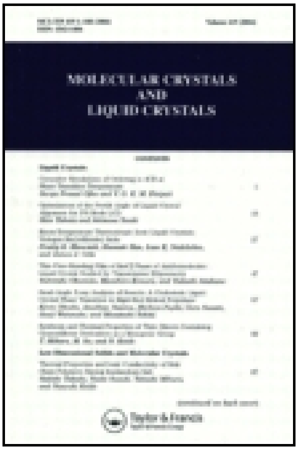

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Characteristics of Thin Films Synthesized from Colloidal Silica-Silane Sols

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Three kinds of colloidal silica (CS)/silane sol solutions were synthesized by using three kinds of CS at different reaction time. Sol solutions were prepared from 1034A CS/methyltrimethoxysilane (MTMS), HSA CS/MTMS and LS CS/MTMS materials. In order to understand their physical and chemical properties, sol-gel coating films were fabricated on glass. Coating film on glass, obtained from 1034A/MTMS sol, had high contact angle and much enhanced flat surface in comparison with those of HSA/MTMS and LS/MTMS sols. Enhanced surface properties were observed in the case of sol solutions left for 7 days. With increasing reaction time in sol solutions, surface free energy and roughness in coating films decreased. Good thermal stability was observed in all used films, i.e., no thermal degradation up to 550°C. In the case of 1034A/MTMS coating film, thermal degradation did not occur up to 600°C. In addition, microhardness of 1034/MTMS coating film was higher than those of HSA/MTMS and LS/MTMS due to active networking and surface treatment reactions between 1034A and MTMS.

Keywords: colloidal silica; nano-hybrid materials; silan; sol-gel reaction

INTRODUCTION

Sol-gel process is a convenient and versatile method for preparing optical thin films at low temperature. In most sol-gel process, colloidal silica and low molecular weight, alkoxide are used as sol-gel precursors [1,2]. Nano-sized colloidal silica particles are being intensively studied until now due to their potential applications in catalysis,

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intelligent materials, optoelectronic devices and coating technology [3,4]. Also, particle size, size distribution and shape are crucial factors to determine various roles they can play as electronic substrates, thin film substrates, electrical and thermal insulators in the field of micro or nano-devices.

Methyltrimethoxysilane (MTMS) is one of representative alkoxide for preparing glassy matrix of films. Hydrolysis and condensation of MTMS during sol-gel process help to form solid silicate around the dopant or molecule in the liquid phase [5–7]. In this case, gelation of a mixture of colloidal silica (CS) and MTMS occurs via networking and surface treatment reactions. These reactions are caused by successive hydrolysis and condensation followed by the subsequent drying and curing [8,9].

In this paper three kinds of CS/silane sol solutions were prepared by using 1034A, HSA and LS as CS materials and MTMS as silane. MTMS is less corrosive and less influenced by impurities [10,11]. To form thin film by sol-gel method, three types of coating technique were usually applied; spin coating, dip coating and spray coating. In this study, dip coating on glass was applied [12]. Here, enhanced properties of sol-gel coating layer on glass have been investigated as a function of reaction time up to 7 days. Also, surface properties of sol-gel films such as contact angle, surface free energy, surface roughness, thermal property and microhardness were investigated in order to understand the behavior of three kinds of CS/silane sol solutions.

EXPERIMENTAL

Preparation of Sol Solutions

Several CS/silane sol solutions were synthesized by using three kinds of CS at different reaction time. 1034A CS (particle size: 20 nm, pH: 2.8) was obtained from Nalco Co. and HSA CS (particle size: 12 nm, pH: 4.2) and LS CS (particle size: 12 nm, pH: 8.2) were obtained from Ludox Co.. MTMS was purchased from Toshiba Co.

CS/silane sol solutions were prepared by 2-step sol-gel reaction. CS/MTMS sol was made from the mixture of CS and MTMS. In the beginning of such sol fabrication, acetic acid was added to HSA and LS CS for pH 3.8, except 1034A CS. Here, following addition of MTMS to three CS was done in the ratio of 30 to 100. The solutions were reacted for 2 days at 10°C. This is the first step for CS/MTMS sol fabrication. Then MTMS was again added to CS/MTMS solutions in the ratio of 60 to 130. The solutions were stirred at 300 rpm for 1–7 days at 10°C. This is the second step for CS/MTMS sol fabrication.

