Interdiffusion during heteroepitaxial Au growth on Pd thin films by electroless Au plating (ELGP) at room temperature

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Received November 14, 2019; revised November 25, 2019; accepted December 3, 2019; published online December 16, 2019

Electroless Au plating (ELGP) on Pd thin films is performed. The ELGP time dependence on the surface morphology is investigated by a scanning electron microscope. Continuous nucleation and growth of hemispherical Au islands are observed as the plating time increases. Heteroepitaxial growth of the electroless plated Au on the Pd surface is confirmed by cross-sectional scanning transmission electron microscope images. Cross-sectional energy-dispersive X-ray spectroscopy reveals interdiffusion between the Pd atoms and the plated Au atoms at room temperature, which allows the formation of Au–Pd alloys. The heteroepitaxial Au growth on Pd is significant for reducing contact resistance of Au/Pd structures.

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Pd-functionalized devices, especially Pd-based hydrogen gas (H₂) sensors, have been intensively studied because Pd exhibits the significant advantage of adsorbing large amounts of H₂. There are a variety of Pd-based H₂ sensors reported in the literature, such as nanogap-based, micro-/nanowire-based, film-based, and nanoparticle-based sensors. 1–19 Pd-based H₂ sensing with a combination of field-effect transistors has also been reported. 20–23

For industrial applications of the Pd-based devices, possessing optimal contact resistance is a crucial factor. Generally, contact points between lead wires and the surfaces of the devices are limited, especially with rough surfaces, which leads to an increase in contact resistance and a decrease in current of the devices. 24,25 Therefore, the contact resistance significantly affects their performance. 26 To reduce the contact resistance, developing flat surfaces and/or covering rough surfaces with low-resistivity metals can be possible solutions. 27 Furthermore, formation of metal bonds at the interface of the contact area would be also effective, especially with soft metals that are hard to be oxidized. 28,29 In that sense, covering Pd surfaces with Au to form Au–Pd metal bonds can be an effective strategy for reducing the contact resistance of the Pd-based devices.

Fabrication processes that are aimed at forming Au over Pd surfaces have been widely developed, such as electroless Au plating. 30–32 However, the method often includes highly-toxic cyanide (CN) compounds in the plating solutions. 30–32 When it comes to industrial applications, an environment- and human-friendly easy electroless Au plating technique with high plating reliability is strongly demanded.

We have previously developed an unique electroless Au plating (ELGP) method, which can be an optimal solution to form Au over Pd surfaces. 33–35 We have demonstrated self-catalyzed ELGP on Au-based nanogap electrodes, flat surface of polycrystalline Pt electrodes, and ultrafine-linewidth Pt-based nanogap electrodes using commercially available and safe chemicals. 33–37 In our ELGP, hemispherical Au islands exhibiting high wettability were plated on the Pt surfaces with contact angles smaller than 90°. 35 Physical adsorption of the Au islands produced inside the ELGP solution could be restricted on the surfaces. 33–35 Moreover, cross-sectional scanning transmission electron microscope (STEM) images revealed that the plated Au was hetero-epitaxially grown on the polycrystalline Pt surface. 35 Owing to the heteroepitaxial Au growth, thermal stability test showed that the heteroepitaxial spherical Au/Pt nanogap electrodes maintained up to 573 K in spite of large self-diffusion coefficient of Au. 35

Based on the reports, our ELGP can be a promising technique to form Au over Pd surfaces with high robustness, which would contribute to reduce the contact resistance.

In this study, we demonstrate ELGP on Pd thin films for the purpose of reducing the contact resistance of Pd-based devices. The ELGP time dependence on the surface morphology is investigated by a scanning electron microscope (SEM). Cross-section of the films after ELGP and their elemental maps are observed by an STEM and energy-dispersive X-ray spectroscopy (EDX), respectively. The characteristics of our ELGP on Pd and its effectiveness are discussed.

Pd thin films were fabricated by electron-beam (EB) evaporation. Ti (3.0 nm) was firstly deposited on SiO₂ (50 nm)/Si substrates as an adhesion layer. Pd (10.0 nm) was subsequently deposited on the Ti layer. The base pressure of the deposition was around 5.0 × 10⁻⁷ Pa.

