

Direct electroless nickel plating on silicon surface

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Abstract Direct electroless nickel plating on *n*-Si(100) wafers in alkaline solutions was demonstrated without any activation procedure in advance, the effect of pH and temperature of the solutions on size of metal particles in deposits was examined, and also the element contents of deposits were analyzed by energy disperse spectroscopy (EDS). The results indicated that the size of metal particles increases with increasing temperature or decreasing pH. The possible mechanism of nickel deposition on *n*-Si(100) was discussed in terms of semiconductor electrochemistry, and the formation of nickel seed crystal on Si was mainly attributed to the generation of atomic hydrogen by electron capture of water molecule from the semiconductor in alkaline solutions.

Keywords: single crystal silicon, electroless nickel plating, atomic hydrogen mechanism.

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With the development of microelectronic devices, the technology of chemical deposition of metals on silicon surfaces has been growing, recently there are a number of reports on applications of electroless plating to the preparation of nano-materials on silicon surfaces^[1–3], and to the ultralarge scale integration (ULSI) technology of integrated circuits (ICs) and microelectro-mechanical systems (MEMS)^[4]. The key step of electroless plating on silicon surface is to initiate the process, many activation procedures have been developed to trigger this process, such as sensitization in a solution of SnCl₂ followed by activation in a solution of PdCl₂^[5], Pd ion implantation^[6,7], or activation in a mixed solution consisting of HF with HNO₃ or HCl^[8–12]. Unfortunately, those procedures would bring about undesirable effects on fabrication of devices. It was found^[12] that electroless nickel plating could take place on silicon surface in alkaline solutions without any activation procedure in advance, however, the mechanism and feasible operation condition still need to be thoroughly investigated. In this work, direct electroless nickel plating on single crystal Si wafers in alkaline solutions was demonstrated, the effects of pH and temperature of plating solution on the size of metal particles in Ni deposits, and the mechanisms for initiating nickel deposition were discussed.

1 Experimental

Single crystal *n*-type Si(100) wafers (1.0×1.0 cm², 525±20 μm in thickness), with specific resistivity of 4–7 Ω·cm, from Silicon Materials Factory of Huajing Microelectronics Co. (Ltd.), Wuxi, were used as the substrates. Prior to electroless nickel-plating, the substrates were degreased with alcohol, soaked in 50% HNO₃ to remove impurity, finally washed with deionized water. After being pretreated, some of the *n*-Si wafers were sputtered with gold on one side by half for special use, and called partially Au-sputtered Si specimen.

The solution for electroless nickel plating was made up of NiSO₄·6H₂O 25 g·L⁻¹, NaH₂PO₂·H₂O 20 g·L⁻¹, sodium citrate Na₃C₆H₅O₇·2H₂O 20 g·L⁻¹, and anhydrous sodium acetate NaAc 5 g·L⁻¹, pH 8.0 and 10.0. The plating was carried out in a beaker of 250 mL without stirring, the temperatures were controlled at 60 and 80 °C, respectively, with an HH-S thermostatic water-bath.

Surface topography of the deposits was observed by a LEO field emission scanning electron microscope (LEO, German), and the composition of deposit (EDS) was measured by an INCA energy spectrometer (Oxford Instrument, Britain). The structure of deposit was analyzed by a D/MAX-RC X-ray powder diffractometer (RIGAKU, Japan), Cu-target Kα rays, tube voltage 40 kV, tube current 30 mA, graphite monochromator filtration, scanning rate 8°/min.

2 Results and discussion

(i) Electroless nickel plating on Si wafers in alkaline solutions. After cleaning treatment, *n*-Si wafers were put into nickel-plating solution immediately without any activation beforehand, then the electroless process takes place. Fig. 1 depicts the SEM images of the Ni-P deposits obtained at different pH and temperatures. As shown in Fig. 1(a), well-distributed spherical particles of 0.82 μm in average are dispersed on the surface under the condition of 80 °C, pH 10 and plating duration of 10 min, while the voids exist on the surface where Ni deposits have not yet covered. If plating was conducted at 60 °C, the particle size reduces to 0.34 μm (Fig. 1(b)), indicating that higher temperature is favorable to growth of particles. As the plating duration increases to 30 min, Si surface is fully covered with Ni deposits, the boundaries between grains reveal themselves clearly, and the particles are further extended to 1.86 μm at 80 °C, and to 1.33 μm at 60 °C, as shown in Fig. 1(c) and (d). The enlargement of particles with time is related not only to growth of single particle, but also to congregation of little ones (Fig. 1(e)). In the initial stage of chemical deposition, there are adequate sites for growth of particles on surface, so that the growing particles are relatively independent and disperse spherically with almost the same size. With the chemical deposition prolonged, however, the number of particles

ARTICLES

increases gradually, and it becomes inevitable for the particles to contact and to aggregate each other, which results in the deformation of spherical particles.

