Articles

Spectroscopic Studies on Electroless Deposition of Copper on Hydrogen-Terminated Si(111) Surface in NH₄F Solution Containing Cu(II) Ions

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The electroless deposition of copper on the hydrogen-terminated Si(111) surface was investigated by means of attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, scanning tunneling microscopy (STM), and energy-dispersive spectroscopy (EDS). The hydrogen-terminated Si(111) surface prepared was stable under air atmosphere for a day or more. It was found from ATR-FTIR that two bands centered at 2000 and 2260 cm^{-1} appeared after the H-Si(111) surface was immersed in 40% NH₄F solution containing 10 mM Cu^{2+}. On the other hand, STM image included the copper islands with a height of 5 nm and a diameter of 10-20 nm. The EDS data displayed the presence of copper, silicon and oxygen species. The results were rationalized in terms of the redox reaction of surface Si atoms and Cu^{2+} ions in solutions, which are changed into Si(OH)$_x$(F)$_y$ containing SiF$_6^{2-}$ ions and neutral copper islands.

Key Words : Silicon, Copper, Ammonium fluoride, ATR, STM

Introduction

In the conjunction with the development of ultra-large-scale integration circuits, the investigation of the control of contaminants in cleansing solutions and also the technology for making a flat hydrogen-terminated Si single crystal surface should be developed in the near future. To obtain ideal H-terminated Si(111), Higashi *et al.* used a basic solution[1] and Watanabe *et al.* used boiling water[2] as an etching solution. It is interesting to note that the method by Higashi et al. has simple processing for an ideal hydrogen termination. An ideal hydrogen-terminated Si(111) surface is stable[3,4,5] in air because the topmost silicon atoms have only one dangling bond.[6] The pH of fluoride solution, miscut angle of Si(111) wafer, orientation, and dissolved oxygen and contaminants in cleansing solution are very important factors to get atomically flat terrace on Si(111) surface. Metal contaminants in HF solution were often electrolessly deposited on a Si(111) surface and caused a rough Si(111) surface. Because of the tendency of copper-electroless deposition on a Si(111) sample, copper contaminants in HF solution have received a special attention.[7-15] These metal contaminants can cause serious malfunction or dielectric breakdown in semiconductor diode.

In this work, firstly the flat hydrogen-terminated Si(111) surface, which was very stable in air, was prepared in 40% NH₄F solution. And then the influences of Cu concentrations and immersing time on Cu deposition on the hydrogen-terminated Si(111) surface were investigated by using ATR-

FTIR spectroscopy, scanning tunneling microscopy and energy-dispersive spectroscopy (EDS). In addition, it is reported about the forming processes of the neutral Cu islands.

Experimental Section

The parallelogram ATR prism (36 × 20 × 0.5 mm, 45° bevel angle) was prepared from phosphorous doped n-type Si(111) wafers (1.0-10 Ω·cm), which were polished on both sides for the ATR-FTIR measurements in a multiple internal reflection geometry. The internal reflection number inside the ATR prism was 72. The samples for STM measurement
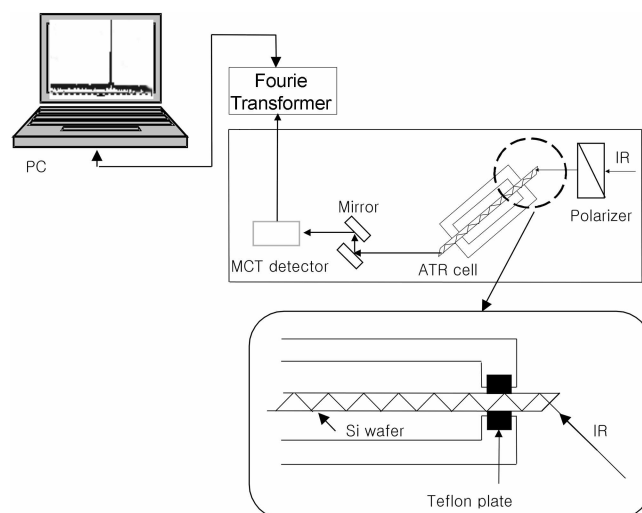

Figure 1. Schematic setup for ATR-FTIR experiment.

