JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Selected Deposition of High-Quality Aluminum Film by Liquid Process

Zhongrong Shen,*[†,‡] Yasuo Matsuki,[‡,⊥] and Tatsuya Shimoda*[∥,‡]

[†]Green Devices Research Center and [∥]School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1245, Japan

[‡]Japan Science and Technology Agency, ERATO, Shimoda Nano Liquid Process Project, 2-5-3 Asahidai, Nomi, Ishikawa 923-1211, Japan

[⊥]Yokkaichi Research Center, JSR Corporation, 100 Kawajiri-cho, Yokkaichi, Mie 510-8552, Japan

Supporting Information

ABSTRACT: For generation of a fine aluminum pattern by conventional vacuum processing, it is necessary not only to use complex and costly instruments but also to perform an additional etching process, which may result in physical and chemical damage to the target film surface. Herein we report a simple solution process for the selected deposition of an Al pattern. Al is obtained from the decomposition of alane under dehydrogenation catalysis of a Pt nanocrystalline pattern on a substrate at ∼105−120 °C, while the self-decomposition of alane in solution is avoided in the presence of high-boiling-point amine. This deposited film generates Al crystals with a diameter of several hundred nanometers, following an epitaxial growth to a continual film. The obtained film shows high conductivity, with a resistivity close to that of bulk Al.

Aluminum is commonly used as an electrode material in a variety of applications because of its high conductivity and low cost. Until now, the main processes used to synthesize Al film or pattern have been vacuum deposition techniques[1] (e.g., physical vapor deposition (PVD) and chemical vapor deposition (CVD)), although some researchers have succeeded in synthesizing film by electrodeposition.[2] For fine patterning of Al films, an etching process is conventionally used. However, conventional etching can result in physical and chemical damage to the target film surface because the etching needs to be performed in plasma containing reactive free radicals and ions for dry etching, or acidic or alkaline solution for wet etching. The principle of fabricating devices by a liquid process has sparked intensive research from the viewpoint of reducing processing costs. We have previously synthesized silicon thin-film transistors from polysilane solution by thermal decomposition,[3] platinum nanoelectrodes from large-sized Pt nanocubes,[4] and Pt patterns by seed growth in an alcohol solution.[5] Reports of the use of liquid processes to prepare metal patterns are rare. In addition to our preparation of Pt fine patterns by solution processes, the silver mirror reaction can also provide fine patterns in liquid.[6] However, both deposited films show a porous structure with much lower conductivity than the bulk metals. High-temperature annealing is necessary to improve the film quality. The direct preparation of high-quality metal patterns remains a challenge. In this Communication, we report the first preparation of a high-quality Al pattern with low resistivity under the catalysis of Pt nanocrystals (Pt NCs) using triethylamine alane (AlH_3NEt_3) as an Al precursor.

Triethylamine alane and its isomer have been used as CVD precursors to prepare Al films, AlN films, and others by eliminating amine and H_2 gas.[7] Formation of an Al film in solution is problematic because of the ease with which it self-decomposes into polyalane and Al nanoparticles at high temperatures (higher than 100 °C); further, it precipitates out of solution with the elimination of an amine molecule. Some research groups achieved the synthesis of Al nanoparticles via thermal and/or catalytic decomposition in solution,[8] indicating the instability of alane at high temperatures. To resolve this problem, there are two critical issues: (1) to improve the selected deposition by using the Pt NC pattern for a catalyst and seed and (2) to prevent alane from self-decomposition by use of additional high-boiling-point (bp) amine. In contrast to our previous work on Pt patterning, Al patterning provides a novel mechanism, i.e., selected growth on a Pt NC pattern as shown in Figure 1. In this case, Pt NC serves as both seed and catalyst for dehydrogenation of alane.