Preparation of Coating Films

CS/silane sol solutions were coated on glass substrates using dip coater. Dip coating was performed using a rate of 4 cm/min at room temperature. After drying in air for about 30 min, the coated glasses were kept in an oven at 60°C for 1 h. Then Coating films were cured for 3 h at 300°C. Properties of sol-gel coating layer on glass have been investigated as a function of reaction time up to 7 days. Qualities of coating films with reaction time are described in Table 1. Figure 1 describes the process of preparing sol solutions and coating films.

Characterization of Coating Films

Dynamic contact angle meter (Surface and Electro-Optics) was used to measure the hydrophobic property of coating film surfaces. Surface free energy was measured by Phoenix (Surface and Electro-Optics), using Lewis Acid/Base equation. The surface roughness of coating films was measured by alpha-step 500 surface profiler. Thermal resistances were identified by TGA (TA Q50) to 800°C at a heating rate of 20°C/min in N_2 atmosphere. The microhardness of coating films was measured by H100 XYp Microhardness Indentor (Fischerscope).

RESULTS AND DISCUSSION

In Table 2, there are summaries on contact angles of 1034A/MTMS, HSA/MTMS and LS/MTMS coating films. Contact angle of coating film depends on surface free energy of composition of materials. CS is hydrophilic. However, silanes, intermediate and silane treated CS are hydrophobic. When silanes enclose the CS surface, hydrophilic

TABLE 1 Observation of Sol-Gel Coating Films Prepared from 1034A/MTMS, HSA/MTMS and LS/MTMS Solutions

Materials	Reaction times	Quality of coating film
1034A/MTMS	1 day	transparent, flat
	4 days	transparent, flat
	7 days	transparent, flat
HSA/MTMS	1 day	hazy, rough
	4 days	a little hazy, rough
	7 days	a little hazy, rough
LS/MTMS	1 day	transparent, flat
	4 days	transparent, flat
	7 days	transparent, flat

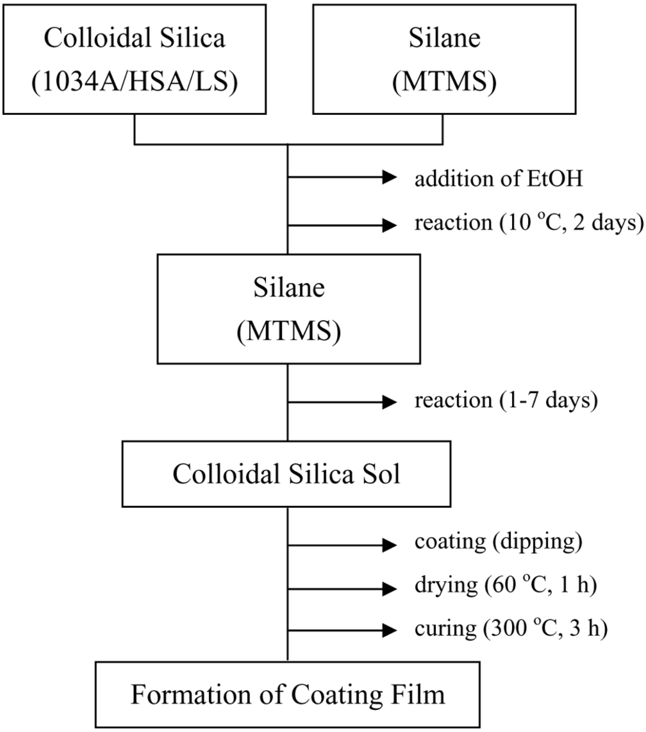

FIGURE 1 The process of preparing coating films obtained from 1034A/MTMS, HSA/MTMS and LS/MTMS solutions.

property of CS changes to hydrophobic surface according to reaction time. So contact angle of CS/silane sol-gel coating films increases. Contact angle of 1034A/MTMS and LS/MTMS coating films increased with reaction time. Contact angle of HSA/MTMS coating film decreased a little. Surface treatment reaction was active between surface of

TABLE 2 Contact Angle of Sol-Gel Coating Films in Variation of Sol Reaction Time in Three Kinds of Sol Solutions, 1034A/MTMS, HSA/MTMS and LS/MTMS

	Kinds of materials (degree)		
Reaction time	1034A/MTMS	HSA/MTMS	LS/MTMS
1 day	85.1	70.1	84.2
4 days	88.1	71.9	85.7
7 days	89.6	69.6	87.9

1034A and LS CS and MTMS. However, it is likely that surface treatment reaction between HSA CS and MTMS was inactive.

