Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 2511–2518

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Investigation of phase separation of nano-crystalline anatase from TiO_2–SiO_2 thin film

Y. Farhang Ghoje Biglu, E. Taheri-Nassaj*

Department of Materials Science and Engineering, Tarbiat Modares University, PO Box 14115-143, Tehran, Iran

Received 19 July 2012; received in revised form 2 September 2012; accepted 3 September 2012
Available online 25 September 2012

Abstract

In this work, a set of SiO_2–TiO_2 mixed oxides was prepared by the polymeric sol–gel route and deposited on glass substrate through the dip coating technique. Then, the effect of different important preparation parameters (sol–gel stabilizers, Ti content, and heat treatment) on the phase separation was investigated. The developed films were heat treated at 500 °C and characterized using TGA/DTA, FTIR, XRD, SEM, and AFM. The results showed that TiO_2 segregation can be controlled by selecting an appropriate composition of diethanolamine (DEA) and methyl methacrylate (MMA) for preparation of polymeric silica–titania sol. Besides, anatase phase in the samples were crystallized without any stabilizers within heat treatment procedure at 500 °C; however, using appropriate composition of DEA and MMA crystallization rate significantly decreased.

Keywords: A. Films; A. Sol–gel process; D. SiO_2; D. TiO_2

1. Introduction

Owing to their potential applications SiO_2–TiO_2 based systems, whose properties depend on their composition, homogeneity, and structure, have attracted considerable interest [1]. The desired arrangement of species significantly depends upon the application, e.g. applications such as super-paramagnetic powders for use in magnetic refrigeration technology require dispersion of small domains of the magnetic species in a nonmagnetic matrix [2]. Other applications such as low thermal expansion glass require complete solution of titania in silica [3]. Titania–silica materials have been extensively used as catalysts and supports for a wide variety of reactions [1], and can be used as protective coating on stainless steel [4], antireflection coating for optical glasses [5], and selective top layer for membranes [6]. The acidic properties of TiO_2–SiO_2 mixed oxides largely depend on the preparation method, synthesis condition, and chemical composition, which are in turn related to the Ti–O–Si connectivity modes. The use of the sol–gel route to prepare raw SiO_2–TiO_2 solids allows obtaining materials with high homogeneity and good titanium dispersion, without any need for control of their composition and properties [7–11].

Producing homogenous SiO_2–TiO_2 gels is considered as a real challenge due to the fast reactivity of titanium alkoxide since it affects the quality of the produced films. Some organic stabilizers are used to accelerate or control the rate of hydrolysis in the metal alkoxides as well as to improve the adherence, transparency, and the quality of the corresponding films. The stabilizing action of complexing agents is an outcome of these stabilizers chelate forming ability with the alkoxides [12–16]. Regarding these reasons, in this study an attempt was made to investigate effect of adding different sol–gel stabilizers, such as (a) diethanolamine and (b) methyl methacrylate.

In this work homogenous SiO_2–TiO_2 films were prepared using DEA and MMA from amorphous SiO_2 matrix without any TiO_2 segregation. Then, the effects of gel synthesis parameters and heat treatment on the phase separation were investigated.

*Corresponding author. Tel.: +98 21 82883306; fax: +98 21 82883381.
E-mail address: taheri@modares.ac.ir (E. Taheri-Nassaj).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.09.010

2. Experimental

2.1. Precursors

The materials applied for preparation of SiO_2–TiO_2 films were as follows: isopropanol (ISP), tetraethyl orthotitanate ($Ti(OCH_3)_4$; TEOT), tetraethyl orthosilicate ($Si(OCH_3)_4$; TEOS), nitric acid (65%), methyl methacrylate ($H_2C{=}C(CH_3)COOCH_3$; MMA), diethanolamine ($C_4H_{11}NO_2$; DEA), and distilled water. It must be noticed that all consumed precursors were purchased from Merck®.

2.2. Preparation of sols

Due to the great differences in electronegativity values of silicon and titanium, hydrolysis rate for TEOT and TEOS were reported rather different. Therefore, to prepare SiO_2–TiO_2 sols, each sol was first produced separately and then mixed with others. The flowchart of polymeric SiO_2–TiO_2 sol is depicted in Fig. 1. In this study, TEOS and ISP were mixed with stirring and then TEOS was hydrolyzed with the addition of distilled water and HNO_3 to the solution.

The polymeric titania sol was produced using TEOT which was partially hydrolyzed with a less than equivalent amount of H_2O in the presence of HNO_3. Prior to hydrolysis reactivity of the precursor was reduced by adding DEA and MMA. Moreover, to investigate stabilizers effect on phase separation, different amounts of MMA and DEA (MMA:DEAvolume ratios of 0:0, 1:1, and 2:1)–named as ST-MD0, ST-MD1, and ST-MD2, respectively–were applied.

2.3. Preparation of SiO_2–TiO_2 films

In this research, acetone washed and dried transparent glass substrates and micro glass slides were dip coated by precursor sols using an automatic dip-coating device (withdrawal speed of 2 mm/s and support/sol contact time of 4 s). This process was repeated 3–4 times so as to obtain the required thickness of the films. Afterwards, they were dried for 72 h in an ambient temperature with 80% humidity at 30 °C. The coatings were heat treated at 500 °C and heating rate of 5 °C/min and then kept at 500 °C for 1 h.

