Preparation of Au fine particle dispersed TiO_2 film by sol-gel and photoreduction process

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Abstract

Au fine particle dispersed TiO_2 film was prepared on silica glass substrate by sol-gel dip and firing process. The films were fabricated from the system of titanium tetraisoproxide-EtOH-HCl-H_2O-hydrogen tetrachloroaurate(III) tetrahydrate. The conditions for the formation of the clear solution and dissolving high concentration of Au compound were examined. And a photoreduction process was adopted to control the size of gold metal particles. Phase evolution of matrix TiO_2 and variation of Au particle with UV irradiation were investigated by XRDA, SEM, TEM and UV-visible spectrophotometer. And the effect of CPCl(Cetylpyridinium chloride monohydrate) as a dispersion agent was evaluated.

I. Introduction

In the beginning Au metal particle embeded oxide films have been studied for the use of optical color filter[1]. Recently many researchers have atttempted to make the TiO_2 film containing nanometer size Au metal particle because of its nonlinear optical properties[2]. There are some important conditions in preparing the film having high nonlinearity. First gold concentration should be as high as posible. Second the size of gold partcile should be around 20 nanometer without aggregation to cause high nonlinear optical susceptability.

In this study proper solution composition including dispersion agent and reduction process were examined to fabricate TiO_2 thin film containing nanometer size Au metal

particles by sol-gel dip & firing process from the titanium tetraisoproxide-EtOH-HCl-H_2O-hydrogen tetrachloroaurate(III) tetrahydrate system.

II. Experimental Procedures

Titanium tetraisopropoxide($Ti(i\text{-}OC_3H_7)_4$), Ethanol, H_2O, HCl, Hydrogen Tetrachloroaurate(III) Tetrahydrate($HAuCl_4 \cdot 4H_2O$) were used as starting materials. Experimental procedure is shown in Fig. 1. First $Ti(i\text{-}OC_3H_7)_4$ and ½ethanol were mixed and stirred. Solution dissolving $HAuCl_4 \cdot 4H_2O$, H_2O and HCl in ½ethanol was added drop-wise to the mixture. All mixing process was conducted at a constant temperature of 30℃ because the stability and clearness of the final mixture depended on its temperature. Compositions of coating solutions are shown in table 1. The basic TiO_2 film composition (S0) of $Ti(i\text{-}OC_3H_7)_4$: H_2O : HCl : C_2H_5OH = 1 : 1 : 0.28 : 8 was adopted from the previous paper[3]. The solubility of Au compound increased with ethanol content and stable mixture was obtained when it was over 90 mols. The maximum TiO_2/Au ratio in the mixture (SS5) was 7/3. Fig. 2. shows maximum Au solubility according to ethanol content in a stable mixture. Au content was expressed as Au wt% in the final solid film and ethanol content as molar ratio to $Ti(i\text{-}OC_3H_7)_4$. Films were prepared on the silica glass substrate by dipping coating with withdrawl

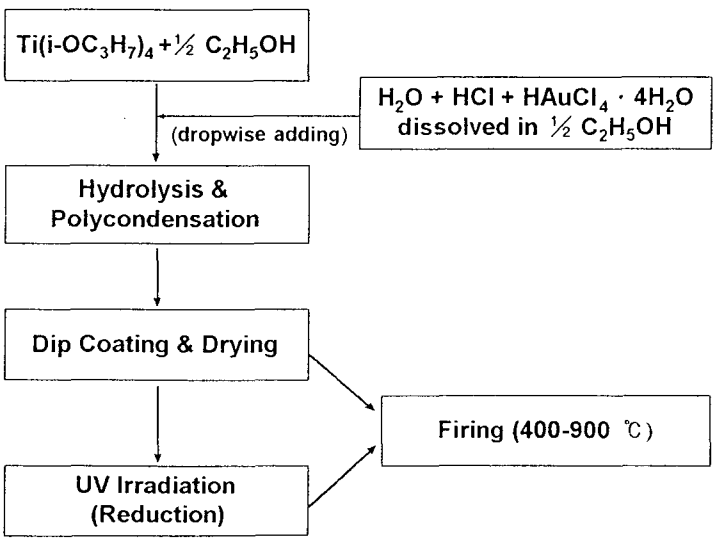


Fig.1 TiO_2 thin film fabrication Process

Table 1. Composition of the coating solutions (molar ratio)

