

Gold Nanoparticles in Silica-titania Thin Layers Prepared by the Sol-gel Procedure

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Abstract

Gold nanoparticles in silica-titania or silica-zirconia thin layers were prepared on glass or silicon substrates by the sol-gel procedure. Tetraethylorthosilicate, tetrabutyltitanate, tetrabutylzirconate, and a gold complex were employed as raw materials. The gold complex was prepared from sodium tetrachloroaurate and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane. The color of the thin layers was altered depending on the compositional ratio of silica-titania or silica-zirconia. The maximal absorption band was affected by the refractive index of the thin layers. The thin layers were observed using scanning electron microscopy and Kelvin probe force microscopy. Gold particles in the layers were analyzed by X-ray diffraction and energy dispersive X-ray spectroscopy. The diameter of the particles was estimated to be from 1 to 20 nm by topography and surface potential images. The coloration of thin layers is considered to be caused by the localized surface plasmon resonance of gold nanoparticles.

Keywords: Sol-gel procedure, Gold nanoparticles, Thin layers, Kelvin probe force microscopy (KFM)

1. Introduction

Metallic nanoparticles embedded in stained glasses are known to have bright colors. For instance, glasses dispersed with rare metal particles such as gold, silver, and copper exhibit red, brown, and yellow colors, respectively. These metallic nanoparticles absorb visible light due to localized surface plasmon resonance (LSPR). In LSPR, free electrons on the metallic nanoparticle are collectively oscillated by resonating with the visible light (Fig. 1). The oscillation frequency is usually in the visible region for gold and silver causing strong surface plasmon resonance absorption. The color of thin layers containing metallic nanoparticles is known to depend on the particle diameter, shape, interparticle distance, and the refractive index of the thin layer matrix [1-4]. There are a number of potential applications for pigments, bio-sensing devices, and surface enhanced Raman scattering since plasmonic materials have characteristic properties such as the light confinement effect, the field enhancement effect, and the shift of resonance conditions [1, 3]. Thus, it is important to reveal the relation between rare metal nanoparticles and the coloration of their thin layers.

In this paper, gold nanoparticles in silica-titania or silica-zirconia thin layers were prepared by the sol-gel procedure. These particles were analyzed by X-ray diffraction (XRD) and observed by field emis-

sion scanning electron microscopy (FE-SEM) and Kelvin force microscopy (KFM). The effect of the refractive index on the color of thin layers was investigated.

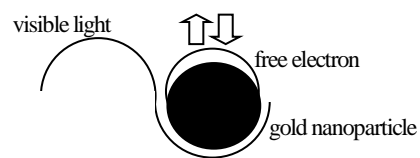


Fig. 1 Schematic of plasmon resonance.

2. Experiment

The coating solution for gold nanoparticles in the silica-titania layer matrix was prepared as follows. Tetraethyl-orthosilicate (TEOS), methyltriethoxysilane (MTES), and 0.1 M HNO₃ (quarter moles of the total silicates amount) were stirred in methanol for 30 min at 40 °C to partially hydrolyzed TEOS. The resulting solution was mixed with a gold complex. The gold complex was prepared by stirring tetrachloroaurate (III) dihydrate and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (entms) for 10 min at room temperature at an entms to tetrachloroaurate molar ratio of 2 to 1. Tetrabutyltitanate (TBT) was dissolved in isopropanol and acetylacetone (acac) at an acac to TBT molar ratio of 3 to 1. The coating solution was

prepared by mixing TEOS, MTES, the gold complex, and TBT solutions with stirring for 30 min at room temperature. For the silica-zirconia matrix layer, tetrabutylzirconate (TBZ) was used instead of TBT.

Glass or silicon substrates were dipped in the coating solution and subsequently heated at 400 °C in air. Micro slide glasses were purchased from Matsunami Glass Ind., Ltd. and used as glass substrates. They were pre-cleaned with water and surfactant, and then dried, while silicon substrates were already pre-cleaned by the manufacturer. The substrate was removed from the coating solution at a withdrawal rate of 40 mm min⁻¹.

