

## Preparation of Au fine particle dispersed TiO<sub>2</sub> film by sol-gel and photoreduction process

Buh-Sung Hyun, Byeong-Il Kim and Won-Ho Kang\*

National Institute of Ceramic Technology, Seoul 153-023, Korea

\*Department of Materials Science and Engineering Dankook University, Cheonan 330-714, Korea

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## Sol-Gel and photoreduction 공정에 의한 Au 미립자분산 TiO<sub>2</sub> 박막 제조

현부성, 김병일, 강원호\*

국립요업기술원, 서울, 153-023

\*단국대학교 재료공학과, 천안, 330-714

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**Abstract** Au fine particles dispersed TiO<sub>2</sub> film was prepared on silica glass substrate by sol-gel dipping and firing process. The TiO<sub>2</sub> films were fabricated from the system of titanium tetraisopropoxide-EtOH-HCl-H<sub>2</sub>O-hydrogen tetrachloroaurate (III) tetrahydrate. The conditions for the formation of clear solution and dissolving high concentration of Au compound were examined. Photoreduction process was adopted to control the size of gold metal particles. Phase evolution of matrix TiO<sub>2</sub> and variation of Au particle with UV irradiation were investigated by XRD, SEM, TEM and UV-visible spectrophotometer. The effect of CPCI (Cetylpyridinium chloride monohydrate) as a dispersion agent was evaluated.

**요 약** Au 미립자가 분산된 TiO<sub>2</sub> 박막을 졸겔담금법과 열처리공정으로 실리카 유리기판위에 제조하였다. TiO<sub>2</sub> 박막제조는 titanium tetraisopropoxide-EtOH-HCl-H<sub>2</sub>O-hydrogen tetrachloroaurate(III) tetrahydrate계를 이용하였다. 고농도로 Au 화합물을 함유하면서 투명한 코팅용액을 형성하는 조건을 검토하였다. Au 금속미립자의 크기를 조절하기 위하여 광환원공정을 채택하였다. UV 조사에 따른 Au 입자의 변화와 TiO<sub>2</sub> 매트릭스의 상전이과정을 XRD, SEM, TEM and UV-visible spectrophotometer로 관찰하였다. 분산제로서 CPCI(Cetylpyridinium chloride monohydrate)의 효과를 평가하였다.

### 1. Introduction

In the beginning Au metal particles embeded oxide films have been studied for the use of optical color filter [1]. Recently many researchers have attempted to make the TiO<sub>2</sub> film containing nanometer size Au metal particles 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 possible. Second the size of gold particle should be around 20 nanometer without aggregation to cause high nonlinear optical susceptibility.

In this study proper solution composition including dispersion agent and reduction process were

examined to fabricate TiO<sub>2</sub> thin film containing nanometer size Au metal particles by sol-gel dipping & firing process from the titanium tetraisopropoxide-EtOH-HCl-H<sub>2</sub>O-hydrogen tetrachloroaurate (III) tetrahydrate system.

### 2. Experimental procedures

Titanium tetraisopropoxide (Ti(i-OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) [4], Ethanol, H<sub>2</sub>O, HCl, Hydrogen Tetrachloroaurate (III) Tetrahydrate (HAuCl<sub>4</sub> · 4H<sub>2</sub>O) were used as starting materials. Experimental procedure is shown in Fig. 1. Ti(i-OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> and 1/2 ethanol were mixed and stirred. Solution dissolving HAuCl<sub>4</sub> · 4H<sub>2</sub>O, H<sub>2</sub>O and

