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THERMAL BEHAVIOR OF PRECURSOR GELS TiO_2 THIN FILMS

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ABSTRACT: In this research the TiO_2 sols were prepared by sol-gel process. The precursor sols consist of a mixture of titanium alkoxide ($Ti(OPr)_4$), isopropanol, water and nitric acid. The sols were stabilized by different amount of acetylacetone. Differential thermal analysis was performed on the precursor powders. The gels DTA anylysis shows the bands attributed to water removal and pyrolysis of organics which are formed by the acetylacetonato complexes. When the heating rate increases the peaks of decomposition extend and their position moves toward higher temperatures.

KEY WORDS: sol-gel, TiO_2 gel, DTA, crystallization

1. INTRODUCTION

Sol-gel processing of metal oxide have been increasingly employed to produce nanomaterials for innovative applications, especially in the field of composites, porous materials and coatings [1]. Titanium oxide films on glass are the most currently investigated functional materials with a large application potential in sensors [2]. During the past years, a possibility was found to improve the properties of TiO_2 thin films obtained by sol-gel process by means of suitable modification of the precursor with different organic agents. The thermal treatment of the modifies gel films leads to their crystallization and oxide films formation. Chemical modification of transition metal alkoxide by acetylacetone leads to slowing down of the alkoxide hydrolysis and polycondensation rates and thus stabilizes the sol [3].

2. EXPERIMENTAL SECTION

Experimental procedure used for preparation of TiO_2 sols was modified to that reported in [4]. The precursor sols consist of a mixture of titanium alkoxide ($Ti(OPr)_4$), isopropanol (IPA), water (H_2O) and nitric acid (HNO_3). The stabilizing agent used in our system was acetylacetone (AcAc). The molar ratio of the component in the basic solution for TiO_2 sol preparation was $Ti(OPr)_4$: IPA : H_2O : HNO_3 = 0.0188 : 0.5657 : 0.0415 : 0.0143. The added amount of acetylacetone was 0 to 0.0388 mol; the amount of isopropanol was adequate reduced. The volume amounts of components for TiO_2 sols preparation of are in Tab. 1.

Tab. 1: Composition of solutions for preparation of TiO_2 sols

Amount [ml] / Sample	$Ti(OPr)_4$	IPA	AcAc	H_2O	HNO_3
Ti0Ac	5.5	43.3	0	0.2	1
Ti0,5Ac		42.8	0.5		
Ti1Ac		42.3	1		
Ti1,5Ac		41.8	1.5		
Ti2Ac		41.3	2		
Ti3Ac		40.3	3		
Ti4Ac		39.3	4		

The obtained sols were transparent. The sols with AcAc were orange color, which is typical for chelate complex formed [3]. The reaction of the complex formation is exothermic. After vigorous stirring at room temperature, the obtained sols were stored in closed PE vessels for 10 days. After that the samples were dried for 5 days at 80 °C. We obtained the powdery samples.

Differential thermal analyses were performed on derivatograph MOM Budapešť which was made-over and digitized. The samples were heated from 50 to 980 °C at rates of 2, 5 and 10 °C.min^{-1}. Before analysis the samples (fraction 0.16 - 0,2 mm) were stored in environment with the humidity of 52,9 %.

3. RESULTS AND DISCUSSION

DTA analysis was performed to determine the temperature of possible decomposition and phase changes. Figure 1 shows the DTA curves of TiO_2 gels measured for the different heating rates. The form of DTA curves (the intensity of peaks and its maximum temperature) changes when the AcAc amount increases and the heating rate increases, too. The band which corresponds to water removal occurs in temperature range 100 - 200 °C for all samples [5]. The exothermic peak occurs between 300 to 400 °C. When the amount of AcAc increases, this peak increases too and moves to high temperature especially for higher heating rates. The sample Ti1Ac is the exception. Another exothermic peaks appear in temperature range 400 - 700 °C. These peaks extend and overlap themselves when the heating rate increases. DTA curves measured at 2 °C.min^{-1} for two highest AcAc amounts show three peaks in this temperature range. This exothermic peaks are due to decomposition and pyrolysis of organic compounds in gels. The organic compounds in gels are probably formed by the acetylacetonato complexes. This complexes are the result of reaction between AcAc, $Ti(OPr)_4$ and IPA. This is confirmed by FTIR analysis reported in [6].

