Deposition of platinum patterns by a liquid process†

Zhongrong Shen,*[a] Jinwang Li,*[a] Yasuo Matsuki,[ab] and Tatsuya Shimoda*[ac]

[a] *Shimoda Nano Liquid Process Project, ERATO, Japan Science and Technology Agency, 2-5-3 Asahidai, Nomi 923-1211 Japan Fax: +81-761-51-7791; Tel: +81-761-51-7781; E-mail: z-shen@ishikawa-sp.com, lijw@ishikawa-sp.com*

[b] *Tsukuba Research Laboratories, JSR Corporation, 25 Miyukigaoka, Tsukuba, Ibaraki, 305-0841 Japan*

[c] *School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi 923-1292 Japan Fax: +81-761-51-1149; Tel: +81-761-51-1550; E-mail: tshimoda@jaist.ac.jp*

In contrast to traditional chemical vapor deposition technique under high vacuum, we introduce a deposition method in liquid to prepare Pt pattern on substrate near 100 ºC by seed growth.

Metal films, such as platinum films, are commonly used as electrodes in a variety of applications. Till now, directly deposited Pt film are prepared by conventional vacuum processing and vapour-phase deposition which utilizes only a small portion of the expensive Pt source in addition to other demerits associated with vacuum deposition techniques. The idea to fabricate devices by a liquid process has sparked intensive research with a view to reducing processing costs according to our previous research.[1] Besides the deposition method in vacuum, directly imprint gold nanoparticles can also get pattern according to Grigoropoulos and co-workers' pioneer works.[2] However this method is not applicable to platinum nanoparticles because stable Pt nanoparticles are always covered by polymer and their film is too hard to use thermal imprinting according to our unpublished result. Ink-jet printing techniques were also used to directly deposit metallic conductive patterns to produce wiring boards, antennas, electrodes and so forth[3] while the preparation of suitable Pt ink is difficult till now. Cremer and co-workers investigated to write metal nanoparticle pattern inside sealed microfluidic channels.[4] However this method is difficult to be used in manufacture because of its complex and limited efficiency. Recently, Ma's group used one-step wet chemical method to fabricate gold nano-prism thin films on ITO substrate, where film is discontinuous.[5] The only remained deposition method in liquid for continuous metal film on substrate is the silver mirror reaction since 1843.[6] Till now, no other continuous metal film can be deposited by using liquid process, indicating the difficulty for this process. If other metal films could be prepared by solution process, this situation might change drastically. Seed-growth process is generally

used in the synthesis of nanoparticles with various shapes in solution.[7] However, there are rare reports using it in the preparation of metal film in liquid. Here, we introduce that platinum film with metallic luster can be selectively deposited on the silicon substrate by a seed growth process.

In our experiments, there are two critical points to selectively deposit Pt on substrate. The first is to form a Pt seed monolayer with TiO_2 precursor (titanium bis(ethyl acetoacetato) diisopropoxide) on substrate by spin-coating. Pt nanocrystals serve as seeds while TiO_2 precursor can enhance the adhesion between SiO_2 and Pt after curing. In this experiment, we synthesized Pt nanoparticles stabilized by polyvinylpyrrolidone (PVP) with the diameter of 7.5 nm (Support Information, Fig.S1) by an alcohol reduction similar to Yang and co-workers' work.[8] In details, 1.5 g chloroplatinic acid (H_2PtCl_6) and 2.5 g PVP (MW: 55,000) was dissolved into 200 mL ethyl glycol. The mixture was heated to 150 ºC and kept for 1 hour. Pt nanoparticles were obtained after reprecipitation with ethanol and hexane. The Pt nanoparticles were dissolved into 2-ethoxy-ethanol with a concentration of 10 mg/mL. Then the Pt solution was mixed with TiO_2 precursor (2 wt% in propylene glycol 1-monomethyl ether 2-acetate) with the volume ratio of 2/1. This mixture is marked as 'TP12' ink. TP12 was spin coated onto silicon substrate and then annealed at 600 ºC for 10 minutes under oxygen atmosphere to remove organic compound and to cure titanium oxide. The second is to put this substrate into Pt developing solution (10mM H_2PtCl_6 in 2-ethanoxy-ethanol) at 100-120 ºC for 1-3 hours. The Pt atoms are easy to crystallize on Pt seed surface to realize selected deposition. The thickness can be controlled by deposition time. After the deposition, the substrate is rinsed with excess water and ethanol. The Pt film shows nice metallic luster.