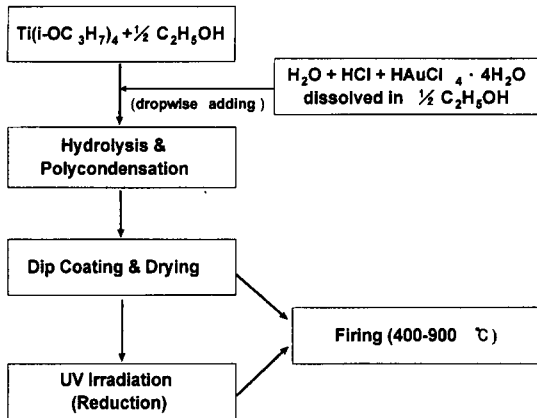
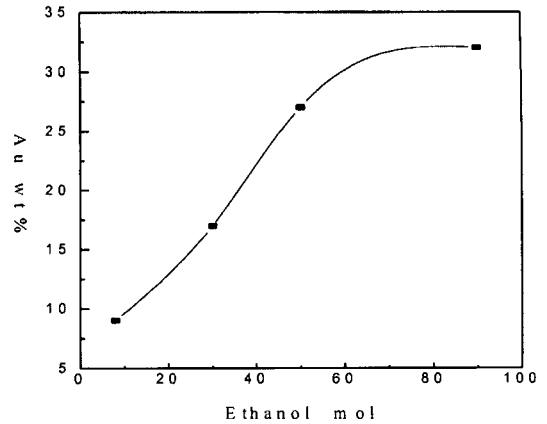
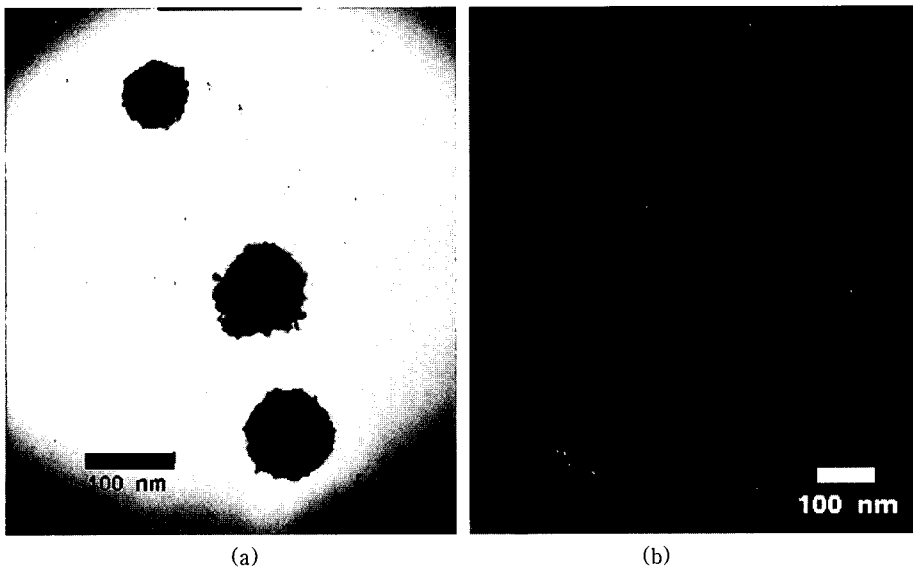
Fig. 1. TiO<sub>2</sub> thin film fabrication process.

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

Table 1  
Composition of the coating solutions (molar ratio)

Sol. No.	Ti(i-OC <sub>3</sub> H <sub>7</sub> ) <sub>4</sub>	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> OH	HCl	TiO <sub>2</sub> /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. 3. TEM photograph of AuCl<sub>4</sub><sup>-</sup> (a) No CPCI and (b) CPCI 0.105 mmol/dm<sup>3</sup>.

HCl in 1/2 ethanol was added dropwise to the mixture solution. All mixing process was conducted at a constant temperature of 30°C because the stability and clearness of the final mixture solution depended on its processing temperature. Compositions of coating solutions are shown in Table 1. The basic TiO<sub>2</sub> film composition (S0) of Ti(i-OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>:H<sub>2</sub>O:HCl:C<sub>2</sub>H<sub>5</sub>OH=1:1:0.28:8 was adopted from the previous paper [3]. The solubility of Au compound increased with ethanol content and stable mixture solution was obtained when ethanol content was over 90 mols. The maximum TiO<sub>2</sub>/Au ratio in the mixture (SS5) was 7/3. Figure 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-OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>. TiO<sub>2</sub> thin films were prepared on the silica glass substrate by dip coating with withdraw speed of 10 cm/min., drying at 100°C for 10 min. and firing at 400–900°C after 5 times dipping and drying. Some dried films were UV-irradiated by 300 W high pressure mercury lamp for 10 min to 2 h. CPCL (cetylpyridinium chloride monohydrate) or CTAC (cetyltrimethyl ammonium chloride) or PVP (polyvinylpyrrolidone) was added to SS5 composition as dispersion agents.

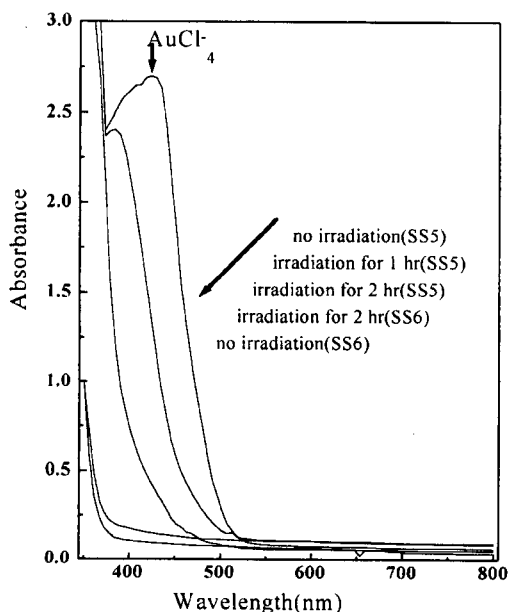


Fig. 4. Change of UV-visible spectra with irradiation time.

