Nucleation Behavior at Electroless Displacement Deposition of Metals on Silicon from HF Solutions

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Electroless displacement deposition of metals on silicon from HF solutions has been paid much attention [1-3]. Various kinds of metals can be deposited on Si by this method. Electrochemical behaviors, such as kinds of carbon dioxide photoreduction products [4] and structures of porous Si produced by metal enhanced HF etching [5, 6], were influenced by the kind of the metals. The modification of Si electrodes with fine metal particles is substantial for preparation of efficient photoelectrochemical (PEC) solar cells [4, 6, 7]. The control of size and distribution density of metal particles is the most important for this type of solar cells. In the present work, the nucleation behavior at the electroless displacement deposition of Pt, Pd, Au and Ag has been investigated.

Single-crystal n-Si wafers (CZ, (100), ca. 1 Ωcm) were used. Three types of pretreatments were employed; washed with acetone and etched with CP-4A (a mixture of HF, HNO_3, CH_3COOH and H_2O) and a 7.3 M (M = mol dm $^{-3}$) HF solution (treatment A), washed by the RCA method and etched with a 7.3 M HF (treatment B), and immersed in 14 M HNO_3 at 353 K for 30 min after treatment A (treatment C). The electroless displacement deposition of metals was carried out by immersing the n-Si wafers in 1.0 or 0.25 mM metal salt (H_2PtCl_6, $HAuCl_4$, $AgNO_3$ or $PdCl_2$) solution including 15mM HF for 120 s at 313 K. The surface inspection of the n-Si wafers and the measurement of distribution density of metal particles were performed with a high-resolution scanning electron microscope.

Figure 1 shows the SEM images of n-Si wafers after immersion into the metal salt solutions including HF. Fine metal particles were deposited on the wafers. The distribution density of metal particles was varied with the kinds of metals, ca. 10^8 (Pt), 10^9 (Pd), 10^{11} (Ag) and 10^{12} cm^{-2} (Au). The density of metal particles, except for the Ag case, increased with the thermodynamic potential of metal deposition. The 1.0 mM H_2PtCl_6 and 15 mM HF solution gave clear dependence of deposited particle density upon the type of pretreatments (Fig. 2). This result would indicate the ability of pretreatment to remove defects or impurities on the n-Si wafers. Prior to the immersion into the metal salt solution including HF, the application of pulse potential to the n-Si wafers in an electrolyte solution was performed, the application increased the distribution density of metal particles. The kinds of ions such as lithium, sodium and potassium in the electrolyte solution induced different distribution density of deposited metal particles.

It was elucidated that the nucleation of electroless displacement deposition of metals on n-Si wafers depends on the kind of deposited metals and the surface conditions of Si wafers. Application of this deposition method to preparation of efficient PEC solar cells will be reported.

References

[1] L. A. Nagahara, T. Ohmori, K. Hashimoto, and A. Fujishima, J. Vac. Sci. Technol. A **11**, 763 (1993).
[2] P. Gorostiza, P. Allongue, R. Díaz, J. R. Morante, and F. Sanz, J. Phys. Chem. B **107**, 6454 (2003).
[3] T. Homma, N. Kubo, and T. Osaka, Electrochim. Acta **48**, 3115 (2003).
[4] R. Hinogami, Y. Nakamura, S. Yae, and Y. Nakato, J. Phys. Chem. B **102**, 974 (1998).
[5] X. Li and P. W. Bohn, Appl. Phys. Lett. **77**, 2572 (2000).
[6] S. Yae, Y. Kawamoto, H. Tanaka, N. Fukumuro, and H. Matsuda, Electrochem. Comm. **5**, 632 (2003).
[7] Y. Nakato and H. Tsubomura, Electrochim. Acta **37**, 897 (1992).

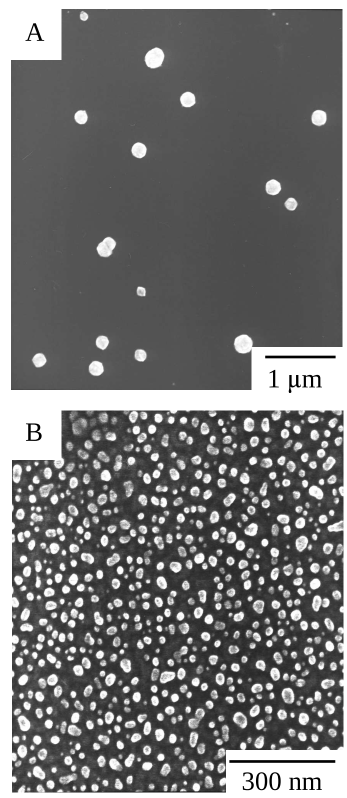

Figure 1. SEM images of n-Si wafers after immersion into the metal salt solutions including HF. A: H_2PtCl_6, B: $AgNO_3$, Pretreatment: treatment A.

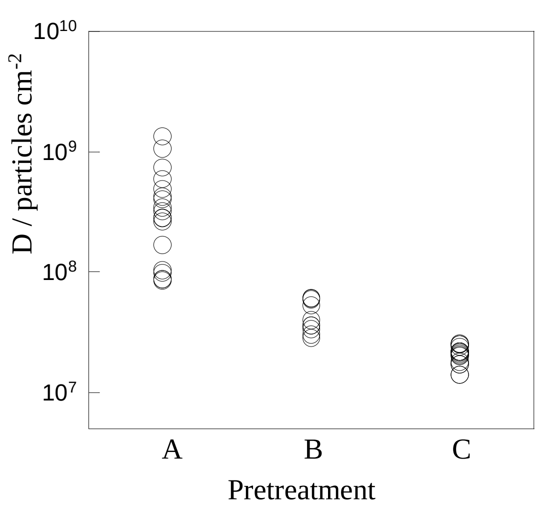

Figure 2. Distribution density (D) of Pt particles deposited on n-Si wafers.