2.4. Characterizations

Morphologies of the SiO_2–TiO_2 films were investigated by a XL30 Philips scanning electron microscopy (SEM) and atomic force microscopy (AFM, CPresearch, USA). A D4ENDEA-VOR Siemens X-ray diffractometer was applied for determination of the crystalline phases present in the film. Powder samples were combined with KBr in a 1:200 mass ratio and pressed into pellets for analysis using a nicolet670 Nexus Fourier transform infrared (FTIR) spectrometer. Thermal gravity analysis (TGA) investigation of the selected films was performed on a STA 429 thermogravimetric analyzer (Netzsh, Germany). The temperature was programmed to increase at a rate of 10 °C/min from ambient temperature to 800 °C under circulation of dried air.

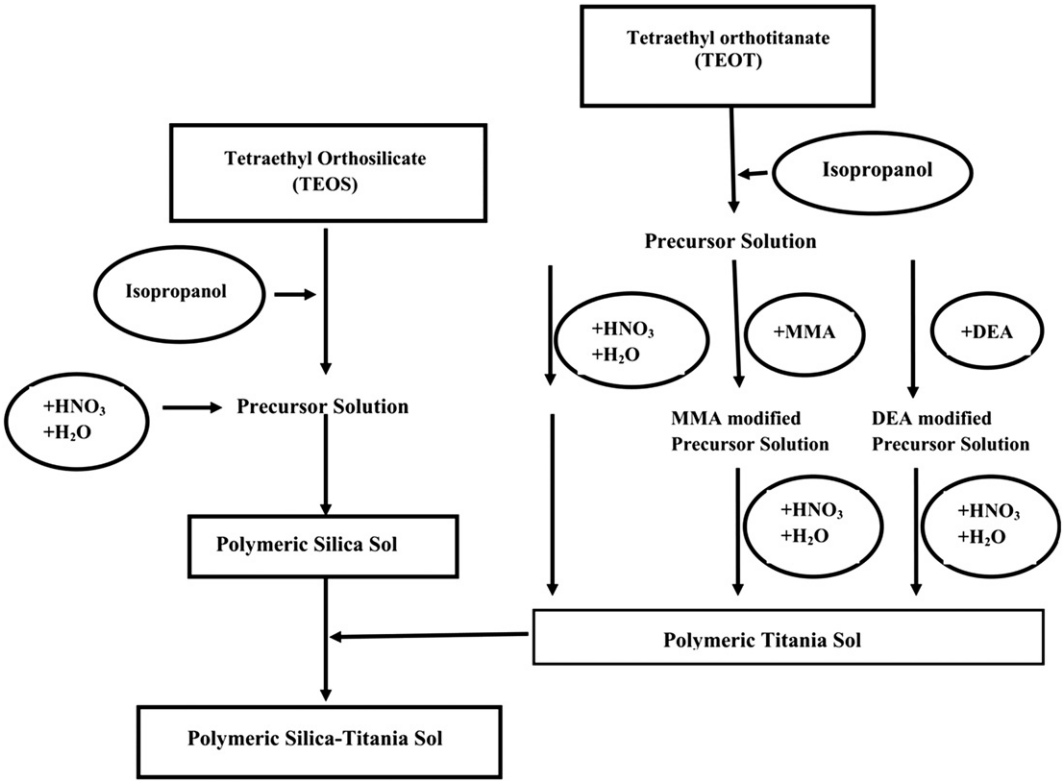


Fig. 1. Schematic representation of fabrication procedure for polymeric SiO_2–TiO_2 sol.

3. Results and discussion

3.1. Morphology of SiO_2–TiO_2 films

Fig. 2 shows the topography images of SiO_2–TiO_2 thin films heated at 500 °C with different amount of stabilizers after the same aging time of 3 h (ST2-MD0 and ST2-MD1 (SiO_2–20 wt% TiO_2 = ST2)). The most significant difference between the two samples is lack of any segregation of TiO_2 in the ST2-MD1 sample (Fig. 2a) and presence of segregation in the ST2-MD0 sample (Fig. 2b). The dimensional information inherent in AFM images (Fig. 3) was used to describe TiO_2 particles separated from silica matrix. The results of AFM and SEM devices were in agreement in showing that separation phase occurred in the surface of the ST2-MD0 nano-composite film. The atomic force microscopy (AFM) indicated that the surface of the nano-composite film becomes locally curvier with eliminating stabilizers content. Two dimensional surface topography and height profile of the ST2-MD0 surface from AFM software is depicted in Fig. 4. Information acquired by height profile and AFM analyzer software indicates an average roughness of 71 nm with maximum peak and valley of 25 nm. The presence of strong peaks in height profile is probably due to the anatase particles separated from SiO_2 matrix. Therefore separation phase increases, the physical and chemical properties of SiO_2–TiO_2 film would be rather different [17]. For further investigation, the effect of synthesis parameters on gel structure and the effect of heat treatment on oxide crystallization and therefore on phase separation are discussed in the following lines.