### 3. Results and discussion

TiO<sub>2</sub> thin film containing a certain kind of particles by drying at 100°C could be prepared from

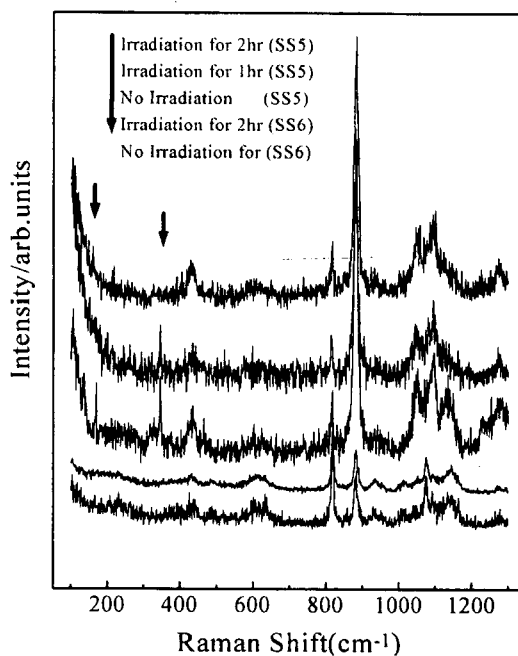


Fig. 5. Raman spectra with irradiation time.

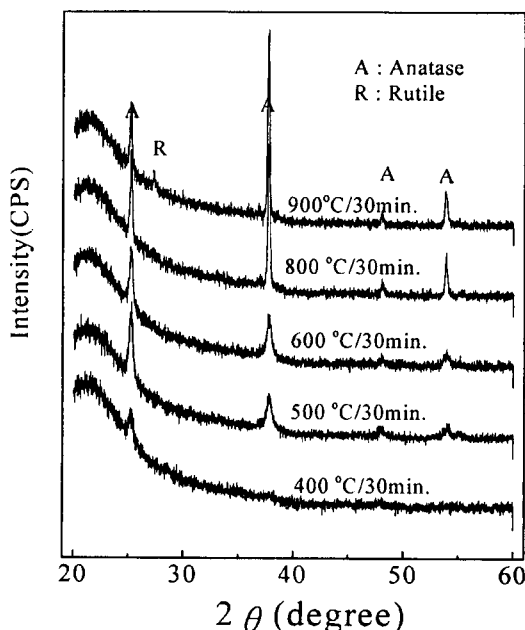


Fig. 6. Phase evolution of TiO<sub>2</sub> film on silica substrate with firing temperature.

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 Cl,  $\text{AuCl}_4^-$ . Some dispersion agents were added to SS5 to reduce the particle size and CPCI was most effective among those. Figure 3(b) shows the particle size when  $0.105 \text{ mmol/dm}^3$  CPCI was added. Firing process at about  $500^\circ\text{C}$  was needed to reduce gold compound into metallic gold. When the film containing  $\text{AuCl}_4^-$  was heated, the reduction and particle growth of metallic gold occurred at a time. As a result firing process changed fine  $\text{AuCl}_4^-$  particles into coarse metallic gold particles. It has been reported that  $\text{Cl}^-$  of  $\text{AuCl}_4^-$  could be removed by UV irradiation at a low

temperature. When  $\text{AuCl}_4^-$  is exposed to UV light photo-decomposition of  $\text{AuCl}_4^-$  is initiated by the excitation of LMCT (ligand to metal charge transfer) band.  $\text{AuCl}_4^-$  is reduced to  $\text{Au}^0$  by the following reactions [4].