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had an area of 1 × 1 cm². Acetone and DI water were used for rinsing Si(111) samples in sonication and piranha solution (H₂SO₄(95%) : H₂O₂(34.5%) = 1 : 1) was used for making oxidation layer on Si(111) surfaces.[16] To obtain hydrogen-terminated Si(111) surface, the ATR prism was immersed in 40% NH₄F solution and dried in flowing nitrogen gas. The sample was immersed in copper containing 40% NH₄F solution (10, 20, 50, and 100 μM Cu²⁺ solution) for 3, 5, 15, and 20 min and dried in flowing nitrogen gas without the sample being rinsed by DI water except the case described otherwise.

ATR-FTIR measurement was performed using a Bio-Rad Excaliber™ spectrometer equipped with HgCdTe (MCT) detector cooled with liquid nitrogen. Ar gas was continuously introduced into the FTIR chamber. The ATR-FTIR spectra were recorded with p- and s-polarization for an oxidized Si(111) surface as a background. STM experiment was carried out using a PicoSPM (Molecular Imaging Corp.).[17] STM was used to investigate copper deposition on the H-Si(111) surface to compare with immersing time dependence in 10 μM copper solution. EDS was obtained by using Oxford Model INCA Energy for JSM-5600.

Results and Discussion

Figure 2 shows the ATR-FTIR spectra of the hydrogen-terminated Si(111) surface measured under dry air environments with p- and s-polarization. A sharp peak at 2083.7 cm⁻¹ was observed in p-polarization mode only (Figure 2(a)). This peak can be attributed to the Si-H stretching mode of the monohydride termination on the Si(111) surface, characterized by a polarization perpendicular to the surface. The facts that no peaks were observable in s-polarization but that the only and strong peak with full with at half maximum of 1.0 cm⁻¹ was observed at 2083.7 cm⁻¹ in p-polarization suggest that the Si(111) was covered homogeneously with H atoms on the (111) terrace, without significant vertical dihydrides present at the step edge.[12] The present result is in good agreement with some previous reports.[1,5,6,10,12] The same H-Si(111) surface was probed under nitrogen gas atmosphere by means of STM and the result is shown in Figure 3. The surface has a wide terrace of 50 nm or more with a step height of 3.1 Å. Thus from both ATR-FTIR and STM results we can conclude that hydride is mostly bound on the ideal (111) terrace as a monohydride. We believe that this is the first ATR-IR and STM data on the same H-Si(111), although either ATR-IR or STM observations have been often separately made on the substrate.

Both the intensity and the full width at half maximum (FWHM) of the peak of the Si-H stretching on the H-Si(111) surface remained unchanged under dry air environments even after 24 hours or more as is shown in Figure 2(b). In addition, no bands related to carbon contaminants were detectable in the region of 2800-3000 cm⁻¹ in the present experimental conditions, which means that the H-covered Si(111) surface was prepared carefully and was kept to be very stable. The results are against the Uosaki's recent article
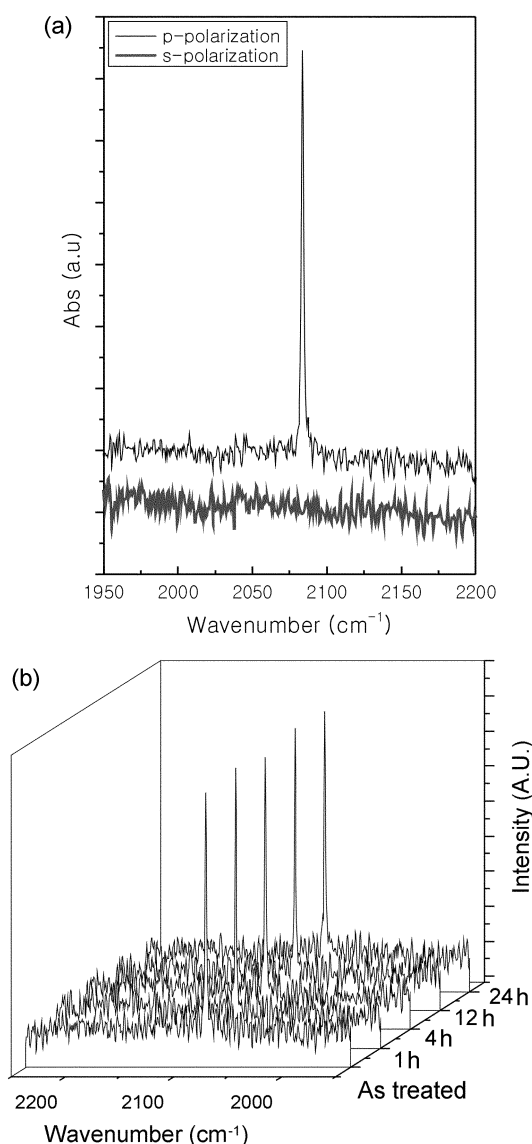