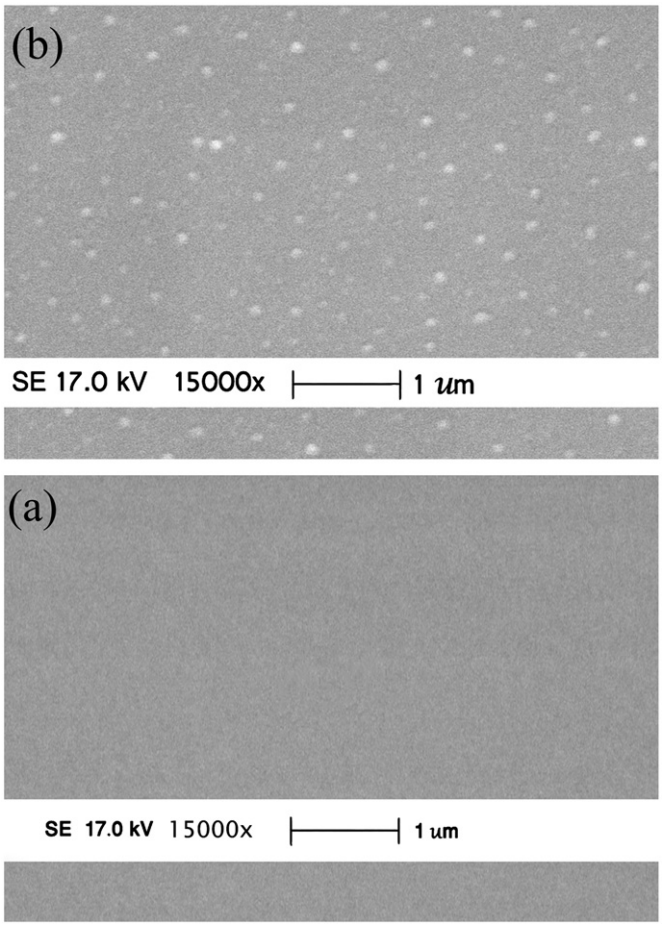
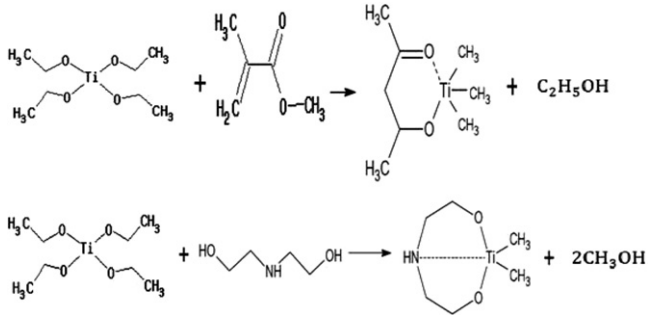


Fig. 2. SEM micrograph of the surface of the SiO_2–TiO_2 film heat treated at 500 °C (a) presence of stabilizers and (b) without stabilizers.

3.2. Effect of gel synthesis parameters on phase separation

3.2.1. Effect of stabilizers

In order to control of hydrolysis rate and precipitation of the titanium alkoxide in TiO_2–SiO_2 sols, MMA and DEA were exclusively used as stabilizers in the experiments. Complexing reactions taking place when both MMA and DEA are mixed with TEOT precursor are presumed as follows:



Followed by complexing reaction, the hydrolysis process of TEOT precursor occurs after adding water into sol of titania. Once stabilizers are separately used, the complexing potential of MMA is stronger than DEA. This is owing to the fact that DEA is a weak base that is neutralized with HNO_3 and makes additional water which accelerates condensation rate and therefore develops phase separation of TiO_2 sols. Through these experiments, a similar experiment was conducted using only DEA and MMA and then both DEA and MMA with the same amount of water. Once only using DEA, the developed sol showed a heavy precipitation. Besides, when using both stabilizers the MMA in sols played a crucial role. This may be attributed to this fact that MMA involves stronger chelate forming ability with the alkoxides and therefore the rate of hydrolysis and precipitation of titanium alkoxide is reduced and as a result a significant reduction of phase separation takes place.

Effect of stabilizers on Si–O–Ti linkages was investigated by Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra of SiO_2–TiO_2 with different amounts of MMA and DEA are shown in Fig. 5. The homogeneity is evaluated by peak intensity of the Si–O–Ti linkage that is observed at 955 cm^{-1}, the IR absorbance at 1097 and 797 cm^{-1} can be assigned to symmetric v_s(Si–O–Si) stretching vibrations, and asymmetric v_{as} (Si–O–Si) stretching vibrations, respectively [18]. The band at 465 cm^{-1} corresponds to Si–O–Si bending modes. The

