Electrochemical Oscillation of Open Circuit Potential during Immersion Plating of Copper on Silicon

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Current or potential oscillations have been observed during the anodic polarization of Si in fluoride-containing solutions. The behavior is generally understood as the repetition of the formation of an oxide layer, the break-down, and the recovery of the Si bare surface. This kind of oscillation usually takes place at quite high voltage. We have found a different type of oscillatory behavior on Si, which is immersed in HF solution containing cupric ions and without external power supply.[1,2] The oscillation occurs under limited conditions of type of dopant and concentration of HF. In this work the behavior is studied further.

EXPERIMENTAL

Porous silicon (PS) samples were prepared by anodizing a *p*-type Si (100) wafer, the resistivity of which was 10-20 Ωcm, in 22 wt% HF-ethanol solution with the current density of 2 $mAcm^{-2}$ and for 20 min. Thus prepared sample was immersed in 0.01 M $CuSO_4$ solution containing different concentrations of HF. The open circuit potential (OCP) was measured against a Cu reference electrode. The values were converted to the ones of the Ag/AgCl (3.3 M KCl).

RESULTS

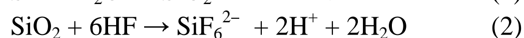
Figure 1 is an example of the oscillation of OCP, which was observed when the PS sample was immersed in 0.01 M $CuSO_4$ and 0.1 wt% HF solution under a stagnant condition. The oscillation is affected by the stirring of the solution. Under the stagnant condition, the oscillation appears about 1200 s after immersion. With stirring the oscillation starts at a much earlier stage. Moreover, the period of the oscillation becomes shorter with the stirring. The periodicity is not random but is a little irregular in both cases; this can be confirmed also by the deviation from a complete circle in the phase map plotting dE/dt vs. E. The results indicate that mass transfer contributes to the oscillation. Similar oscillatory behavior is observed also with a flat Si wafer. According to this result, the presence of a PS layer on top of the Si wafer turns out not to be a key factor for the oscillation. However, it affects the kinetic behaviors during the oscillation. This is also confirmed by the influence of solution viscosity on the oscillatory behavior.[3] The periodicity is much more ordered than in the case of a PS substrate. The phase map forms an almost closed circle. However, the shape is slightly deviated from a complete circle. The type of substrate affects the oscillatory behavior. A heavily doped p^+-type Si, 0.01 Ωcm, did not show the oscillation at all. The oscillation was not observed also in *n*-type Si.

HF concentration in 0.01 M $CuSO_4$ base solution is an important issue. By adding 0.01 wt% HF, the OCP oscillations emerge. No visible Cu deposition is observed on the surface of the Si wafer in this case. In the solutions of 0.05 and 0.1 wt% HF the oscillations become very pronounced and regular. The amplitude of the oscillation is about 0.1 V. In this case the surface is covered with Cu without peeling off. More concentrated HF than 0.1 wt% causes peeling off of deposited Cu foil. With increasing the HF concentration, the amplitude of the oscillations of the OCP decreases and the oscillations finally disappear at 1 wt%. It can be seen that the lower end of the OCP during the oscillation keeps at around -0.15 V until this HF concentration. However, in more concentrated solutions, the OCPs are located at more negative potentials.

DISCUSSION

To consider the mechanism of the oscillatory behavior, it is assumed that oxidation of Si with successive dissolution of SiO_2 and reduction of Cu^{2+} take place in the system as it was first observed by dos Santos et al.[4] These reactions can be written as

$$Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e^- \quad (1)$$



$$SiO_2 + 6HF \rightarrow SiF_6^{2-} + 2H^+ + 2H_2O \quad (2)$$

and

$$Cu^{2+} + 2e^- \rightarrow Cu \quad (3).$$

Electrode potentials for the reactions (1) and (3) are -1.22 V (pH 3) and 0.07 V, respectively; therefore the OCP would stay in between them. It actually varied in the potential rage of 0.05 to -0.35 V under the present conditions.

Cu deposition starts and the OCP is located at negative potential when a PS or Si sample is immersed in a $CuSO_4$ solution without HF. Then the deposition rate decreases and finally the deposition ceases, where the OCP shifts toward the positive potential and then settles.[2] According to the observation of the formation of Cu foil and its detachment, it seems reasonable that the repetition of the surface coverage by deposited Cu accompanied by SiO_2 formation and the partial recovery to the bear surface after the detachment in the presence of HF would lead to the oscillation. This explains the effect of HF concentration on the oscillatory behavior on *p*-type Si. However, this interpretation cannot apply to the behavior observed on p^+- and *n*-type Si. The interfacial energy structure between semiconductor and solution may takes part in the oscillation.

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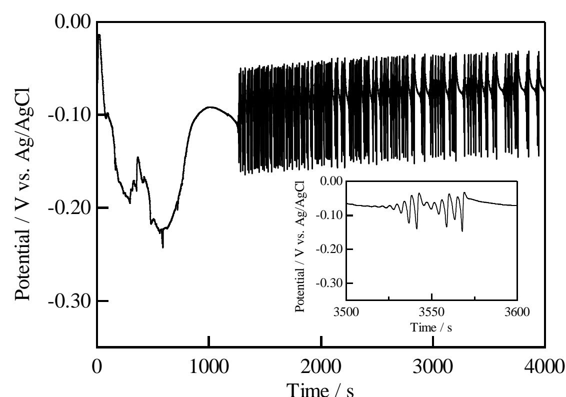

Fig. 1 OCP oscillation of PS during immersion plating in 0.01 M $CuSO_4$ + 0.1 wt. % HF under stagnant condition. The inset is the magnification.