It is reported that the transformation of the anatase phase into the rutile phase occurs between 450 and 800 °C, and the difference in the transformation temperature depends on the kind of precursors, the preparation conditions and the properties of materials [7]. The exothermic peak which may be represent the rutile formation is the highest at the smallest amounts of AcAc. This peak is located in temperature range 760 - 880 °C in dependence on the heating rate and the AcAc amount.

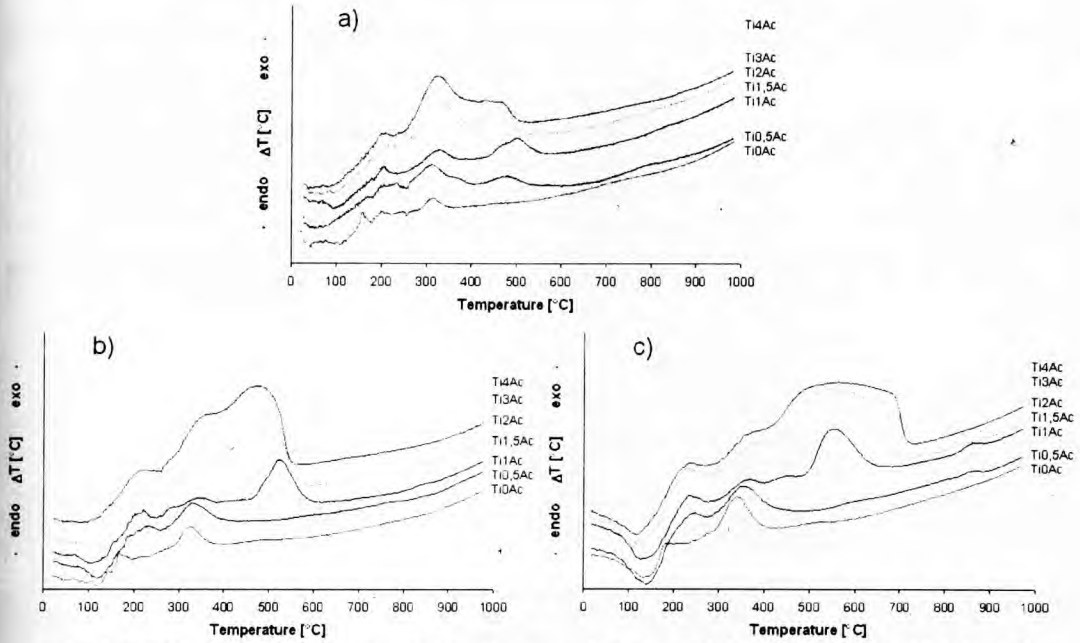
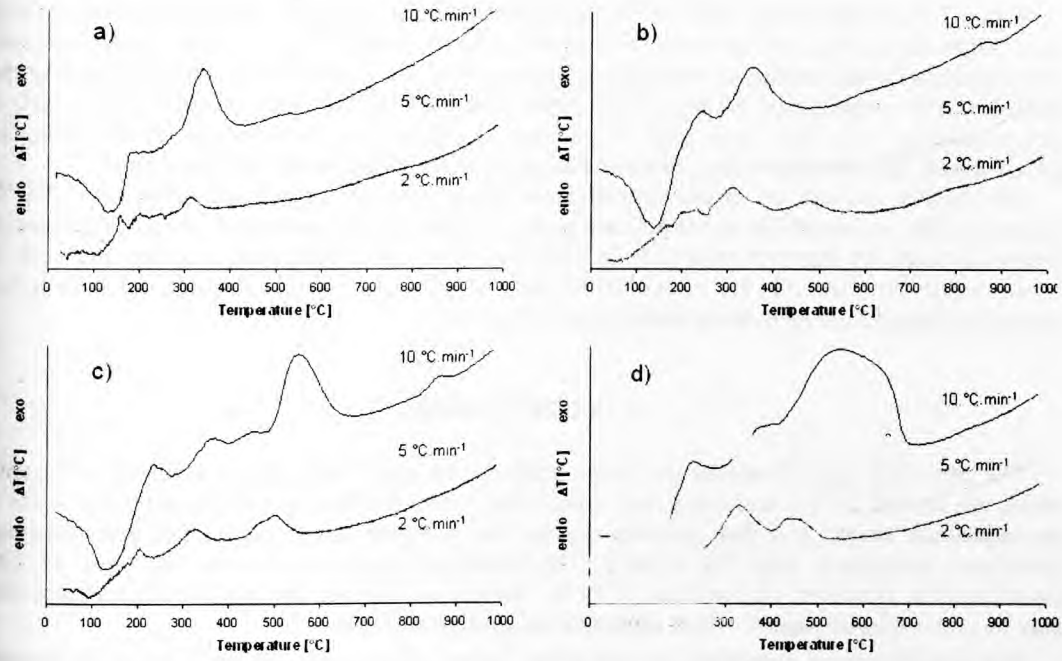