Changing pH value of solution has influence on the size of metal particles. It is found that the higher the pH value the smaller the particle size, which explains that the size of metal particles in Fig. 1(f) for pH 8.0 is larger than that in Fig. 1(a) for pH 10.0 by about 1.15 μm . This may be attributed to that higher pH of solution will facilitate oxidation of NaH_2PO_2 so that the rate of nucleation is raised and nucleation density on the surface becomes larger.

(ii) Reduction of nickel ions on silicon in the absence of NaH_2PO_2 . In order to explore the mechanism of direct electroless nickel-plating on silicon without pre-activation, the following experiment was designed. Put the cleaned silicon wafers in alkaline nickel plating solution without

NaH_2PO_2 , of which pH value was adjusted to 10.0 with NaOH and T set at 80 $^\circ\text{C}$, and several minutes later, particulate metallic nickel appears on the surface of silicon substrate, which is tentatively referred to as “reduced nickel” for differentiation from that formed in electroless plating. In the meanwhile, some bubble departs and rises from the surface. The hydrogen evolution reaction might occur at Si surface in hot alkaline solution, written as

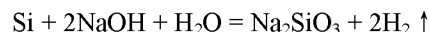


Figure 2 shows the SEM images of “reduced nickel” formed in the condition mentioned above, where many fine spherical particles were observed, of which the average size is about 0.27 μm , smaller obviously than that in Fig. 1(a) and (b). Furthermore, the deposits are present as numerous individual spherical particles rather than as a complete thin metal layer. These results demonstrate that