This experiment relies on two steps to selectively deposit Al on the substrate. The first step is to prepare Pt NC pattern by microcontact printing or nanoimprinting lithography according to our previous work.[5] To enhance the adhesion between Pt crystals and substrate, we introduced a thin titanium oxide (TiO_2) adhesive layer, as shown in Figure 1a. Experimentally, we synthesized a Pt NC pattern by using a mixture ink of TiO_2 precursor (titanium bis(ethylacetoacetato)diisopropoxide) and Pt nanoparticles stabilized by poly(vinylpyrrolidone) in 2-ethylethanol, followed by spin-coating and nanoimprinting lithography or direct microcontact printing. The patterned substrate is annealed at 600 °C for 10 min under an oxygen atmosphere to remove organic compounds and to cure TiO_2. The second step (Figure 1b) is to put the substrate into 2 wt % triethylamine alane solution in 4-methylanisole (bp 174 °C) in the presence of additional 2 wt % *N*-dimethyloctylamine with a high bp (195 °C) under a nitrogen atmosphere. The reaction was maintained for between 30 min and 2 h at 105−120 °C until the desired thickness. The triethylamine alane was

Received: February 28, 2012
Published: April 30, 2012

 © 2012 American Chemical Society

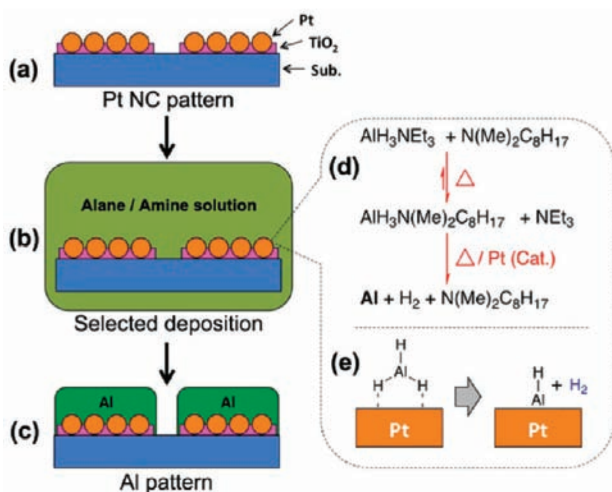

Figure 1. Schematic illustration of selected deposition of Al on a Pt nanocrystal pattern. (a) Pt nanocrystalline pattern whose top surface is naked and bottom is fixed by a TiO_2 thin layer. (b) Deposition process by immersing the substrate with a Pt nanocrystalline pattern into alane solution at ~105−120 °C. (c) Final Al pattern on substrate. (d) Formula for the decomposition of alane in the presence of high-boiling-point amine and Pt NCs. (e) Dehydrogenation of alane on the Pt surface.

synthesized by a procedure similar to that reported by Frigo and co-workers.[9] Normally, triethylamine alane readily polymerizes into an insoluble polymer ($(AlH_3)_n$) when the temperature is higher than the bp of the stabilizer (triethylamine with a bp of 89 °C). This decomposes into Al nanoparticles after further thermal treatment. We introduced additional *N*-dimethyloctylamine with a high bp to stabilize the alane precursor and prevent it from polymerization or the formation of Al nanoparticles under 105−120 °C (Figure 1d). After immersion of the substrate with a Pt NC pattern into alane−amine solution, Pt NCs serve as a catalyst for the dehydrogenation of alane. Catalyzed degradation of alkane or alcohol on Pt surfaces has been studied by several research groups by using density functional theory calculations.[10] Our calculations (Figure S1) showed that when AlH_3 is adsorbed onto a Pt surface, two of the Al−H bonds are broken by interactions between substrate Pt atoms and the Al atom in AlH_3 (Figure 1e), accompanied by dihydrogen elimination. After Al metal covers the Pt surface, Al serves as a seed for continual Al growth because the Al surface can also help to break Al−H bonds catalytically. Deposited Al film is expected to enhance nucleation because of its strong metallic bonding with Al and its relatively high surface free energy.[11] After the deposition, the substrate (Figure 1c) was washed with excess dehydrated toluene. In this reaction, the optimized temperature was 105−120 °C. When the temperature was higher than 125 °C, the amine−alane complex decomposed readily even without Pt catalyst. A white solid was precipitated from solution, which may be the polyalane or Al particles.