Figure 2. (a) and (b) ATR-FTIR spectra of H-Si(111) surface in the region of H-Si stretching for p- and s- polarization (a) and after the sample was exposed to dry air for 0, 1 h, 4 h, 12 h, and 24 h (b).

that the intensity of the Si-H peak started to decrease but some new peaks of C-H stretching in the region of 2852, 2923, 2931, 2960 cm⁻¹ due to carbon contaminants were observed with increasing the exposure time to dry air.[5] Our experimental conditions appear to be cleaner.

Figure 4(a) and 4(b) show STM images observed in nitrogen with the H-terminated Si(111) surface which was immersed in 40% NH₄F solution containing 10 μM Cu²⁺ for 5 and 15 min, respectively. It was found that the STM images had bright spots associated with Cu deposition over the H-Si(111) surface. The bright spots started to be formed on the step edge of the terrace surface, which is consistent with the work reported by Homma *et al.*[9] The size of the bright spots was mainly 10-20 nm in diameter with a height of 5 nm. Maximum size of such spots remained unchanged irrespective of the change in immersing time in the solution containing Cu(II) ions. However, the density of the spots
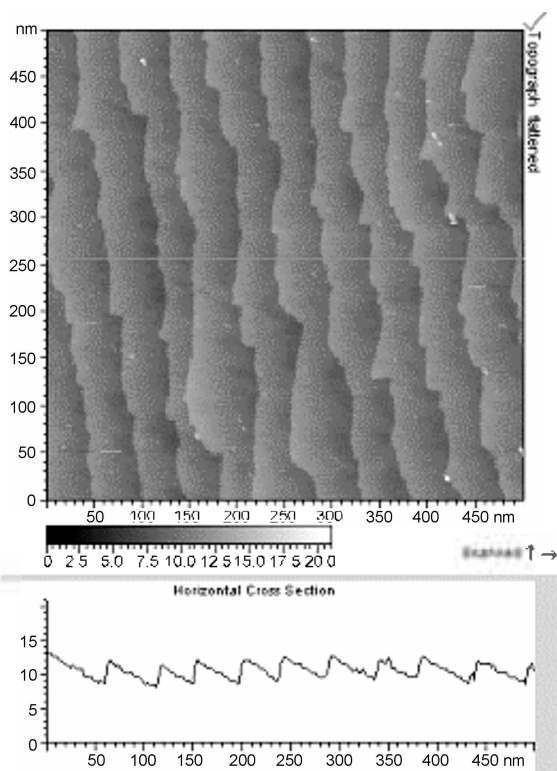
Figure 3. STM image of H-Si(111) surface (Fig. 2) under nitrogen atmosphere: Frame is 0.5 × 0.5 μm^2.
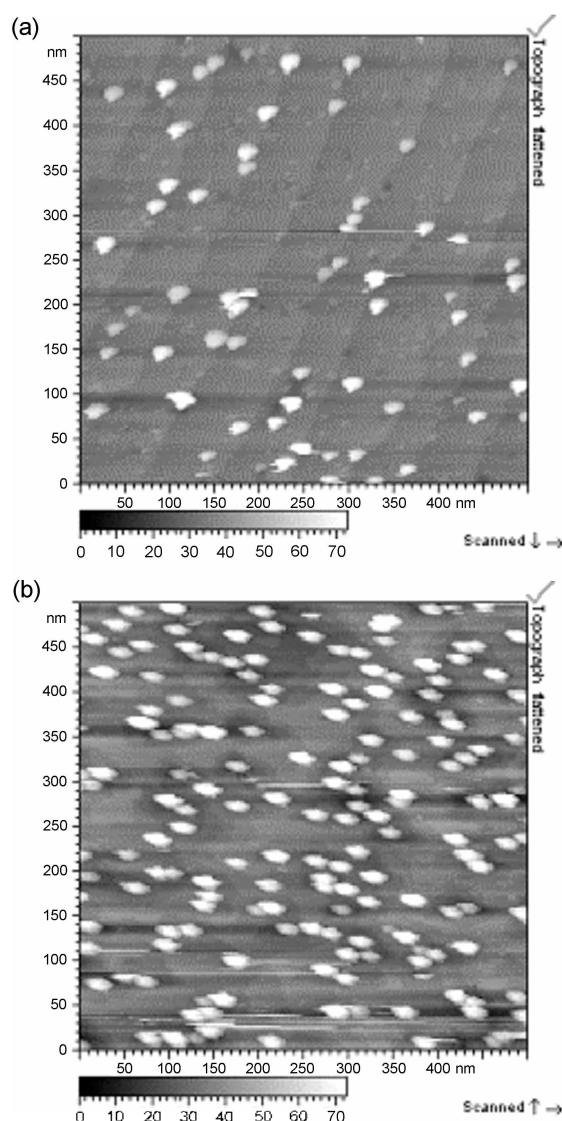

