

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

F. A. Harraz,^{a,z} T. Tsuboi,^{b,*} J. Sasano,^a T. Sakka,^{a,*} and Y. H. Ogata^{a,*}

^aInstitute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan

Immersion plating of metals (Ag, Cu, Ni) onto a porous silicon (PS) layer from aqueous and nonaqueous solutions has been studied. The modified PS layers after the immersion plating were analyzed by X-ray diffraction and X-ray photoelectron spectroscopy. Fourier transform infrared spectroscopy and scanning electron microscopy were also performed to investigate the structural changes and microstructure of PS samples after the plating process. In both solutions, the deposition of metal oxidizes PS simultaneously to SiO_2 . The different deposition behaviors are discussed in terms of different rest potentials of PS in these solutions and electrode potential of each metal. Immersion plating in nonaqueous organic solutions shows that a trace of residual water affects the metal deposition. Based on the results obtained, the mechanism of metal deposition is proposed. The metal deposition proceeds by nucleation and growth via the local cell mechanism. It is also found that metal deposition proceeds very differently on Si wafer and PS surfaces. The different deposition behaviors on both surfaces are discussed. © 2002 The Electrochemical Society. [DOI: 10.1149/1.1498841] All rights reserved.

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Porous silicon (PS) is quickly becoming an important and versatile electronic material in different fabrication technology. It was initially observed about 45 years ago as black resist on Si after electropolishing of c-Si.¹ Since the first report on its ability to emit very efficient visible photoluminescence at room temperature,² significant development has been made toward the understanding and applicability of such material for electronics and the material has been investigated for possible optoelectronic applications.³

Another interesting chemical property of PS is its ability to act as a modest reducing agent.⁴ In contrast to its optical properties, much less attention has been given to using PS as both a reducing agent and a substrate for metal deposition. In addition, it is important to establish good electrical contact with the volume of the PS structure for realizing the potential applications in the microelectronics industry. Furthermore, PS layers have also been proposed for potential application as the host matrix for polymers or metals, which have interesting optical properties.⁵ For example, Pt-coated n-type PS electrodes have shown good solar energy conversion, which is one of the highest for n-Si photoelectrochemical solar cells.⁶ Consequently, metal deposition on PS is a subject of interest.

Dry processes such as physical and chemical vapor deposition⁷ are widely used to deposit metals in the field of Si technology. However, it appears that such a process leads to poor penetration of metal inside the pores of the PS due to what is called pore mouth blockage. However, such blockage is not expected when applying electrodeposition method^{8,9} in solution. Under the electrochemical reaction the charge carriers are provided by the bulk silicon, and it is expected that the deposition process can take place preferentially at the pore bottom, as in the case of the formation of the PS layer. In addition, electroless plating¹⁰ and immersion plating,¹¹⁻¹⁴ as wet methods, are expected to be quite effective to deposit various metals. In both methods there is, in principle, no great problem of mass transport inside the pores, which may limit the process. In recent work, Belyakov et al.¹⁵ reported that Ag metal could penetrate inside the PS layer during the deposition from solution. They also observed that the structures obtained with chemically prepared metal contacts show better photoelectric properties and more intense electroluminescence compared to the structures with vacuum-evaporated contacts.

In this study the immersion plating method is highly nominated, where no electrical contact is required as in the case of electroplating. The method has another virtue over electroless plating since no catalyst is needed to deposit the metals of interest as the PS surface

^b Present address: Canon, Incorporated, Eltran Business Center, Hiratsuka, Kana-

itself is catalyzing the deposition. In addition, such a technique allows the formation of metal deposits in the form of island-like structure with simplicity in operation and lower cost. In this case, controlling the size and distribution of the island metal particles could enhance the catalytic activity of the semiconductor electrodes for photoelectrochemical cells, as has been reported.^{16,17} Furthermore, it is also possible to obtain patterned metallization of PS structure since the deposition of some metals can be localized to the illumination area.

However, in most cases the deposition of metals is accompanied by a quenching of the photoluminescence, most likely due to the nonradiative defects generated by the surface modification.¹² Meanwhile, the PS luminescence could be retained if the deposited metal is dissolved by acid treatment.¹³ In a different trend of PS formation, it has been reported that the film formed by chemical etching in the presence of Fe³⁺ improved the photoluminescence properties.¹⁸ Other authors were concerned to deposit various conducting polymers to PS layers.^{19,20} Their results showed that after a certain time of immersion in different polymer-containing solutions, the hardness and the thermal conductivity for the resulting structure were improved without affecting the photoluminescence. For more details, the different deposition methods, with special attention to the requirements and specific drawbacks of each method, are reviewed in a recent report.²¹

An anodic reaction occurring on the same substrate surface is important for the immersion plating process to be completed. It is assumed that the anodic reaction accompanying metal ion reduction from aqueous solution is the oxidation of Si in the presence of water into SiO₂.^{14,22} However, due to the lack of water, the oxidation of Si or PS is not expected to occur as a counter reaction for metal deposition in nonaqueous solutions.