Figure 2 illustrates the AFM, cross-sectional TEM, HAADF-STEM, and elemental mapping results of Pt NC substrate before deposition (Figure 2a,b) and Al film after deposition (Figure 2c−e). Figure 2a shows the surface morphology of a Pt NC monolayer on the silicon substrate. We used elemental mapping of a cross-section of the Pt NC substrate to experimentally demonstrate that the Pt NCs are fixed on the substrate by a TiO_2 thin layer. As shown in Figure 2b, the

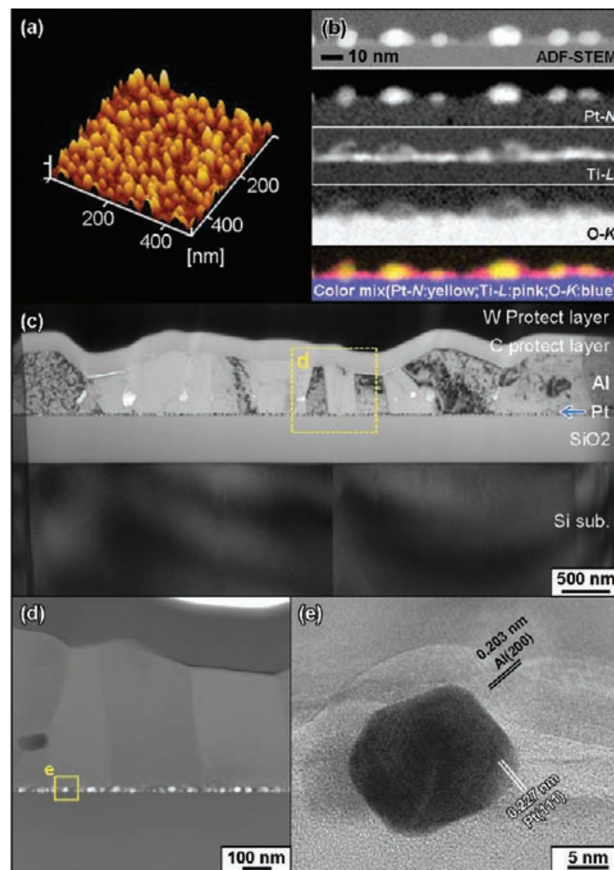

Figure 2. (a) AFM topography image of Pt NC substrate. (b) Elemental mapping of cross-section of Pt NC substrate. (c) Overview of Al film deposited on substrate by cross-section TEM. (d) HAADF-STEM image for an enlarged area of Al film and Pt NCs (yellow mark in (c)). (e) High-resolution TEM image of one Pt NC and the deposited Al film (yellow mark in (d)).

bottom of the Pt NCs dip into the TiO_2 layer, while the top side of the Pt is exposed, as shown in Figure 1a. Figure 2c shows typical ridge−valley morphology for an Al film after deposition. Unlike the flat surface achieved by sputtering, this natural ridge−valley surface has potential application in solar cells as a reflection and backscattering electrode. The Al film comprises single-crystalline grains with a size of several hundred nanometers (Figure 2c,d). After 1 week, the substrate showed no obvious diffusion at the interface between Pt and Al. High-resolution TEM (Figures 2e and S2) shows the crystalline structure of Al and Pt with a tight interface. This Al film passed a convenient tape test. Although there are several voids in this Al film, it shows low resistivity of ~2.8−3.5 $\mu\Omega$ cm by a four-point probe measurement (Mitsubishi Chemical Corp. MCP-T360).

To investigate the mechanism of the growth step, we used SEM for monitoring the growth at different deposition times (10, 20, and 40 min). As shown in Figure 3a, single-crystalline Al crystals with a diameter of several hundred nanometers form initially under the catalysis of Pt NCs. The size of Al crystals greatly depends on the concentration of alane and the reaction temperature. Al crystals show a large size (~1−5 μm) when using higher concentrations of alane and at high reaction temperatures. In contrast, the crystals formed in this process were small, with a diameter of several hundred nanometers. Maintaining the reaction for 20 min, the Al tends to epitaxial

