

# Metal Deposition onto a Porous Silicon Layer by Immersion Plating from Aqueous and Nonaqueous Solutions

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It is important to create a good contact between porous silicon (PS) and metal to realise the potential applications in the microelectronics industry. Wet processes such as electrodeposition, electroless plating and immersion plating (1,2) are expected to be quite effective to deposit various metals. Of these techniques, the immersion-plating method is highly nominated because it has the virtue of simplicity and lower costs. Moreover, it is desirable for some applications to deposit metal on the substrate without the need for an electrical contact. This study reports on the immersion plating of metals (Ag, Cu, Ni) onto a PS layer from aqueous and nonaqueous solutions, with the aim to compare and realise the different deposition behavior of each metal and to investigate the effect of residual water in nonaqueous solutions on the anodic reaction of the process.

## EXPERIMENTAL

PS was prepared from a *p*-type Si (100) wafer (10-20  $\Omega$ cm) by anodization in 20 wt% HF alcoholic solution. Purification of Methanol (MeOH) and acetonitrile (MeCN), as organic solvents, was performed by drying over molecular sieves. The residual water was measured by Karl Fisher's titration method. The preparation and experiments in nonaqueous solutions were conducted in a glove box under Ar gas atmosphere. Different metal salts of Ag, Cu and Ni were investigated. PS samples were immersed in these solutions, and the samples were observed using x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The electrochemistry of the pure organic solvents was investigated by measuring *i*-E curves using Si RDE. The rest potentials were measured by immersing PS and bare Si in the solutions.

## RESULTS AND DISCUSSION

Ag metal was deposited from aqueous solution containing all  $\text{Ag}^+$  ions while proceeding of Cu deposition depends upon the type of salt used:  $\text{CuSO}_4$  deposits Cu,  $\text{CuCl}_2$  inhibits deposition whereas no Cu was detected from  $\text{Cu}(\text{NO}_3)_2$  aqueous solution. In nonaqueous solutions, Ag and Cu were deposited from the MeOH solution containing metal ions, but in contrast no metal was detected from the MeCN solution containing either  $\text{Ag}^+$  or  $\text{Cu}^{2+}$ . The inhibition effect of  $\text{CuCl}_2$  was also observed in nonaqueous solution. Ni could not be deposited onto PS in aqueous nor nonaqueous solutions. The oxidation of PS to  $\text{SiO}_2$  was observed to occur simultaneously with the metal deposition as confirmed by FTIR spectra; see Fig.1.

The different deposition behavior can be related to the different electrode potential of each metal. Nickel has the most negative electrode potential and therefore the reduction of nickel ions on PS surface is not favored. On the contrary, the potential of both  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Ag}^+/\text{Ag}$  couple is more positive than that of Ni and consequently the reduction of metal ions is more easily occurred. On the other hand, absence of Cu deposition from  $\text{Cu}(\text{NO}_3)_2$  solution is due to that  $\text{NO}_3^-$  ion is thermodynamically easier to be reduced than  $\text{Cu}^{2+}$ . In addition, nitrate ions can oxidize silicon, resulting in absence of Cu deposition.

The same behavior was observed when we used  $\text{NaNO}_3$  solution.

The rest potential of the PS in  $\text{Ag}^+$ -nonaqueous solutions was measured. The result shows that the rest potential in the MeOH solution, from which Ag was deposited, stays at less noble (negative) value, while the value in the MeCN solution shifts to noble (positive) direction indicating the unfavorable Ag deposition. The same behavior of potential shift was observed in the copper system. The potential shift in case of the MeCN solution may be due to a complex formation.

The average level of residual water was 30-50 ppm in  $\text{Cu}^{2+}$ -MeOH solutions. The concentration of 50 ppm water content corresponds to about  $2 \times 10^{-3}$  M and hence, the water concentration in the organic solutions cannot be neglected. Further, the current-potential curves revealed that MeOH exhibits a wide potential window during the measurements. This suggests that MeOH is a stable solvent and is not expected to involve in the reaction where the reduction of metal ions occurs. Accordingly, the trace of residual water in organic solutions strongly affects the deposition process.

According to the above results, the difference in deposition behavior is attributed to the different redox couple of each metal on the one hand. On the other hand, it is also related to the different rest potential of the PS in these solutions. The immersion process is characterized by coupled redox reactions, one corresponding to metal formation, the other to the silicon oxidation.

We also tested the possibility of metal deposition onto Si wafer in nonaqueous solutions. Metal plating inspected by naked eye revealed no deposition. However, XPS measurements revealed that minute amount of Cu and Ag was adhered on the Si surface from MeOH solution accompanied by the oxidation of silicon. These results show that the metal plating occurs at a much higher rate on the porous surface compared to that on Si wafer. The difference in behavior may be attributed to the chemical changes produced during the formation of the porous layer. This difference leads to a potential shift of the PS toward less noble (negative) potential, as observed from rest potential measurements. Much further work is needed in this area for complete understanding.

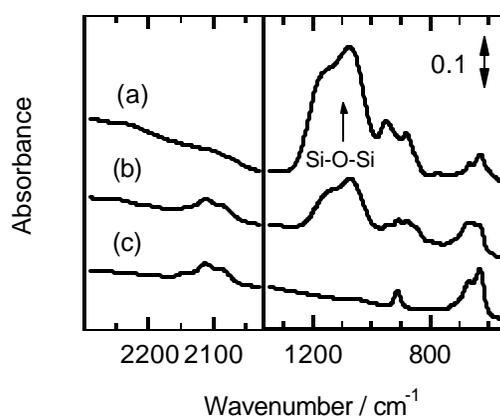


Fig.1 Transmission FTIR spectra of PS after 10 min immersion in MeOH solution of; (a)  $3 \times 10^{-3}$  M  $\text{CuSO}_4$ , (b)  $10^{-2}$  M  $\text{CuCl}_2$  and (c) as prepared PS.

## REFERENCES

1. M. Jeske, J. W. Schultze, M. Thönissen, and H. Munder, *Thin Solid Films* **255**, 63 (1995).
2. T. Tsuboi, T. Sakka, and Y. H. Ogata, *Appl. Surf. Sci.* **147**, 6 (1999).