Methanol (MeOH), a protic solvent as water, and acetonitrile (MeCN), an aprotic solvent containing no oxygen atom, were used as organic solvents in this study. The physicochemical properties of water and these solvents are different.²³ Therefore, different conditions for metal deposition may be required. Further, our previous work²⁴ is the first report concerning metal deposition from nonaqueous solutions.

With respect to the reaction mechanism during the immersion plating, Jeske *et al.*¹¹ have proposed that the reaction proceeds with injection current multiplication and hydrogen evolution is indispensable for deposition. In contrast to this model, chemical processes for the deposition reaction have been proposed by Tsuboi *et al.*²² However, the prior mechanism is put in question because the reaction with electrons in the conduction band of a p-type silicon cannot proceed without illumination and gas evolution was never observed during our experiments. On the other hand, the latter model does not give information either about the generation of nuclei at the initial

^{*} Electrochemical Society Active Member.

gawa 254-0013, Japan.

^z E-mail: farid@iae.kyoto-u.ac.jp

stage of immersion or how the deposition proceeds after a prolonged time of exposure. In this article, this information is identified and thoroughly discussed.

This study reports on the immersion plating of metals (Ag, Cu, Ni) onto PS layers from aqueous and nonaqueous solutions, in order to compare and realize the different deposition behaviors of each metal and to investigate the effect of residual water in nonaqueous solutions on the anodic counter reaction of the process. We did not perform analysis to quantify the metal penetration into PS; therefore, we do not discuss the pore filling in this study. Another objective of this work is to clarify the detailed reaction mechanism during the immersion plating event. In addition, the different deposition behaviors of the PS layer and the Si wafer are also discussed.

Experimental

The Si(100) single crystals used in this study were p-type borondoped (10-20 Ω cm in resistivity). The starting wafers (0.6 mm thick) were cut into 1.3×1.3 cm pieces. The PS layers were prepared by electrochemical anodization in a cell made of trifluoroethylene resin utilizing a current density of 2 mA cm⁻² for 20 min. A silicon wafer and a copper current collector were mounted at the bottom of the cell by using an O-ring that allowed 0.785 cm² of the Si crystal to be exposed to the homogeneously mixed electrolyte composed of 20 wt % HF (47 wt % HF:99.5 wt % ethanol = 1:1.35 in weight). Prior to each experiment, the Si wafers were rinsed in acetone and dipped for a few minutes in 5 wt % HF solution to remove any native surface oxides. The PS thus prepared was dried by blowing Ar gas onto it. PS layers about 2 µm thick were produced having porosity in the range of 75-80%. Then PS was immersed in the solution containing different metal ions at room temperature. AgClO₄, AgNO₃, Ag₂SO₄, CuSO₄, CuCl₂, Cu(NO₃)₂, (CF₃SO₃)₂Cu, NiSO₄, and NiCl₂ were used as metal salts. Purification of organic solvents, MeOH and MeCN, was performed by drying over molecular sieves. The residual water was measured by the conventional Karl Fischer titration method.²⁵ The concentration of metal ions prepared was 10⁻² M, unless otherwise specified. The preparation and experiments in nonaqueous solutions were conducted in a glove box under Ar gas atmosphere. After the immersion, the PS sample was rinsed in the pure solvent and dried by blowing Ar gas.

X-ray diffraction (XRD) patterns were measured with Cu K α radiation (1.54 Å) using a Rigaku RAD 2 C system with an attachment for thin-film measurement. X-ray photoelectron spectroscopy (XPS) measurements were performed using a JPS-9010 MC, JEOL. Fourier transform infrared spectroscopy (FTIR) spectra were taken by means of a Nicolet Avatar 360. A Si wafer was used as a reference to remove Si bulk absorption. The data were averaged over 64 times with a resolution of 4 cm⁻¹.

The rest potential of PS in contact with the solutions was measured using Ag/AgCl as a reference electrode. A potentiostat/ galvanostat, Princeton Applied Research model 273A, was used. The ohmic contact on the rear side of the samples was made with an InGa eutectic alloy. The measurements were conducted in the dark. Current-potential curves using a Si rotating disk electrode (RDE) in pure organic solvents were measured using an automatic polarization system, Hokuto Denko HZ-3000. A three-electrode cell was used with an Ag/AgCl electrode as a reference and a Pt wire as a counter electrode. The rotation rate was 2000 rpm and the scan rate was 2 mV s⁻¹. We used 0.1 M tetra-*n*-butylammonium perchlorate as a supporting electrolyte during the rest potential and currentpotential measurements. Scanning electron microscopy (SEM), JSM-5600 JEOL, was used to examine and characterize the morphology of the specimens after the plating process.

