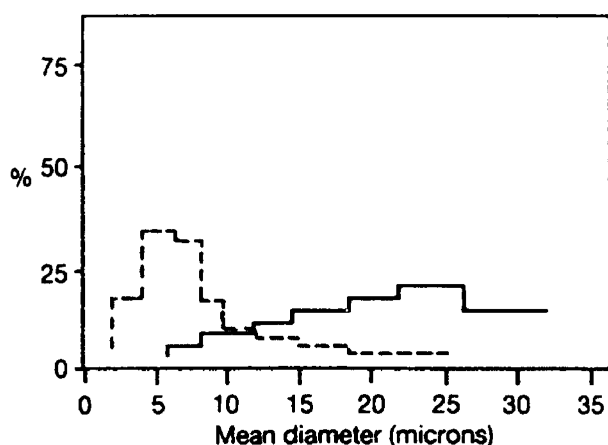

Figure 3. Mass (- - -) and volume (—) distribution of water droplets obtained by pneumatic atomization [6]

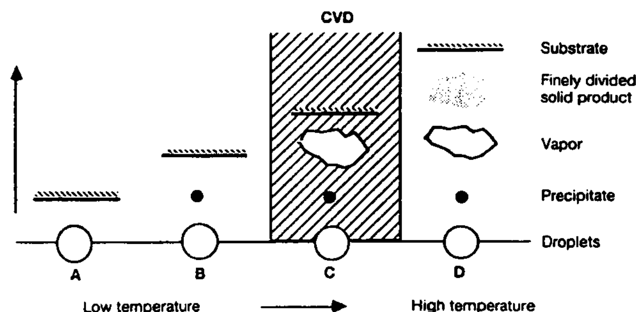

Figure 4. Deposition reaction schemes for pyrosol process [9]

Process A: At low temperature, the droplets reach the substrate in liquid state. The solvent vaporizes leaving a dry precipitate in which decomposition occurs.

Process B: At higher temperatures, the solvent evaporates before the droplet reaches the substrate and the precipitate reaches the substrate in the solid state.

Process C: The solvent evaporates as the droplets approach the substrate, the precipitate sublimates and the obtained vapors diffuse to the substrate where they chemically react in the heterogeneous phase. This is a typical case of CVD.

Process D: At the highest temperatures, the chemical reaction takes place in the vapor phase and the reaction product deposits on the substrate in the form of a fine powder.

The best deposit is obtained when deposition occurs by process C. In the case of ultrasonic spraying, the droplets diameter size distribution is narrow, so all the droplets vaporize at the same time giving a homogenous deposit.

PARAMETERS OF THE PYROSOL PROCESS

The parameters of the pyrosol process may be divided into two categories, depending on whether they are attributed to the atomization or the deposition process.

1. Atomization parameters

The aerosol flow rate (quantity of aerosol per unit time) is a function of:

a) the ultrasonic power

b) the carrier gas flow rate

c) the physical properties of the solution (vapor pressure, surface tension and viscosity)

2. Deposition parameters

a) the chemical parameters (precursor solution, substrate, carrier gas)

b) the deposition temperature (substrate surface temperature)

DEPOSITION KINETICS

The Pyrosol process may be considered as a CVD process, which is divided into three stages:

1. evaporation of the solution in the vicidity of the substrate

2. transport of the species to the substrate surface

3. reaction of the species on the substrate surface

Two categories of parameters influence the deposition kinetics:

1. the quantity of transported precursor per unit time
2. the substrate surface temperature

A linear relationship may be established between the quantity of material deposited per unit time and these parameters:

$$\frac{de}{dt} = \lambda \, c \, Q$$

where de/dt – is the deposit growth rate, c – the precursor solution concentration, Q – the aerosol flow rate and λ is the constant which depends on the temperature and gas flow rate.

APPLICATION OF THE PYROSOL PROCESS

The major application of the pyrosol process is for the deposition of noble metals, sulphide and oxide thin films and coatings (Table 1). This technique is also used in the synthesis of nanostructured and ultra–fine powders [10].

Tin(IV)–oxide, SnO_2, due to its wide range of application, including transparent conductive electrodes, gas sensors, antistatic coatings, resistors, microwave shields, protective coatings, etc. [2,11–13], is one of the most common materials deposited as a thin film by the pyrosol process.

The results of the deposition of SnO_2 thin films on glass substrates by the pyrosol process will be presented in this paper. Beside on glass, SnO_2 thin films have been deposited on alumina or silicon wafers [12, 14]. Mineral salts ($SnCl_4$, $SnCl_2x2H_2O$) or organ–metallic (dibutyltindichloride, dibutyltindiacetate and dibutyldidilaurate) have been frequently used as tin precursors. The solvents used are methanol, ethanol, butanol, acetyl acetone or de–ionized water [10–16].

