Formation of Porous Silicon by Metal Particle Enhanced Chemical Etching in HF Solution

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Porous silicon is usually prepared by electrochemical (p-Si) or photoelectrochemical (n-Si) etching under anodic bias. In the present work, chemical etching in HF solution without a bias has produced porous layers on Si wafers that had been modified with metal particles, and micrometer-sized porous Si layers have improved the conversion efficiency of solar cells.

Single crystal n-Si wafers (CZ, (100), ca. 1 Ω cm, 1.0 x 1.0 cm^2) were modified with metal particles by electroless (displacement) deposition. The n-Si wafers were immersed in a 1.0 mM (M = mol dm^{-3}) hexachloroplatinic (IV) acid and 15 mM HF aqueous solution for 120 s. Au, Ag and Pd particles were deposited on n-Si by the similar displacement method. The metal-particle-deposited n-Si wafers were immersed in a 7.4 M HF aqueous solution at a temperature of 298 K for 24 hours. In some cases, Ar or O_2 gas was bubbled into the HF solution before and during immersion of n-Si wafers. The n-Si wafer was fixed to a Teflon holder and used for measurements of photoelectrochemical (PEC) solar cell characteristics. The n-Si electrode and a Pt plate counter electrode were immersed in an 8.6 M HBr and 0.05 M Br_2 redox electrolyte solution. The n-Si electrode was irradiated with a tungsten-halogen lamp. The illumination intensity was adjusted such that it gave the same photocurrent as simulated solar illumination (AM 1.5G, 100 mW cm^{-2}) for single crystal Si solar cells.

Figure 1a shows SEM image of Pt-particle-deposited n-Si wafer after immersion in the HF solution without any gas bubbling. Many pores of 0.5 – 1.5 µm in diameter were formed. The surface of n-Si changed color to gray, and showed the photoluminescence of orange color under a black light illumination. The O_2 bubbling enlarged the number and depth of micrometer-sized pores (Fig. 1b). The weight loss of n-Si was increased by the O_2 bubbling. The Ar bubbling stopped the etching and gave no change on the surface of Pt modified n-Si. Neither the weight nor surface of bare n-Si was changed with immersion in the HF solution with or without gas bubbling. n-Si(111) and p-Si gave similar results. Pd particles enhanced the etching rate of n-Si more than Pt particles, but decreased the number of pores and the intensity of luminescence (Fig. 2a). Thick nanometer-sized porous layer was formed on Ag-particle-deposited n-Si (Fig. 2b). The morphology of porous Si layers formed on Au-particle-deposited n-Si changed from Fig. 2b like to Fig. 1a like with decreasing of particle density. These results show that micrometer- and nanometer-sized porous layers are formed by metal particle enhanced HF etching in the presence of dissolved O_2.

The photocurrent density of a PEC solar cell using a Pt-particle deposited n-Si electrode was increased from 24 to 34 mA cm^{-2} by etching in the HF solution with O_2 bubbling (Fig. 3). The maximum power output reached to 11.4 mW cm^{-2} corresponding to 11.4 % of conversion efficiency.

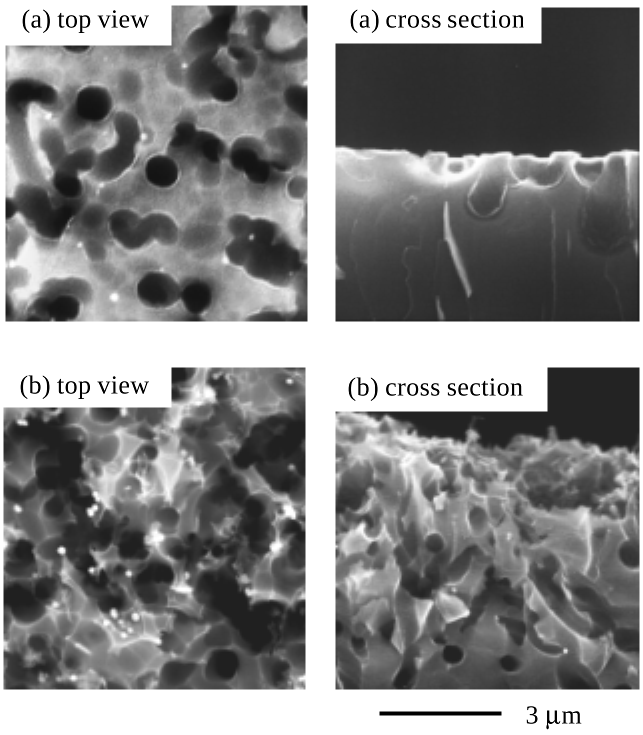

Figure 1. SEM images of Pt-particle-deposited n-Si wafers after immersion in 7.4 M HF solution without any gas bubbling (a) and with O_2 bubbling (b).

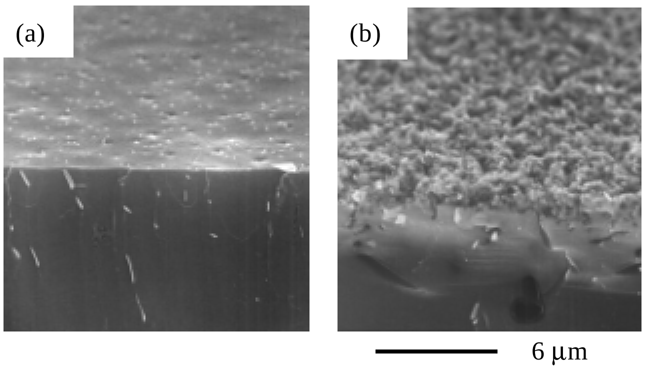

Figure 2. SEM images of metal-particle-deposited n-Si wafers after immersion in 7.4 M HF solution without any gas bubbling. Metal particles: (a) Pd and (b) Ag.

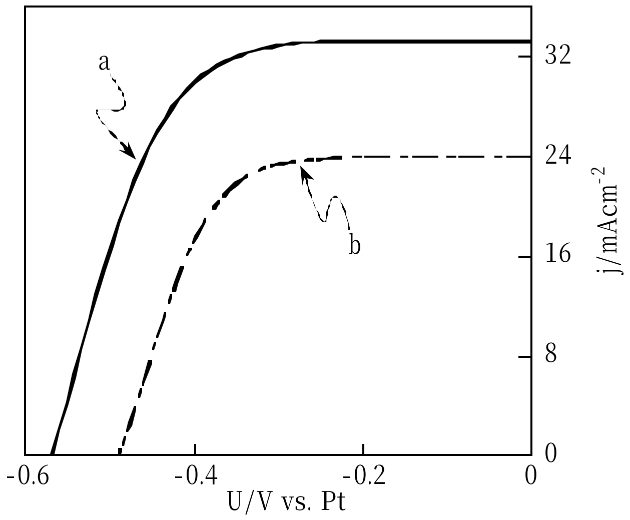

Figure 3. Photocurrent (j) vs. potential (U) curves for the Pt-particle-deposited n-Si electrodes. (a) after immersion in 7.4 M HF solution without gas bubbling and (b) no immersion.