Sol.No.	$Ti(i\text{-}OC_3H_7)_4$	H_2O	C_2H_5OH	HCl	TiO_2/Au	Appearance
S0	1	1	8	0.28	-	clear
S0-1	1	1	8	0.28	70:30	precipitate
S0-2	1	1	8	0.28	82:18	precipitate
S0-3	1	1	8	0.28	90:10	unstable
SS0	1	1	15	0.28	82:18	unstable
SS1	1	1	20	0.28	82:18	unstable
SS2	1	1	40	0.28	82:18	unstable
SS3	1	1	50	0.28	82:18	unstable
SS4	1	1	90	0.28	82:18	clear
SS5	1	1	90	0.28	70:30	clear
SS6	1	1	90	0.28	-	clear

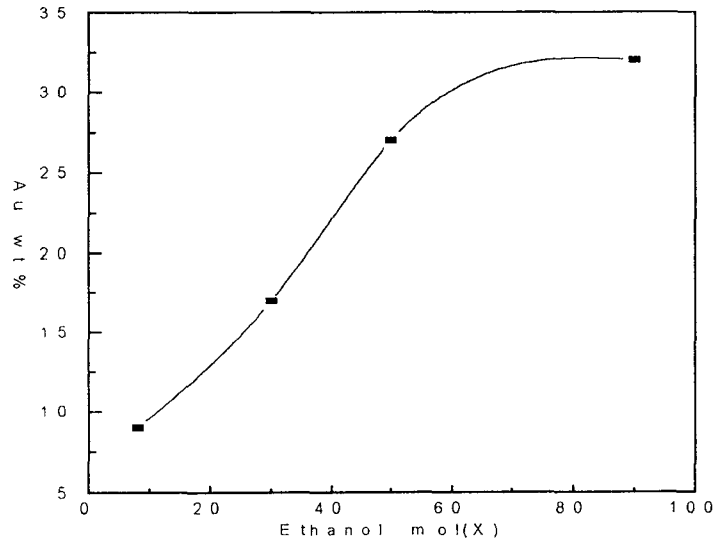
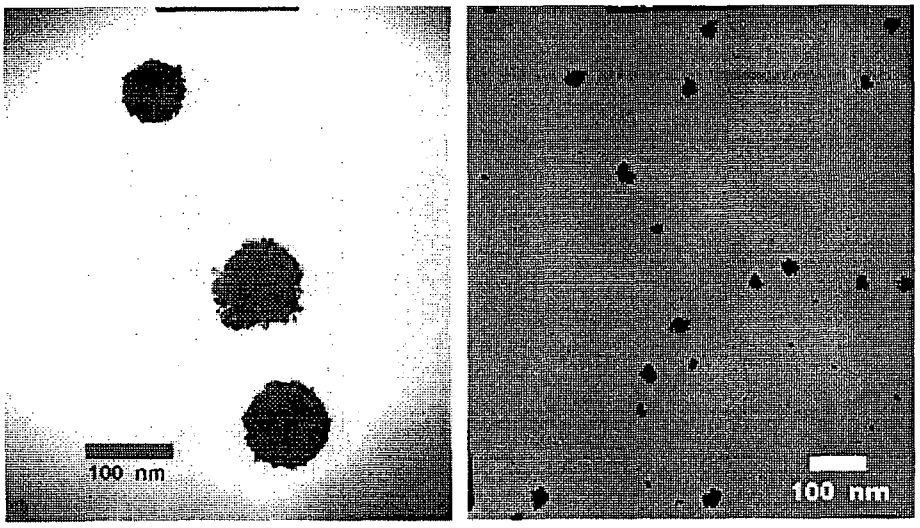


Fig. 2 Maximum solubility of Au compound vs. ethanol content in the stable solutions

speed of 10 cm/min, drying at 100℃ for 10 min and firing dried film at 400~900℃ after 5 times dipping and drying. Some dried film was UV-irradiated by 300W high pressure mercury lamp for 10 min~2hrs. CPCl(cetylpyridinium chloride monohydrate) or CTAC(cetyltrimethyl ammonium chloride) or PVP(polyvinylpyrrolidone) was added to SS5 composition as dispersion agents.