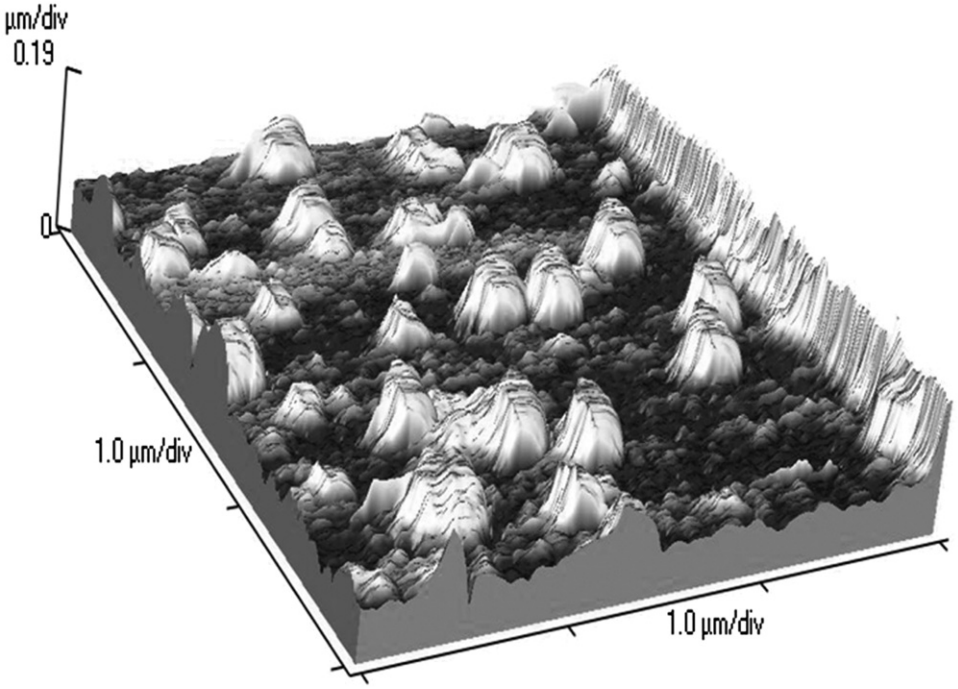


Fig. 3. AFM image of the surface of the SiO_2–TiO_2 film heat treated at 500 °C.

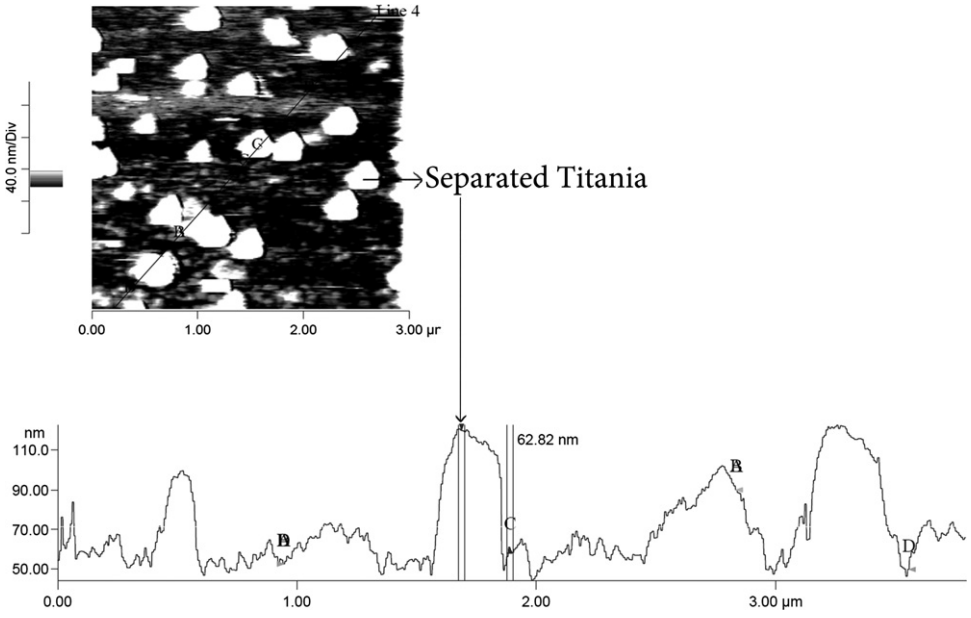


Fig. 4. Two dimensional AFM image and height profile of the surface of the SiO_2–TiO_2 film heat treated at 500 °C.

band at 955 cm^{-1} is usually coupled with the hint of tetrahedral coordination of Ti^{4+} ions which should substitute for Si^{4+} ions in the bulk matrix of SiO_2–TiO_2 mixed oxides with low titanium content [19].

SiO_2–20TiO_2 films without any stabilizers show strong absorption signal around 645 cm^{-1}. Absorption at 645 cm^{-1} corresponding to Ti–O–Ti bonds is clearly observed in the ST2-MD0 sample, suggesting the phase separation of titania from amorphous silica matrix. The remarkable decrease in the 645 cm^{-1} band with increasing total stabilizers content indicates that steric repulsion in organic media is generated through the interaction of organic shells of DEA and MMA around titanium oxide clusters. These ligands act as a functionality blocker and prevent TiO_2 formation and, consequently, TiO_2 phase separation. It is worth to mention that, this band is not detected for the ST2-MD2 sample.

The intensity of absorbance at 955 cm^{-1} decreases as the separation of titania into a second phase increase. This band increases and decreases in intensity respectively by adding stabilizers in the ST2-MD1 sample and stabilizers content in the ST2-MD2 sample. A simple explanation for this is that the