The absorption spectra of thin layers on the glass substrates were recorded using a spectrophotometer (V-670, JASCO). For the visible absorption measurement, the coating procedure was repeated five times. XRD patterns were measured with CuK α radiation at 30 kV and 15 mV (MiniFlex II, Rigaku). For preparation of the XRD samples, the coating procedure was repeated forty times on the glass substrates. Silica-titania particles in the thin layer matrix were observed by FE-SEM (S4800, Hitachi High-Technologies), which is a scanning probe microscope (SPM), equipped with an energy-dispersive X-ray spectrometer (EDX). Surface morphology and contact potential difference images were obtained by KFM (SPM-9600, SHIMADZU). The refractive indices at 550 nm and thicknesses of the thin layers were measured using a spectroscopic ellipsometer (HORIBA Jobin Yvon). The thicknesses of the thin layers were also determined using a contact probe surface profiler (Veeco Japan) and a X-ray reflectometer (ULTIMAIII, Rigaku).

3. Results and discussion

3.1 Absorption spectra

Absorption spectra of the thin layers are shown in Fig. 2. Their compositional atomic ratios estimated from the raw materials are shown in Table 1. Although as-prepared thin layers were colorless, they exhibited colors after the heat treatment. For the result of the surface plasmon-based absorption of gold nanoparticles, the color changed from pink to blue due to the compositional molar ratio of titania to silica, that is, the wavelength of the maximal absorption (λ_{max}) of the thin layers was red-shifted depending on the refractive index of the silica-titania layer. The red-shifting trend was the same as altering titania to zirconia.

Differential absorption spectra of thin layers before and after soaking in the iodine solution, as shown in Fig. 3, were calculated from absorption spectral data. Although the thin layers exhibited colors before soaking, only the color of the silica thin layer with a Si: Ti: Au atomic ratio of 97.1: 0.0: 2.9 faded after soaking. This suggests that the gold nanoparticles in the silica matrix were dissolved, and that the absorption of the visible light based on the LSPR was reduced. Since the content ratio of titania in the silica-titania matrix is more than

about 50 %, its absorption peak height was unchanged by the soaking. This result suggests that gold nanoparticles are not eluted by the soaking. Since MTES used as a raw material has a methyl group bonded to silicon, the pores of the network structure of the silica layer matrix may be larger than those of the silica-titania or titania layer matrix. Consequently, gold nanoparticles in the silica layer matrix were dissolved and eluted into the iodine solution.

3.2 Color and refractive index

Refractive indices (n) of thin layers containing silica, titania, and zirconia were calculated from the following expression [6].

$$n = 1 + \rho \sum p_i k_i$$

where ρ , p_i , and k_i are the density, mass fraction, and weight refractive index, respectively. The values of ρ for silica, titania, and zirconia are 2.2, 3.8, and 5.6 g cm⁻³, respectively [7], while those of k_i are 0.21, 0.40, and 0.20, respectively [6]. The relation between refractive indices (n) and wavelengths of the maximal absorption (λ_{max}) of the thin layers is shown in Fig. 4. Depending on the refractive index, the wavelengths (λ_{max}) for both silica-titania and silica-zirconia thin layers were red-shifted. The ratio of titania or zirconia to silica altered the refractive index. However, when the refractive index of silica-titania was the same as that of silica-zirconia, the wavelengths of their maximal absorption band (λ_{max}) were also roughly the same. This result shows that the refractive index of the thin layers caused the absorption band peak to be red-shifted. The refractive indices of samples O and P on the silicon substrates were 1.82 and 2.04, respectively (Table 2). The wavelengths (λ_{max}) for samples O' and P' on the glass substrates were 568 and 580 nm, respectively. Although the samples are on different substrates, the chemical components of samples O' and P' are the same as those of samples O and P, respectively.

