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# Low-Temperature Crystallization of $TiO_2$ Films on Arranged Mono-Layers by Sol-Gel Method

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$TiO_2$ gel films were deposited on self-assembled monolayers (SAMs) of octadecy ltrichlorosilane (OTS) and $SiO_2$ glass substrates using $Ti(OC_3H_7^i)_4$-derived titania sols. It was found that OTS SAM induces precipitation of anatase phase at a rather low temperature of 200°C when a molar ratio of $H_2O/Ti(OC_3H_7^i)_4$ was as low as 0.5 for sol preparation.

*Keywords:* molecular templates; SAMs; crystallization; $TiO_2$ films; sol-gel method

## INTRODUCTION

It is known that temperatures above 400~500°C are usually necessary for the crystallization of most functional materials in sol-gel method. To satisfy the needs for some devices in which the functional films or the substrates are not durable against the high-temperature treatment, much lower heat-treatment temperature is strongly requested in recent years.

In the present study, an idea of utilizing ordered arrangement of molecules such as SAMs as templates[1] to induce the oriented nucleation in functional films at low temperature was introduced to the sol-gel method.

## EXPERIMENTAL

Octadecyltrichlorosilane (OTS) monolayer was prepared on quartz glass substrate in dried $N_2$ atmosphere first. Titanium tetraisopropoxide ($Ti(OC_3H_7^i)_4$), ethanol and 35% HCl aq. were used for preparing precursor sols with different $r = H_2O/ Ti(OC_3H_7^i)_4$ molar ratios. The gel films were obtained by dipping the monolayer substrates and the bare glass substrate into the prepared sols repeatedly, and then successively heat-treated at given temperatures.

## RESULTS AND DISCUSSION

$TiO_2$ films (r =1) were first deposited on the bare glass substrate and OTS SAM and heat-treated at various temperature. Anatase was found to be formed above 400°C, and no great difference in crystallization behavior among the films deposited on different substrates when r = 1.

$TiO_2$ films (r =0.5) were then deposited on the glass substrate and OTS SAM and heat-treated at various temperature successively. Influence of the substrate on the crystallization behavior of the films clearly appeared after post-heating at 200°C for 1 h (Fig. 1). The anatase (101) peak was observed for the $TiO_2$ gel films deposited on the OTS SAM, while those on the bare glass substrate were still amorphous. The most intense anatase (101) peak was observed for the films on the OTS SAM post-heated at 700°C for 10 min. In addition, a weak rutile (110) peak was also observed. The anatase phase on the OTS SAM completely transformed into the rutile one when further post-heating was carried out at 900°C for 10

min. For the films deposited on the glass substrate, no rutile peaks were observed even at 900°C.

This crystallization temperature (~200°C) found in the film on the OTS SAM is much lower than those usually observed for alkoxide-derived $TiO_2$ films deposited on glass substrates. Since the extent of the crystal nucleation occurring interior the gel films is supposed to be similar irrespective of the substrate surface, the nucleation at the film/substrate interface is thought to play a critical role in the crystallization behavior of the gel films.

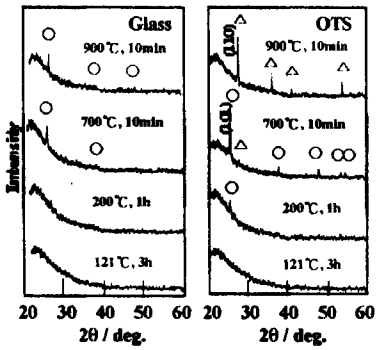


FIGURE 1 XRD patterns of the $TiO_2$ films deposited on glass substrates and OTS SAMs. ○ : anatase, △: rutile.

It should be noted that the appreciable effects of the substrate were found on the crystallization behavior of the gel films only when a smaller r (0.5) was employed for the sol preparation in the present study. Yoldas[2] have indicated that r, a basic parameter in sol-gel method, affects the kinetics of hydrolysis and polymerization and then determines the nature of the resultant polymer. A hydrolytic polycondensation reaction can be written as follows:

$$nTi(OR)_4 + (4n + x - y)H_2O \rightarrow$$
$$Ti_nO_{2n-(x+y)/2}(OH)_x(OR)_y + (4n-y)ROH \qquad (1)$$

According to this equation, the concentration of alkyl (OR) terminal

groups in the polymer increases as the amount of water is decreased in the system. That is, a smaller r (0.5) leads to the presence of a large amount of alkyl terminal groups unhydrolyzed. Therefore, the arrangement and/or rearrangement of the titania polymers at the gel film/OTS SAM interface is expected to more easily occur in the gel film deposition and/or drying processes due to the interaction between the methyl groups in OTS SAM and the (OR) terminal groups in the gel film when a smaller r was employed for the sol preparation.

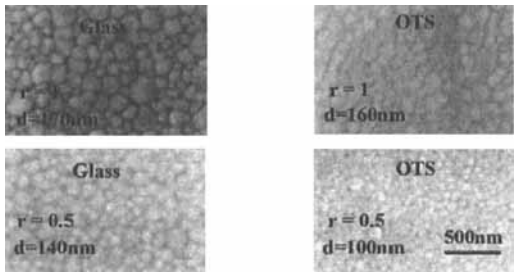


FIGURE 2 SEM images of the $TiO_2$ gel films coated on the glass substrate and OTS SAM surface after post-heated at 900℃ for 10min.

Fine grains of submicrometer in size for the films on glass were observed (see FIGURE 2). The grain size decreased by several tens nanometers for the films on OTS. This may be due to the strong molecular interaction at the film/OTS substrate interface which accelerated the crystal nucleation there. Therefore, a larger number of nuclei formed at the interface, which in turn realized the smaller grain size in this film.

## *References*

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