Table 1. Materials and condition for thin film deposition by the Pyrosol process

Categorie	Material	Source	Solvent	Gas	T_S, °C
Noble metal	Pd	Pd acetyl-acetonate	buthanol	N_2, H_2	300–350
Noble metal	Pt	Pt acetyl-acetonate	buthanol	N_2, H_2	400
Metal	Ru	Ru acetyl-acetonate	buthanol	N_2, H_2	400
Sulphide	CdS	$CdCl_2$, $(NH_2)_2CS$	water	Ar	300
Selenide	CdSe	$CdCl_2$, $(NH_2)_2CSe$	water	Ar	200–300
Oxide	In_2O_3	Pd acetyl-acetonate	acetyl-aceton.	air	500
Oxide	ZnO	Zn acetate	methanol	air	300–500
Oxide	Al_2O_3	Al iso-propoxide	buthanol	air	650
Spinel	$NiCo_2O_4$	Ni, Co nitrate	water	air	350–400

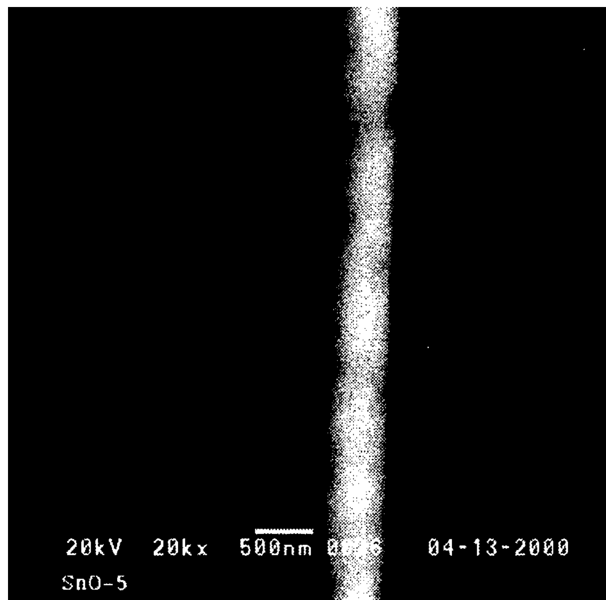

Figure 5. SEM fracture micrograph of SnO_2 thin film

Ethanol solutions of $SnCl_2x2H_2O$ of the concentrations 0.05, 0.1, 0.2 and 0.4 mol/dm^3 were sprayed on microscope glass in the experiments. The aerosol was carried by compressed air (Q = 100 l/h), which was also the oxygen source for oxidation. The substrates were placed on a ceramic holder (Fig. 1), electrically heated to obtain the substrate temperatures 300, 350, 400 and 450°C. The temperature was measured by a Pt/Pt–Rh thermocouple, fixed on the substrate surface.

The film thickness was measured on scanning electron microscopy (SEM) fracture micrographs (Fig. 5). The crystal structure of the deposited films was determined by X–ray diffraction (XRD). The surface topology and grain morphology were determined by SEM.

Fig. 6 shows the linear dependence between the thickness and deposition time at fixed temperature (400°C) and precursor solution concentration (0.1 mol/dm^3). The mean deposition (growth) rate may be calculated from the slope, and it is about 24 nm/min.

The temperature dependence of the growth rate at fixed concentration shows two regimes (Fig. 7). In the first regime, below 325°C, the growth rate markedly increases with increasing temperature. From the Arrhenius plot of the deposition rate and the deposition temperature (v vs. 1/T at Fig. 7), the activation energy of 33 kJ/mol implies that the deposition process is thermally activated. This suggests that the deposition process is surface–reaction controlled, where the kinetics are slower than the mass transfer. Above this temperature the dependence of the growth rate on the temperature significantly decreases, which suggests that the deposition process is diffusion controlled [17].

Fig. 8. presents a linear dependence between the growth rate (thickness) and precursor solution

concentration. Considering the temperature dependence of the growth rate, this linear dependence suggests that the process is limited by gas–phase diffusion and the growth mechanism corresponds to a CVD process [17].