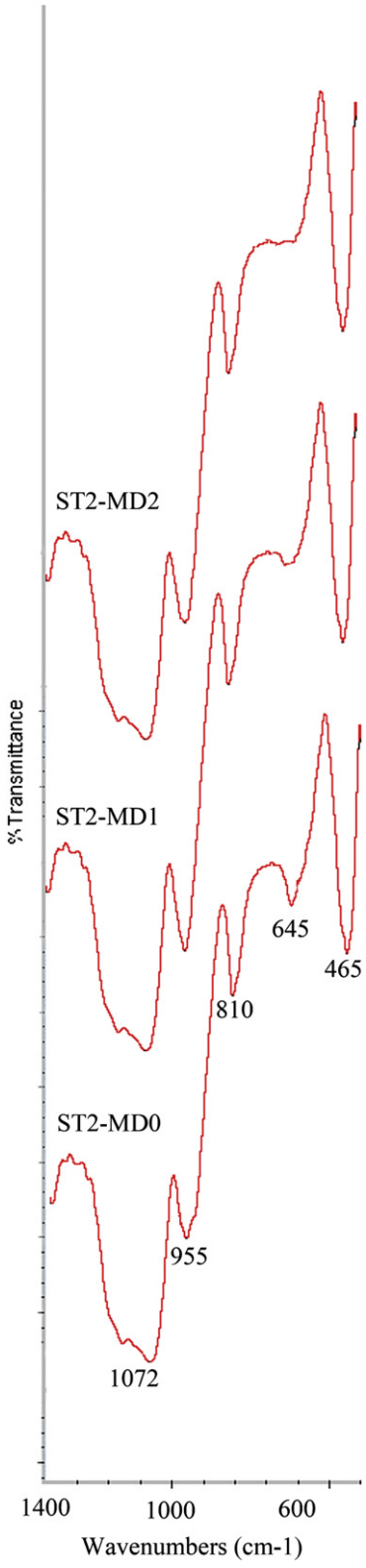


Fig. 5. Effect of stabilizers on FTIR spectra in the low wave number region for SiO_2–20 wt% TiO_2 films.

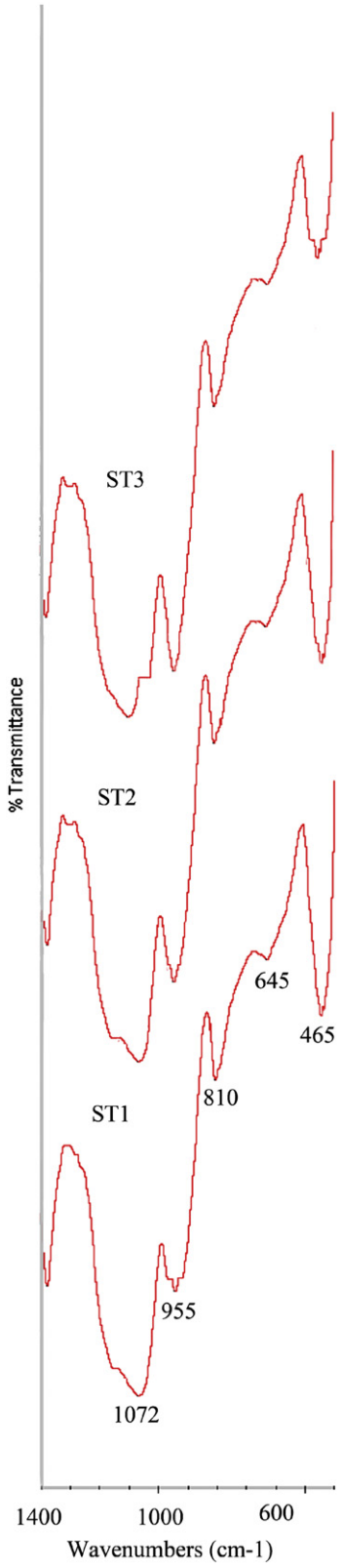


Fig. 6. FTIR spectra in the low wavenumber region for SiO_2–TiO_2 films with various Si/Ti ratios.

thickness of organic shell increases and prevents Si–O–Ti linkages formation.

It is known that the phase separation is induced parallel to the aging time; in other word, the more aging time is, the higher separated would be. The phase-formation time would be shortened according to the amount DEA added to the system; this in turn initiates hydrolysis process. Since MMA,

on the other hand, behaves differently, the aging time was slightly decreased by rising DEA amount. As a result, DEA noticeably influenced the separation phase since the admixture-DEA significantly accelerates the process of hydrolysis and condensation and therefore retards the aging time.

3.2.2. *Effect of Si/Ti molar ratio*

Influence of Si/Ti molar ratio on phase separation between SiO_2 and TiO_2 was studied under the following conditions (between sol and stabilizers), SiO_2–TiO_2 sol:-DEA:MMA as relative volume ratios were 20:0.75:0.75 at reaction temperature of 25 °C. To investigate titanium content influence on the relative abundance of Si–O–Ti linkage of SiO_2–TiO_2 films, FTIR studies were performed. FTIR spectra of SiO_2–TiO_2 films with Si/Ti = 10, 4, and 2.3 (ST1, ST2, and ST3, respectively) are shown in Fig. 6. The remarkable increase in the 955 cm^{-1} band and decrease in the 465 cm^{-1} band with increasing titanium content indicates that the structure of Si–O–Si is possibly ruined in local regions and more Si–O–Ti linkages are produced [19–21]. Nevertheless, no variation of weak titania bands at 645 cm^{-1} can be observed. Therefore, the FTIR spectrum shows the homogeneity of the samples prepared even for TiO_2 content as high as 30 wt%.

When Si/Ti molar ratio changed from 10 to 2.3, the gelation time decreased from 45 h to 3 h. As previously mentioned, the more aging time leads to the higher separation amount. This is attributed to the increase in the percentage of titanium, since electronegativity of $Ti(OE)_4$ (0.63) is higher compared to that of $Si(OE)_4$ (0.32) [19,22]. Thus, titanium has duplex silicon of electropositive charge, which explains why the hydrolysis and condensation kinetics of titanium alkoxide is much faster than that of TEOS. This causes a more compact structure compared to the state of gel without titanium. Accordingly, titanium introduced into the gels in the form of