Figure 1 illustrates the AFM, cross-sectional TEM, SAED and elemental mapping results of Pt seed substrate before deposition (a-c) and Pt film after deposition (d-f). Fig. 1a shows the surface morphology of Pt seeds monolayer on silicon substrate. After spin-coating TP12 ink on silicon substrate, the Pt nanoparticles shrink into 10nm after annealing under oxygen atmosphere at 600 ºC. As shown in the cross-sectional HRTEM image (Fig. 1b), the aggregated Pt nanoparticles are single-crystal. The lattice spacing of 0.23 nm corresponds to Pt(111). Simultaneously, TiO_2 layer was formed with a thickness of 4-5 nm as shown in the inset of Fig. 1b. Parts of TiO_2 film show crystalline structure with the lattice spacing of 0.35 nm, which is the anatase-TiO_2(101). To study the Pt seed substrate in more detail, we use elemental mapping of cross-section of seed substrate to confirm that Pt nanoparticles was well fixed on the substrate under the help of TiO_2 layer. As shown in Fig. 1c, the bottom of Pt nanoparticles are well wetting with TiO_2 layer while one can see the top of Pt is naked, which coincides with the cross-sectional TEM image (Fig. 1b). Fig. 1d shows the AFM image of Pt film after deposition. The film is flat with a small root mean square (RMS = 5.21nm). To confirm the quality of Pt film, cross-sectional

TEM and SAED are employed as shown in Fig. 1e and 1f, respectively. The film shows a thickness of 120 nm after 2 hours deposition. The selected area (as marked in Fig. 1e, circle) electron diffraction (SAED) of Pt film after deposition indicates the Pt film is polycrystalline with random orientation because of the randomly arranged Pt seeds on the substrate. As shown in Fig.S2 (Support Information), one can see that the same crystal orientation of Pt in film (area '1') as on the interface (area '2'). That is to say, Pt seeds can orientate the crystallization of Pt during the deposition. For the detailed structure, please see high resolution TEM image in support information.

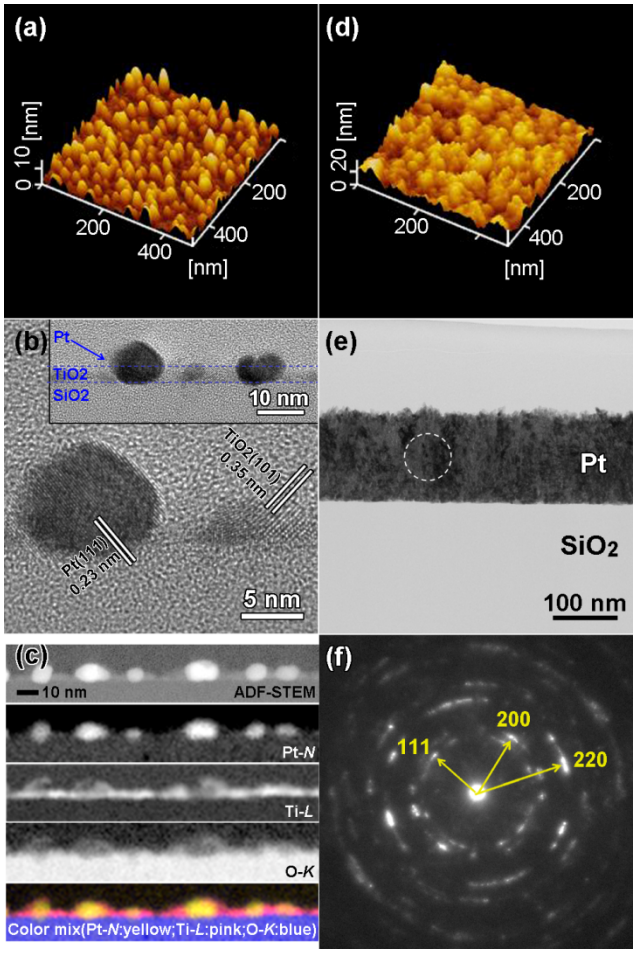

Fig. 1 a) AFM topography image of Pt seed substrate. b) Cross-sectional HRTEM of Pt seed substrate. Inset shows the wide area with high contrast. c) Elemental mapping of cross-section of Pt seed substrate. d) AFM morphology of Pt film after deposition. e) Cross-sectional TEM of the deposited Pt film on silicon substrate. f) Selected area (as marked in Fig. 1e, circle) electron diffraction of Pt film after deposition.