Results and Discussion

Immersion plating of metals from aqueous solutions.—Metal deposition on PS was inspected by measuring the XRD pattern. Nickel deposition was not detected on the PS surface from aqueous



Figure 1. XRD patterns of PS after 1 min immersion in (a) 5×10^{-3} M Ag₂SO₄, (b) 10^{-2} M CuCl₂, (c) 10^{-2} M NiCl₂, and (d) untreated PS.

solutions of NiCl₂ or NiSO₄; there was no change either in XRD pattern or in color. Copper was deposited during the immersion in CuCl₂ and CuSO₄ aqueous solutions, whereas deposition was not detected from Cu(NO₃)₂ solution. Silver deposition resulted from the immersion in Ag₂SO₄, AgClO₄, and AgNO₃ solutions. Figure 1 shows the XRD patterns of the PS samples after 1 min immersion in different metal ion aqueous solutions. Dipping the PS in 10^{-2} M NiCl₂ leads to no change in the XRD pattern. However, the pattern of PS after immersion in 10^{-2} M CuCl₂ exhibits two peaks at 43.4 and 50.4°, corresponding to Cu(111) and Cu(200), respectively. Furthermore, the sample exposed to 5×10^{-3} M Ag₂SO₄ reveals two peaks related to silver deposition.

The different deposition behaviors can be discussed according to the different electrode potentials of each metal. Half-cell reactions and electrode potentials in different solutions²⁶⁻²⁹ are summarized in Table I. CIO_4^- is not concerned with the reaction since it is difficult to be reduced, although it has the highest positive potential. Nickel has the most negative electrode potential and therefore the reduction of nickel ions on PS surfaces is not favored. Nickel cannot deposit on the PS by immersion plating from its simple salts. On the contrary, the potential of Cu^{2+}/Cu couple is more positive than that of Ni^{2+}/Ni and consequently, copper ions are more easily reduced to Cu metal. Cu deposits under simultaneous oxidation of PS as confirmed by FTIR measurements (discussed later). Cu was not detected during the immersion in Cu(NO₃)₂ aqueous solution although the oxidation of PS occurred. Nitrate ion has more positive potential than $\mathrm{Cu}^{2+}.$ This means that NO_3^- ion is thermodynamically easier to be reduced than Cu²⁺. In addition, nitrate ion can oxidize silicon, resulting in absence of Cu deposition. The oxidation of Si in HF/HNO3 solution during PS formation by stain etching is well known.³⁰ The same surface oxidation was also observed when we used NaNO₃ solution.

The deposition of Ag after dipping PS in aqueous solution of Ag^+ is also related to the positive standard potential of Ag. The potential of Ag^+/Ag couple is more positive than that of Cu^{2+}/Cu couple. The difference has an influence on the metal deposition.

	Electrode potential (V vs. SHE) ^b		
Half-cell reaction	H ₂ O	MeOH	MeCN
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.32		_
$\mathrm{Cu}^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Cu}$	0.28	0.41	-0.34
$Ag^+ + e^- \rightarrow Ag$	0.68	0.75	0.11
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.40	—	_
$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$	0.78	—	

Table I. Half-cell reactions and electrode potentials at 25°C in different solutions.^a

^a The potential is referred to a standard hydrogen electrode (SHE) in an aqueous solution. In all solutions, pH is set equal to 7 and the activities of Ni²⁺, Cu^{2+} , Ag^+ , NO_3^- , NO, ClO_4^- , and ClO_3^- are set equal to 10^{-2} .

^b References 26-29.

Unlike Cu, Ag was deposited from $AgNO_3$ solution because Ag^+ has more positive potential than NO_3^- ion.

The behavior of PS during the immersion in aqueous solutions is classified into two categories on the basis of XRD and FTIR results: (*i*) no change and (*ii*) silicon oxidation to SiO_2 . The classification of all samples is summarized in Table II. It is worth noting that the oxidation of silicon to SiO_2 is indispensable to the metal deposition.

Metal deposition from nonaqueous solutions and structural changes.—All the preparations and plating experiments reported in this section were conducted in a glove box under Ar gas atmosphere. We investigated the influence of anhydrous NiSO₄ and NiCl₂ dissolved in purified MeOH and MeCN solutions on PS substrates. We utilized 10^{-2} M metal ion concentration. XPS measurements revealed that Ni was not detected in all solutions after the immersion process. This behavior can also be attributed to the more cathodic redox potential of Ni in these solutions, as mentioned in the previous section.