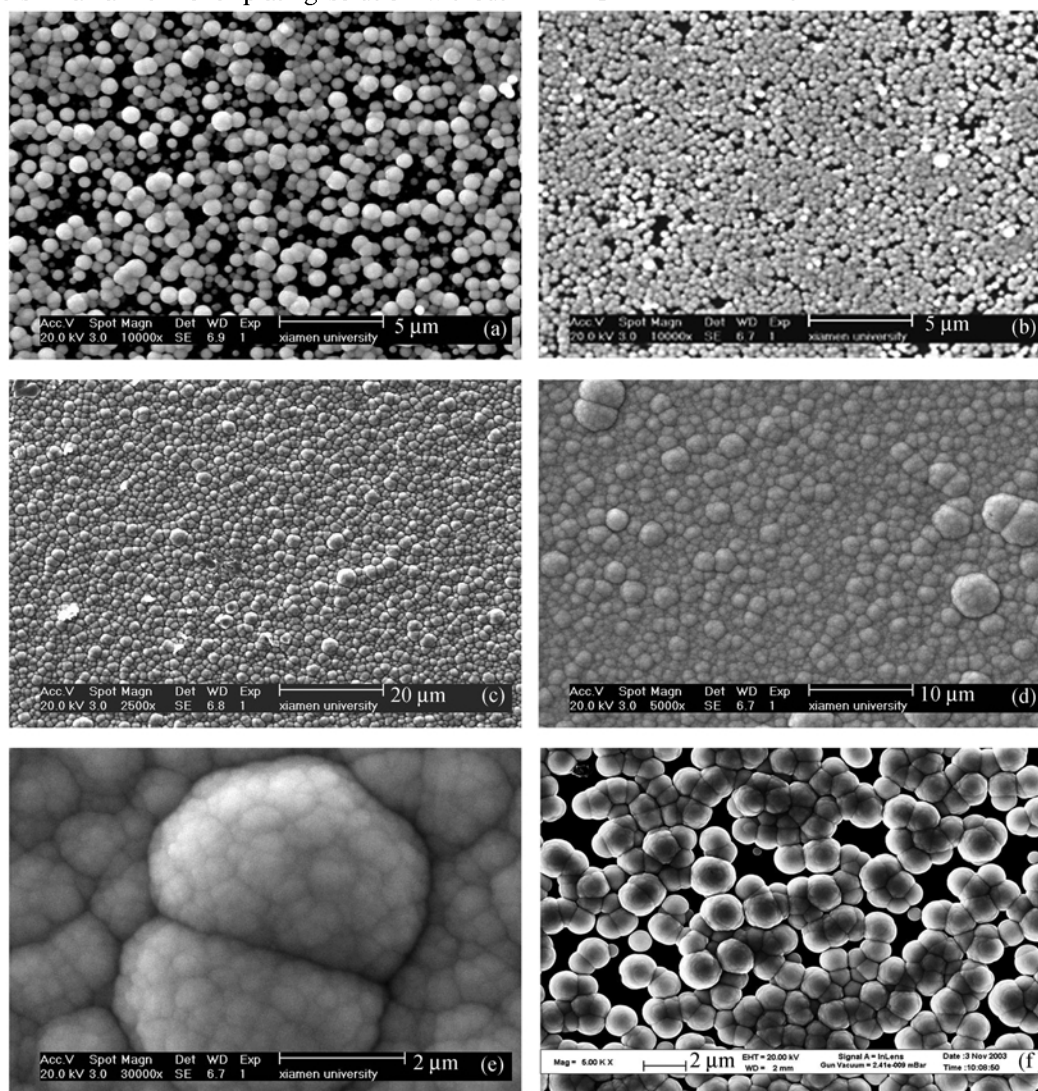


Fig. 1. SEM images of the deposits on silicon wafers. (a) $T = 80^\circ\text{C}$, pH 10.0, plating duration 10 min; particle size 0.82 μm , $\times 10.0$ K; (b) $T = 60^\circ\text{C}$, pH 10.0, 10 min; 0.34 μm , $\times 10.0$ K; (c) $T = 80^\circ\text{C}$, pH 10.0, 30 min; 1.86 μm , $\times 2.5$ K; (d) $T = 60^\circ\text{C}$, pH 10.0, 30 min; 1.33 μm , $\times 5.0$ K; (e) magnification of (d); $\times 30.0$ K; (f) $T = 80^\circ\text{C}$, pH 8.0, 10 min; 1.97 μm , $\times 5.0$ K.

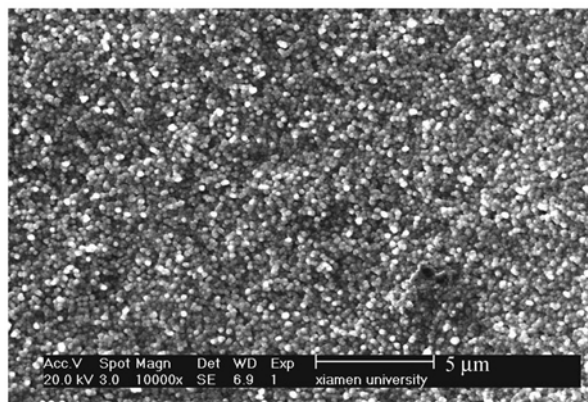


Fig. 2. SEM images of “reduced nickel” produced spontaneously on silicon in alkaline solution pH 10.0, at 80 °C for 30 min.

nickel ions could be spontaneously reduced on *n*-Si in alkaline solution and the resulting “reduced nickel” would provide the active catalytic centers for electroless Ni-P plating.

Table 1 lists the results of EDS of “reduced nickel” as well as electroless plating Ni-P alloy, for the former the content of Si is remarkable, associated with the fact that the surface of Si is not wholly covered with metallic nickel. On the other hand, element Si is not detected in the specimen of electroless plating Ni-P alloy, instead P (assigned from the band at 2.0 kV) and Ni exist, indicating that the deposit matrix fully covers the surface of Si substrate and the Ni-P layer is thick enough. From Table 1 it is also recognized that O is detected in “reduced nickel”, not in electroless plating Ni-P alloy, inferring that O exists in SiO₂ on the silicon surface.

It is noteworthy that analogous to the formation of “reduced nickel”, on the silicon surface without pre-activation “reduced copper” can be also deposited in alkaline electroless copper plating solution without reductant, implying that direct electroless copper plating on *n*-Si is feasible.

Table 1 The composition of “reduced nickel” and electroless plating Ni-P alloy

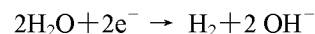
Deposit	Element	Weight percent	Atom percent
Reduced nickel	O	2.67	8.14
	Si	12.51	21.64
	Ni	84.82	70.22
Electroless ^{a)} plating Ni-P alloy	P	11.24	19.36
	Ni	88.76	80.64

a) Plating condition: pH 10.0, 60 °C, 30 min.