In order to get a better insight of selectivity, Pt seed pattern on silicon substrate was prepared for this purpose. There are several methods to fabricate Pt seed pattern with TP12 ink, for example, inkjet, micro-contact printing (μCP), nano-imprinting lithography (NIL), and etc. Here we employ NIL to get Pt seed pattern by partial removing Pt seed on silicon substrate with argon plasma. The pattern is the squares of 100 μm by 100 μm with 10 μm spacing. This patterned Pt seed substrate was used for Pt deposition in liquid. Fig. 2 illustrates the result of selectivity after Pt deposition. As shown in SEM image (Fig. 2a), a clear Pt pattern was obtained. Figure 2b shows an enlarged image with a cross, where Pt seeds were removed by NIL. There are only few Pt nanoparticles attach on SiO_2 because of physisorption (such as van der Waals force) while almost all Pt grows on square pattern with Pt seeds. Finally we use I-V curve to investigate the selected deposition on the intra-pattern (solid line) and inter-pattern (dash line) as shown in Fig. 2d. For inter-pattern measurement, no current can be detected while obvious metal property is shown when applying a voltage on the same Pt square pattern. Furthermore, we checked the resistivity of our Pt film by a four-point probe measurement (Mitsubishi Chemical Corp. MCP-T360). It shows a resistivity of 84.4 μΩ·cm for an as-depo film while the resistivity drops drastically to 12.7 μΩ·cm after annealing at 600 ºC for 5-10 minutes, which is close to the Pt bulk (10.2 μΩ·cm).

We investigated the mechanism of selected deposition in Fig 2c. Pt seed substrate shows a terrace structure after NIL. The right part is covered by Pt seeds and TiO_2 layer for Pt deposition. On the contrary, the left part was etched by argon plasma, where Pt and TiO_2 were totally removed during NIL, leaving an inert SiO_2 surface only. Different from the synthesis of Pt nanocrystals in ethyl glycol at high temperature (higher than 150 ºC), we use a slightly low temperature (100~120 ºC) to slowly reduce H_2PtCl_6 to Pt atoms in 2-ethoxy-ethanol. Before the atoms aggregate into nanoparticles and precipitate from solution, Pt atoms or clusters (green dots in Fig. 2c) tend to attach on Pt seed because of the stronger interaction between Pt atoms/clusters and Pt seeds on substrate[9] although a small amount of Pt precipitates from solution. Note that this seed growth manner includes not only vertical growth but lateral one as well as shown in the cross-sectional SEM image (Fig. 2c), where the Pt film spreads out with an additional width of 300 nm, which is nearly two times of the thickness of Pt film (150 nm). The higher lateral growth speed may be attributed to the Pt source not only from top but also from side (red arrows). Interestingly, Pt film shows low interaction with SiO_2 surface, remaining an obvious gap between them. That is why we introduce TiO_2 adhesive layer between Pt pattern and SiO_2 substrate.

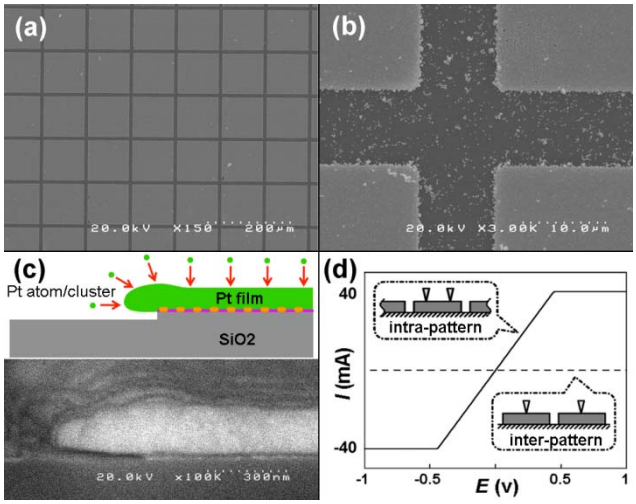

Fig. 2 a) SEM image of a selectively deposited Pt square pattern on Pt seed substrate by liquid process. b) Enlarged SEM image of Fig. 2a. c) Illustration of growth mechanism (top) and cross-sectional SEM image of Pt pattern (bottom). d) I-V curves of Pt pattern when applying voltage on same square (intra-pattern) and neighbour patterns (inter-pattern).