Deposition of Ag onto PS was inspected by measuring XPS and also visually. Ag deposition was commenced immediately from MeOH solution, as evident from a metallic silver appearing on the PS surface. On the contrary, no metal was observed from MeCN solution. Figure 2 shows the Ag $3d_{5/2}$ and Si 2p XPS spectra of PS after 10 min immersion in 10^{-2} M AgClO₄-MeOH and MeCN solutions. The charge correction was made by setting the binding energy of C 1s to 284.5 eV as an energy reference. These spectra show that the Ag metal-related peak appears at 368.5 eV from MeOH solution, whereas no signal is detected in the case of the MeCN solution. The reduction of Ag⁺ ions was accompanied by the oxidation of PS: two peaks were detected at 99.4 and 103.0 eV, which can be assigned to Si(0) and SiO₂, respectively.³¹ This behavior is due to the different electrode potentials of Ag in both solutions. The electrode potential in MeOH solution is more positive than that in MeCN solution by more than 0.5 V (see Table I).

The measurement of rest potential is quite interesting because this parameter is characteristic of the anodic and cathodic reactions taking place on the Si surface. The rest potential is the potential that PS substrate spontaneously attains when it is immersed in the elec-

Table II. Summary of the results of immersion plating on PS from aqueous solution. PS was immersed in 10^{-2} M solution for 10 min.

Solute	Deposited metal	Silicon oxide
NiSO ₄	None	None
NiCl ₂	None	None
CuSO ₄	Cu	SiO_2
CuCl ₂	Cu	SiO ₂
$Cu(NO_3)_2$	None	SiO ₂
AgNO ₃	Ag	SiO ₂
AgClO ₄	Ag	SiO ₂

trolyte. We measured the rest potential of PS in 10^{-2} M AgClO₄-MeOH and MeCN solutions. The Ag/AgCl reference electrode was connected to the electrolyte by means of a saturated KNO₃-agar salt bridge made of a polyethylene tube. The measurements were reproducible within a few millivolts. The result is shown in Table III. The rest potential of PS in the MeOH solution, from which Ag was deposited, stays at less noble (more negative) value, while the value in the MeCN solution shifts to noble direction (less negative), indicating the unfavorable Ag deposition. The result of rest potential is dependent on the electrolyte composition and the surface site reactivity of the electrode material. We used PS samples prepared under the same conditions and the same metal ion concentration; hence, the different rest potentials are mainly related to the solvent. The potential shift in the case of MeCN solution may be due to a complex formation with Ag⁺ ions. It should be noted that MeCN forms a stable complex with Ag⁺ ions.²³

CuSO₄ and CuCl₂ solutions of MeOH and MeCN were prepared. Since CuSO₄ is sparingly soluble in these solvents, we prepared a concentration of 3×10^{-3} M in MeOH and 2×10^{-4} M in MeCN solution. We prepared 10^{-2} M CuCl₂ solutions. Cu metal was deposited from CuSO₄-MeOH solutions while only a trace of Cu was observed from CuCl₂-MeOH solutions. Figure 3 shows the Cu 2p_{3/2} and Si 2p XPS spectra of PS immersed in these CuSO₄ and CuCl₂-MeOH solutions for 10 min. A sharp peak at 932.4 eV corresponding to Cu deposition from CuSO₄-MeOH solution was detected while only a small peak from CuCl₂ was observed. This trace



Figure 2. Ag $3d_{5/2}$ and Si 2p XPS spectra of PS after 10 min immersion in 10^{-2} M AgClO₄ of (a) MeOH and (b) MeCN solutions.

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Table III.	Rest potentials (V vs	. Ag/AgCl) of PS	immersed in 0.01
M of (CF	₃ SO ₃) ₂ Cu and AgClO) ₄ in MeOH and	MeCN solutions. ^a

Organic solvent	System	Rest potential, V	Deposited metal
MeOH	Cu	-0.20	Yes
MeCN	Cu	+0.34	No
MeOH	Ag	-0.62	Yes
MeCN	Ag	-0.10	No

^a 0.1 M tetra-*n*-butylammonium perchlorate was added as a supporting electrolyte.

amount of Cu deposition is attributed to the inhibition of Cu deposition by Cl⁻ ions. Tsuboi *et al.*¹⁴ have investigated that Cu deposition from its halide aqueous solution was inhibited as the concentration of halide ions increased. They attributed the inhibition to the reversible contact adsorption of halogen ions on the PS surface. We have investigated in detail the effect of Cl⁻ ions on Cu deposition onto PS from a methanol solution,³² and we attributed this inhibition to the stabilization of Cu(I) species in this solution. From the XPS measurements it is also revealed that the deposition of Cu was accompanied by the oxidation of Si. The oxidation of Si was also confirmed by measuring FTIR spectra, as explained latter.