(iii) The mechanism for triggering direct electroless nickel plating on Si surface. There are various explanations for the formation of metallic nickel seeds on silicon surface. It was proposed^[9,11,13] that nickel reduction arises from the presence of Si-H on silicon, the argument for this is reasonable since the Si wafers used by those authors

were pretreated with HF solution, as a result, Si-H could be generated and the atomic hydrogen as reductant could reduce nickel ions into metal, in the literature the chemical deposition processes of metals are often interpreted based on the reducibility of atomic hydrogen. In this work, however, no HF is applied to pretreatment of Si surface so whether Si-H exists is in question. Takano and his co-workers^[12] considered that the main factor to initiate the metal deposition was the galvanic cell rather than Si-H, that is, Si was supposed to act as an anode to emit electrons, and the metallic nickel as cathode that was formed with nickel ions-captured electrons from Si as soon as the Si substrate was immersed into the solution. To test and verify the galvanic cell mechanism, we put the partially Au-spattered Si wafer into the alkaline nickel-plating solution without NaH₂PO₂. The results are shown in Fig. 3, where metallic nickel were simultaneously deposited on both bare and Au-spattered parts of Si surface. According to the galvanic cell mechanism the nickel deposition should occur only on the Au-spattered part but not on the bare silicon, and it is not the case. Therefore, we believe that as silicon is a semiconducting material, the reduction of nickel ions on Si should be discussed in terms of semiconductor electrochemistry.

Cattarin and his coworkers^[14] measured the flat-band potential of *n*-Si(100) in 2 mol·L⁻¹ NaOH as -1.15 V versus SCE (all the potentials below are referred to SCE). According to the relation of flat-band potential to pH value of solution^[15], namely negative shift of 2.303RT/F with increased per pH, the flat-band potential of *n*-Si(100) in pH 10.0 solution at 80 °C, in conformity with the condition in this work, is estimated to be about -0.95 V. If the conduction band edge is located at 0.15 eV over Fermi level, then the conduction and valence band edges are at -1.10 and 0.0 V, respectively. In the alkaline solution, the hydrogen evolution reaction can be written as



where the standard equilibrium potential is -1.07 V, and the equilibrium potential changes to -0.833 V in the solution of pH 10.0 at 80 °C. The oxidation-reduction potential of Ni₃(C₆H₅O₇)³⁺/Ni is about -0.67 V under the condition in this work, which can be calculated on the basis of Nernst equation^[16] and the stability constant of the complex $K=6.9$ ^[17]. Accordingly the energy level distribution of both solid and redox species in solution is shown in Fig. 4, from which it is concluded that both H₂O and Ni₃(C₆H₅O₇)³⁺ seem to be able to capture electrons from conduction band of *n*-Si, however, it is more favorable for the reaction of H₂O since the level for H₂O/H₂ system is more close to the conduction band edge. Therefore, the atomic hydrogen is probably produce on the Si surface. Here the emphasis is placed on thermodynamics of reaction on the semiconductor, aiming at clarifying the importance in pH control. If pH value is lowered, the energy overlap between the solid and redox species in solution