ELGP was performed on the Pd films by our method described earlier. 33–35 Briefly, the Pd films were cleaned to remove organic impurities adhered on the Pd surface prior to ELGP. To prepare ELGP base solution, Au foils (109 × 109 mm², 99.99%, 65 mg) were dissolved in 3 ml of iodine tincture consisting of I₂ and KI in ethanol with ultrasonic agitation. Subsequently, L(+) -ascorbic acid as a reducing agent was added into the Au-dissolved iodine tincture solution until the solution was saturated. To perform ELGP, 8 ml of de-ionized water (18.1 MΩ) was used to dilute 8 μl of the ELGP base solution in 1000 times. Finally, the cleaned Pd films were immersed into the diluted ELGP solution to perform self-catalyzed ELGP. After the plating, the films were rinsed to terminate the plating, and were dried with N₂ gas. The plating times were varied from 6 to 150 s in this study. The temperature of the plating solution was room temperature.

Surface morphology of the Pd films after ELGP was observed by a field-emission SEM (Hitachi High-Technologies, SU8000). To observe and analyze cross-section
of the films, an STEM sample was prepared by a focused ion beam (JEOL, JIB-4500). Cross-sectional STEM images and EDX elemental maps of the films were observed and analyzed by an STEM (Hitachi High-Technologies, HD-2700).

Top-view SEM images of the Pd films after ELGP with different plating times are shown in Fig. 1. The plated Au islands can be observed as bright spots with different size in each SEM image [Figs. 1(a)–1(d)]. By increasing the plating time from 6 to 30 s, the nucleation density and the size of the plated Au islands on the surface increased. This indicates that the nucleation and growth of the Au islands continuously occurred during the plating process. After ELGP for 90 s, continuous plated Au partially covered the Pd surface. This surface morphology was obtained by connecting the isolated Au islands with their neighboring ones as increasing the plating time. The Pd surface was fully covered by the plated Au after ELGP for 150 s, where isolated Au islands no longer existed; once the Pd surface was completely covered by the plated Au, the remaining reduced Au ions would rather diffuse and form uniform Au surface than form isolated Au islands due to large self-diffusion coefficient of Au.

Cross-sectional bright-field (BF)-STEM and high-angle annular dark field (HAADF)-STEM images of the Pd films after ELGP for 30 s are shown in Fig. 2. The hemispherical Au islands, marked by the yellow arrows in Fig. 2(a), were observed on the relatively flat Pd surface. Some of the hemispherical Au islands appear to be overlapped in the cross-sectional images, which corresponds to the isolated Au islands observed in top-view SEM images in Fig. 1(d). The hemispherical Au islands showed high wettability with contact angles smaller than 90°, and physical adsorption of the Au islands produced inside the plating solution was not confirmed, which is in agreement with the previous result.35)

Cross-sectional EDX elemental maps of the Pd films after ELGP for 30 s are shown in Fig. 3. From the EDX results, Ti atoms were uniformly formed on the SiO2/Si substrate and did not diffuse. On the other hand, the Pd atoms slightly diffused into the plated Au region. Moreover, the plated Au

![Fig. 1](image1.png)  
**Fig. 1.** Top-view scanning electron microscope (SEM) images of the Pd thin films after electroless Au plating (ELGP). The plating times are (a) 6, (b) 10, (c) 20, (d) 30, (e) 90, and (f) 150 s, respectively.

![Fig. 2](image2.png)  
**Fig. 2.** (Color online) Cross-sectional scanning transmission electron microscope (STEM) images of the Pd thin film after ELGP for 30 s. (a) Bright field (BF)-STEM and (b) high-angle annular dark field (HAADF)-STEM images. (a) The plated hemispherical Au islands are marked by the yellow arrows.
atoms diffused into the entire Pd film region. It is worth noting that the density of the Au atoms was higher at the position located just below the plated hemispherical Au island. Therefore, interdiffusion between the Pd atoms and the plated Au atoms was confirmed by our ELGP at room temperature, while it was not confirmed by ELGP on Pt.\textsuperscript{35)} Based on the phase diagram of Au–Pd binary alloys, Au and Pd are miscible at any atomic ratio.\textsuperscript{38)} Hence, the formation of all proportional solid solution of Au–Pd alloys is expected.

