Self-Assembling Formation of Ni Nanodots on SiO₂ Induced by Remote H₂-plasma Treatment and Their Electrical Charging Characteristics

K. Makihara, K. Shimanoe, M. Ikeda, S. Higashi and S. Miyazaki

Graduate School of Advanced Sciences of Matter, Hiroshima University
Kagamiyama 1-3-1, Higashi-Hiroshima 739-8530, Japan
Phone: +81-824-24-7648, FAX: +81-824-22-7038, E-mail: semicon@hiroshima-u.ac.jp

1. Introduction
Charge storage in metal nanodots embedded into dielectric layers has received much attention because superior charge retention to semiconductor nanodots can be expected for metals with proper work functions [1]. For the nonvolatile memory application, the formation control of metal nanodots with good size uniformity and an areal density as high as $\sim 10^{12}$ cm$^{-2}$ in gate dielectrics is a crucial issue. So far, metal nanodots, including Au, Ag, Pt, W [2, 3] and Ni [4] have been applied to a floating gate in nonvolatile memories. To settle reliability issues, minimizing the thermal budget is of great importance because metal diffusion often occurs through the oxide [5].

In this work, we have demonstrated a new fabrication method of nanometer-scale Ni dots on SiO₂ from ultrathin Ni films by exposure to a remote hydrogen plasma. Electron charging to and discharging from the Ni nanodots have been studied by an AFM probe technique to confirm the electrical isolation among Ni nanodots.

2. Experimental
A ~1.3nm-thick SiO₂ was thermally-grown on p-Si(100) and treated by a dilute HF solution to terminate the surface with OH bonds. A ~1.3nm-thick Ni film was evaporated on the SiO₂ by electron beam without any extra heating. Subsequently, Ni films were exposed to a remote plasma of pure H₂ as schematically illustrated in Fig. 1. The plasma was generated in a quartz tube with a size of 10cm in diameter by inductively-coupling with an external single-turn antenna connected to 60MHz generator through a matching circuit. The substrate was placed on the susceptor at a distance of 32 cm away from the position of the antenna to minimize ion damages. For the remote H₂ plasma treatment, gas pressure and VHF power were changed in the range from 0.1 to 0.6 Torr and 100 to 350W, respectively, at room temperature. The exposure time to the remote H₂ plasma was kept constant at 5min. The dot density and size uniformity were evaluated by Atomic force microscopy (AFM). Also, Electron charging to and discharging from Ni nanodots so-prepared were carried out by scanning the sample surface with an electrically-biased AFM probe tip in a tapping mode at room temperature in clean room air, where a Rh-coated Si₃N₄ cantilever with a radius of tip apex of ~100nm was used. Before and after electron charging or discharging, the topographic and corresponding surface potential images were simultaneously taken with a non-contact Kelvin-probe mode.

3. Results and Discussion
AFM images for as-evaporated Ni films show a fairly smooth surface morphology with a root-mean-square roughness of 0.16nm and are almost identical to those for as-grown SiO₂ surface as shown in Fig. 2. By exposing the Ni films to the remote H₂ plasma under a gas pressure of 0.26 Torr with VHF powers of 350W at room temperature, the formation of Ni dots with an areal dot density of ~6.7x10¹¹ cm⁻² and an average dot height of ~2.0nm was clearly observed (Fig. 2(c)). It is likely that surface migration of Ni atoms is induced by atomic hydrogen and results in agglomeration with cohesive action. H₂ pressure dependence of Ni nanodot density at a VHF power of 350W is shown in Fig. 3. With decreasing the H₂ pressure down to 0.1 from 0.26 Torr, the dot density is decreased to 6.7x10¹¹ from 6.5x10¹⁰ cm⁻², and the increase in the pressure from 0.26 to 0.6 Torr causes a reduction in the dot density down to 8x10⁹ cm⁻². In the pressure region below 0.26 Torr, the generation of atomic hydrogen is likely to limit the dot nucleation density. The reduction of the dot density over 0.26 Torr suggests diffusion loss of atomic hydrogen before reaching the sample surface due to the increased collisions in gas phase. We have also evaluated the effect of VHF power on the dot density as represented in Fig. 4. In the case of remote H₂ plasma treatment with a VHF power of 100W, the Ni dot density was as low as 5.6x10⁸ cm⁻². By changing VHF power...
from 100 to 350W, the Ni dot density is markedly increased by a factor of 13.

To confirm electrical isolation among Ni nanodots so prepared, the surface potential changes due to electron injection to and extraction from Ni dots with ~2nm in height and an areal dots density as high as 6x10^11cm^-2 have been studied as shown in Fig. 5. When the surface is scanned with the AFM tip biased at -0.5V with respect to the substrate in the tapping mode, a distinct decrease in the surface potential of corresponding area, which is associated with electron injection to the dot, is observed but, in the unbiased area, no change in the surface potential is detectable. Subsequently by scanning with the tip biased at +0.5V in the central part of electron pre-injected region, the surface potential raises by almost double the change caused in electron injection, which makes the reverse contrast in the surface potential image as shown in Fig. 5 (b) and (c), indicating that Ni nanodots are separated electrically each other. No change in topographic images with electron injection and extraction was confirmed. The changes in the surface potential evaluated from surface potential images after applied various tip biases were summarized in Fig. 6. The tip bias dependence of surface potential change in a stepwise manner confirms multistep electron charging and discharging characteristics of Ni nanodots associated with the charging energy of Ni dot. Notice that, positively charged states occur even at a tip bias of 0V, which can be interpreted in terms of the work function difference between Ni and Rh.

Summary
The formation of Ni nanodots by the remote H_2 plasma treatment of ultrathin Ni films deposited on SiO_2 has been successfully demonstrated at room temperature. The Ni nanodot density can be controlled in the range from 10^9 to 10^12cm^-2 by changing the VHF power, the H_2 plasma pressure and the substrate temperature. This technique is very promising for low temperature fabrication of metal-based dots acting as charge storage nodes on the SiO_2.

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References