Fabrication of Nickel Dots Using Selective Electroless Deposition on Silicon Wafer

Tetsuya Osaka,* Nao Takano, and Shinichi Komaba
Department of Applied Chemistry, School of Science and Engineering, Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Shinjuku-ku, Tokyo 169-8555

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The selective deposition of nickel on n-Si(100) wafer in aqueous solution was investigated. It was confirmed by cross-sectional FE-TEM examination that the deposition of nickel occurred from a solution of nickel ions prepared by excluding the hypophosphite reducing agent from the conventional electroless nickel plating bath, and that this deposition reaction accompanied the formation of SiO_2. This finding shows that the electrons needed to reduce the nickel ions to the metal are supplied directly from the Si wafer. By utilizing this galvanic displacement reaction, nickel metal in the form of minute dots measuring 1 μm in diameter was selectively deposited using a silicon oxide layer as the resist in combination with a two-step process, which consisted of the first step of immersing a Si wafer into a solution containing nickel ions but no reducing agent to form nuclei of nickel metal, and the second step of immersing the wafer with the nuclei into a conventional electroless nickel plating bath to cause the growth of the nuclei to the desired size.

In the semiconductor-device industry, attempts have been made to utilize the method of electroless deposition. In the past several years, filling via holes and trenches[1] have been attempted for producing ultra large scale integration (ULSI) interconnects.[2] In this case, there is a great potential of success with electroless deposition because of the simplicity and the via-hole filling ability of the electroless plating method. Furthermore, in our opinion, the fabrication of metal dots in the size of approximately 10 nm on Si wafer by electroless deposition will contribute to the realization of ultra high density (over 1 Tbits cm^{-2}) ROM devices. If the metal dots are fabricated with a ferromagnetic element such as Ni or Co, RAM devices should result.[3] In this future system, the read device of dot information for ROM and RAM will use electron beam and MFM (magnetic force microscope) tip systems, respectively.

Electroless metal deposition on Si wafer was investigated by several researchers.[1,4,5] Also, the deposition of metals on Si from impurities in solution was investigated with the aim of preventing it.[6,7] In these investigations, the metal deposition was proposed to accompany anodic oxidation of silicon.[6,7] In the present study, selective nickel deposition was tried to form nickel metal dots with the size of approximately 1 μmφ on Si wafer using a wet process of plating.

The substrates used were n-type Si(100) wafers (phosphorus-doped with a resistivity of 8 to 12 Ω cm, Shin-Etsu Handotai Co., Ltd.). The wafers were cut to 2 x 2 cm^2. For electroless deposition of nickel, three types of baths listed in Table 1 were employed. Bath A was a typical NiP electroless deposition bath,[8] operated at 80 °C and pH 8.0. The reducing agent, NaH_2PO_2, was absent in Baths B and C. Bath B contained sodium citrate as the complexing agent for Ni^{2+}, and $(NH_4)_2SO_4$ as the buffering agent. Bath C contained only $(NH_4)_2SO_4$ and no complexing agent. Baths B and C were both operated at the same condition as Bath A. Wafers were cleaned by the RCA method,[9] which is one of the standard cleaning procedures for Si wafers. After cleaning, these wafers were rinsed in distilled water with the resistivity of $1.5 \times 10^6 \sim 2.0 \times 10^6$ Ω cm, which was used in all stages of experiment, and then they were immersed in the various deposition baths. The catalyzation of Si wafer was performed, when necessary, by simple immersion for 10 s in aqueous $PdCl_2$ solution (0.1 g dm^{-3} of $PdCl_2$ in dilute HCl). All deposition experiments were performed on a class 100 clean bench. The 300 nm thick SiO_2 resist was formed by plasma CVD, and 1 μmφ dots were produced by reactive dry etching.

The samples were examined by a field emission transmission electron microscope (FE-TEM; Hitachi, Ltd., HF-2000) equipped with energy dispersive X-ray spectrometer (EDX; Kevex Instruments, Inc., Sigma) and a scanning electron microscope (SEM; Hitachi, Ltd., S-2500CX). The sample for cross sectional FE-TEM observation was prepared by a submicron-scale fabrication technique using a focused ion beam machine (FIB; Hitachi, Ltd., FB-2000A). An electron probe microanalyzer (EPMA; JEOL Ltd., JXA-8600) was used for elemental analysis of the deposits.

Table 1. Bath compositions and its operation conditions

Chemicals / mol dm^{-3}	Bath A	Bath B	Bath C
$NiSO_4 \cdot 6H_2O$	0.10	0.10	0.10
$NaH_2PO_2 \cdot H_2O$	0.15	–	–
$(NH_4)_2SO_4$	0.50	0.50	0.50
Sodium citrate	0.20	0.20	–

pH : 8.0 (Adjusted with NH_4OH).
Temperature : 80°C for all baths.

The nature of nickel deposition on Si wafer was first examined. The NiP[10] electroless plating was initially performed on a Si wafer with the catalyzation, but the NiP film obtained from Bath A easily peeled off. On the other hand, when plating was done without catalyzation, a more adherent metallic film deposited on the wafer. From these results, we conducted the electroless NiP plating on Si wafer without catalyzation.