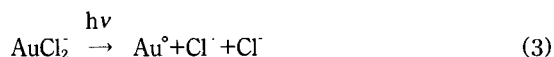
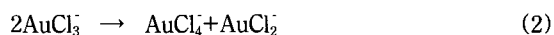


Figure 4 shows the change of UV-visible spectra for coating solution SS5, SS6 with UV irradiation time. The absorption peak at  $\lambda=400\sim 470 \text{ nm}$  of SS5

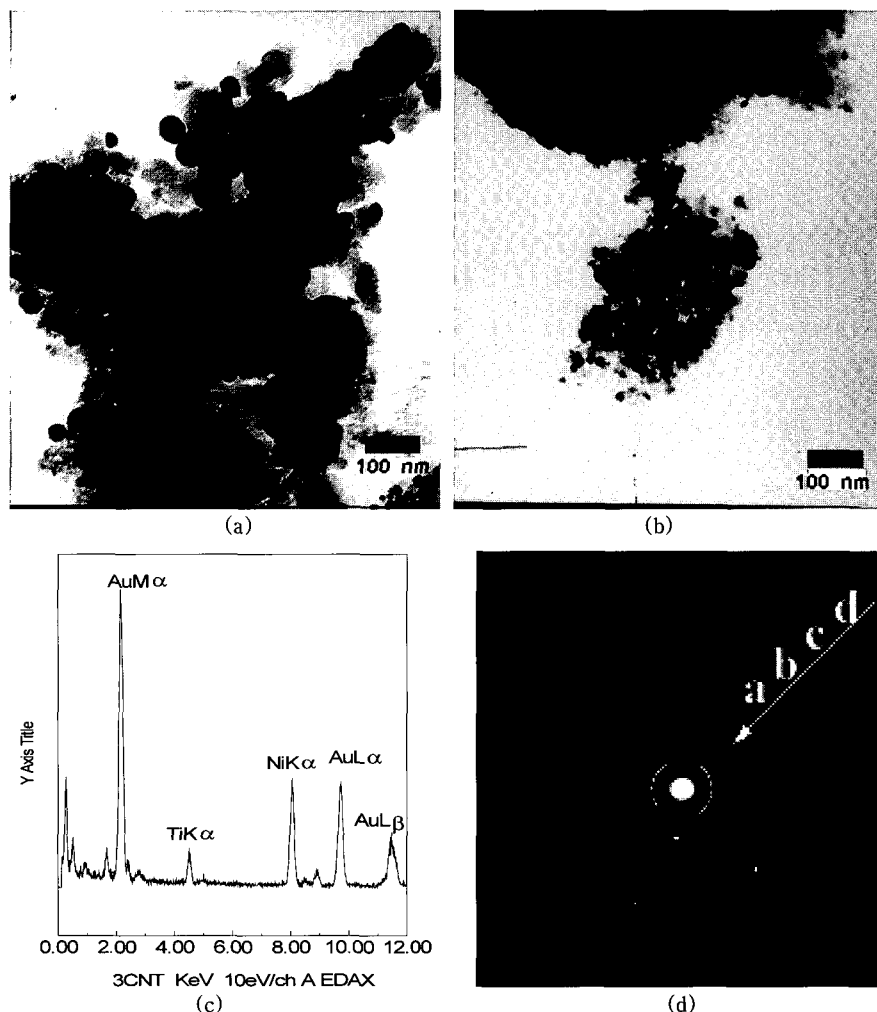


Fig. 7. TEM photographs of nanometer Au metal particles. (a)  $500^\circ\text{C}/30 \text{ min.}$ , (b)  $300 \text{ W}/2 \text{ hr} \rightarrow 500^\circ\text{C}/30 \text{ min.}$ , (c) EDAX of Au (d) Electron diffraction patterns of Au; a: (111), b: (200), c: (220) and d: (311).

was assigned to AuCl<sub>4</sub><sup>-</sup> [4]. As UV irradiation time was longer, the absorption peak of AuCl<sub>4</sub><sup>-</sup> weakened. After 2 hour irradiation, this band disappeared. Before UV irradiation, the solutions SS5, SS6 were yellowish. Color of solutions was changed 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<sub>4</sub><sup>-</sup> peak appears at  $\lambda=347, 324, 171$  cm<sup>-1</sup> [5], and AuCl<sub>2</sub><sup>-</sup> peak appears at  $\lambda=350, 329, 116$  cm<sup>-1</sup> [6]. The peaks at about  $\lambda=170$  cm<sup>-1</sup> and 350 cm<sup>-1</sup> appeared for SS5 without UV irradiation. 1 hour irradiation made the peak at  $\lambda=170$  cm<sup>-1</sup> disappeared. And the second peak at about 350 cm<sup>-1</sup> disappeared with 2 hour irradiation. This result was consistent with the result of UV-visible spectra.

Figure 6 shows phase evolution of TiO<sub>2</sub> thin film fired at various temperature on silica glass substrate. Anatase phase appeared at 400°C and phase transformation to rutile phase began at 900°C.

