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Effects of additives on properties of Sol-Gel derived TiO_2 coating films for nonlinear optics

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Sol-Gel법에 의한 TiO_2 비선형 광학 박막 특성에 미치는 첨가물의 영향

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Abstract TiO_2 films of rutile and anatase phase have been prepared on silica glass substrates by the sol-gel method using $Ti(i\text{-}OC_3H_7)_4$. The effect of additives on the polymorph of TiO_2 film has been examined in view of degree of crystallization. Third-order nonlinear optical properties of the both films have been investigated by the third harmonic generation method. The measured 3rd-order nonlinear optical susceptibility of rutile and anatase thin films were about 1.4×10^{-12} and 9.7×10^{-13} esu, respectively.

요 약 $Ti(i\text{-}OC_3H_7)_4$ 알콕사이드를 출발 원료로 사용한 sol-gel법을 이용하여 Rutle, Anatase 결정상의 TiO_2 박막을 제조하였다. 결정화 정도란 관점에서 TiO_2 박막의 결정상에 미치는 첨가물의 영향을 조사하였다. 3차 비선형 광학 감수율을 THG법을 이용하여 측정하였으며, Rutle 과 Anatase 결정상의 TiO_2 박막의 3차 비선형 광학 감수율은 각각 1.4×10^{-12} 과 9.7×10^{-13} esu의 값을 얻었다.

1. Introduction

As far as oxide film coatings are concerned, metal alkoxide process is one of the most important techniques for the synthesis of various functional films because it is possible to coat large surface and to form a homogeneous multi component film at low temperature. So far many reports on TiO_2 film coatings with special attention have been published [1-4]. Recently, TiO_2 is considered to be a promising nonlinear optical material because of the high refractive index more than 2.5 and high transparency in the visible range.

The importance of additives for obtaining transparent titania sol and its application in coating have been pointed out. Chemical modification of alkoxides with additives has proved to be important in sol-gel processing. It has been shown that additives such as acetylacetone, ethanolamines and acetic acid react with alkoxides, forming modified molecular precursors which control the degree of hydrolysis and subsequent polycondensation reactions. Therefore, these additives assist in easy handling of sol and precise control over the thickness of the film. In the course of our investigation concerning the solvent effect, it was found that ethanol amine can accelerate the crystallization.

In the present study, TiO_2 films of rutile and anatase have been prepared on silica glass substrates by the sol-gel method. Nonlinearities of the both films have been investigated by THG method. The effects of heating temperature and additives on the morphology, crystallographic orientation of the resultant TiO_2 coating film have been examined.

2. Experimental

2.1. Preparation of Film

TiO_2 thin films were prepared by sol-gel method. As a starting standard solution, $Ti(i\text{-}OC_3H_7)_4$-H_2O-EtOH-HCl solution was selected and the chemical composition of the solution was 1 : 1 : 8 : 0.28 in molar ratio as listed in Table 1. Titanium tetraisopropoxide was first dissolved in a solution of additives (Acetylacetone, acetic acid, ethanolamines (MEA, DEA, TEA) and (DiMF) and half of a prescribed amount of alcohol (EtOH Ethoxy EtOH, i-PrOH, 1(2)-BtOH). Then, the solution was mixed with a solution of H_2O and the remainder of alcohol. Resultant coating solutions were allowed to stand

at room temperature for 30 minutes prior to dip-coating. Dip-coating was used for film formation. A SiO_2 glass substrate was immersed in a coating solution, and pulled up at a rate 3.5 cm min^{-1}. The film was heated at 600, 700, 800 and 900℃ for 10 min immediately after each coating procedure. This cycle was repeated 10 times to obtain the desired film thickness.

2.2. Characterization of film

The crystalline phases preciptated in the films were identified by X-ray diffraction method using CuKα radiation. The refractive index of TiO_2 film was determined by an ellipsometer in the wavelength range of 500 to 1000 nm. The absorption spectra were measured in the region from 200 to 2000 nm by a UV-visible spectrophotometer. The third harmonic generation intensity $I_{3\omega}$ was measured by a nonlinear optical measurement apparatus (Tokyo Instruments, Co.) The surface and cross-sectional morphology of the films was observed by TEM.