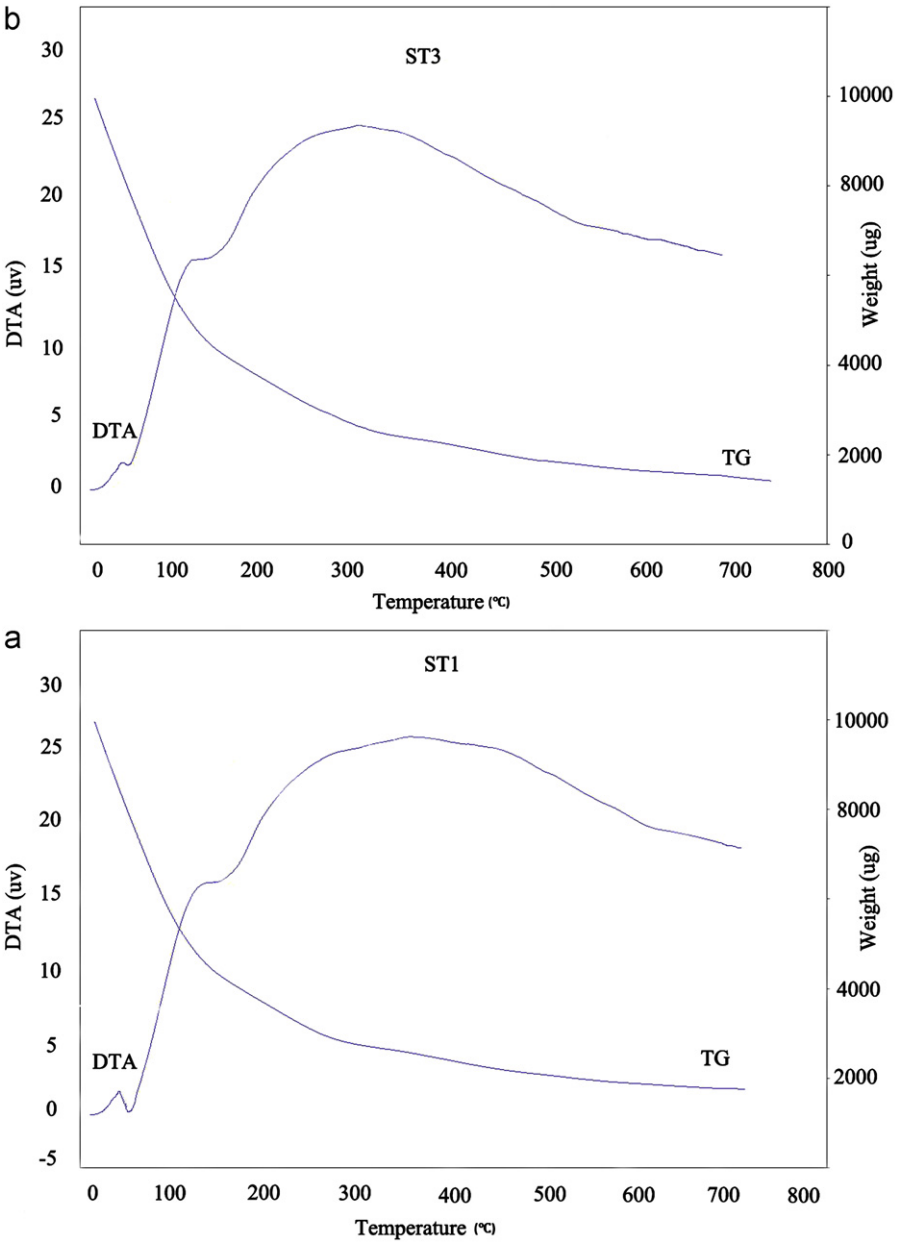


Fig. 7. TG and DTA curves of (a) SiO_2–10 wt% TiO_2 and (b) SiO_2–30 wt% TiO_2.

TEOT significantly speeds up the gelation process and then, as a result, phase separation decreases.

3.3. Effect of heat treatment on phase separation

3.3.1. Thermal analysis

Fig. 7a and b show typical TG and differential thermal analysis (DTA) curves for ST1 and ST3 samples, respectively. The DTA curve for ST1 sample exhibits a strong endothermic peak at approximately 70 °C, while for ST3 intensity of this peak remarkably decreases. In both cases, three weight losses were observed. The TG curves for both ST1 and ST3 indicate an initial weight loss of 16.8% between ambient temperature and 120 °C. These changes are induced by elimination of physical water and alcohols trapped in the porous texture [7]. There is a further weight loss of 12.3% and 10.15% in the TG curves in the range 120–500 °C for ST3 and ST1, respectively. This is associated to a wide exothermic peak at around 420 °C for ST1 and at around 370 °C for ST3, that both correspond to the decomposition of organic residues [23]. When the stabilizers content decreases, this process is shifted into the higher temperature ~450 °C. Hence, it can be found that the temperature of CH_3 group carbonization depends on the amount of MMA and DEA and increases with decreasing amount of stabilizers. This also results in generation of samples with uniform pore size structure, which allows gradual elimination of organic residue. For ST3, this process occurs at a lower temperature, indicating a more homogenous pore size structure compared to the ST1. Then, it can be concluded that there is more Si–O–Ti linkages in the ST3 compared to the ST1; so separation phase decreases with increasing TiO_2 and in fact increasing MMA and DEA in SiO_2–TiO_2 films.