Figure 2 shows surface free energy of 1034A/MTMS, HSA/MTMS and LS/MTMS coating films. Here, CS has higher surface energy than water due to its ionic surface. Also, surface energy decreases when CS was rounded with silanes. In Figure 2, the surface energy of coating films decreased with increasing reaction time of sols, also, 1034A/MTMS coating film showed higher contact angle than those of HSA/MTMS and LS/MTMS in Table 2. Therefore, surface energy of 1034A/MTMS coating film showed lower than those of HSA/MTMS and LS/MTMS. This means that coating film of 1034A/MTMS formed more stable surface than those of HSA/MTMS and LS/MTMS.

Figure 3 shows surface roughness of sol-gel coating films with reaction times. Here, surface roughness of coating films is affected by homogeneity of composition of materials. In the beginning of sol-gel reaction, roughness of coating film showed high. However, it decreased with increasing reaction time. Coating film of HSA/MTMS MTMS had rougher surface than those of 1034A/MTMS and LS/MTMS. This means poor homogeneity occurs due to inactive reaction. Surface of 1034A/MTMS and LS/MTMS coating film was smooth. Their surface smoothness of coating films got better through the surface treatment reaction between CS and silane.

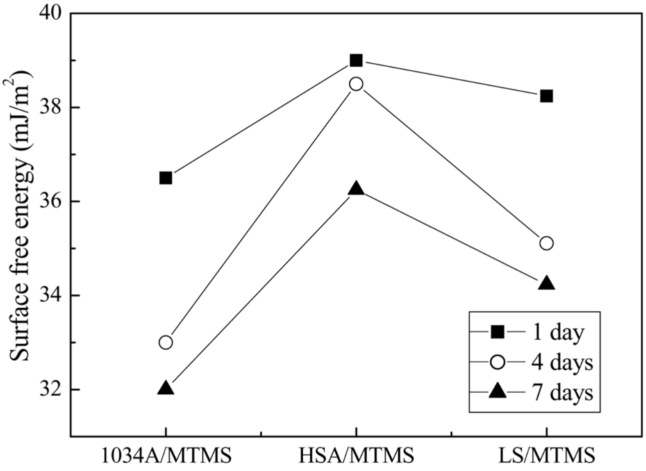

FIGURE 2 Surface free energy of sol-gel coating films in variation of sol reaction time in three kinds of sol solutions, 1034A/MTMS, HSA/MTMS and LS/MTMS.

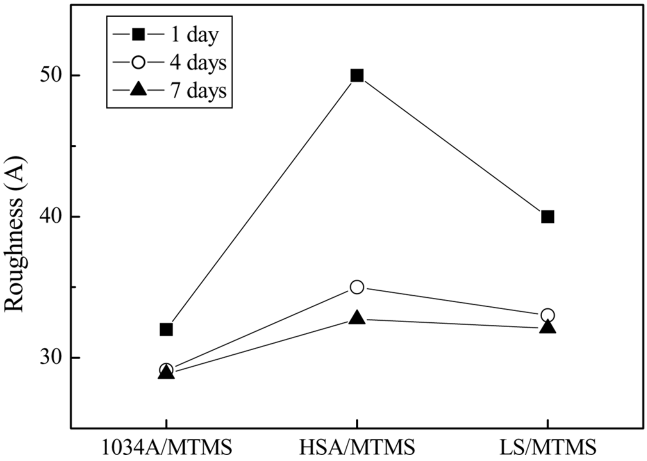

FIGURE 3 Roughness of sol-gel coating films in variation of sol reaction time in three kinds of sol solutions, 1034A/MTMS, HSA/MTMS and LS/MTMS.