On the contrary, no Cu was detected from MeCN solution containing either CuSO₄ or CuCl₂. Since we could not prepare the 10^{-2} M CuSO₄ in organic solutions and CuCl₂ seems to inhibit the deposition, we used trifluoromethanesulfonic acid copper(II) salt, (CF₃SO₃)₂Cu, to prepare other solutions. The concentration of Cu ions was 10^{-2} M. We carried out the immersion plating process under the same experimental conditions. Copper deposition was inspected by XPS, XRD, and visually. Copper was found to deposit from MeOH solution, whereas no metal was observed from MeCN solution. We also measured the rest potential of PS in these solutions. The results, given in Table III, show that the rest potential of PS in MeOH solution containing Cu²⁺ ions stays at less noble potential, (-0.2 V vs. Ag/AgCl), indicating the possibility of Cu deposition, while the value in MeCN solution shifts to the noble direction, (+0.34 V), explaining the inhibition of metal deposition. It is most plausible that the observed potential shift stems from a complex formation with Cu ions. It is also reported that MeCN forms a stable complex with Cu(I) ions.²³ In addition, the negative value of the potential of Cu²⁺/Cu couple in MeCN solution com-



Figure 3. Cu $2p_{3/2}$ and Si 2p XPS spectra of PS immersed in (a) 3 $\times 10^{-3}$ M CuSO₄ and (b) 10^{-2} M CuCl₂-MeOH solutions for 10 min.

2 Current density (mA/cm² 0 , **i**i^{i;} -2 (b) (a) -6 -8 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 Potential (V vs. Ag/AgCI)

Figure 4. Current density-potential curves of Si RDE in (a) pure MeOH (\longrightarrow) and (b) pure MeCN ($\cdots \cdots$) containing 0.1 M tetra*n*-butylammonium perchlorate as a supporting electrolyte. The rotation rate and scan rate were 2000 rpm and 2 mV s⁻¹, respectively. The scans were started at the OCP.

pared with that in MeOH solution, (see Table I) might be related to the absence of Cu deposition from MeCN solution.

In addition to the two factors mentioned (rest potential of PS and redox couple of each metal) that affect and determine the deposition behavior in organic solvents, one should not neglect the influence of the different physicochemical properties of both solvents. As mentioned earlier, MeOH is classified as a protic solvent, whereas MeCN is aprotic, containing no oxygen atom. MeOH has a greater Gutmann's donor number than MeCN (20.0 and 14.1, respectively),³³ *i.e.*, MeOH has a higher donor ability (basicity). As a consequence, the solvation power of MeOH toward ions is greater than MeCN and it is quite similar to water (MeOH molecules can donate one and accept two hydrogen bonds). In view of these facts, it is expected that the solvation states of metal ions (Cu or Ag) in the two solvents are not similar and consequently, this may also have an effect on the deposition behavior.

It is also of interest to note that Cu was found to deposit much faster on the PS from MeOH solution than aqueous solution. The amount of deposited Cu from both solutions for the same Cu ion concentration and immersion time was estimated by inductively coupled argon plasma emission spectroscopy (ICP) technique. The potential of Cu^{2+}/Cu couple in MeOH solution is more positive than that in aqueous solution. This means that Cu ions are more easily reduced in MeOH than in aqueous solution thermodynamically.

The average level of residual water was 30 ppm in CuSO₄ and (CF₃SO₃)₂Cu-MeOH solutions, while it was around 50 ppm in CuCl₂-MeOH solution according to Karl Fischer titration. 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. We applied vacuum distillation to improve the residual water content after drying over molecular sieves. However, further reduction of water content was not attained. Current-potential curves using a Si RDE were measured to investigate the electrochemical behavior of pure MeOH and MeCN solvents. We used 0.1 M tetra-n-butylammonium perchlorate as a supporting electrolyte during the measurements. The result is depicted in Fig. 4. It reveals that both solvents exhibit a wide potential window during the measurements. The oxidation of MeOH starts at potentials higher than +0.3 V vs. Ag/AgCl. A similar oxidation potential of MeOH was reported in aqueous solution.³⁴ The rest



Figure 5. Transmission FTIR spectra of PS after 10 min immersion in (a) 3×10^{-3} M CuSO₄-MeOH solution, (b) 10^{-2} M CuSO₄-aqueous solution, (c) 10^{-2} M CuCl₂-MeOH solution, and (d) freshly prepared PS.

potential of PS in MeOH *vs.* solution, where Cu and Ag were deposited, is -0.2 and -0.62 V (Ag/AgCl), respectively, as shown in Table III. These results suggest that MeOH is a stable solvent and is not expected to be involved in the reaction where the reduction of metal ions occurs. Furthermore, the immersion of PS in all MeCN solutions containing metal ions, in which the water content was 21-26 ppm, led to oxidation of Si, although the solvent does not contain oxygen atoms (see Fig. 2, for example). Accordingly, we concluded that the trace of residual water in the organic solutions strongly affects the deposition process.