3. Results

3.1. Crystallization behaviour

Table 1

Compositions of the coating solutions

Compositon(Mol ratio)													Remarks		
Sol No.	Ti O(OPr)$_4$	H_2O	Ethoxy EtOH	EtOH	PtOH	BtOH	HCl (1-,2-)	DMF	Acetic Acid	Acetyl Aceton	MEA	DEA	TEA	Appearance of Sol	Film	Phase (700℃)
S0	1	1	-	8	-	-	0.28							Clear	transparant	A
S1	1	1	-	8	-	-	0.28	1						Clear	transparant	R+A
S2	1	1	-	8	-	-	0.28		1					Clear	transparant	R+A
S3	1	1	-	8	-	-	0.28			1				Clear	transparant	A
S4	1	1	-	8	-	-	0.28				1			Clear	transparant	R+A
S5	1	1	-	8	-	-	0.28					1		Clear	transparant	R
S6	1	1	-	8	-	-	-					3		Clear	transparant	-
S7	1	1	-	8	-	-	0.28					5		Clear	transparant	-
S8	1	1	-	8	-	-	0.28					7		Clear	transparant	-
S9	1	1	-	8	-	-	0.28							Clear	transparant	R+A
S10	1	1	8	-	-	-	0.28							Clear	transparant	A
S11	1	1	-	-	8	-	0.28							Clear	transparant	A
S12	1	1	-	-	-	8	0.28							Clear	transparant	A/A
S13	1	1	-	8	-	-	0.15							Clear	transparant	A
S14	1	1	-	8	-	-	0.20							Clear	transparant	A

*R : Rutile Phase, A: Anatase Phase

*Sample S6, S7, S8 and S9 were coated on slide glass for substrate at 600℃

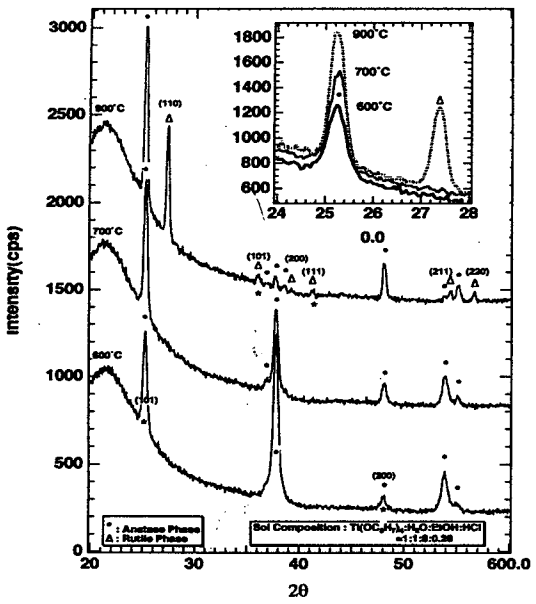

Fig. 1. X-ray diffraction patterns of standard solution S0-derived films heated at 600, 700 and 900℃.

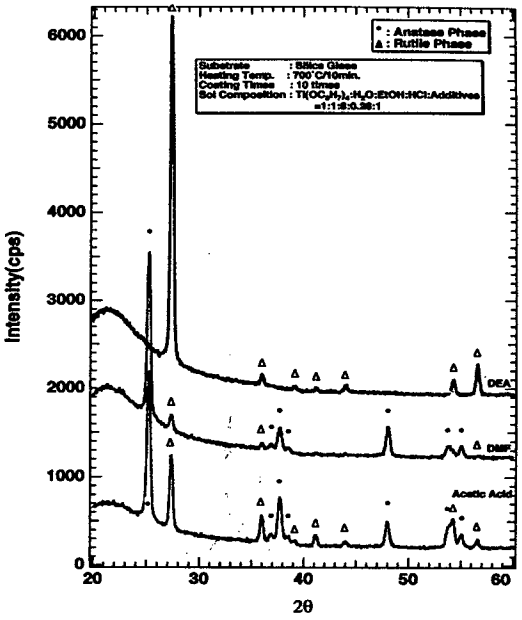

Fig. 2. X-ray diffraction patterns of the TiO_2 films prepared from solutions containing additives (DEA, DMF and acetic acid) at 700℃.