Fig. 1: DTA curves of TiO_2 gels; the heating rate a) 2 °C.min^{-1}, b) 5 °C.min^{-1}, c) 10 °C.min^{-1}



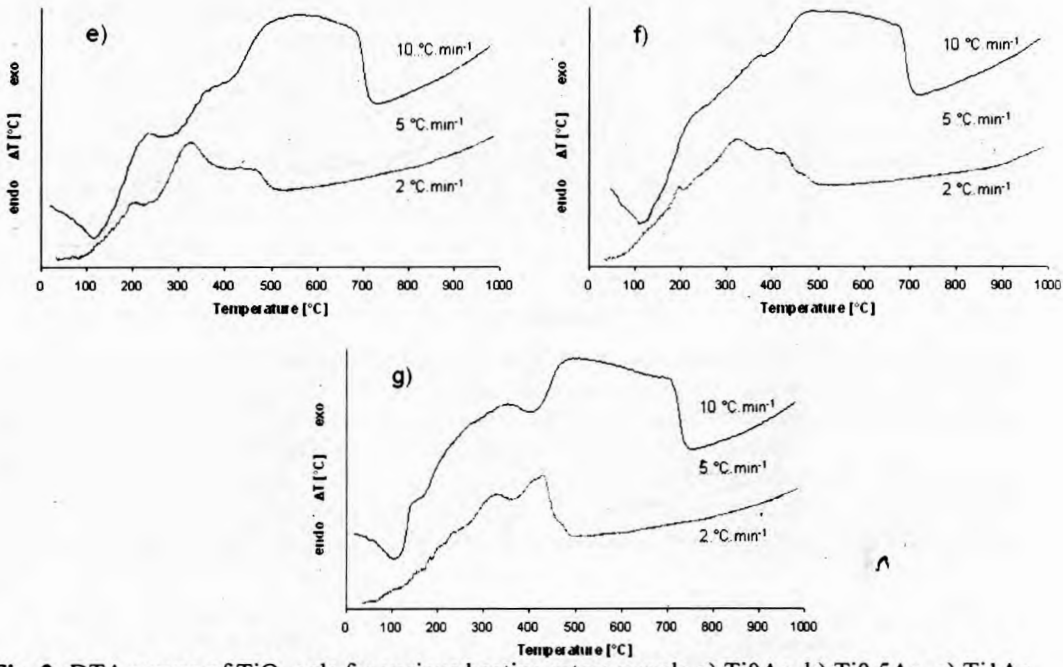


Fig. 2: DTA curves of TiO_2 gels for various heating rates; sample a) Ti0Ac, b) Ti0,5Ac, c) Ti1Ac, d) Ti1,5Ac, e) Ti2Ac, f) Ti3Ac, g) Ti4Ac

Figure 2 shows the DTA curves of TiO_2 gels measured for individual samples at various heating rates. When the heating rate increases the intensity (and the area) of decomposition peaks increases. The position of peaks moves toward higher temperatures. The peaks extend when the heating rate increases. The extension of decomposition peaks is caused by the different conditions in gels at various heating rates. The compounds in gel react slower and the gas products of decomposition diffuse hardly. The decomposition reactions take place in the greater range of temperatures.

We can not exclude the anatas crystallization takes place in temperature range 400 - 700 °C. However, there is impossible to identify the peak of crystallization because it can be overlapped to combined peaks of organics pyrolysis. In addition, when the heating rate increases the peak of crystallization decreases. On the basis of FTIR analysis [6] we suppose the AcAc presence in system causes the change from amorphous nature to crystalline one.

4. CONCLUSIONS

The gels DTA analysis shows the bands attributed to water removal and pyrolysis of organics which are formed by the acetylacetonato complexes. When the heating rate increases the peaks of decomposition extend and their position moves toward higher temperatures. The acetylacetonato complexes decompose after the heating. The decomposition peaks overlap the peak of TiO_2 crystallization. However, on the basis of FTIR analysis we suppose the acetylacetonato complexes may be „the nucleation agent" which supported anatas crystallization.

The suitable sensor properties are depending to the composition and the heating temperature. Therefore, it is important to know the material composition at given temperature.

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5. REFERENCES

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