3.3 XRD and EDX measurements

XRD patterns of the thin layers are shown in Fig. 5. Three diffraction peaks at 38.2°, 44.4°, and 64.6° are respectively attributed to the (111), (200), and (220) planes of gold (Fig. 5a). The peak at 38.2° is common in the three patterns shown in Figs. 5 a, b, and c. Peaks attributed to gold are also observed in the EDX spectrum of the thin layer on the silicon substrate (Fig. 6). These results indicate that gold particles are in the layer matrix. For titania in the thin layer matrix, a trace peak at 31.7° is attributed to the (104) plane of triclinic Ti₄O₇ (Fig. 5b). As for zirconia in the thin layer, two peaks at 31.7° and 56.8° are attributed to the (012) and (032) planes of orthorhombic ZrO₂, respectively (Fig. 5c) [7, 8, 9]. Most of the silica-titania and silica-zirconia layer matrices were amorphous because diffraction peaks assigned to their crystalline phases were not found.

Table 2 Compositional atomic ratios, thicknesses, refractive indices, and wavelengths of the maximal absorption (λ_{max}) of thin layers on silicon substrates containing gold particles in silica-titania. † Wavelengths (λ_{max}) were measured for thin layers on glass substrates.

Sample	Si: Ti: Au atomic ratio	Spectroscopic ellipsometer		Contact probe surface profiler	X-ray diffractometer	λ_{max} / nm
		Thickness / nm	Refractive index	Thickness / nm	Thickness / nm	
N	97.1: 0.0: 2.9	3	—	—	3	530 †
O	58.2: 38.8: 2.9	21	1.82	20 — 6	18	568 †
P	12.6: 84.8: 2.6	39	2.04	41 — 46	38	580 †

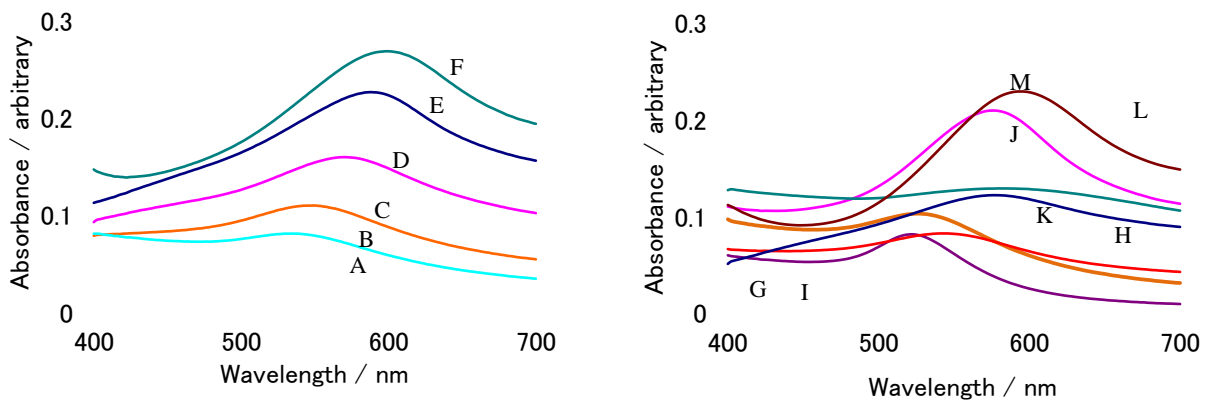


Fig. 2 Absorption spectra of thin layers containing gold nanoparticles in silica-titania (left) and silica-zirconia (right), respectively.