Figure 1 shows X-ray diffraction patterns of standard solution(SO)-derived films heated at 600, 700 and 900℃. The peak intensity of (101) plane (anatase phase) increases with increasing temperature. The peak intensity of (110) plane(rutile phase) was observed at 900℃. Figures 2 and 3 shows X-ray diffraction patterns of the TiO_2 films prepared from solutions(S1−S5) containing additives such as MEA, DEA, DMF, acetic acid and acethyl aceton. TiO_2 film prepared from solution (S5) containing DEA was anatase phase below 600℃ and consisted of a single phase of rutile at 700℃. Preferred orientation along the (110) plane was observed. The other TiO_2 films prepared from solutions containing additives such as MEA, DMF, acetic acid and acethyl aceton consisted of a mixture of anatase and

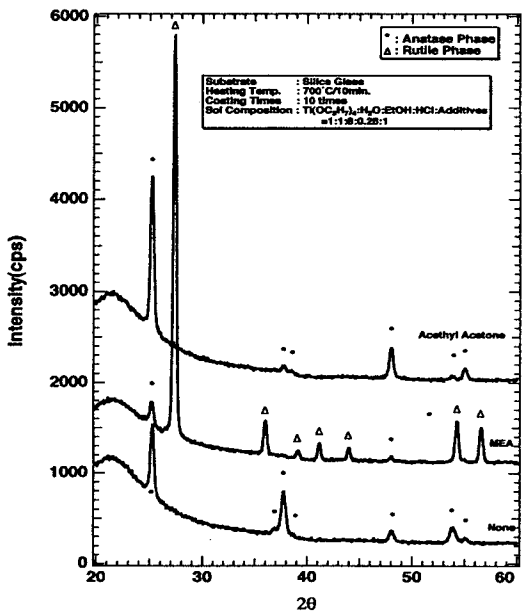

Fig. 3. X-ray diffraction patterns of the TiO_2 films prepared from solutions containing additives (acethyl aceton and MEA) at 700℃.

rutile phase at 700℃.

3.2. *Surface morphologies*

Figure 4 shows the TEM image(a) and electron diffraction pattern(b) of film from solution SO at 600℃. Generally, particle size increases and anatase phase changes to rutile phase with increasing heating temperature. The electron diffraction pattern of anatase phase was observed at 600℃.

In contrast, preferred orientation along the

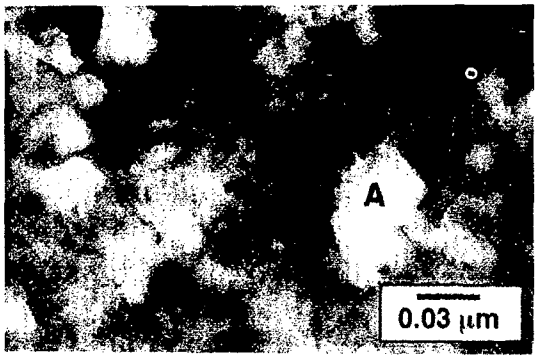

Fig. 4(a). Suface image of thin TiO_2 film.

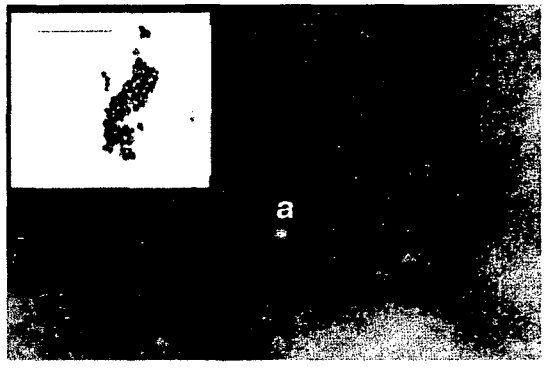

Fig. 5(a). Suface image of thin TiO_2 film.

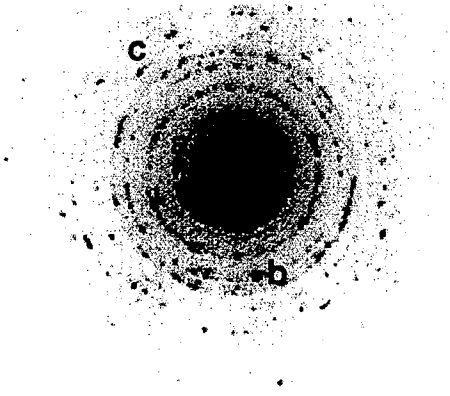

Fig. 4(b). The electron diffraction pattern of selected-area A. Anatase Phase:a:(101), b:(200), C(220).

Fig. 4. Transmission electron micrograph of a thin TiO_2 film at 600℃ (a) surface image and (b) diffraction pattern of selected-area A.[Ti(O-i-Pr)$_4$:H_2O:EtOH:HCl=1:1:8:0.28 and 10 times coatings].

