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Water-adsorption effect on electrical resistivity of nanoporous gold

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ABSTRACT

The effect of water adsorption on the electrical resistivity of nanoporous gold (NPG) thin films, as well as flat gold (FG) with no nanoporosity, has been examined. Both NPG and FG thin films showed higher electrical resistivity in water than in air; however, the difference between the electrical resistivity of NPG in water and in air was quite large. The first-principles calculations suggest that the density of states at Fermi energy of the surface gold atoms decreases as a result of water adsorption, which is responsible for the electrical resistivity change in the NPG.

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The adsorption of various molecules on the surface of a substrate can be detected by monitoring the electrical properties of the substrate material [1–5]. The substrate materials should possess nanostructures with both a high surface area and electrical conductivity. For example, adsorption of oxygen on carbon nanotubes [1,2], protein on silicon nanowires [3,4] and thiol molecules on gold nanowires [5] can be successfully detected.

Nanoporous gold (NPG) has open porous structures with pores and ligaments in the nanometer size range and can be fabricated by dealloying or selective dissolution of less noble elements from binary alloys in an electrolyte [6,7]. Monolithic nanoporous metals with high specific surface areas exhibit adsorption-driven macroscopic actuation in aqueous and gaseous environments [8–14]. In particular, Detsi et al. have revealed the humidity dependence of a macroscopic strain in NPG [12–14]; that is, adsorption of water in gaseous environments actuates NPG. The actuation of NPG by adsorption suggests that the electrical properties of NPG are also altered by the atmosphere. In addition, the conditions used for dealloying and post-treatment determine the pore and ligament sizes of NPG; under conditions that suppresses the self-organization of gold atoms, the pore and ligament sizes are as small as the mean free path of electrons in gold [15,16]. Consequently, the electrical properties of NPG are expected to be sensitive to the adsorption of water. Considering this background, we compare the change in electrical properties of NPG resulting from the adsorption of water. That is, the effects of the atmosphere (air and water) on the electric resistivity of NPG are examined.

NPG films were fabricated by dealloying of Au_{0.25}Ag_{0.75}/pure-Au stacked film sputtered on an insulating glass substrate, as schematically shown in the Supplementary Material. First, a 70-nm-thick gold adhesion layer was sputtered on the glass and then a 140-nm-thick Au_{0.25}Ag_{0.75} layer was sputtered on the gold adhesion layer by radio-frequency magnetron sputtering. A metallic mask was used for the fabrication of a circuit of sputtered film that is suitable for electrical resistivity measurements using a four-probe method. NPG films were produced by dealloying of the prepared film sample in 70 mass% HNO₃ for 24 h at 298 K (denoted as NPG-a), for 24 h at 253 K (denoted as NPG-b) and for 5 min at 298 K (denoted as NPG-c) under free corrosion conditions without anodic electrochemical potential. The dealloyed samples were thoroughly washed with distilled water to remove residual acid. For comparison, a 140-nm-thick flat gold (FG) film without a nanoporous structure was also prepared by sputtering on a glass substrate. The thickness of the sputtered films was confirmed using a probe-type step profiler (Dektak150 by ULVAC Corp.). The microstructure of the samples was observed by scanning electron microscopy (SEM).

The electrochemically active surface area of the gold films was evaluated by cyclic voltammetric (CV) measurements at room temperature using a potentiostat and a three-electrode electrochemical cell with Pt wire as a counter electrode, saturated calomel electrode (SCE) as a reference electrode, and sample film as a working electrode [17]. The electrolyte was 0.1 mol/L H₂SO₄ aqueous solution deoxygenated by bubbling with high purity N₂ for 30 min prior to each experiment. CV was conducted at 0.5 mV s⁻¹ in a potential range from 0 to 1.3 V vs. SCE.

The electrical resistivity of the NPG and FG samples was measured at 298 ± 0.5 K by a direct current four-probe method in air and in ion-exchanged and distilled water. The electrical resistivity of the NPG layers was calculated assuming that the two layers have a parallel connection for electron conductivity [18]. The change in the electrical resistivity ($\Delta\rho/\rho_0$) of NPG and FG resulting from immersion in water was then

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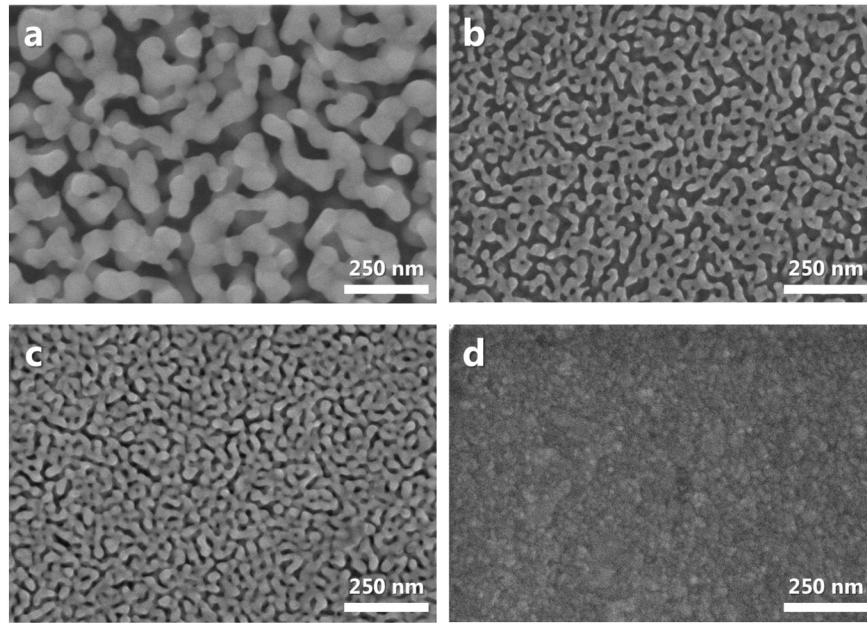