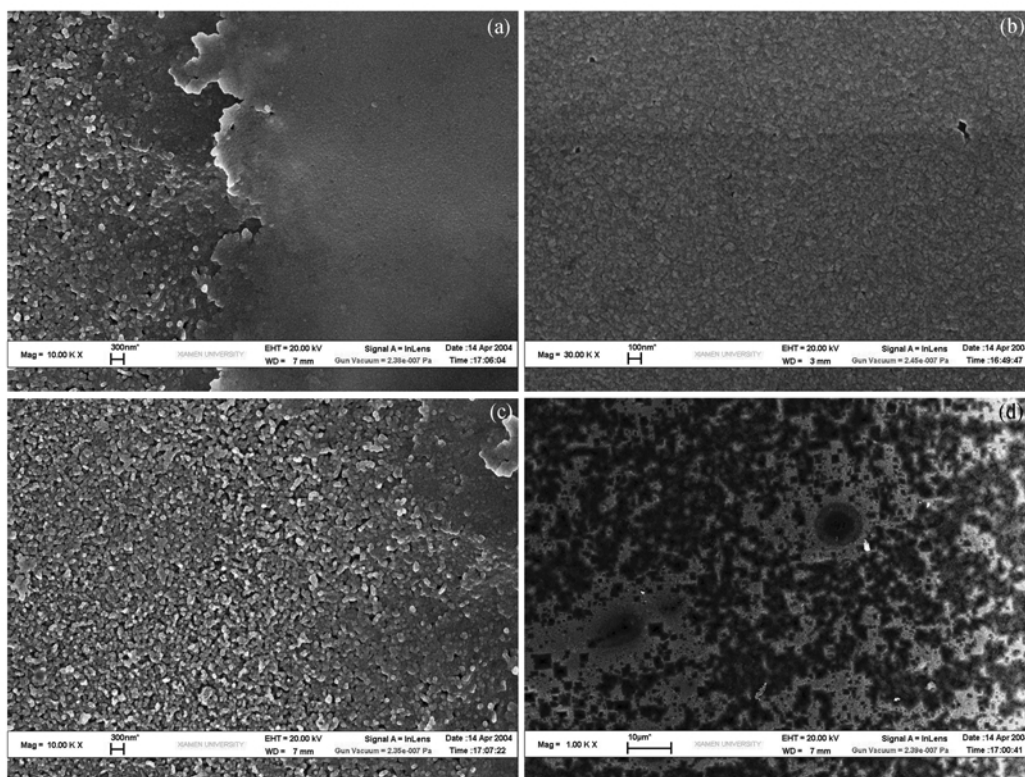
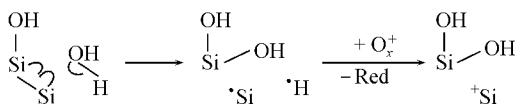


Fig. 3. SEM images of partially Au-spattered Si wafer before and after electroless nickel plating. (a) Before plating, Au-spattered section on right side and bare section of Si surface on left side; $\times 10.0$ K; (b) nickel deposits on Au-spattered section; 50 nm, $\times 30.0$ K; (c) nickel deposits on bare Si surface near the border between two sections; 100 nm, $\times 10.0$ K; (d) nickel deposits on bare Si surface far from the border; $\times 1.0$ K. Deposition conditions: pH 10.0, 80 °C, 30 min.

will change so that the formation of atomic hydrogen may not take place.

As for the kinetic aspects of atomic hydrogen generation, in the studies on etching and passivation of Si(100) in $2 \text{ mol} \cdot \text{L}^{-1}$ NaOH, Xia and his coworkers^[18,19] proposed that with OH^- ions being a catalyst, H_2O molecules will receive electrons easily from the conduction band of *n*-Si, and the formation of atomic hydrogen was presented as^[19]



SiO_2 is produced in the process.

It must be noted that the reduction of Ni^{2+} on *n*-Si and the triggering of electroless plating may occur in different ways, but the reduction by atomic hydrogen is the main path. Secondly, if there exist located electron levels on Si (i.e. surface state), Ni^{2+} ions may be reduced by electrons via the surface state. Once metallic nickel is deposited on silicon, the part of metal on the surface is negatively charged because the work function of *n*-Si is 4.0 eV and that of nickel 4.5 eV, thereby Ni^{2+} ions can be deposited on the part of metal by capturing electrons from sili-

con surface. In a similar way, the result shown in Fig. 3 can be well explained. The work function of Au is 4.8 eV, and Au is negatively charged when contacting *n*-Si, hence Ni^{2+} is reduced on Au. By this mechanism, the formation of multi-layer Ni can be also interpreted.

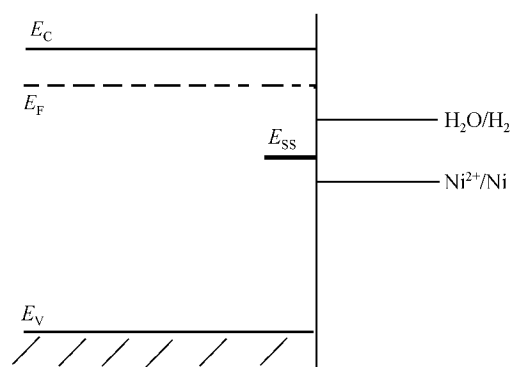


Fig. 4. Energy level distribution of *n*-Si surface and redox species in solution in a solution of pH 10.0 at 80°C.

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