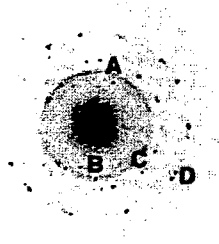

Fig. 5(b). The electron diffraction pattern showed rings composed of bright spots which were assignable to:A:(110), B:(101), C:(210), D:(002) diffractions in selected-area 'a'.

Fig. 5. Transmission electron micrograph of a thin TiO_2 film at 600℃ (a) surface image and (b) diffraction pattern of selected-area A. [fixed at Ti(O-i-Pr)$_4$:H_2O:EtOH:HCl:DEA=1:1:8:0.28:7 and 10 times coatings].

(110) plane of rutile phase at 600℃ was observed in TiO_2 film prepared from solution containing DEA as shown in Fig 5.

3.3. Optical properties

The wavelength dependence of refractive index of TiO_2 film is shown in Table 2. The refractive index decreases with increasing wavelength over a wevelength range from 500 to 1000 nm. The refractive index at 1.9 μm(n_ω) was estimated by extrapolating the linear plot of $1/(n^2-1)$ vs. E^2(E=photon energy). Optical band gap(E_g)was estimated from the extrapolation of a linear portion of the $(\alpha h\nu)^2$ vs $h\nu$ plot ot the $h\nu$-axis. The values obtained are summarised in Table 2, also. The 3rd-order nonlinear optical susceptibility values of rutile and anatase films were determined to be 1.4×10^{-12} and 9.7×10^{-13} esu, respectively.

4. Discussion

4.1. Crystallization effects of organic additives

The amino and hydroxyl groups of alkanolamines are known to coordinate the metal atoms of alkoxides, improving the solubility and stability against hydrolysis of the alkoxide [5].

In the present study, addition of more than 1 mole of alkanolamine to i mole of titanium tetraisopropoxide provided a clear solution. As shown in Figs. 2 and 3, preferred orientation along the(110) plane of rutile phase at 700℃ was observed in TiO_2 film prepared from solution containing DEA. In contrast films prepared from solutions containing MEA consisted of a mixture of anatase and rutile phase.

One possible explanation of the effect of the solvent boiling point on TiO_2 crystallization is that a solvent of higher boiling point would evaporate more slowly on heating, allowing the structure relaxation of gel film before crystallization. Since DEA has a higher boiling point(270℃) than MEA(170℃), the structural relaxation of the TiO_2 film prepared from solutions containing DEA is allowed by the slower vaporization of the solvent, providing denser precursor film than porous one. This consideration suggests that the structural relaxation of the precursor gel before crystallization is necessitated for obtaining homogeneous films with strongly preferred orientation. The fine microstructure as shown in Fig. 5(a) may explain why TiO_2 film prepared from solution containing DEA is consist of a only single rutile phase in contrast with TiO_2

Table 2
Optical properties of TiO_2 film

	$n_{3\omega}$	n_ω	$T_{3\omega}$/%	T_ω/%	E_g/eV	$\chi^{(3)}$/esu
Rutile	2.40	2.27	86.5	81.0	3.0	1.4×10^{-12}
Anatase	2.29	2.16	91.3	82.6	3.2	9.7×10^{-13}

film from solution S0.

4.2. Relationship between $\chi^{(3)}$ and optical band gap

One can expect that an enhancement in $\chi^{(3)}(-3\omega:\omega, \omega, \omega)$ occurs when in a material a frequency of interacting light approaches either one of one, two or three photon resonance frequencies as follows,

$$\chi^{(3)}(-3\omega:\omega, \omega, \omega) \propto \frac{N}{\hbar} \sum_{gnmn'} \rho(g) \cdot F(\omega) \cdot \Omega_{gn} \Omega_{nm} \Omega_{mn'} \Omega_{n'g} \text{ and} \quad \text{(Eq. 1)}$$

$$F(\omega) = \frac{1}{(E_{ng}-3\omega)\cdot(E_{mg}-2\omega)\cdot(E_{n'g}-\omega)} + \frac{1}{(E_{ng}+\omega)\cdot(E_{mg}-2\omega)\cdot(E_{n'g}-\omega)} + \frac{1}{(E_{ng}+\omega)\cdot(E_{mg}+2\omega)\cdot(E_{n'g}-\omega)} + \frac{1}{(E_{ng}+\omega)\cdot(E_{mg}+2\omega)\cdot(E_{n'g}+3\omega)} \quad \text{(Eq. 2)}$$

where $\rho(g)$, E_{ij} and Ω_{ij} are the density matrix element of fundamental state, the energy difference between states i and j $\hbar(=h/2\pi$, h is the Plank's constant) unit and the transition matrix elements between states i and j, respectively. For materials having optical band gep. E_g, higher than three photon energy, 3ω, the three photon resonance makes the greatest contribution to the enhancement of $\chi^{(3)}$. Then, to a good approximation, the most significant term due to the three-photon resonance in the above equation may be expressed as follow.