Changes in FTIR spectra after immersion plating.—The transmission mode of FTIR spectra can provide sensitive information concerning the surface species. However, in order for this technique to work well, many surface sites must be available. PS layers satisfy this condition due to the very large surface area, and that is why the structure of the PS surface has been extensively investigated by transmission FTIR spectroscopy.³⁵⁻³⁸ The spectra were measured on freshly prepared samples to investigate the structure changes after immersion in different solutions.

Figure 5 shows the spectra of an as-prepared PS layer and PS immersed in CuSO₄-MeOH and aqueous solutions and CuCl₂-MeOH solution for 10 min. FTIR spectra of PS and its oxidized state have been investigated and the band assignments have been proposed.³⁹⁻⁴¹ As-formed (fresh) PS displays bands associated with surface hydrides: the spectra show distinctive triplets at 2090-2150 cm⁻¹, a sharp absorption at 910 cm⁻¹, and strong absorption at 630-680 cm⁻¹, Fig. 5d. This absorption is due to SiH_x species. Absence of the absorption at 1100 cm⁻¹ due to Si—O—Si stretching demonstrates that the oxidation does not proceed for the freshly prepared sample; the spectra was measured soon after the PS formation. Further, absorption at 810 cm⁻¹ corresponding to Si-F_x stretching does not appear, indicating that the PS layer contains no fluorine. This result is in good agreement with the result obtained by sputter depth profile measurements.⁴²

A marked change in the spectra is observed for the PS immersed in aqueous and nonaqueous solutions containing Cu^{2+} . An absorption extending from 1000 to 1200 cm⁻¹ due to Si—O—Si stretching appeared in both solutions. No absorption at 2190-2250 cm^{-1} , assigned to $O_v SiH_x$, is observed. The absorption intensities related to SiH_x, namely, at 630-680 cm⁻¹, are decreased. The disappearance of the absorption at 2090-2150 cm^{-1} assigned to SiH_x after the immersion in CuSO4-MeOH and aqueous solutions is also observed. However, the same absorption band is slightly decreased after the immersion in CuCl₂-MeOH solution. It is also of interest to note that the different Si-O-Si peak intensities, Fig. 5a and c, indicate that in CuCl₂-MeOH solution PS is more slowly oxidized compared to CuSO₄-MeOH solution, and this result corresponds well to the result obtained by XPS measurements (see Fig. 3) in which only small peak-related Cu deposition is detected due to the inhibition by Cl⁻ ions. Furthermore, the appearance of an absorption peak at 1100 cm⁻¹ for all the samples immersed in aqueous and nonaqueous solutions of Cu ions demonstrates that the oxidation of PS accompanies the deposition of Cu metal from the solutions.

Mechanism of metal deposition onto PS surface.—In order to clarify the reaction mechanism of metal deposition onto the PS surface, a series of SEM images of Cu deposition from 0.01 M $(CF_3SO_3)_2Cu$ -MeOH solutions was examined at different immersion times. The SEM images obtained are shown in Fig. 6. At the early stage of immersion, after 5 s, many Cu particles in the order of 120-180 nm diam were detected on the surface of PS, Fig. 6a. A prolonged immersion for 30 s produced a size increase of the Cu crystals, in the range of 500 nm, as clearly observed in Fig. 6b. Further morphological investigation revealed that the Cu nuclei increase rapidly both in number and size as the deposition time proceeds. After 5 min immersion in the same solution, the PS surface is almost completely covered by Cu metal, as clearly seen in the SEM image of Fig. 6c.

Copper ions are able to withdraw electrons from the PS substrate, and thus deposition occurs. Here we consider that the reduction of Cu^{2+} proceeds through the galvanic displacement of PS in the plating bath. In other words, Cu^{2+} gains electrons released by the electrochemical oxidation of PS to be reduced and deposit on the surface. A similar reductive deposition of Cu and Ag on PS from aqueous solutions has been reported.^{43,44}

The oxidation of PS and the reduction of metal ions were found to occur simultaneously and can be explained by the following coupled redox reaction^{14,22}

Oxidation

$$Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e^-$$
 [1a]

and

$$SiH_r + 2H_2O \rightarrow SiO_2 + (4 + x)H^+ + (4 + x)e^-$$
 [1b]

Reduction

or

[2a]

$$Ag^+ + e^- \rightarrow Ag$$
 [2b]