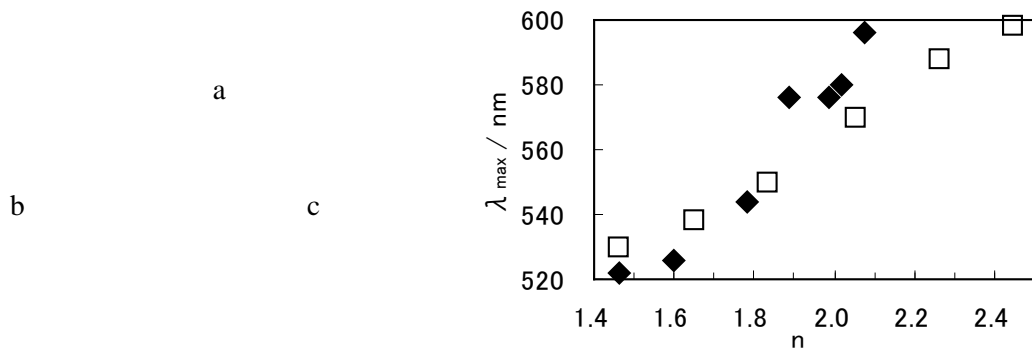


Fig. 3 Differential absorption spectra of thin layers before and after soaking in the iodine solution. The atomic ratio of Si: Ti: Au was (a) 97.1: 0.0: 2.9, (b) 49.9: 47.5: 2.6, and (c) 5.9: 91.3: 2.8, respectively.

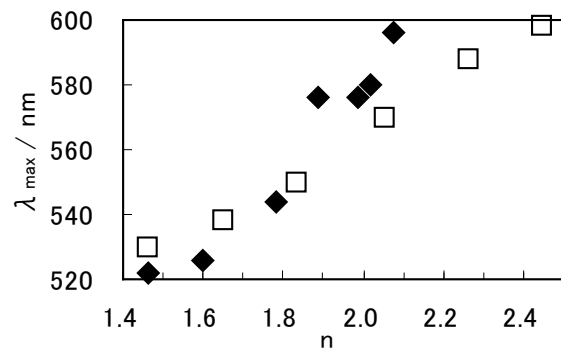


Fig. 4 Wavelengths of the maximal absorption (λ_{max}) vs. refractive indices (n) of thin layers. The \square and \blacklozenge symbols represent silica-titania and silica-zirconia thin layers, respectively.

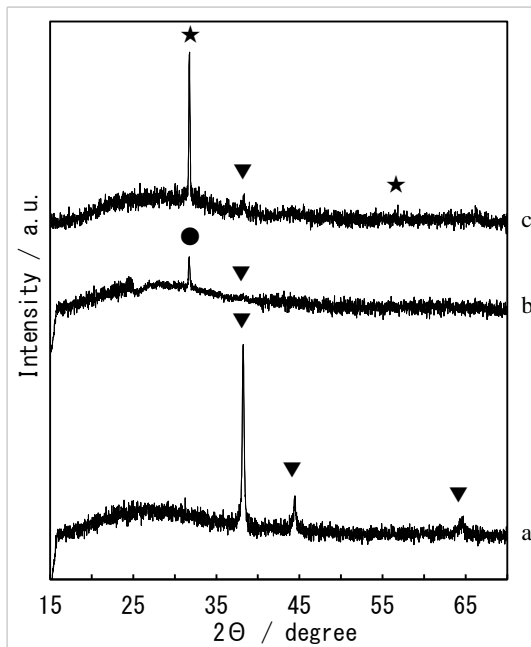


Fig. 5 XRD patterns of thin layers on glass substrates. The atomic ratio of Si: Ti: Zr: Au was (a) 97.1: 0.0: 0.0: 2.9, (b) 5.7: 91.3: 0.0: 2.9, and (c) 5.8: 0.0: 91.3: 2.9, respectively. The ▼, ● and ★ symbols indicate gold, triclinic Ti_4O_7 , and orthorhombic ZrO_2 , respectively.

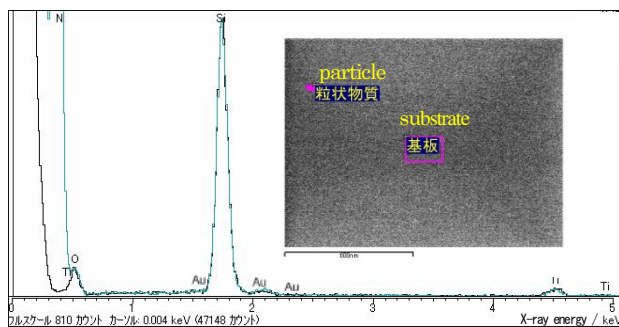


Fig. 6 EDX spectrum of thin layer on silicon substrate. The atomic ratio of Si: Ti: Au was 12.6: 84.8: 2.6.