The TGA spectrum of CS/silane coating film is given in Figure 4. The initial weight loss by 2–3% in all of samples is believed to be results of desorption of the moisture adsorbed on the surface of CS and the dehydration of between CS and silanol during raising temperature. The thermal degradation of 1034A/MTMS coating film

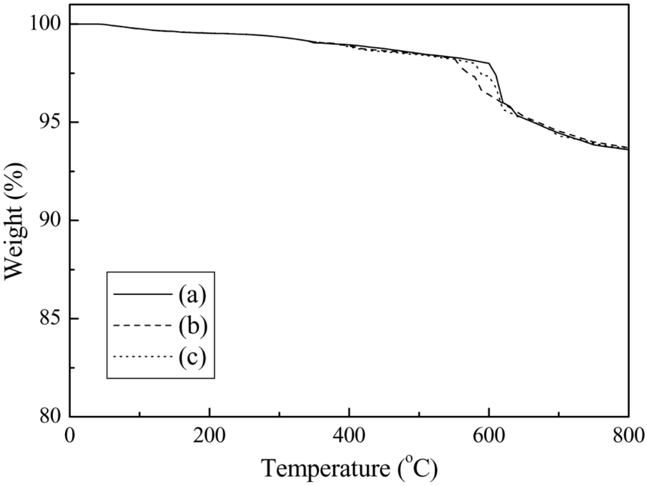

FIGURE 4 TGA thermograms of sol-gel coating films prepared from (a) 1034A/MTMS (b) HSA/MTMS (c) LS/MTMS solutions.

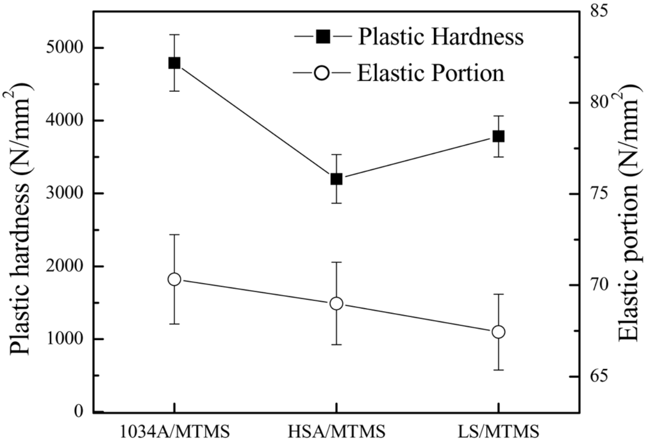

FIGURE 5 Plastic hardness and elastic portion of sol-gel coating films prepared from 1034A/MTMS, HSA/MTMS and LS/MTMS solutions.

occurred at 600°C. The degradation of HSA/MTMS coating film started at 550°C. The thermal degradation temperature of LS/MTMS coating film was 580°C. Thermal degradation of HSA/MTMS coating film occurred at the lowest temperature. When CS solution reacts with MTMS, networking between HSA and MTMS was not actively produced. It is expected that interaction force of HSA/MTMS coating film was weaker than other coating films. 1034A/MTMS coating film endured up at higher temperature of 600°C than in the case of LS/MTMS coating film.

The plastic hardness and elastic portion of coating films are shown in Figure 5. Networking and surface treatment reactions were more active in the case of 1034A/MTMS sol. These results lead to that the plastic hardness of 1034/MTMS film was higher than those of HSA/MTMS and LS/MTMS. Although same amounts of MTMS were added to three different sols, elastic portion showed different values.

CONCLUSIONS

Three kinds of colloidal silica (CS)/silane sol solutions were synthesized by using three kinds of CS at different reaction time. Properties of sol-gel coating layer on glass have been investigated as a function of reaction time up to 7 days. 1034A/MTMS and LS/MTMS sols formed transparent and flat coating films. HSA/MTMS sol was needed enough reaction time to form stable coating film. The surface properties of 1034A/MTMS coating film improved than those of HSA/MTMS and LS/MTMS. 1034A/MTMS coating film had high contact angle and low surface energy. Surface roughness of 1034A/MTMS showed lower than those of HSA/MTMS and LS/MTMS, too. In case of thermal stability, thermal degradation of 1034A/MTMS sol-gel coating films did not occur up to 600°C. Plastic hardness and elastic portion of coating films showed high. The condition of sol-gel reaction was suitable in 1034A CS, so properties of 1034A/MTMS coating film were distinguished such as surface free energy, surface roughness and plastic hardness.

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