Figure 4. (a) and (b). STM images of the Si(111) surfaces immersed in 40% NH_4F solution containing 10 μM Cu^{2+} for 5 min (a) and 15 min (b): Frames are 0.5 × 0.5 μm^2.

increased with increasing dipping time as is shown in Figure 4, indicating that the spontaneous deposition of copper under open-circuit conditions takes more than minutes and does not occur immediately after immersion, which is quite different from what was observed in Figure 1 by Homma *et al.*[9] We note that our STM data are consistent with ATR-IR (Fig. 6). Figure 5 shows the ATR-FTIR spectra for the Cu-deposited Si(111) surface prepared from 40% NH_4F solution containing 20 μM Cu^{2+} for 5 min. The peak at 2083.7 cm^{-1} corresponding to the Si-H stretching mode of the mono-hydride termination decreased in its intensity. However, two new broad bands appeared near 2000 and 2260 cm^{-1} as compared with the only H-terminated Si(111) surface without Cu ions.

The intensity of the 2083.7 cm^{-1} peak corresponding to Si-H stretching mode of the monohydride termination on the Si(111) surface decreased as Cu^{2+} concentration (Fig. 6) or immersing time increased. The latter result is in agreement with the Uosaki's.[10] On the other hand, the two broad bands at 2000 and 2260 cm^{-1} started to grow with increasing Cu^{2+} concentration or immersing time. The two broad bands were not detectable once the Cu-deposited Si(111) surface was rinsed off by DI water. Thus it is clear from the above results that the two broad bands are stable only under the environments of coadsorption of the deposited Cu atoms. The broad peak centered at 2000 cm^{-1} is assigned to the combination mode of NH_4^- deformation (1484 cm^{-1}) and NH_4^+ torsional oscillation (523 cm^{-1}).[5,10] The frequency of 2260 cm^{-1} is reported to correspond to vibration of $Si(O)_x(F)_y$, but it has

not been clear. To confirm the ATR-FTIR and STM results, we measured an EDS spectrum for Cu islands deposited on H-Si(111) surface from the sample immersed in 40% NH_4F solution containing 10 μM Cu^{2+} ions for 5 min and the result is shown in Figure 7. The EDS data displayed clearly the presence of Si, Cu and O species in agreement with ATR-FTIR (Si and O species) and STM data (Cu). Especially, it is noted that the intensity of O species on EDS data is much higher than that of Cu species. We believe that such a high intensity of O species could not originate only from oxidation of Cu or Si during the sample handing for EDS measurement. Thus we suggest that the broad peak near 2260 cm^{-1} originates from the vibration of $Si(O)_x(F)_y$. It has been known that infrared absorption of silicon oxide species appear near this region, supporting the present argument.[14,15]