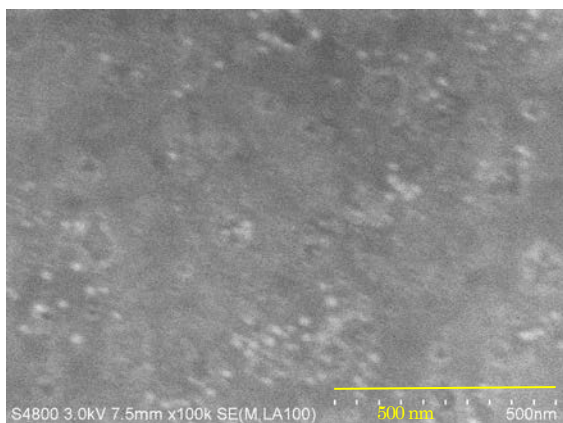


Fig. 7 Backscattered electron image of thin layer containing gold particles in silica. The atomic ratio of Si: Au was 97.1: 2.9.

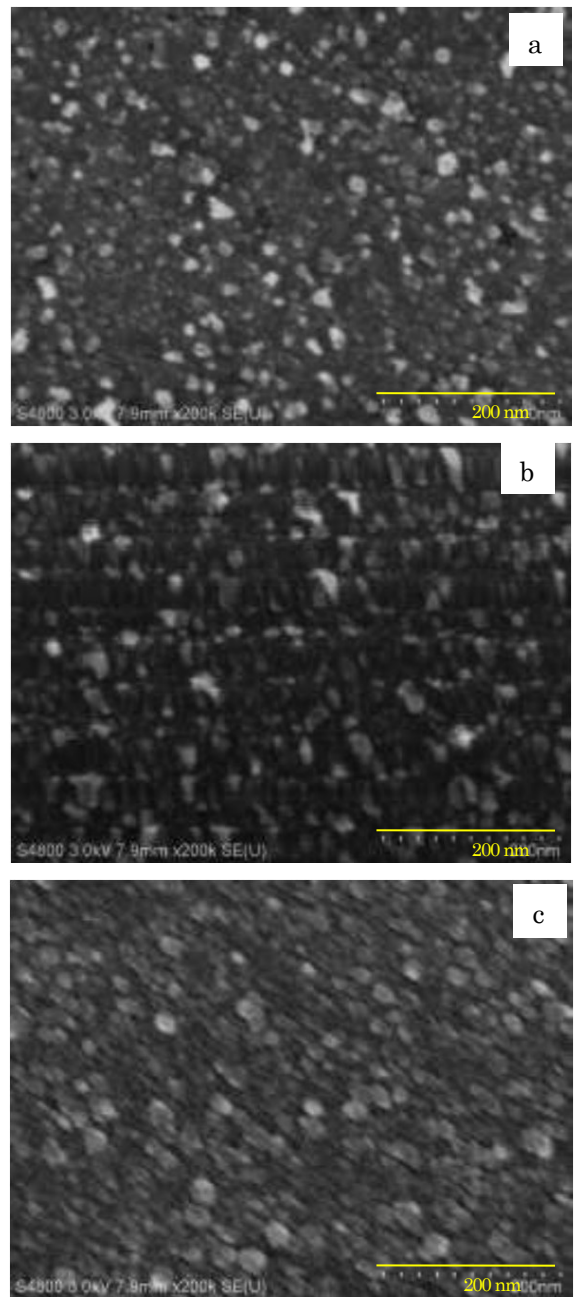


Fig. 8 Secondary electron images of thin layers containing gold particles in silica-titania. The atomic ratio of Si: Ti: Au was (a) 97.1: 0.0: 2.9, (b) 38.7: 58.4: 2.9, and (c) 8.0: 89.3: 2.7, respectively.