$$\chi^{(3)} = \frac{A}{(E_g-1.96)\cdot(E_g-1.31)\cdot(E_g-0.65)(\text{esu})} \quad (E_g > 1.96) \quad \text{(Eq. 3)}$$

where A is the phenomenological constant (1.4×10^{-11}).

In the relationship between $\chi^{(3)}$ and optical band gap of TiO_2 thin film, $\chi^{(3)}$ shows a tendency to increase asymptotically as the E_g approaches 1.96 eV corresponding to the photon energy of 3rd harmonic generation signal. From this equation, $\chi^{(3)}$ values were estimated to be 3.4×10^{-12} and 2.3×10^{-12} esu for rutile and anatase films, respectively.

4.3. Theoretical $\chi^{(3)}$ value based on modified lines's model

So far, several simple models have been proposed to describe the third-order optical nonlinearity such as Boling's and Miller's model. Lines introduced an influence of empty d-orbitals on the nonlinear optical response of various transparent transition-metal oxides on the basis of the bond-orbital theory. The empty d-levels fall rapidly bellow the conduction sp-band as a function of decreasing the equilibrium bond length and increasing $\langle d/p \rangle$ overlap. This d-orbital contribution to linear and nonlinear optical response is negligible for bond length $d \geq 2.3$ Å, but in

creases rapidly with decreasing bond length, becoming dominant when $d \leq 2.0$ Å. The angular average nonlinear refractive index n_2 ws expressed only in terms of measurable physical quantities by the following equation,

$$n_2(av) = \frac{f^3 \cdot f_L \cdot d^2 (n_\omega^2 - 1) \cdot E_s^6}{n_\omega (E_S^2 - E^2)^4} \times 10^{-13} \quad \text{(Eq. 4)}$$

where $f_L = (n_\omega^2 + 2)/3$ is the Lorentz local field factor, f is the local enhancement factor, n_ω^2 is the refractive index at the wavelength $\lambda = 1.9$ μ m, and d the bond length between cation and anion in Å unit. For frequency of $\omega^2 \langle\langle E_S / h^2$, E_S in eV unit is the one paramenter Sellmeier gap which is in practice equal to E_0 in Wemple's equation and L is an empirical factor which suggested might be reasonably constant for a group of related materials. In the present study, on the assumption of absence of any local field correction factor(i.e., $f=1$). Since the third-order nonlinear optical susceptibility $\chi^{(3)}$ is related n $_2$, it is possible to estimate the theoretical $\chi^{(3)}$, giving the following equation,

$$\chi^{(3)} = L \cdot \frac{f_L^3 \cdot d^2 (n_\omega^2 - 1) \cdot E_S^6}{(E_S^2 - E^2)^4} \quad \text{(Eq. 5)}$$

Where L is an empirical factor which suggested might be reasonably constant for a group of related materials. This approach has considerable merit for calculating the theoretical $\chi^{(3)}$ value since the above equation is composed of measurable parameters, experimentally. From this relation, one can obtain $\chi^{(3)}$ values of 4.7×10^{-12} and 2.7×10^{-12} esu for rutile and anatase films, respectively. Therefore, the higher $\chi^{(3)}$ values of both TiO_2 polymorphs compared with silica glass can be ascribed to the higher refractive index and narrow optical band gap, which result from the significant contribution of 3d orbitial due to the large p-d overlapping in the short Ti-O bond length.

5. Conclusions

TiO_2 films of rutile and anatase phase have been prepared on the silica glass substrates by the sol-gel method. The effect of additives on the degree of crystallization of TiO_2 film has been examined. Third-order nonlinear optical properties of both films have been investigated by the third harmonic generation method. The following results were obtained

1) A single rutile phase was observed at 700℃ in a TiO_2 film prepared from solution containing DEA in contrast with TiO_2 film from solution containing other additives.

2) The measured 3rd-order nonlinear optical susceptibilities of rutile and anatase thin films were about 1.4×10^{-12} and 9.7×10^{-13} esu.

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