Now we discuss the processes of the Cu deposition on the Si(111) surface in NH_4F solution containing Cu^{2+} ions.
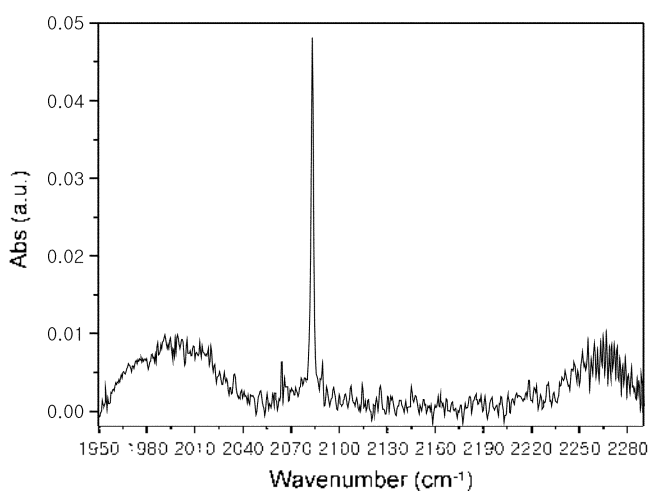
Figure 5. P-polarized *ex-situ* ATR-FTIR spectra of the Si(111) surface immersed in 40% NH₄F solution containing 20 μM Cu²⁺ for 5 min after preparation of H-Si(111) surface.
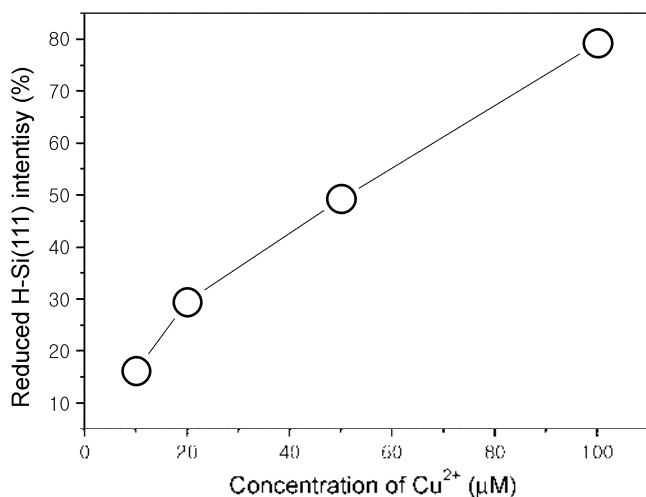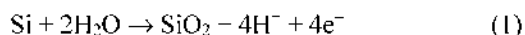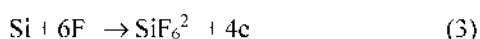

Figure 6. Reduction ratio of the H-Si(111) peak as a function of Cu²⁺ concentration in 40% NH₄F solution.

Figure 7. EDS spectrum of copper particle deposited on H-Si(111) surface in 40% NH₄F solution containing 10 μM Cu²⁺ for 5 min.

reduced into the neutral copper atoms, which started to form the Cu islands on the silicon surface. Thus Cu^{2+} ions switch the dissolution pathway of Si surface atoms from the one occurring in NH_4F solution not containing Cu^{2-} ions.

As the reaction of Si atoms and Cu^{2-} ions proceeds over the surface, the byproducts of $Si(O)_x(F)_y$ containing SiF_6^{2-} ions start to accumulate near the surface, as indicated in reaction (2). SiF_6^{2-} ions formed may be surrounded with counter ion NH_4^-. This is compatible with the facts that the two broad bands of 2000 cm⁻¹ and 2260 cm⁻¹, indicating the presence of the NH_4^+ and $Si(O)_x(F)_y$ with SiF_6^{2-} ions, respectively, were found to be observed and that the intensities of the 2000 cm⁻¹ and 2260 cm⁻¹ increased monotonously as Cu^{2+} concentration or immersing time increased. Therefore, it is speculated that the two NH_4^- and SiF_6^{2-} ions remain such a salt form on the surface, since the both broad bands were not detectable after rinsing the Cu-deposited Si(111) surface by DI water.

There are two possible reduction processes on the Si surface in fluoride solutions.[10,11] One is a combination reaction of the two consecutive processes including the oxidized silicon as an intermediate.

$$Si + 2H_2O \rightarrow SiO_2 - 4H^- + 4e^- \qquad (1)$$
$$SiO_2 + 6F^- + 4H^+ \rightarrow SiF_6^{2-} + 2H_2O \qquad (2)$$

The other is the direct oxidation reaction of silicon surface atoms without an intermediate.