Due to removal of structural hydroxyls from the structure, the TG curves indicate a slight weight loss of 0.69 and 1.82% between 500 and 700 for ST1 and ST3, respectively. The higher third step weight loss of the higher Ti contents samples during heating process can be explained by existence of some titanium linkages like Ti–O–R, as burning of the organic content of MMA and DEA in the sample containing higher titanium content is more difficult to eliminate. The existing Si–O–Ti bonds would be broken at this stage, leading to the formation of Ti–O–Ti structural units but having no concern with weight loss. Therefore, our method could attain better homogeneity even for much higher Ti contents (30 wt%) as compared to 15 wt% value reported earlier [12,24].

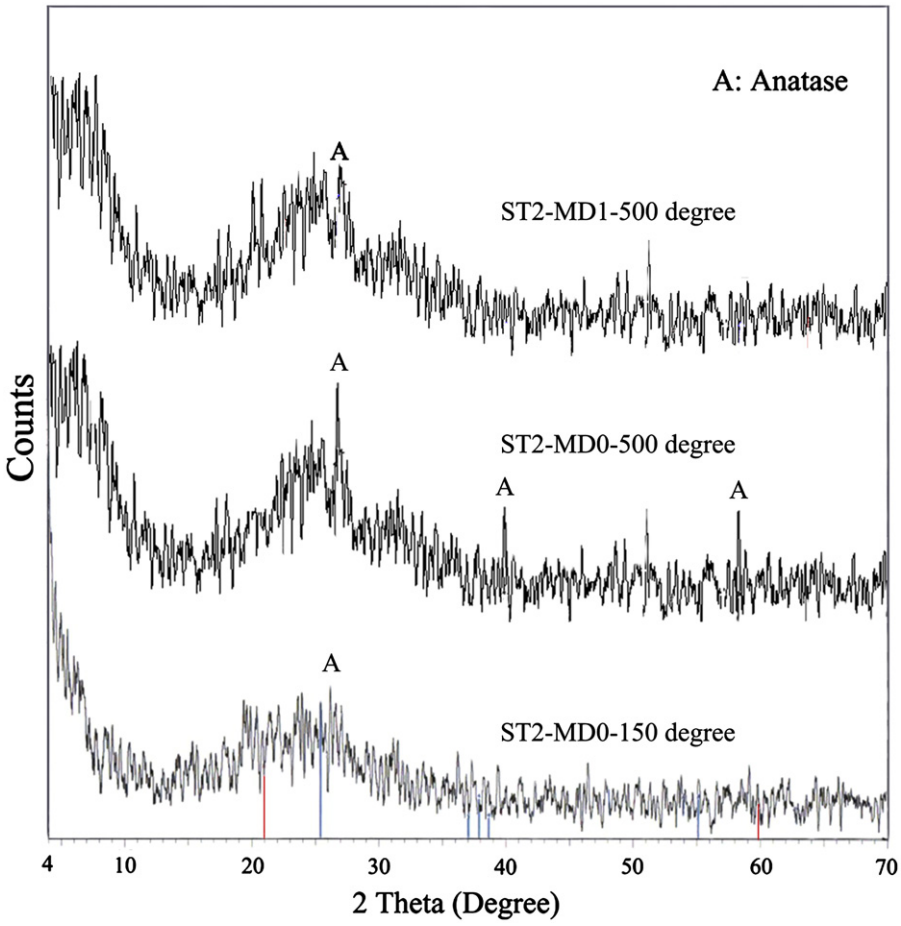


Fig. 8. X-ray diffraction pattern of SiO_2–TiO_2 films heat-treated at various temperatures.

3.3.2. Crystal structure

In this work, X-ray diffraction (XRD) analysis for three samples (ST2-MD0 at 150 °C, ST2-MD0 and ST2-MD1 at 500 °C) has been performed as shown in Fig. 8. For samples without stabilizers, as the temperature rises TiO_2 is found in anatase form, whereas SiO_2 was formed in an amorphous phase. For the ST2-MD0, the amorphous TiO_2 segregates to form crystals when the samples are heated at 500 °C. Sample ST2-MD1 proves to be a better candidate in comparison with ST2-MD0. Also, sample ST2-MD0 produces its titanium oxide phases on heat treatment. The patterns for ST2-MD1 exhibit a broad diffraction peak within the 2θ range 10–40° characteristic of amorphous silica. This indicates that titanium is highly dispersed in the silica matrix and a few numbers of crystals exist as the size is appropriate to be detected by XRD. Since very small diffraction peaks related to species are observed, it can be stated that the Ti^{4+} ions may enter the SiO_2 network and take the place of some Si^{4+} ions, leading to a homogenous distribution of isolated Ti^{4+} species in the silica matrix. The results of this study, therefore, show that the mixing of Si and Ti at an atomic level occurs in the sol–gel process, while higher amounts of Ti addition without using stabilizers lead to segregation of TiO_2 particles.

The experiments conducted in this project revealed that application of DEA and MMA enhances the homogeneity of SiO_2–TiO_2 films at higher temperature and prevents more anatase segregation.

4. Conclusions

In this work, titanosilicate films were prepared with 10, 20, and 30 wt% TiO_2 by the polymeric sol–gel route. SEM and AFM images showed TiO_2 separation in surface of the SiO_2–TiO_2 films without using any stabilizer. The intensity of Si–O–Ti linkages peak was increased with using appropriate composition of diethanolamine (DEA) and methyl methacrylate (MMA) as stabilizers, proving the homogeneity of the samples. However, it was reduced with further stabilizer content. XRD spectra showed the evolution of TiO_2 anatase phase with elimination of stabilizers and with heat treatment.