The oxidation of PS was confirmed by FTIR spectra, and in all cases the form of silicon oxide is SiO_2 , as revealed by XPS measurements (peak at about 103 eV in Fig. 3 and 4). The formation of a SiO_2 layer was also reported as the product of Cu deposition on Si from solutions containing Cu²⁺ as traces of impurity.^{45,46}

 $Cu^{2+} + 2e^- \rightarrow Cu$

On the basis of the morphological analysis obtained by SEM and the information received from XPS and FTIR, it is revealed that the oxidation of PS and the deposition of Cu occur from the very beginning of immersion. The detailed mechanism of metal deposition (Cu or Ag) is illustrated in Fig. 7. The metal deposition is suggested to initiate from a finite number of nucleation sites which is dependent on the properties of PS surface and the plating bath constitu-





(b)

15kV X5,000 5Am

Figure 6. Plan-view SEM images of PS layers after immersion in 0.01 M $(CF_3SO_3)_2Cu$ -MeOH solutions for different periods: (a) 5 s, (b) 30 s, and (c) 5 min immersion.

ents. The generation of nuclei is observed at the early stage of immersion (step 2 and 3). As the exposure time proceeds, the electrons released by the anodic oxidation of PS are supplied to the metal ions through the deposited metal, resulting in the growth of crystals (step 4). Consequently, the immersion plating process proceeds by a nucleation and growth mechanism.

(c)

The thickness of the deposited Cu layer on PS was estimated according to the following formula

$$t = m/(a \times d)$$
[3]

where *m* is the mass of deposited Cu as measured by ICP, *a* is the geometrical surface area of the PS, and *d* is the density of bulk Cu metal. The estimated thickness after 5 min immersion was found to be 0.38 μ m. The interesting question is now to understand how this thick Cu layer is formed after 5 min immersion. This result cannot be explained by the general corrosion-type mechanism, since the deposition reaction is inhibited and ceased after a short time of immersion, when the PS surface is no longer in contact with the solution. Therefore, we suggest that the immersion plating process should proceed via the local cell type scheme rather than the general corrosion type at this stage, although both the mechanisms may be possible at the early nucleation and growth stages. The deposited nuclei act as local cathodes for further crystal growth. On prolonged immersion the coalescence of the nuclei occurs and hence, the exposed area of the PS substrate is reduced. Then the unoxidized PS

underneath act as local anodes from which the electrons are supplied to the metal ions through the deposited metal or intergrain boundaries. Based on these observations, the deposition process proceeds by nucleation and growth via the local cell mechanism.

Comparison of metal deposition on silicon wafer and PS surfaces.—To investigate the possibility of metal deposition onto p-type Si(100) wafers, immersion plating under the same experimental conditions was carried out in nonaqueous solutions. Metal plating inspected by the naked eye revealed no deposition. However, XPS measurements revealed that a minute amount of Cu and Ag was adhered on the Si surface from MeOH solution accompanied by oxidation of silicon. A similar cementation process was also reported on c-Si in aqueous solution.⁴⁷

In order to demonstrate the different deposition behaviors, Fig. 8 shows plan-view SEM micrographs of 2 min Ag deposition from 0.01 M AgClO₄-MeOH solution on bare Si and PS surfaces. As seen in Fig. 8a, Ag crystals, 100-180 nm diam, are deposited on the Si wafer surface in the form of island-like structures. However, in Fig. 8b it is apparent that the density of Ag nuclei considerably increased both in number and size when the substrate is PS. These results show that much more metal plating occurs on the porous surface compared to that on the Si wafer. In other words, metal deposition proceeds very differently on bare Si and PS surfaces.

Metal deposition by immersion plating takes place at the opencircuit potential (OCP, no current) of the substrate upon dipping in



Figure 7. Schematic representation of the mechanism of metal deposition onto PS substrate during the immersion plating.

the plating bath. Since the rest potential is dependent on the electrolyte composition and the surface reactivity of the electrode material, the measurements of the rest potential may provide good information concerning the different deposition behaviors between PS and Si electrodes. We measured the rest potential of both substrates immersed in 0.01 M (CF₃SO₃)₂Cu and 0.01 M AgClO₄-MeOH solutions. The results are shown in Table IV. An inspection of the data shows that the rest potential of PS in both solutions has a more negative value (less noble potential) compared to that of Si wafers. Less noble potential obtained for the PS indicates the promotion of the anodic reaction, *i.e.*, the oxidation of PS. Historically, it has been noted since its discovery that PS layers are significantly more chemically reactive than bulk Si. Upon exposure to hot wet air or metal ion solutions, the freshly prepared PS samples are oxidized rapidly. The speed and extent toward oxidation is much higher compared to Si wafers.