Figure 7(a) shows TEM photograph of Au particle embedded in TiO<sub>2</sub> film fired at 500°C for 30 min. without UV irradiation. These particles was proved metallic gold by EDAX and electron diffraction pattern. Figure 7(b) shows Au metallic particles formed with firing at 500°C for 30 min. after 2 hour UV irradiation. The size of 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, CPCI as a dispersant and UV irradiation for reduction of AuCl<sub>4</sub><sup>-</sup> to Au metal before firing were essential to make nanometer size

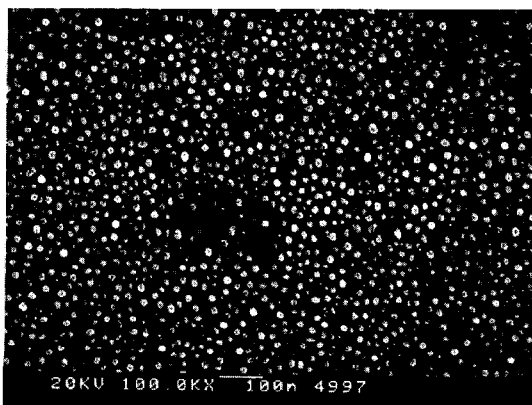


Fig. 8. SEM photograph of TiO<sub>2</sub> film dispersed Au metal on silica glass substrate (SS5, 2 h → 500°C/30 min.).

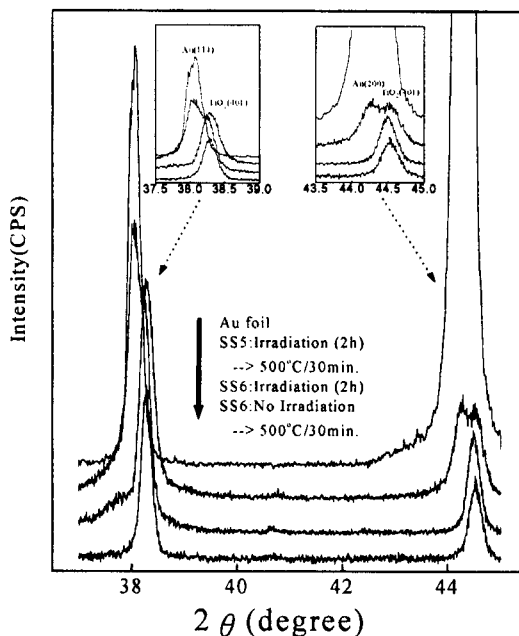


Fig. 9. X-ray diffraction patterns as UV irradiation time and heat treatment.

metallic gold particles in TiO<sub>2</sub> thin film using sol-gel process.

Figure 8 shows TiO<sub>2</sub> thin film containing metallic Au particles fabricated on silica glass substrate which was coated with composition SS5, UV-irradiated for 2 h and fired at 500°C for 30 minutes. TiO<sub>2</sub> grains of about 20~30 nm were observed. Although Au metal particle was not distinguished from TiO<sub>2</sub> particles because of similarity in size and shape, existence of Au particles were confirmed by XRD analysis as shown in Fig. 9.

#### 4. Conclusions

TiO<sub>2</sub> thin film containing 10~20 nm Au particles on silica glass substrate was fabricated from titanium tetraisopropoxide-EtOH-HCl-H<sub>2</sub>O-hydrogen tetrachloroaurate (III) tetrahydrate system. SS5 composition with 30 wt% Au on the basis of final solid film remained no precipitation and clear for 3 weeks. Addition of 0.105 mmol/dm<sup>3</sup> CPCI (Cetylpyridinium chloride monohydrate) as a dispersion agent was effective to control the size of Au compound before firing. UV irradiation was needed to reduce AuCl<sub>4</sub><sup>-</sup> to Au metal and Au metal growth was suppressed in the subsequent firing process.

**Acknowledgments**

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**References**

- [ 1 ] B.S. Hyun and B.I. Kim, Color generation by gold colloid in silica film, Commision Research Report, Institute of Ceramic Technology (1996).
- [ 2 ] Y. Katayama, M. Sasaki and E. Ando, J. Non-Cryst. Solids 178 (1994) 227.
- [ 3 ] S.H. Kim, Y.S. Chung, I.K. Kim, S.M. Kang, B.S. Hyun, B.I. Kim and W.K. Park, J. Kor. Asso. Crys. Grow. 8(2) (1998) 315.
- [ 4 ] T. Sato, H. Iwabuchi and Y. Yonezawa, J. Mat. Chem. 7(9) (1997) 1837.
- [ 5 ] P. Hendra, J. Chem. Soc. (A) (1967) 1298.
- [ 6 ] P. Braunstein and R. Clark, J. Chem. Soc. Dalton (1973) 1845.