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Study of the initial stage of electroless Ni deposition on Si (100) substrates in aqueous alkaline solution

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Abstract

We investigated electroless nickel deposition in aqueous alkaline solution with and without conventional palladium catalyzation and found that nickel deposition was initiated and sustained on silicon substrates even without the palladium nuclei activation of the surface. But the resulting quality of the nickel film was not as good as the one with the prior activation. The reason was observably directed to the initial stage of the deposition processes. Nickel deposits nucleation on silicon surface was considered crucial for subsequent achievement of a well adhered, least damage influenced film. Effects of ammonia fluoride, nickel ion concentration and bath temperature in the aqueous nickel bath without reducing agent were studied over the nucleation results. The existence of fluorine ions in the solution increased the density of nickel nuclei particles and refined nickel particle sizes to the most extent, while concentrated nickel bath enhanced the nucleation as well. Consequently the improved quality of nickel film that was obtained from the electroless baths can be attributed to the fine and dense nickel particles formed in the initial stage by virtue of the fluorine ion, concentrated nickel ion and elevated temperature.

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1. Introduction

Among modern methods of Si manufacturing, wet processes such as electrodeposition and electroless deposition are attractive in mass-production of fine structures [1–4]. Practically, the electrodeposition technique is attracting a great attention in recent Cu interconnection technology, and various types of applications have been studied [1,5]. The electroless deposition technique is also notable in many aspects and is extensively applied in electronic circuitry fabrication [6,7]. In industry, applications of electroless plating are diverse, ranging from printed circuits to coating of plastics and ceramics. Electroless plating on Si has been used in ultra-large scale integration (ULSI) metallization [8–10], ohmic contact [11] etc. Electroless metal deposits are obtained by reduction of metal ions present in the solution by means of a chemical reducing agent that is also present in solution. However, previous activation of the surface is often necessary to obtain a good quality electroless deposits. Activation is usually achieved by depositing small amounts of Pd on the surface. Pd nuclei act as initiators of the following electroless deposition.

Nowadays production of nanostructures on Si wafer surfaces [12–14] is of potential request in the proceeding development of minute devices such as single electron transistors [15,16], patterned recording media [17–19], etc. Regarding metal deposition, it is both desirable and convenient for some applications to have a method that produces deposition on the sample without the need for an electrical contact, thus allowing deposition by simple immersion of the sample in a solution containing the appropriate metallic ions. Particularly, electroless metal deposition on Si wafer has been investigated by researchers recently, for instance, Pt, Au, Fe and Cu etc. In most of those studies for wafer-scale wet formation processes, the HF-containing electrolytes were frequently used [20–23]. We have been studying Ni deposition on Si by wet processes. In this work over open-circuit Ni deposition on Si, an alkaline aqueous solution was used instead since it was found that the deposition was negligibly slow in an acidic solution [24]. Ni deposition on Si wafer with and without conventional

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Table 1
Bath compositions of the first round experiments

Chemicals (mol/l)	Bath A	Bath B
$NiSO_4.6H_2O$	0.1	0.1
$NaH_2PO_2.H_2O$	0.15	0.15
Sodium citrate	0.2	0.2
$(NH_4)_2SO_4$	0.5	0.5
Ammonia	pH adjusted to 8	pH adjusted to 8
Sodium dodecyl sulfate	10 mg	10 mg
Prior Pd catalyzation	Yes	No

prior Pd activation was examined. And for the purpose of studying the initial stage of electroless Ni deposition on Si, the composition of the electroless deposition bath was adjusted so as to clarify the component participation in the deposition processes.

2. Experimental details

The substrates used were p-type Si (100) wafers (Boron doped with a resistivity of 10 ~ 20 Ω cm). The specimens were 1 × 1 cm square pieces cut out of the wafer. Prior to any further steps, the Si wafers must be cleaned first to remove all foreign matters from the surface of Si (dirt, scum, silicon dust, etc.). They were cleaned by APM ($H_2O/H_2O_2/NH_4OH = 5$ parts/1 part/1 part) followed by HF dip, which is one of the standard cleaning procedures for Si wafers [25]. First, APM was used to remove residual organic contamination left over from the solvent cleaning or any other previous processing. Then HF dip was used to remove the native Si oxide and thin oxide layer grown during the cleaning procedure. After cleaning, these wafer pieces were used in all stages of experiments in the prepared solutions.