According to these observations, the question arises as to understand the difference in rest potential values and why metal deposition is faster on PS than on Si surfaces under the same conditions. The different behaviors in the deposition between PS and Si wafers is unclear. A detailed interpretation of the observed results is difficult; however, some distinguishable points between the two surfaces can be outlined as follows: (*i*) PS differs from Si wafers by its high porosity (in this work 75-80%). (*ii*) The specific surface area of PS is known to be very large; of the order of 200 m²/cm³.⁴⁸ (*iii*) The presence of a great amount of silicon hydrides on PS surface. (*iv*) The depression of dopant; the dopant dissolves in HF solution dur-



(a)



Figure 8. Plan-view SEM micrographs of Ag deposits after 2 min immersion in 0.01 M AgClO₄-MeOH solutions on an (a, top) p-Si(100) wafer and (b, bottom) a PS substrate prepared on the same wafer type. The deposition was carried out under identical experimental conditions.

ing PS formation.^{49,50} (v) Quantum confinement caused by the nanometer-size structure in PS.

Since we treated the Si wafers with 5% HF solution prior to the immersion plating, the wafer surface is also terminated by hydrogen atoms. We expect no significant difference in the states of silicon hydrides between the two surfaces and consequently, this cannot be the direct reason for the rest potential shift. Our research group¹⁴ and others^{45,51} have observed no major difference in metal deposi-

Table IV	. Rest p	otentials	(V vs.	Ag/AgCl)	of PS	and Si	wafer	in
0.01 M o	f (CF ₃ S	O ₃) ₂ Cu a	nd Ag	gClO ₄ -Me	OH sol	utions. ^a	ı	

Metal ion solution	Substrate	Rest potential, V
Cu ion solution	PS	-0.20
	Si	-0.11
Ag ion solution	PS	-0.62
	Si	-0.02

^a 0.1 M tetra-*n*-butylammonium perchlorate was added as a supporting electrolyte.

tion when they used different types of dopant, and hence, the depression of dopant during the formation of PS in HF solution does not affect the deposition behavior. Thus, it is doubtful whether point (*iii*) or (*iv*) can interpret the results.

Based on this explanation, we tentatively attribute this difference to the different surfaces. The vast internal surface area of PS compared to that of Si wafer would increase the metal deposition reaction. Furthermore, the promotion of metal ion reduction usually occurs at defects on the surface, such as scratches or contamination area, 52,53 or at the more chemically active sites, such as kinks and steps.⁴⁵ Thus, the presence of pores may provide sufficient increase of metal deposition to the porous layer. Therefore, the difference in the deposition behavior is likely related to the different morphologies between the two surfaces. The different morphology affects the rest potential value and the potential directs the plating process. Much more effort is needed in this area before detailed understanding can be obtained.

Conclusions

Metal deposition onto PS by immersion plating from aqueous and nonaqueous solutions was investigated. Ag was deposited from all the aqueous solutions containing Ag⁺ while Cu deposition depends upon the type of salt used: CuSO₄ deposits Cu, CuCl₂ inhibits deposition, whereas no Cu was detected from $Cu(NO_3)_2$ aqueous solution. In nonaqueous solutions, Ag and Cu were deposited from the MeOH solution containing metal ions. On the contrary, no metal was detected from the MeCN solution of either Ag^+ or Cu^{2+} . The inhibition effect of CuCl₂ was also found in nonaqueous solution. Ni could not be deposited onto PS from its simple salts in neither aqueous nor nonaqueous solutions. The oxidation of PS occurs simultaneously with the deposition of metal. The different deposition behaviors are attributed to the different redox couples of each metal in solution. It is also related to the different rest potentials of PS in these solutions. The rest potential of PS in MeOH solution containing Ag⁺ or Cu²⁺ ions stays at less noble value, indicating the possibility of metal deposition, while the value in MeCN solution is the most positive, explaining the unfavorable metal deposition. Based on these results, we concluded that solution chemistry of metal ions determines the rest potential of PS and the rest potential directs metal deposition. Besides, a trace of residual water was found to affect the immersion plating behavior in nonaqueous solutions.

We have discussed the reaction mechanism for immersion plating. Metal is deposited on the PS by electrochemical displacement deposition. The oxidation of PS occurs simultaneously with the metal deposition. The whole deposition process proceeds by nucleation and growth. At prolonged immersion time, the growth proceeds via the local cell mechanism rather than the general corrosion type.

We have also observed that metal plating occurs at a much higher rate on the porous surface compared to that on the Si wafer. Further, the changes produced during the formation of PS lead to a shift in the rest potential of PS toward less noble direction. This potential shift indicates the promotion of anodic reaction and consequently, the metal ion reduction is enhanced. The difference in deposition behavior between PS and bare Si is likely related to the different morphologies of both surfaces. Much further work is needed in this area for complete understanding.

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