

### Photo-Assisted Controlling of Platinum Electrodeposition on p-Silicon

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#### Introduction

Metal electrodeposition on semiconductor plays a vital role not only in wiring technique in microelectronics but also in electrocatalysis of semiconductor. Especially, silicon has a band structure suitable for evolution of hydrogen from water with the use of sun light. Recently, solar energy conversion has attracted great attention and hydrogen energy system is expected to be a major player in creation of sustainable society. It has been suggested that the electrocatalysis of semiconductor would be improved by controlling the size and density of metal particles on semiconductor.

Electrodeposition of metals on n-Si has been widely investigated by a number of researchers.<sup>1</sup> On the other hand, there is few examples of systematic study on electrodeposition on p-Si. With or without application of cathodic potential, noble metals like Pt can be deposited on p-Si by hole injection via the valence band of Si even in the dark. Due to the low overpotential, growth of deposited particles predominates over nucleation under this condition. In contrast, as charge transfer occurs via the conduction band under illumination, nucleation is prevailing due to the large overpotential.<sup>3</sup> Using this behavior, we tried to control the size and density of Pt particles by adjusting illumination time and light intensity.

#### Experimental

All experiments were carried out with 10-20  $\Omega$  cm boron-doped p-Si (100) as substrates. Al was deposited to the backside of the substrate by evaporation followed by annealing to obtain ohmic contact. Before Pt deposition, the surface was etched in 5 wt% HF aqueous solution to remove the native oxide layer.

A 4 mM  $\text{H}_2\text{PtCl}_6$  and 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution was used as electrolyte. The solution was bubbled with Ar gas for 30 minutes before deposition to remove dissolved oxygen. Electrodeposition of Pt on p-Si was carried out under potentiostatic condition and under illumination. A 60 W tungsten-halogen lamp was used as a light source. Electrochemical measurements were performed with Ag/AgCl as reference electrode.

#### Results and Discussion

Figure 1 shows cathodic curves of p-Si in 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution with or without 4 mM  $\text{H}_2\text{PtCl}_6$  under illumination of 100  $\text{mW cm}^{-2}$ . In the solution containing Pt ions, a current peak appears at -0.20 V (vs. Ag/AgCl). This current seems to result from reduction of Pt ions. At more negative potentials than -0.6 V, large current due to hydrogen evolution is observed.

We investigated the influence of light intensity on the time profile of Pt deposition current at the same applied potential (Fig. 2). When the intensity is higher than 25  $\text{mW cm}^{-2}$ , the initial current peak was observed, followed by a decrease of current. The time of the current peak delays and the current decreases with the decrease of light intensity. The peak disappears for the cases of 12.5 and 20  $\text{mW cm}^{-2}$ . In addition, we confirmed the Pt deposition occurs even in the dark and the particle density obtained in the dark is quite low. The initial current peak is attributed to nucleation. It is considered that once active sites are covered with particles, nucleation stops and then the nuclei grow. The same behavior as Fig. 2 was reported

in case of Au and Cu deposition on n-Si in the dark with changing applied potential. It was also suggested that nucleation rate is the function of applied potential.<sup>1,2</sup>

Figure 2 indicates that light intensity works like applied potential when n-Si is used. The number of excited carriers, electrons in the conduction band, is proportional to the light intensity. Charge transfer proceeds via the conduction band, and as a result, increase of light intensity enhances the nucleation rate. Therefore, Pt nucleation on p-Si can be controlled by changing light intensity without changing applied potential.

Taking these results into account, we succeeded to fabricate Pt deposited Si electrodes having different sizes and densities of particles. Stopping illumination before the current peak in Fig. 2, we could obtain an electrode modified with low density particles. Moreover after nucleation under illumination, we controlled the particle size in the dark by keeping at a constant potential and changing the electrolyzing time.

We are also studying how the size and density of Pt particles influence the electrocatalysis of Si during hydrogen photoevolution with the electrodes fabricated by this method.

#### References

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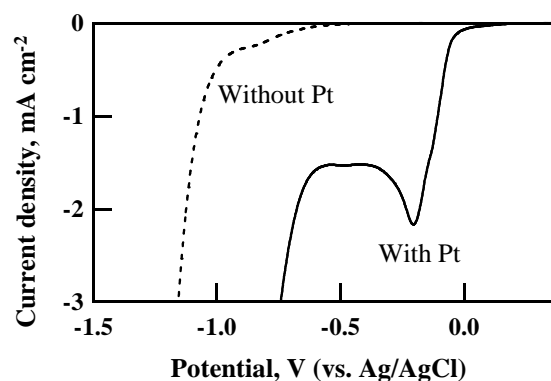


Fig. 1 Current-potential curves for p-Si in 0.5M  $\text{Na}_2\text{SO}_4$  with or without 4mM  $\text{H}_2\text{PtCl}_6$  under illumination of 100  $\text{mW cm}^{-2}$ . Scan rate was 10  $\text{mV s}^{-1}$  in both cases.

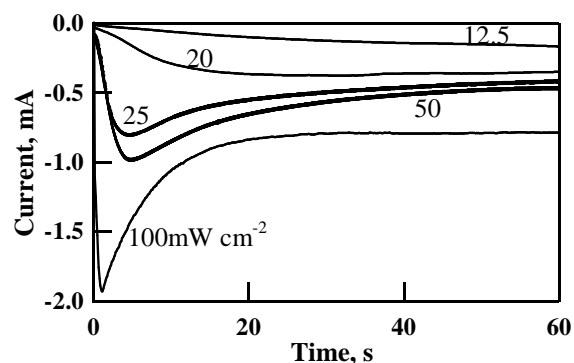


Fig. 2 Current-time curves for the deposition of Pt on p-Si in 4 mM  $\text{H}_2\text{PtCl}_6$  with 0.5 M  $\text{Na}_2\text{SO}_4$  under illumination. Light intensity was 12.5, 20, 25, 50, and 100  $\text{mW cm}^{-2}$ . The potential was -0.2 V (vs. Ag/AgCl).