Magnified BF-STEM and HAADF-STEM images of the Pd films after ELGP for 30 s, highlighted in Fig. 2 by the red dotted squares, are shown in Fig. 4. These images show continuous lattice fringes as parallel lines across the Pd film region to the plated Au region. Thus, heteroepitaxial Au growth on the Pd surface was confirmed in spite of the large lattice mismatch between Pd and Au of about 5%. The lattice fringes are indicated by pairs of parallel red lines with red arrows in Fig. 4(a), where the lattice spacings are (1) 2.22, (2) 2.28, (3) 2.26, and (4) 2.31 Å, respectively. The lattice spacings in Fig. 4(a) were almost in between that of face-centered cubic (fcc) Pd(111) (2.25 Å) and Au (111) (2.35 Å). Considering Vegard’s law,\textsuperscript{39)} the variation of lattice spacings can be explained by the formation of all proportional solid solution of Au–Pd alloys owing to the interdiffusion. Thus, these spacings can be assigned to fcc Au–Pd alloys with different atomic ratio of Au and Pd. The variation of lattice spacings due to lattice expansion or shrinkage, inducing lattice strain in Au–Pd alloys, would also be possible.

Based on the EDX analysis, each lattice fringe would correspond to the crystal located in Pd-rich region or Au-rich region. The lattice spacings of (1) 2.22 and (2) 2.28 Å in Fig. 4(a) would be attributed to Pd-rich crystals even though they were located in the plated Au region. On the other hand, the lattice spacing of (4) 2.31 Å would be attributed to Au-rich crystals even though it was located in the Pd film region. These results also support the interdiffusion between the Pd atoms and the plated Au atoms.

As demonstrated, hemispherical Au islands with high wettability were successfully plated on the Pd films by our ELGP. The plating time required to cover the whole surface was only a few minutes, which is enough short for mass production of Pd-based devices. Heteroepitaxial Au growth on Pd and the interdiffusion between the Pd atoms and the plated Au atoms suggest the formation of robust Au–Pd metal bonds. Moreover, the thickness of the plated Au can be controlled by adjusting the plating time. Since our ELGP is self-catalyzed plating, there is no limitation to the thickness of the plated Au theoretically, as long as the Au ions and the reducing agent are available at the Pd surface.\textsuperscript{34)} Therefore, our ELGP can be considered as a promising technique to reduce contact resistance of Pd-based devices.

Heteroepitaxial Au growth on Pd has been widely reported in the case of Pd@Au core–shell nanoparticle structures and tadpole-shaped structures consisting of Au heads and Pd tails by depositing Au atoms on Pd seed nanocrystals.\textsuperscript{39–42)} However, there has been only a few reports on heteroepitaxial Au growth on Pd surface.\textsuperscript{43,44)} In this study, heteroepitaxial Au growth was demonstrated on the EB-deposited Pd thin films by our ELGP.

Interdiffusion between Au and Pd has been reported in the case of Pd@PdAu nanoparticles with different degrees of alloying in the outer shell, where the alloying of Pd and Au was attributed to galvanic replacement; the Pd atoms of the core surface were substituted by Au atoms when Pd nanocubes were immersed in an HAuCl\textsubscript{4} solution.\textsuperscript{45)} Other studies have shown partial interdiffusion of Pd@Au and Au@Pd nanoparticles synthesized by chemical
The interdiffusion of the Pd atoms and the plated Au atoms was realized in the Pd thin films covered by the plated Au, which can contribute to reduce the contact resistance of Au/Pd structures.

**Acknowledgments** We thank Ms. M. Miyakawa for the technical support of the SEM measurements. We thank Suzukakedai Materials Analysis Division, Technical Department, Tokyo Institute of Technology for the preparation of the STEM sample. We thank Hitachi High-Technologies for the technical support of the cross-sectional STEM and EDX measurements. This study was partially supported by MEXT Element Strategy Initiative to Form Core Research Center (Grant Number JPMPX012101001); and BK Plus Program, the Basic Science Research Program (NRF-2014R1A6A1030419).

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**Fig. 4.** (Color online) Magnified cross-sectional STEM images of the heteroepitaxial Au on Pd thin film after ELGP for 30 s highlighted in Fig. 2 by the red dotted squares. (a) BF-STEM and (b) HAADF-STEM images. (a) The lattice fringes are indicated by pairs of parallel red lines with red arrows, where the lattice spacings are (1) 2.22, (2) 2.28, (3) 2.26, and (4) 2.31 Å, respectively.
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