Semitransparent Conductive Thin Porous Au Films on a Thiol-containing Primer Layer formed from Au Nanoparticle Ink

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We demonstrated that thin porous Au films showing semi-transparency in the region of visible light and electric conductivity were prepared by spincoating an α-terpineol ink containing decanethiol-passivated Au nanoparticles onto silica and silicon substrates modified with 3-mercaptopropyltriethoxysilane and subsequent annealing for sintering the Au nanoparticles. A thin film of the α-terpineol ink was transformed to droplets on unmodified silica and silicon substrates by dewetting after spincoating, while it was changed to a thin porous film on the modified substrates by suppressing a progress of dewetting. The porous structure remained after sintering at 300 °C, resulting in the formation of semitransparent and conductive thin porous Au films with a transmittance of about 40 % in the visible light region and a surface resistivity of 10⁻² – 10⁻³ Ω/square. We also demonstrated that the thin porous Au film was available as a wet etching mask for silicon microprocessing using a hydrogen fluoride (HF) aqueous solution.

Key words: semitransparent conductive porous Au film, Au nanoparticle ink, 3-mercaptopropyltriethoxysilane, dewetting control

1. Introduction

Transparent conductive films have been widely used in optoelectronic applications such as electrodes in flat panel displays [1] and solar cells [2]. The conductive matters are categorized mainly into two: transparent metal oxides and metals. In the case of metal oxides, indium tin oxide (ITO) [3], zinc oxide (ZnO) [4], and titanium oxide (TiO₂) [5] are familiar. The transparent conductive layer is deposited or coated onto transparent inorganic and polymer substrates. In the case of metals, gold (Au), silver (Ag), and copper (Cu) in the thin film state are used as conductive matters, because the thick films are opaque by high reflection. Synthetic metals of carbon nanotubes [6] and poly(thiophene) derivatives [7] are used as other conductive matters.

Semitransparent thin metal films often show higher electric resistivity than the metal bulks, when the thickness is decreased. To avoid the increase in the resistivity, patterning conductive metal films is one approach. For this objective, patterned metal films remaining large aperture areas have been prepared by screen printing [8], ink-jet printing [9], nanoimprinting [10] of metal nanoparticle inks and subsequent sintering.

In this study, we report on spontaneous formation of a porous film from alkanethiol-passivated Au nanoparticle inks on surface-modified substrates. This methodology is very simple. As a result of sintering the porous film, we successfully prepared semitransparent conductive thin porous Au films on silica and silicon substrates. We show the properties of the thin porous Au films.

2. Experimental

A Au-precursor ink dispersing hexanethiol-
passivated Au nanoparticles in α-terpinenol (C6-Au-NPs ink) and a Au-precursor ink dispersing decanethiol-passivated Au nanoparticles in α-terpinenol (C10-Au-NPs ink) were purchased from Tanaka Kikinzoku Kogyo. These inks were diluted by adding α-terpinenol solvent, and the Au concentrations were adjusted to 15 and 20 wt%. The diluted inks were used in this study. 3-Mercaptopropyltriethoxysilane (MPS) was obtained from Wako Pure Chemical. Silicon wafers with a native oxide layer (Ferrotec) and silica substrates (Matsunami Glass) were used as unmodified substrates.

Figure 1. Schematic illustration of the method for preparing a thin porous Au film on a MPS-modified substrate.

Figure 1 shows the schematic illustration of the method for preparing a thin porous Au film on a MPS-modified substrate. The surfaces of silicon wafers and silica substrates were cleaned by exposure to UV/ozone using a UV/ozone cleaner (Nippon Laser Electronics, NL-UV42S) for 30 min. Liquid MPS was coated on the clean substrates by coating using a bar coater (Daiichirika, No.9). The wet MPS films of about 0.1 μm thick were left under an atmosphere for 12 h, resulting in the formation of a thiol-containing primer layer on the substrates. Either the C6-Au-NPs ink or the C10-Au-NPs ink was spincoated at different revolutions per minutes in the range of 1000 – 4000 rpm. The formed ink film was then annealed at 300 °C under an atmosphere for sintering Au nanoparticles, resulting in the formation of a thin Au film on the substrate. In the case of using a silicon wafer, wet etching was carried out by immersion in a 7% hydrogen fluoride (HF) aqueous solution (50% HF: conc. HNO₃ (v/v) = 2:15). The thin Au film used as the etching mask was removed by immersion in a Au wet etchant (Kanto Chemical, AURAM-302). The morphologies of the ink film and the sintered Au films were observed by scanning electron microscopy (SEM: Hitachi, S-3000N). Transmittances for UV-visible light of the silica substrate mounting the thin Au film were measured using a diode-type spectrophotometer (Shimadzu, MultiSpec-1500). The surface resistivity of the substrates was measured using a resistivity meter (Mitsubishi Chemical, Loresta-EP).

3. Results and Discussion

3.1. Formation of thin porous Au film

Figure 2 shows thin Au films after spincoating with the Au-precursor ink and subsequent sintering at 300 °C, with results for unmodified and MPS-modified silica substrates indicated in Figs. 2(a-b) and 2(c-d). The C6-Au-NPs ink and the C10-Au-NPs ink were used in Figs. 2(a,c) and 2(b,d), respectively. It was clear that thin sintered Au films were formed on the MPS-modified silica substrates, while islands of Au were formed on the unmodified silica substrates. Interestingly, porous structures were spontaneously obtained in the sintered Au films prepared from the C10-Au-NPs ink on the MPS-modified substrates. It was found that the formation of the porous structure was dependent on the surface modification and the alkylthiol molecule passivating Au nanoparticles.