Fig. 1. SEM images of nanoporous gold (NPG-a, NPG-b and NPG-c) (a–c) and flat gold (FG) (d).

calculated using the following equation:

$$\Delta\rho/\rho_0 = (\rho_w - \rho_0)/\rho_0, \quad (1)$$

where ρ_0 is the electrical resistivity of NPG or FG measured in air (with humidity of 30%) and ρ_w is the electrical resistivity of NPG or FG measured in ion-exchanged and distilled water. The thermal equilibrium was confirmed by monitoring the electric potential during the measurements. To check reproducibility, three or four identical samples were fabricated and their electrical resistivity was measured.

The microstructures of the fabricated NPG and FG are shown in Fig. 1. Nanoporous structures were observed in NPG-a, b and c, whereas the SEM image of FG showed a featureless surface. The geometric characteristics of pore and ligament sizes in the NPG samples were clearly varied by the dealloying conditions. The roughness factor (RF, ratio of the electrochemically active surface area of NPG to that of FG) can be estimated by the following equation [17]:

$$A_{\text{NPG}}/A_{\text{FG}} = Q_{\text{NPG}}/Q_{\text{FG}}, \quad (2)$$

where A is the surface area and Q is the charge associated with the reduction of adsorbed oxygen, which can be calculated using the cathodic peak in the CV measurements. Table 1 summarizes the calculated roughness factors as well as the pore and ligament sizes, which were measured from the SEM images of the NPG samples. When the pore and ligament sizes of NPG are comparable, the specific surface area (S) can be calculated by

$$S = C/\rho d_L, \quad (3)$$

where ρ is the density of solid bulk gold ($= 19.3 \text{ g/m}^3$), d_L is the ligament size of NPG and C is a constant ($= 3.7$) [19]. In the present study, S of NPG-b with equivalent pore and ligament sizes was calculated and then S of NPG-a and NPG-c with inequivalent pore and ligament

sizes are calibrated by the roughness factor. As a result, S roughly increased as the pore size decreased, assuming that oxygen monoatomically adsorbs (and desorbs) on NPG in the CV measurements, as shown in Table 1.

The measured electrical resistivity of FG was $37.6 \text{ n}\Omega \text{ m}$, which is slightly higher than that reported in the literature [20]. This indicates that the electrical resistivity of FG is dominated by free electron scattering at the surface because the thickness of the FG film is in the same length order of the mean free path of the electrons [15,16]. The electrical resistivity of NPG in air at 298 K was 246 (NPG-a), 426 (NPG-b), and 548 (NPG-c) $\text{n}\Omega \text{ m}$. The measured resistivity of the present NPG was in agreement with other literature data (shown in Supplementary Material) [21–25], which indicates the validity of the present measurement.

The change in the electrical resistivity of NPG and FG after immersion in water ($\Delta\rho/\rho_0$) are shown as a function of specific surface area in Fig. 2. The $\Delta\rho/\rho_0$ of the NPG samples was above 4%, whereas that of FG was 0.8%. The $\Delta\rho/\rho_0$ of NPG increased with specific surface area, suggesting that the adsorption of water on the surface of the gold ligaments clearly affects the electrical properties of NPG. However, $\Delta\rho/\rho_0$ is not simply proportional to specific surface area. The $\Delta\rho/\rho_0$ of NPG-b and NPG-c was lower than that predicted by the extrapolation of data from FG and NPG-a; that is, when the pore size of NPG is smaller than a certain threshold, the smallness of the ligaments and pore sizes has a reverse effect on the electrical resistivity.

Dealloyed nanoporous metals have lattice distortion at the surface owing to a large curvature of the ligaments [26,27]. The coexistence of lattice expansion (positive strain) and compression (negative strain) owing to the peculiar nanostructure is one of the characteristics [26]. The surface adsorption and lattice distortion may synergistically affect the electrical conductivity of gold. In addition, adsorption effects have been investigated by density of states (DOS) of a metal atom at Fermi energy (FE) by electron state calculations [28,29]. Therefore, using first-principles calculations, water molecules are set on a gold (111)

Table 1
Ligament sizes, pore sizes, roughness factors and calculated specific surface areas of NPG samples.

Sample ID	Ligament diameter, d_L (nm)	Pore diameter, d_p (nm)	Roughness factor, $A_{\text{NPG}}/A_{\text{FG}}$	Specific surface area, S (m^2/g)
NPG-a	77	53	16	3.4
NPG-b	24	24	38	8.0
NPG-c	23	14	54	11.3

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