$$Si + 6F^- \rightarrow SiF_6^{2} + 4e \qquad (3)$$

In this work, it was detected from both EDS and ATR-FTIR that oxygen species existed on the Si(111) surface during the electroless copper deposition. Therefore, the oxidation reaction of the silicon surface atoms seems to proceed via the former processes having oxidized silicon species. At the same time Cu^{2-} ions in the solution were believed to be
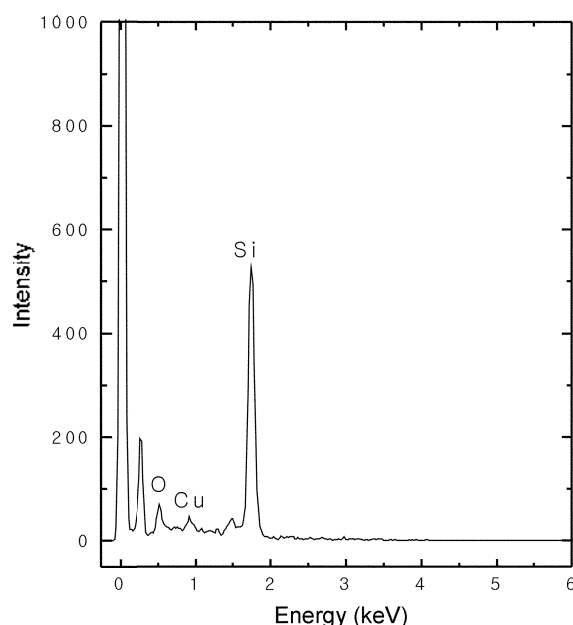
Conclusions

We investigated the hydrogen-terminated Si(111) surface with flat terrace, which was stable without any carbon contaminants for a day or more. When the H/Si(111) surface was immersed in NH₄F solution containing copper(II) ions, the copper species were deposited on the steps of its surface and the two extra broad bands centered at 2000 and 2260 cm⁻¹ appeared in ATR-FTIR spectra. The two peaks were the frequencies of the combination mode of NH_4^- deformation (1484 cm⁻¹) and NH_4^+ torsional oscillation (523 cm⁻¹), and vibration of $Si(O)_x(F)_y$, respectively. The results were rationalized in terms of the redox reaction of Si atoms and Cu^{2+} ions, which were changed into $Si(O)_x(F)_y$ containing SiF_6^{2-} ions and neutral copper islands.

References

1. Higashi, G. S.; Chabal, Y. J.; Trucks, G. W.; Raghavachari, K. *Appl. Phys. Lett.* **1990**, *56*, 656.

2. Watanabe, S.; Nakamura, N.; Ito, T. *Appl. Phys. Lett.* **1991**, *59*, 1458.

3. Graf, D.; Gruder, M.; Schulz, R. *J. Vac. Sci. A* **1989**, *7*, 808.

4. Neuwald, U.; Hessel, H. E.; Feltz, A.; Memmert, U.; Behm, R. J. *Appl. Phys. Lett.* **1991**, *60*, 1357.

5. Ye, S.; Ishihara, T.; Uosaki, K. *Appl. Phys. Lett.* **1999**, *75*, 1562.

6. Trucks, G. W.; Raghavachari, K.; Higashi, G. S.; Chabal, Y. J. *Phys. Rev. Lett.* **1990**, *65*, 504.

7. Hiraiwa, A.; Itoga, T. *IEEE Trans. Semicond. Manufact.* **1994**, *7*, 60.

8. Li, G.; Jiao, J.; Seraphin, S.; Raghavan, S.; Jeon, J. S. *J. Appl. Phys.* **1999**, *85*, 1857.

9. Homma, T.; Wade, C. P.; Chidsey, C. E. D. *J. Phys. Chem.* **1998**, *102*, 7919.

10. Ye, S.; Ishihara, T.; Uosaki, K. *J. Electrochem. Soc.* **2001**, *148*, C421.

11. Morinaga, H.; Suyama, M.; Ohmi, T. *J. Electrochem. Soc.* **1994**, *141*, 2834.

12. Watanabe, S. *J. Chem. Phys.* **2000**, *113*, 2423.

13. Niwano, M.; Kaseyama, J.; Kurita, K.; Takahashi, I.; Miyamoto, N. *J. Appl. Phys.* **1994**, *76*, 2157.

14. Bensliman, F.; Fukuda, A.; Mizuta, N.; Matsumura, M. *J. Electrochem. Soc.* **2003**, *150*, G527.

15. Chelma, M.; Homma, T.; Bertagna, V.; Erre, R.; Kubo, N.; Osaka, T. *J. Electroanal. Chem.* **2003**, *559*, 111.

16. Lee, H.-Y.; Lee, C.-H.; Jeon, H.; Jung, D. *Bull. Korean Chem. Soc.* **1997**, *18*, 737.

17. Song, M.-B.; Jang, J.-M.; Lee, C.-W. *Bull. Korean Chem. Soc.* **2002**, *23*, 71.