X–ray diffraction analysis data shows that the films are crystalline and have a tetragonal rutil structure for all the examined samples (Fig. 9). The preferred orientation of the deposited films calculated from the X–ray diffraction patterns [18] is in [110] and [200] directions. The major orientation for films of smaller thickness,

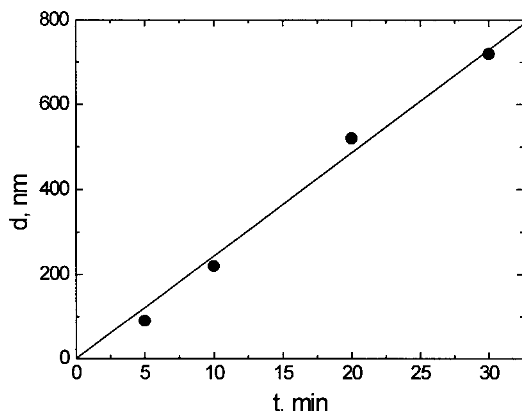

Figure 6. The dependence to thickness on deposition time

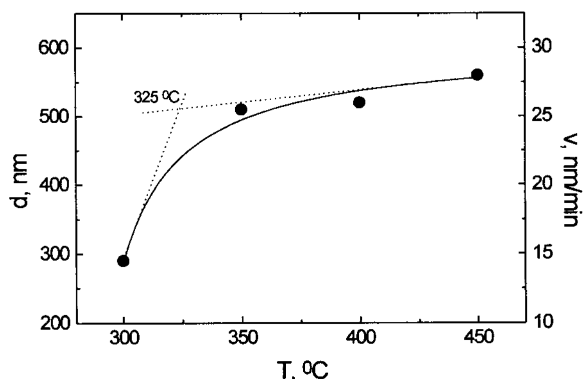

Figure 7. The dependence of the film thickness and the growth rate on the deposition temperature

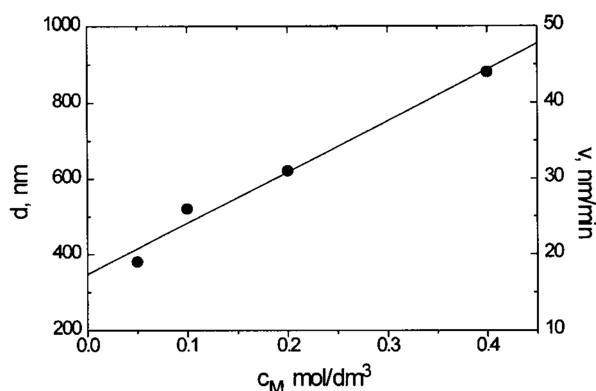

Figure 8. The dependence of the film thickness and the growth rate on the precursor solution concentration

substrate temperature and precursor solution concentration correspond to the (110) plane [19].

It may be seen from the SEM micrographs, that the surface morphology and structure characteristics are quite different with changing the process parameters (Fig. 9). The mean grain size varies in the range 150 – 570 nm.

The thinner films (90 and 220 nm) are non–uniform, with noticeable voids on the surface (Fig. 9a). With increasing film thickness (520 and 720 nm), the surface becomes homogeneous. The films deposited at 300°C are homogeneous with a smooth surface and uniform grain size (about 150 nm) (Fig. 9b). With increase of the surface temperature to 350°C, the

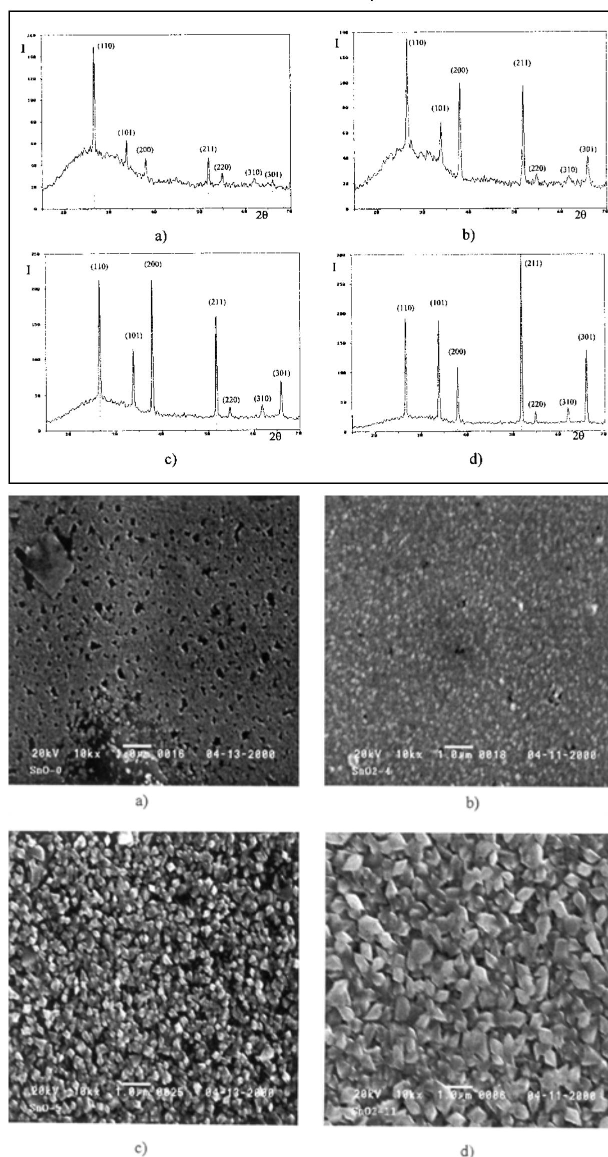

Figure 9. XRD patterns and SEM micrographs for SnO_2 films deposited under the conditions:
a) T = 400°C, c_M = 0.1 mol/dm^3, t = 5 min (d = 90 nm);
b) T = 350°C, c_M = 0.1 mol/dm^3, t = 20 min;
c) T = 300°C, c_M = 0.1 mol/dm^3, t = 20 min;
d) T = 400°C, c_M = 0.4 mol/dm^3, t = 20 min