Figure 2. SEM images of (a-d) thin Au films prepared by spincoating (a, c) 15 wt% C6-Au-NPs ink and (b, d) 15 wt% C10-Au-NPs ink on (a, b) unmodified and (c, d) MPS-modified silica substrates at 3000 rpm and subsequent sintering at 300 °C for 2 h.
In general, dewetting contributes about 0.06 \( \mu \)m, decreased with an increase in the preparation revolutions. The holes had a homogeneous, with an increase in the revolutions. As shown in Fig. 3(d), the holes had a size of \( \frac{1}{50} \) m at 1000 rpm, \( \frac{1}{20} \) m at 2000 rpm, \( \frac{1}{100} \) m at 3000 rpm, and \( \frac{1}{400} \) m at 4000 rpm and annealed at 300°C for 2 h.

We wondered when the porous structure of the sintered Au film was formed. To reveal this, the wet ink film just after spincoating was observed by SEM. Figure 3(a) shows the ink film prepared by spincoating 20 wt% C10-Au-NPs ink onto the MPS-modified silica substrate at 3000 rpm. The porous structure had been already formed after spincoating. The porous structure remained after sintering at 300°C for 2 h, as shown in Fig. 3(d).

To investigate the effect of revolution on the structural formation, we observed thin sintered Au films prepared under different revolutions. Figures 3(b) – 3(d) show the SEM images of the sintered Au films prepared at 1000, 2000, 3000, and 4000 rpm, respectively. Small random holes were formed in the case of the preparation at 1000 rpm, as shown in Fig. 3(b). The holes gradually turned enlarged and homogeneous, with an increase in the revolutions. As shown in Fig. 3(d), the holes had a diameter of about 0.5 \( \mu \)m. The thickness of the sintered Au film decreased with an increase in the preparation revolution. The thickness was 0.2 \( \mu \)m at 1000 rpm and 0.06 \( \mu \)m at 4000 rpm.

The influence of the revolutions means contribution of dewetting to collapse the wet ink film. In general, dewetting of a film starts from nucleation. Holes grow from film rupture. The film is eventually transformed into droplets [11, 12]. Taking the facts into consideration, we can understand the difference between the unmodified and MPS-modified silica substrates. In the case of using the unmodified silica substrates, the dewetting of the wet ink film proceeded to the formation of droplets. In the contrast, the dewetting stopped at the formation of hole growth in the case of using the MPS-modified silica substrates. The suppression of proceeding the dewetting is responsible for the strong interaction between the thiol group of MPS and Au surfaces. It was considered that the decanethiol-passivated Au nanoparticles were reacted with the thiol groups of MPS-modified silica substrates at the outermost surface by exchanging surfactants. Therefore, in the case of the high revolution at 3000 and 4000 rpm, larger holes grew in the wet film of the C10-Au-NPs ink, because the dewetting suppression by the thiol group gradually proceeded. The thin porous Au film after sintering had durability to exfoliation by an adhesive tape. This indicated that the strong interaction generated between the surface thiol groups and the Au film surface.

3.2. Transmittance and resistivity of thin porous Au film

Figure 4 shows the optical transmittance of the thin Au films on MPS-modified silica substrates after sintering at 300°C for 2 h. As the revolution in the spincoating was increased, the optical transmittance in the range of 300 – 800 nm was gradually increased. The optical transmittance was 5 – 6 % at 1000 rpm, 14 – 24 % at 2000 rpm, 27 – 41 % at 3000 rpm, and 37 – 52 % at 4000 rpm. The increase in the optical transmittance with the increase in the revolution was

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rent and (b) easing a surface area to contact pm and (c) (a) 26 the MPS porous Au film. As seen in Fig. 5(a), holes grew on wet etching and the silicon wafer after removal of the porous Au mask by Au wet etching. The porous sintered Au thin film was prepared by spincoating C10-Au-NPs ink at 3000 rpm and annealed at 300 °C for 2 h.

The surface resistivity of the thin sintered Au films was measured by a four probe method using a Loresta-EP meter. The thin porous Au films prepared at the revolution of 2000, 3000, and 4000 rpm had a surface resistivity of $0.71 \times 10^3$, $0.59 \times 10^3$, and $0.68 \times 10^2 \ \Omega$/square. We could prepare the porous Au films on MPS-modified silica substrates having optical transparency and electrical conductivity by the simple method consisting of spincoating and thermal annealing.

Au is well known as a chemically stable material. We noted the property for silicon microprocessing. To have a surface of a silicon wafer rough has an advantage of increasing a surface area to contact other functional materials. Here, we used the thin porous Au film as a wet etching mask for silicon microprocessing. In a manner similar to a silica substrate, a silicon wafer with the native oxide layer was modified with MPS. The C10-Au-NPs ink was spincoated on the MPS-modified silicon wafer and sintered at 300 °C for 2 h. Figure 5 shows SEM images of the porous Au film formed on the MPS-modified silicon wafer before and after silicon wet etching and the silicon wafer after removal of the porous Au film. As seen in Fig. 5(a), holes grew on the MPS-modified wafer. After the wet etching with a HF aqueous solution, the regions inside the holes were made rough as shown in Fig. 5(b). As shown in Fig. 5(c), it was clear that the regions inside holes were etched. The regions masked with the porous Au films had smooth surfaces. This indicates that the porous Au thin film was functioned as a wet etching mask for an aqueous solution.

4. Conclusion
We demonstrated that semitransparent and conductive thin porous Au films were successfully obtained by the simple method of spincoating the alkylthiol-passivated Au nanoparticle ink and sintering under an atmosphere. The surface modification of silica and silicon substrates with 3-mercaptopropyltrimethoxysilane (MPS) was necessary to obtain the porous Au film. The thiol groups located at the outermost surface of the MPS-modified substrates had a suppressive effect on proceeding dewetting of the thin ink film prepared by spincoating. The porous Au film could be used as a wet etching mask.

References