III. Results and discussion

TiO_2 film containing a certain kind of particles by drying at 100℃ could be made from SS5 composition as shown in Fig. 3(a). These particles were too larger and later analysis revealed that particles were not metal but a compound composed of Au and



(a) (b)

Fig. 3 TEM photograph of $AuCl^-_4$-
(a) No CPCl (b) CPCl 0.105 mmol/dm^3

Cl, $AuCl_4^-$-. Some dispersion agents were added to SS5 to reduce the particle size and CPCl was most effective among those. Fig. 3(b) shows the particle size when 0.105 mmol/dm^3 CPCl was added. Firing process at about 500℃ was needed to reduce gold compound into metallic gold. When the film containing $AuCl_4^-$- was heated, reduction and particle growth of metallic gold occurred at a time. Resultantly firing process changed fine $AuCl_4^-$- particles into coarse metallic gold particles. It has been reported that Cl^- of $AuCl_4^-$ could be removed by UV irradiation at low temperature. When $AuCl_4^-$ is exposed to UV light photo-decomposition of $AuCl^-_4$ is initiated by the excitation of LMCT(ligand to metal charge transfer)band. $AuCl^-_4$ is reduced to Au^0 by the following reactions[4].

$$AuCl_4^- \xrightarrow{h\nu} AuCl_3^- + Cl^{\cdot} \quad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

$$2AuCl_3^- \rightarrow AuCl_4^- + AuCl_2^- \quad \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

$$AuCl_2^- \xrightarrow{h\nu} Au^{\circ} + Cl^{\cdot} + Cl^- \quad \cdots\cdots\cdots\cdots\cdots\cdots (3)$$

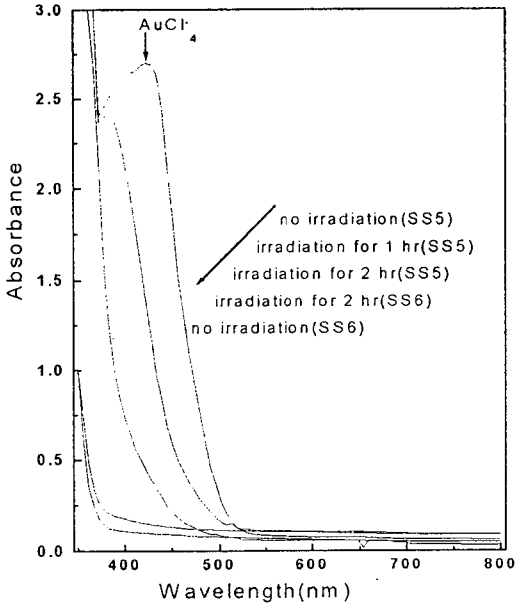
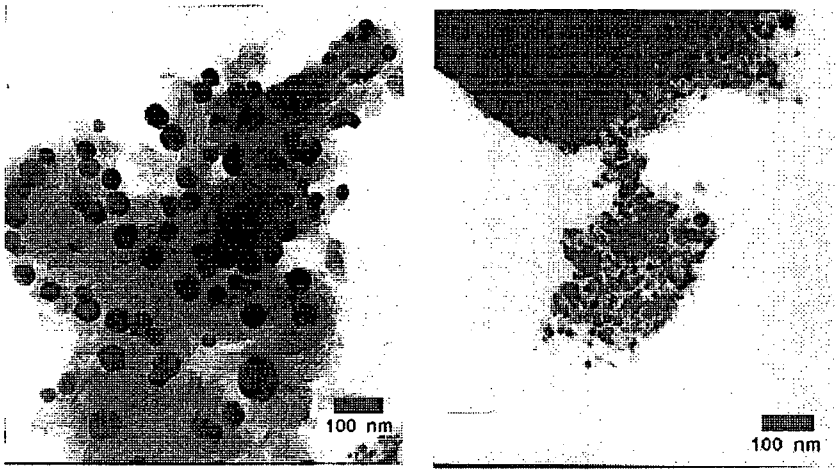