dx.doi.org/10.1021/ja301956s | J. Am. Chem. Soc. 2012, 134, 8034−8037

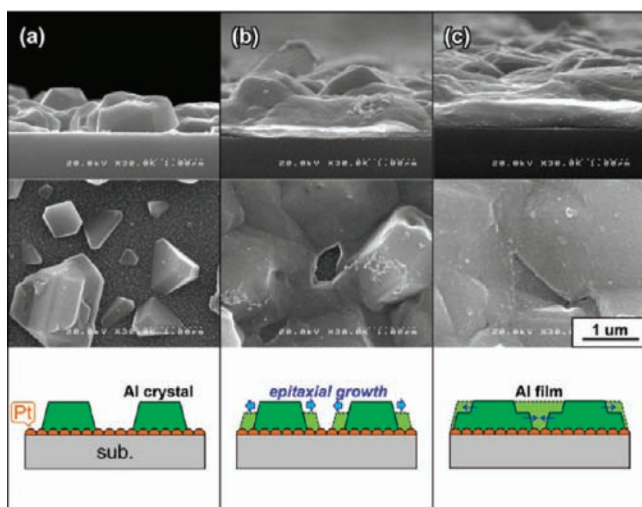

Figure 3. SEM image of Al deposition at different reaction times: (a) 10, (b) 20, and (c) 40 min. The bottom images indicate the possible mechanism of Al deposition. Initially, Al crystals form under catalysis of Pt NCs. Next, crystals connect together via epitaxial growth.

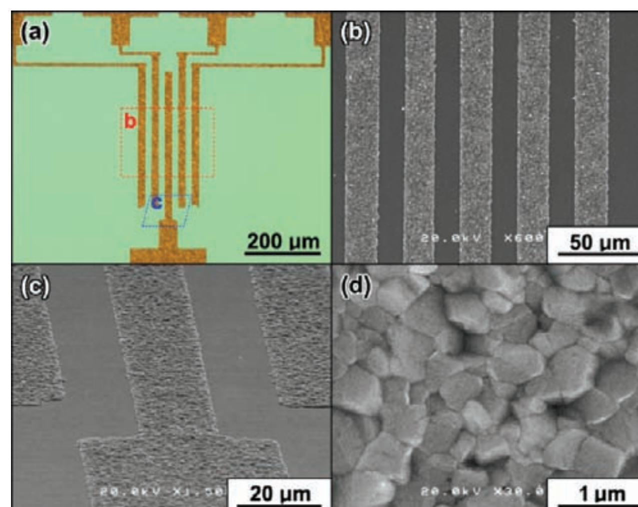

Figure 4. Selected deposition of Al pattern on silicon substrate. (a) Optical microscopy of 20 μm Al electrode pattern. (b) SEM image of electrode pattern (red mark in (a)). (c) SEM image of enlarged area (blue mark in (a)) with a tilt angle. (d) Top-view high-magnification SEM image of Al film.

growth on the Al crystals (Figure 3b). After 40 min, the Al crystals connect with neighboring crystals, resulting in the formation of a continual Al film on the substrate (Figure 3c). Furthermore, the film thickness gradually increases from several hundred nanometers to several micrometers under different reaction times.

Here we give an example of the selectivity of Al on substrate. Selected deposition of Al has potential for use in a variety of device electrodes because of its low cost of synthesis and because it avoids damage owing to dry- or wet-chemical etching. The selectivity originates from the catalytic activity of Pt and the reaction temperature. By using the current experimental conditions, the self-decomposition clearly begins when the reaction temperature is higher than 125 °C. The Al nanocrystals formed in reaction solution are randomly absorbed on the substrate, resulting in poor selectivity (Figure S3). When the reaction temperature is maintained at ~105−120 °C, alane is stable in the presence of excess high-bp amine in the reaction solution. The Pt surface catalytically weakens the Al−H bonding because of the dehydrogenation interaction, which provides a good selectivity. Experimentally, well-defined 20 μm wide electrode pattern composite Pt NCs and TiO_2 layers were formed by a spin-coating process and nanoimprinting lithography. After this substrate is kept in developing solution for 1 h, Al grows on the area with Pt NCs. Figure 4a shows the Al electrode pattern measured by optical microscopy. The pattern shows a golden color, which may be caused by the reflection of the microscope. We also used SEM to observe this Al pattern (Figure 4b−d). We observed a clear electrode pattern with a width of 20 μm. Figure 4c indicates the clear surface of the silicon substrate without a Pt nanocrystalline pattern. Figure 4d demonstrates that the Al pattern comprises Al crystals with few voids, and no individual Al nanoparticle attaches on the surface of the Al pattern. By this experiment, we demonstrated the high selectivity of Al by a solution process.