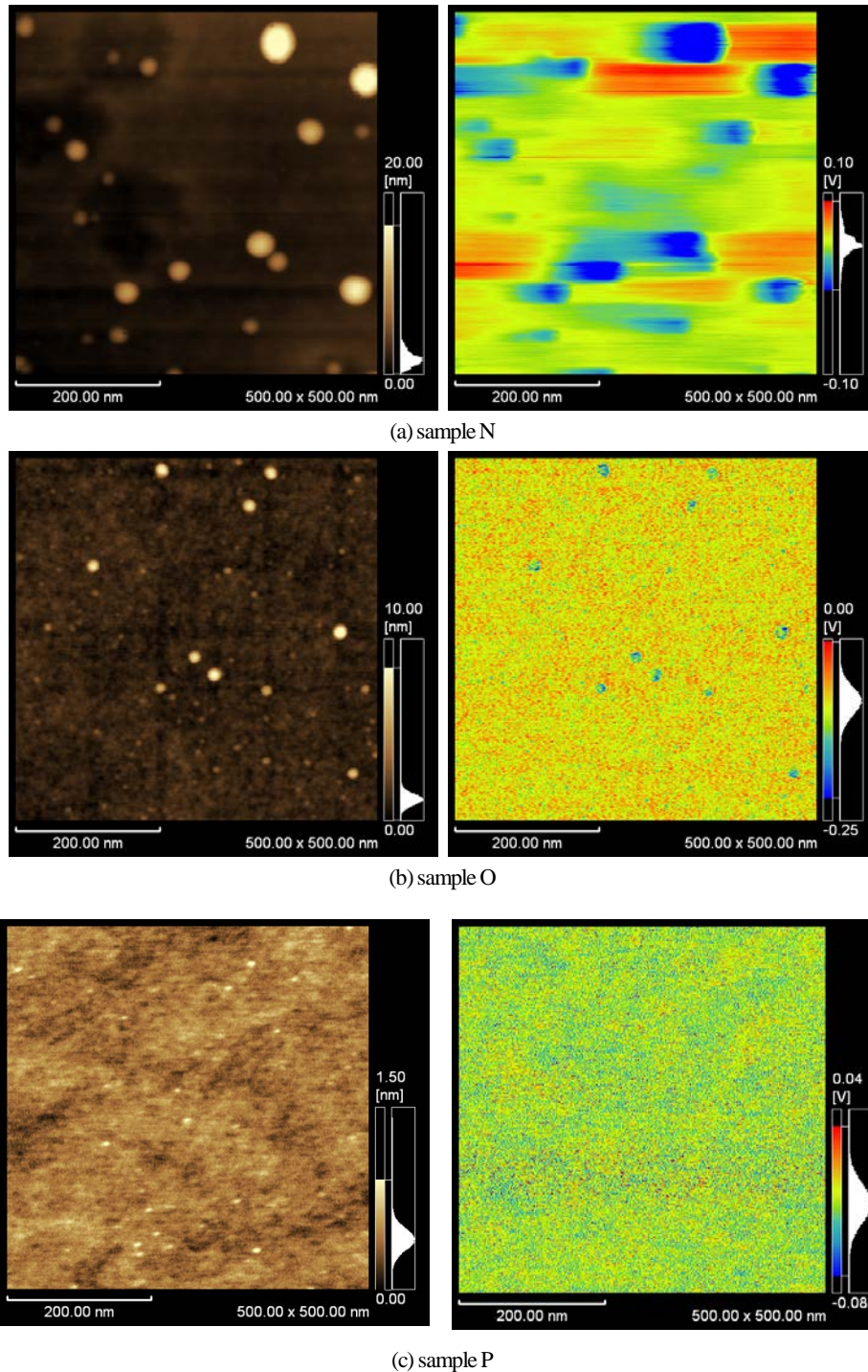


Fig. 9 Topography (left) and surface potential (right) images of thin layers containing gold particles in silica-titania.