surface becomes rougher (Fig. 9c). The grains are polygonal with sharp edges and uniform size. As the temperature increases, larger grains may be observed. At 450°C some grains are twinned as a result of crystal growth. Increase of the precursor solution concentration from 0.05 to 0.4 mol/dm^3 (as well as the film thickness), leads to the deposition of very homogeneous films with fine–grained morphology) (Fig. 9d).

The obtained results show the great influence of the process parameters on the film morphology, which leads to their further application. It may be seen that films of the best quality are deposited at a lower surface temperature or a higher precursor solution concentration.

CONCLUSION

The pyrosol process as a simple, low cost technique is very suitable for the deposition of oxide thin films. Thin SnO_2 films of different morphology can be prepared by control of the process parameters. The chosen parameters (the deposition time, the substrate temperature and the precursor solution concentration) illustrate the possibilities of running the pyrosol process as a CVD method. Assimilation of the film deposition conditions to a CVD is the main aim of this technique.

ACKNOWLEDGEMENT

This paper was financially supported through the project "Synthesis of functional materials in accordance with the synthesis–structure–properties–application relationship" of the Ministry of Science, Technologies and Development of the Republic of Serbia.

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IZVOD

SINTEZA PREVLAKA PIROLIZOM

(Naučni rad)

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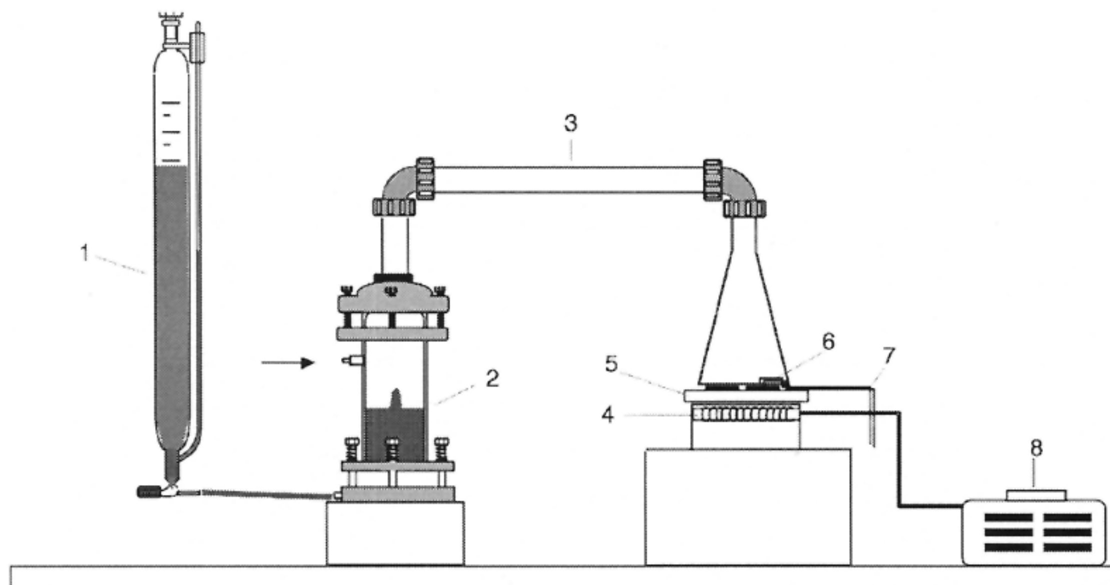
Među brojnim tehnikama sinteze materijala reakcijama u aerosolu, Pirosol proces predstavlja izglednu tehniku za sintezu tankih filmova pre svega zbog svoje jednostavnosti, ekonomičnosti i kvaliteta sintetisanih prevlaka. Proces je baziran na ultrazvučnom generisanju aerosola, njegovom transportu i depoziciji na zagrejanom substratu. U radu su prikazani teorijski principi Pirosol procesa, kao i uticaj nekih od parametara sinteze pri depoziciji SnO_2 tankog filma.

Ključne reči: Reakciono raspršivanje • Pirosol • SnO_2 • Tanki filmovi •
Key words: Ultrasonic atomizing • Pyrosol • SnO_2 • Thin films •



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