Fig.4 Change of UV-Visible Spectra with Irradiation time

Fig. 4 shows the change of UV-visible spectra for coating solution SS5, SS6 with UV irradiation time. The absorption peak at λ=400~470nm of SS5 was assigned to $AuCl^-_4$-[4]. As UV irradiation time was longer, the absorption peak of $AuCl^-_4$ weakened. After 2 hour irradiation, this band disappeared. Before UV irradiation, the solutions SS5, SS6 were yellowish. Color of solutions became lighter by UV irradiation and finally colorless with 2 hour irradiation. We expected from this spectra change that reduction process finished with 2 hour irradiation. Raman spectra for the solutions to examine further accurate reduction process is shown in Fig. 5 Generally $AuCl^-_4$- peak appears at λ=347, 324, 171 cm^{-1} [5], and $AuCl^-_2$ peak appears at λ=350, 329, 116 cm^{-1} [6]. The peaks at about λ=170cm^{-1} and 350 cm^{-1} appeared for SS5 without UV irradiation. One hour irradiation made the peak at λ=170cm^{-1} disappeared. And the



(a) (b)

Fig. 7 TEM photographs of nanometer Au metal particles
(a) 500℃.30min. (b) 300W/2hr --> 500℃/30min.

second peak at about 350 cm^{-1} disappeared with 2 hour irradiation. This result was consistent with the result of UV-visible spectra.

Fig. 6 shows phase evolution of TiO_2 thin film fired at various temperature on silica substrate. First anatase phase appeared at 400℃ and rutile phase started to appear at 900℃.

Fig. 7(a) shows TEM photograph of Au particle embeded in TiO_2 film fired at 500℃ for 30 min without UV irradiation. These particles was proved metallic gold by EDAX and electron diffraction pattern. Fig. 7(b) shows Au metallic particle formed with firing at 500℃ for 30 min after 2 hour UV irradiation. Gold particle size was about 10~20 nm in the latter case. This means that UV irradiation before firing is effective to control the size. Consequently, chemicals for good dispersion and UV irradiation for reduction of $AuCl^-_4$ to Au metal before firing were essential to make nanometer size metallic gold particles in TiO_2 thin film using sol-gel solution.

Fig. 8 shows TiO_2 thin film containing metallic Au particles fabricated on silica glass substract which was coated with composition SS5, UV-irradiated for 2 hours and fired at 500℃ for 30 minutes. TiO_2 particles of about 20~30 nm uniformly arranged. Although Au metal particle was not distinguishable from TiO_2 particles because of similarity in size and shape, existence of Au particle was confirmed by XRD patterns shown in Fig. 9.