3.4 Surface observation of thin layers

Thin layers of silica-titania on the glass substrates were observed by FE-SEM. The backscattered electron image of the thin layer containing silicon and gold with an atomic ratio of 97.1: 2.9 is shown in Fig. 7. Every particle in the image appears brighter than the surroundings because the contrast of the backscattered electron image depends on the atomic number. The brighter parts in the image indicate gold particles. Secondary electron images of thin layers

containing silicon, titanium, and gold with an atomic ratio of 97.1: 0.0: 2.9, 38.7: 58.4: 2.9, and 8.0: 89.3: 2.7 are shown in Figs. 8 a, b, and c, respectively. The thin layers were carbon-coated to prevent electrification. Secondary electron images cannot discriminate gold particles from silica-titania. Silica-titania particles were presumed to be dispersed more closely than gold ones. The average particle diameter was estimated to be in the range from 10 to 30 nm.

KFM can distinguish each gold particle from silica-titania since

work potentials for gold and silica-titania are different. Topography and surface potential images are shown in Fig. 9. In these images, the vertical axis indicates the height from the substrate or relative surface potential. Surface potential images of samples N and O show that the potential distributions observed on the surfaces of the thin layers are different, that is, nanoparticles were observed with relatively lower surface potential than the surroundings; moreover, the particles in the surface potential image overlapped those in the topography image. These results suggest that gold nanoparticles are distinguished from silica-titania. The color of the thin layers is attributed to the localized surface plasmon resonance of their gold nanoparticles. Gold nanoparticles of sample P were distinguished from the silica-titania matrix by the topography image, however, they were not observed by the surface potential images due to the extremely small particle size.

From three topography images, spherical gold nanoparticles were dispersed in a broad size distribution on the surface of the thin layers and their particle diameter was estimated to be from 1 to 20 nm. Gold nanoparticles were smaller than silica-titania particles as shown in Fig. 8. As the ratio of titania in silica-titania increased, the diameter of the gold nanoparticles tended to decrease. Consequently, the matrix refractive index affected the coloration of thin layers, but the effect of the diameter of gold nanoparticles on the color was not confirmed.

4. Conclusions

Thin layers containing gold nanoparticles in silica-titania were prepared by the sol-gel procedure using alkoxide compounds mixed with a gold complex. Gold nanoparticles in thin layers were characterized by XRD, EDX, SEM, and KFM. It was shown that the colors of thin layers depend on the matrix refractive index; however, a relation between color and particle size was not confirmed.

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ゾル-ゲル法で調製したシリカ-チタニア薄膜中の金ナノ粒子

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要 旨

ガラスまたはシリコンを基板として、シリカ-チタニアおよびシリカ-ジルコニア薄膜に含まれる金ナノ粒子をゾル-ゲル法で調製し、薄膜マトリックスが金粒子のプラズモン共鳴に及ぼす影響について検討した。原料としてテトラエチルオルトシリケート、テトラブチルチタネート、テトラブチルジルコネート、及び金錯体を用いた。金錯体は塩化金(III)酸ナトリウムとN-(2-アミノエチル)-3-アミノプロピルトリメトキシシランから合成した。これらを含むアルコール溶液をガラスまたはシリコン基板にディップコーティングした後、400°Cで熱処理して薄膜を得た。これらの薄膜の色は、シリカに対するチタニアまたはジルコニアの量比に依存してピンクから青色に変化し、薄膜の最大吸収波長と薄膜のマトリックスの屈折率とは直線関係にあることが確認された。薄膜中の金粒子は、走査型電子顕微鏡およびケルビンプローブ顕微鏡で観察し、X線回折法およびエネルギー分散X線分光法で分析した。ケルビンプローブ顕微鏡観察の凹凸像と表面電位差像より、金粒子の直径は1~20nmと推測された。表面プラズモン共鳴による金粒子の色は、マトリックスの屈折率の影響を受けていることは確認できたが、粒子径の色への効果については確認できなかった。

キーワード：ゾル-ゲル法、金ナノ粒子、薄膜、ケルビンプローブ顕微鏡