For electroless deposition of Ni, two baths listed in Table 1 were employed in the first round of examination. They were the same baths (marked as A and B), but affiliated with and without prior catalyzing activation step. In principle, non-metallic materials are classified as extrinsically catalyzed materials. Usually for such substrates, those catalytically active nuclei of metal must be deposited on the surface prior to the following immersion in the electroless plating bath. Catalyzation of Si surface was performed simply by immersion in an aqueous $PdCl_2$ solution (0.1 ~ 0.5 g/l of $PdCl_2$ in dilute HCl with HF) [8,9] at room temperature for 1 min. Nevertheless, in order to examine the inherent nature of direct Ni deposition on Si surface, plating was done in the same bath without catalyzation. Temperature was set at 80 °C. Both bath A and B contained sodium citrate as the complexing agent for excess free Ni^{2+} to stabilize the solution and ammonium sulfate as the buffering agent for a longer term pH control. Surfactant worked as wetting agent to prevent hydrogen inclusion.

Table 2
Bath compositions of the second round experiments

Chemicals (mol/l)	Bath C	Bath D
$NiSO_4.6H_2O$	0.1	0.1
$NaH_2PO_2.H_2O$	–	–
Sodium citrate	–	–
$(NH_4)_2SO_4$	0.5	0.5
Ammonia	pH adjusted to 8	pH adjusted to 8
Sodium dodecyl sulfate	10 mg	10 mg
$(NH_4)F$	No	2.5

Table 3
Bath compositions of the third round experiments

Chemicals (mol/l)	Bath E	Bath F
$NiSO_4.6H_2O$	1.0	1.0
$(NH_4)_2SO_4$	0.5	0.5
Ammonia	pH adjusted to 8	pH adjusted to 8
Sodium dodecyl sulfate	10 mg	10 mg
$(NH_4)F$	2.5	2.5
Temperature	80 °C	60 °C

In the second round of inspection, it made us choose two types of solutions listed in Table 2 due to the interest in mechanistic study of initial Ni deposition behavior on Si with the absence of prior surface catalyzation. In bath C and D, the reducing agent, NaH_2PO_2 was excluded. Both bath C and D contained Ni ions and buffering agent but no complexing agent. Particularly, NH_4F was added to bath D. Both deposition experiments were performed without activation processes, again at 80 °C and pH was adjusted to 8.0.

In the third round of investigation, we increased the Ni salt concentration from 0.1 M to 1.0 M while other solution components remained the same as those in bath D. In bath E and F, the plating was conducted at 80 °C for E and at 60 °C for F, as highlighted in Table 3.

The deposited specimens were examined by using the scanning electron microscope (SEM; JOEL JSM 6360) equipped with an energy dispersive X-ray spectrometer (EDX; Kevex Instruments, Inc., Sigma). The cross-sectional observation of the electroless Ni deposits involved a metallographic sectioning followed by the inspection with SEM. The initial stage of deposition was also studied by atomic force microscope (AFM; Nanoscope II, Digital instruments, Inc.) since it offers a relatively simple and inexpensive means with nanometer resolution.

3. Results and discussion

3.1. Electroless Ni deposition on Si wafers with and without catalyzation

Conventional electroless Ni deposition provides a continuous build-up of metal coating on a substrate. If the substrates (usually non-metallic and some metallic) are not intrinsically catalytic, previous activation of the surface is needed by depositing a certain amount of Pd nuclei that initiates the following electroless Ni deposition. Now by immersion in bath A, electroless Ni was deposited over the catalyzed Si surface sites from reduction of metal ions in the solution by reducing agent that provides electrons. Fig. 1 shows the progress. On the other hand, without Pd activation as catalyzation, electroless Ni film was also formed on Si after immersion in bath B (same bath as A but no catalyzation step included). From the SEM images in Fig. 2, formation of Ni (P) deposits was confirmed on the uncatalyzed Si wafer surface after aqueous bath B treatment. Further in Fig. 3 we can see that Ni film formed in bath A with catalyzation was more adherent and continuous without evident cracks. In contrast, Ni film formed in bath B was easily