In conclusion, we demonstrate the first preparation of Al fine pattern with low resistivity of ~2.8−3.5 $\mu\Omega$ cm by a liquid process. The Al can selectively grow on a Pt nanocrystalline pattern. This selectivity originates from the dehydrogenation of catalysis of Pt nanocrystals. By introducing a TiO_2 layer, Al shows good adhesiveness. This is a simple method for the preparation of high-quality Al films or patterns at low cost and might dramatically change the concept for Al deposition in a vacuum. This technique has great potential for use in various fields involving electrodes and the gratings of projectors. Now we are attempting to use this technique to prepare back electrodes for amorphous silicon solar cells by whole-solution processes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Quantum chemical calculation of the adsorption of an alane molecule on a Pt(111) surface, high-resolution cross-sectional TEM image of the Al film, and SEM image of a negative example of an Al pattern prepared at 150 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

z-shen@jaist.ac.jp; tshimoda@jaist.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Prof. Shinichi Katayama and Dr. Pham Tien Lam of Japan Advanced Institute of Science and Technology for their kind discussion on the preparation of manuscript.

■ REFERENCES

(1) For example: (a) D'Heurle, F. M. *Metallurgical Mater. Trans. B* **1970**, *1*, 725−732. (b) Rhee, S.-W. *Korean J. Chem. Eng.* **1995**, *12*, 1−11.

(2) For example: (a) Keyes, D. B.; Sherlock, Swann, Jr.; Klabunde, W.; Schicktanz, S. T. *Ind. Eng. Chem.* **1928**, *20*, 1068−1069. (b) Jiang, T.; Chollier Brym, M. J.; Dube, G.; Lasia, A.; Brisard, G. M. *Surf. Coat. Technol.* **2006**, *201*, 10−18.

(3) Shimoda, T.; Matsuki, Y.; Furusawa, M.; Aoki, T.; Yudasaka, I.; Tanaka, H.; Iwasawa, H.; Wang, D.; Miyasaka, M.; Takeuchi, Y. *Nature* **2006**, *440*, 783−786.

(4) Shen, Z.; Matsuki, Y.; Shimoda, T. *Chem. Commun.* **2010**, *46*, 8606–8608.
(5) Shen, Z.; Li, J.; Matsuki, Y.; Shimoda, T. *Chem. Commun.* **2011**, *47*, 9992–9994.
(6) For example: (a) Shen, L.-Y.; Ji, J.; Shen, J.-C. *Langmuir* **2008**, *24*, 9962–9965. (b) Hozumi, A.; Inagaki, M.; Shirahata, N. *Appl. Surf. Sci.* **2006**, *252*, 6111–6114.
(7) For example: (a) Jones, A. C.; Hitchman, M. L. *Chemical Vapour Deposition*; RSC Publishing: London, 2008. (b) Liu, Y.; Overzet, L.; Goeckner, M. *Thin Solid Films* **2007**, *515*, 6730–6736. (c) Karpov, I.; Bratina, G.; Sorba, L.; Franciosi, A.; Simmonds, M. G.; Gladfelter, W. L. *J. Appl. Phys.* **1994**, *76*, 3471–3478. (d) Glass, J. A., Jr.; Kher, S. S.; Spencer, J. T. *Chem. Mater.* **1992**, *4*, 530–538.
(8) (a) Meziani, M. J.; Bunker, C. E.; Lu, F.; Li, H.; Wang, W.; Guliants, E. A.; Quinn, R. A.; Sun, Y.-P. *ACS Appl. Mater. Interfaces* **2009**, *1*, 703–709. (b) Haber, J. A.; Buhro, W. E. *J. Am. Chem. Soc.* **1998**, *120*, 10847–10855. (c) Foley, T. J.; Johnson, C. E.; Higa, K. T. *Chem. Mater.* **2005**, *17*, 4086–4091. (d) Jouet, R. J.; Warren, A. D.; Rosenberg, D. M.; Bellitto, V. J.; Park, K.; Zachariah, M. R. *Chem. Mater.* **2005**, *17*, 2987–2996.
(9) Frigo, D. M.; van Eijden, G. J. M. *Chem. Mater.* **1994**, *6*, 190–195.
(10) For example: (a) Xu, Z.-F.; Wang, Y. *J. Phys Chem C Nanomater Interfaces* **2011**, *115*, 20565–20571. (b) Adlhart, C.; Uggerud, E. *Chem.—Eur. J.* **2007**, *13*, 6883–6890. (c) Kua, J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1999**, *121*, 10928–10941.
(11) Tanaka, T.; Nakajima, T.; Yamashita, K. *Thin Solid Films* **2002**, *409*, 66–73.