References

[1] X. Gao, I.E. Wachs, Titania–silica as catalysts: molecular structural characteristics and physic chemical properties, Journal of Catalysis Today 51 (1999) 233–254.

[2] R.D. Shull, R.D. Michael, L.J. Swartzendruber, L.H. Bennett, Proceedings of the International Workshop on Studies of Magnetic Properties of Fine Particles and Their Relevance to Material Science, North-Holland, Amsterdam, 1992.

[3] P. Rejikumar, N. Unnikrishnan, Phase segregation in binary SiO_2/TiO_2 and SiO_2/Fe_2O_3 nanoparticle aerosols formed in a premixed flame, Journal of Materials Research 14 (1999) 4551–4561.

[4] P. Sun, H. Liu, H. Yang, W. Fu, S. Liu, Synthesis and characterization of TiO_2 thin films coated on metal substrate, Applied Surface Science 256 (2010) 3170–3173.

[5] C.J.R. Gonzalez, P.F. James, H. Rawson, Silica and silica–titania glasses prepared by the sol–gel process, Chemistry of Materials 14 (2002) 2429–2432.

[6] A.J. Burggraaf, L. Cot, Fundamentals of Inorganic Membrane Science and Technology, Elsevier, Amsterdam, 1996 (pp. 141–225).

[7] J. Ren, Z. Li, Sh. Liu, Y. Xing, Silica–titania mixed oxides: Si–O–Ti connectivity, coordination of titanium, and surface acidic properties, Catalysis Letters 124 (2008) 185–194.

[8] A. Ulatowska, I. Holowacz, K. Wysocka, Silica-based versus silica–titania sol–gel materials—comparison of the physical properties: surface tension, gelation time, refractive index and optical transmittance, Applied Optics 1 (2009) 202–212.

[9] M. Beghi, P. Chiurlo, L. Costa, Structural investigation of the silica–titania gel/glass transition, Journal of Non-Crystalline Solids 145 (1992) 175–179.

[10] C. Perry, X. Li, D.N. Waters, Structural studies of gel phases—IV. An infrared reflectance and fourier transform raman study of silica and silica/titania gel glasses, Spectrochimica Acta Part A: Molecular Spectroscopy 47 (1991) 1487–1494.

[11] J.H. Lee, S.Y. Choi, C.E. Kim, The effects of initial sol parameters on the microstructure and optical transparency of TiO_2–SiO_2 binary aerogels, Journal of Materials Science 32 (1997) 3577–3585.

[12] T. Fernandez, G. Jose, S. Mathew, An ultra-low hydrolysis sol–gel route for titanosilicate xerogels and their characterization, Journal of Sol Gel Science and Technology 41 (2007) 163–168.

[13] J. Zhai, L. Zhang, Xi Yao, Effects of composition and temperature on gel-formed TiO_2/SiO_2 films, Journal of Non-Crystalline Solids 260 (1999) 160–163.

[14] A.A. Ismaeil, I.A. Ibrahim, Impact of supercritical drying and heat treatment on physical properties of titania/silica aerogel monolithic and its applications, Applied Catalysis 346 (2008) 200–205.

[15] K.M. Hunga, W.D. Yanga, Preparation and characterization of TiO_2–SiO_2 glass ceramics via the sol gel process by adding organic additives, Materials Manufacturing Processes 17 (2002) 323–338.

[16] C.H. Kwon, J.H. Kim, I.S. Jung, H. Shin, K.H. Yoon, Preparation and characterization of TiO_2–SiO_2 nano-composite thin films, Journal of Ceramics International 29 (2003) 851–856.

[17] S. Permpoon, M. Houmard, D. Riassetto, L. Rapenne, G. Berthome, Natural and persistent superhydrophilicity of SiO_2/TiO_2 and TiO_2/SiO_2 bi layer films, Journal of Thin Solid Films 516 (2008) 957–966.

[18] M. Aizawa, FTIR liquid attenuated total reflection study of TiO_2–SiO_2 sol–gel reaction, Journal of Non-Crystalline Solids 128 (1991) 77–85.

[19] M. Nocun, S. Siwulski, E. Leja, Structural studies of TEOS-tetraethoxytitanate based hybrids, Optical Materials 27 (2005) 1523–1528.

[20] C. Liu, Q. Fu, J.B. Wang, W.K. Zhao, Y.L. Fang, Structural characterization of nanocrystalline TiO_2 and TiO_2:SiO_2 powders and thin films at 35 °C, Journal of the Korean Physical Society 46 (2005) 104–108.

[21] E. Pabon, J. Retuert, R. Quijada, A. Zarate, TiO_2–SiO_2 mixed oxides prepared by a combined sol–gel and polymer inclusion method, Journal of Microporous and Mesoporous Materials 67 (2004) 195–203.

[22] R.S.A. Lange, K.N.P. Kumar, J.H.A. Hekkink, Microporous SiO_2 and SiO_2/MO_x (M = Ti, Zr, Al) for ceramic membrane applications: a microstructural study of the sol-stage and the consolidated state, Journal of Sol–Gel Science and Technology 2 (1994) 489–495.

[23] P. Cheng, M. Zheng, Y. Jin, Q. Huang, M. Gu, Preparation and characterization of silica-doped titania photocatalyst through sol–gel method, Materials Letters 57 (2003) 2989–2994.

[24] C. Sanchez, J. Livage, M. Henry, Chemical modification of alkoxide precursors, Journal of Non-Crystalline Solids 10 (1988) 65–76.