In order to understand the initial deposition reaction of electroless NiP plating on Si without catalyzation, we prepared Baths B and C without adding the reducing agent of NaH_2PO_2. The deposition rate in Bath B was much slower than that in Bath A, but Ni deposition did clearly take place. In the case of Bath C, the quantity of Ni deposit obtained was clearly greater than that from Bath B. This result implies that the reduction of nickel ion is restrained by the complexing agent, i. e., citrate anion, which has a strong ability to coordinate with Ni^{2+}. The deposition of Ni was confirmed by using an EPMA.

In view of the results obtained with Baths B and C, it is apparent that the reaction of the initial Ni deposition from Bath A does not involve the reducing agent, NaH_2PO_2. After the initial stage, the NiP deposition in Bath A must proceed by the autocatalytic mechanism involving the reducing agent.

The cross section of a sample obtained from Bath C was examined by FE-TEM. The images are shown in Figure 1, in which the white area in the upper part of the image shows the carbon deposited for the conductivity of the sample surface. The gray area at the bottom portion of the image shows Si substrate, and the black area in the mid portion is Ni deposit. The sample was investigated by EDX, which confirmed the presence of the elements of Si, Ni, O, and C. A significant amount of oxygen was present between Si substrate and Ni deposit. The silicon oxide layer was clearly observed in Figure 1 with a thickness of *ca.* 20 nm. No silicon oxide was present before the immersion in Bath C, because the Si surface had been cleaned by the RCA process, which includes treatment with an aqueous solution of HF.

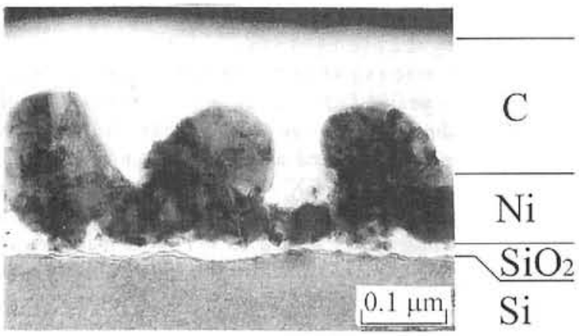

Figure 1. Cross sectional FE-TEM image of a sample obtained from Bath C.

Thus, it is apparent that the Ni deposition from the bath containing no reducing agent occurred by the mechanism of galvanic displacement accompanying the formation of silicon oxide. The deposition of copper metal on Si from a solution containing Cu^{2+} as an impurity is also known to take place as a result of galvanic displacement.[7]

In the Ni deposition by galvanic displacement, the electrons consumed for the reduction of nickel ions are supplied by the Si substrate. Therefore, the deposition of Ni is expected to occur on Si, and not on the silicon oxide. Based on this consideration, selective Ni deposition was performed by using a layer of thermal oxide of silicon as the resist. When Bath A containing the reducing agent was used for the selective deposition, the number density of NiP nuclei formed was small, and they grew in size to form patches or large particles of NiP on the surface. This nucleation-growth behavior is not compatible with the purpose of producing metal dots of minute geometry. The above observation indicates that in Bath A the growth of NiP occurs preferentially to the formation of new nuclei. On the other hand, it was found that the Ni nuclei formation occurred more easily and preferentially when the reducing agent was excluded (Bath C). Therefore, for the first step we employed Bath C to deposit nuclei on the Si surface. This step was performed by immersing a patterned Si wafer for five min. in the bath containing no reducing agent. Then, the wafer was transferred into the electroless bath (Bath A). Figure 2 shows the NiP dots measuring 1 µm in diameter produced by using the two-step process. The shape of the NiP dots shows that each dot consists of only a few particles of NiP. These results indicate that the formation of a grater number of nuclei would be necessary to produce dots even smaller than 1 µm in diameter.

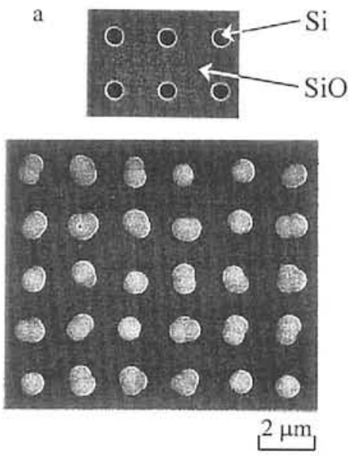

Figure 2. SEM images of: a) a substrate with a layer of thermal oxide of silicon as the resist before plating. b) selective nickel deposition on a).

In conclusion, minute nickel dots measuring 1 µm in diameter were clearly formed on Si wafer. To fabricate these nickel dots, a process consisting of two separate steps of nucleation and particle growth was utilized with success.

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10 When Bath A is used, phosphorus is included in the deposit because this bath contains NaH_2PO_2 as reducing agent. Therefore, we use the terms 'NiP' and 'Ni' to designate the deposits produced in Bath A, and C, respectively.