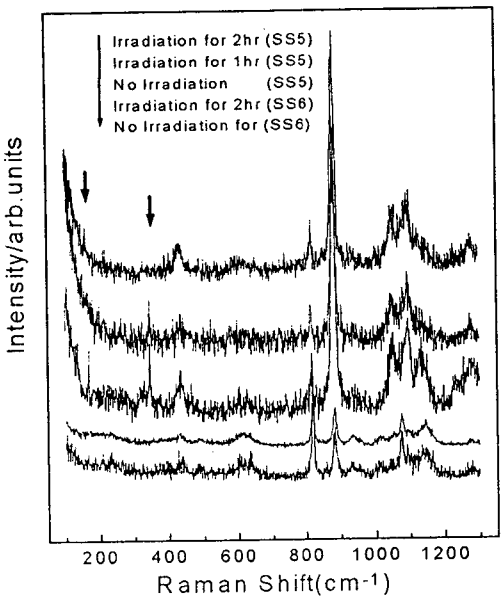


Fig. 5 Raman Spectra with Irradiation time

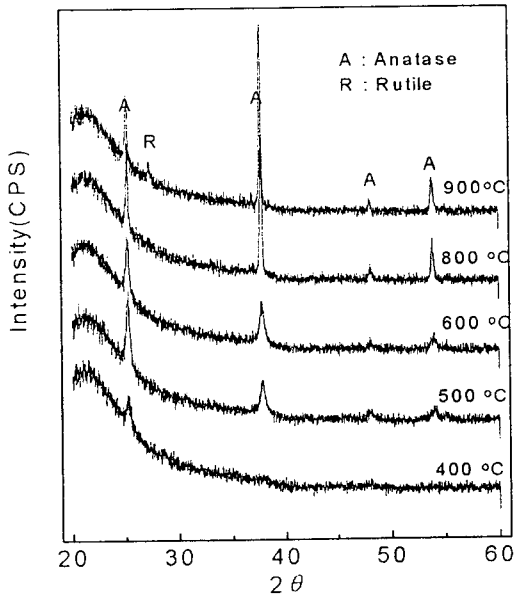


Fig.6 Phase evolution of TiO_2film on silica substrate with firing temperature

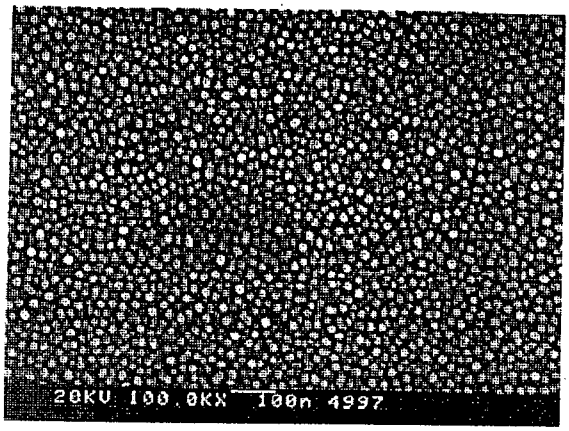


Fig. 8 SEM Photograph of TiO_2 Film dispersed Au metal on silica glass substract(SS5, 2h-->500℃/30min.)

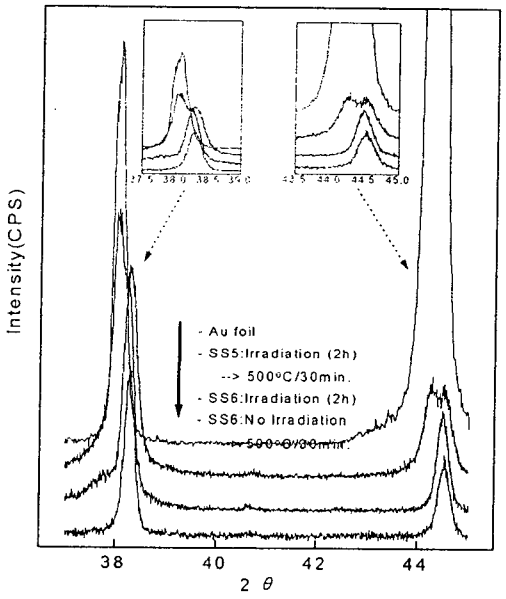


Fig. 9 X-Ray Diffraction Patterns as UV Irradiation time and Heat treatment

IV. Conclusions

TiO_2 thin film containing 10~20nm size Au metal on silica glass substrate was successfully fabricated from titanium tetraisoproxide-EtOH-HCl-H_2O-hydrogen tetrachloroaurate(III) tetrahydrate system. SS5 composition having 30 wt% Au on the basis of final solid film remained no precipitation and clear for 3 weeks. Addition of

0.105 mmol/dm^3 CPCl(Cetylpyridinium chloride monohydrate) as a dispersion agent was effective to control the size of Au compound before firing. And UV irradiation was needed to reduce $AuCl^-_4$- to Au metal, by which Au metal growth was suppressed in the subsequent firing process.

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