Piezoelectric oxide materials have drawn recent research interest due to their potential in many applications ranging from sensors to radio frequency devices, micro electro mechanical systems (MEMS), and memories.[10] Pt substrate has a popular application that it serves as an electrode to orientate the crystallization of ferroelectric materials such as lead zirconate titanate (PZT).[11] Here we employ the prepared Pt substrate to orientate the crystallization of solution-processed PZT, which can enhance the utility of these materials for practical purposes due to the possibility for cost reduction and better compatibility. In the experiment, the Pt film by our deposition method was firstly treated by annealing at 650 ºC for 5 minutes. PZT precursor (8wt%, Pb/Zr/Ti = 120/40/60, Mitsubishi Materials Corp.) was spin-coated on our Pt substrate, then dried at 150 ºC for 5 minutes and then pyrolyzed at 310 ºC for 5minutes on hot plate. This procedure was repeated several times to obtain a film thickness of 230 nm (Fig. 3a, inset). The PZT was finally crystallized at 600 ºC by rapid thermal annealing (RTA) for 10 minutes in air. The well crystalline structure is shown in Fig. 3a with perovskite PZT (100), (110), (111) and (200) (marked by squares) while there is no pyrochlore phase. Two additional diffractions are attributed to Pt(111) and Pt(200) (marked as dots). The topographic AFM image is shown in Fig. 3b with a small roughness (RMS = 3.64 nm). The polarization versus electric field (P-E) hysteresis loop of the film is presented in Fig. 3c, where top Pt electrode was prepared by vacuum deposition. The loop and the low leakage current (Support Information, Fig. S3) show the typical feature of PZT on a usual sputtered Pt film. The apparent remnant polarization (Pr) is about 42 μC/cm^2, and the corresponding coercive electric field (Ec) is

about 80 kV/cm, which is close to PZT on a sputtered Pt film (Tanaka Kikinzoku) with a Pr of 43 μC/cm^2 and an Ec of 83 kV/cm (Support Information, Fig. S4). On the basis of the above results, the deposited Pt film is of high quality and can be used for practical devices, and this method provides the possibility to fabricate PZT-based devices by a WHOLE-LIQUID Process.

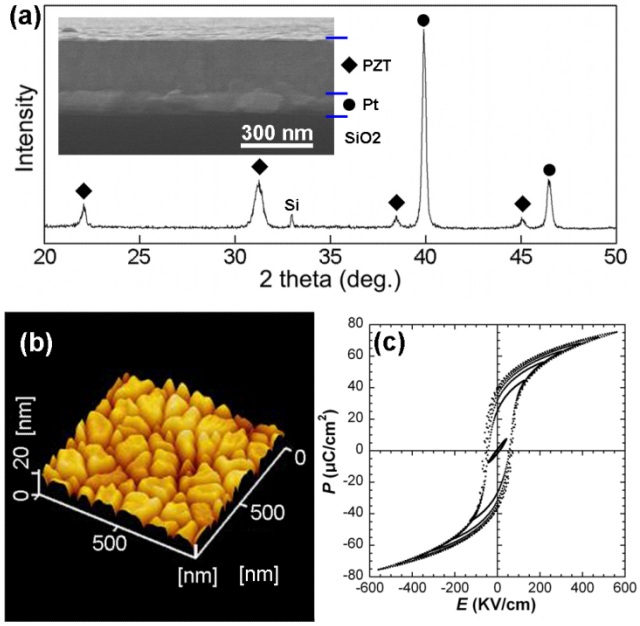

Fig. 3 (a) XRD pattern of crystalline structure of PZT on deposited Pt film. Inset shows the cross-sectional SEM image of this PZT film; (b) AFM topography image of PZT on an area of 500 nm x 500nm; (c) P-E hysteresis loops of PZT on deposited Pt substrate.

Conclusions

In summary, we introduce a new generation of deposition method in liquid to prepare Pt pattern on substrate near 100 °C by a seed growth process. There are two critical steps to realize the selected deposition: to pattern Pt nanocrystals on the substrate under the help of TiO_2 layer; and to deposit Pt on this substrate under an mild reducing system in 2-ethoxy-ethanol. Pt nanoparticles on substrate serve as seeds for Pt crystallization and orientation. Finally we gave one application of this Pt film for the crystallization of PZT film. It gave a new concept to fabricate the nano-device by a whole-liquid process with cost reduction.

Notes and references

† Electronic Supplementary Information (ESI) available: TEM and SAED pattern of Pt nanoparticles, cross-sectional deposition film, leakage current of PZT film, and P-E hysteresis loops of PZT on sputtered Pt film for comparason. See DOI: 10.1039/b000000x/

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