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Formation mechanism of metal nanodots induced by remote plasma exposure

KATSUNORI MAKIHARA*, KAZUHIRO SHIMANOE, AKIRA KAWANAMI,
MITSUHISA IKEDA, SEIICHIRO HIGASHI, SEIICHI MIYAZAKI
Graduate School of Advanced Sciences of Matter, Hiroshima University
Kagamiyama 1-3-1, Higashi-Hiroshima, 739-8530, Japan

We have demonstrated formation of Pt nanodots by remote H_2, He or Ar plasma treatments of ultrathin Pt films deposited on SiO_2 and studied the effect of remote H_2 plasma on the Pt nanodot formation in comparison with the results obtained with rare gas plasmas. The surface migration of Pt atoms induced by remote H_2 plasma is suppressed with Ar or He dilution. By exposing the Pt foil to remote plasma of pure H_2, the surface temperature was increased up to ~500 °C. The migration of Pt atoms is driven by local heating caused by the efficient recombination of atomic hydrogen on pure Pt surface.

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1. Introduction

The application of metal nanodots to a floating gate of MOS memories has been attracting much attention because of an advantage in charge storage characteristics reflecting metal work function and spin polarity [1-4]. In the floating gate memory application of metal nanodots, one of key issues is to minimize metal diffusion into a gate dielectric layer [5] which often degrades oxide reliability and causes a large variation in the memory window. So far, we have demonstrated the self-assembling formation of nanometer-scale metal (Ni, Pt and Pd) dots on thermally-grown SiO_2 with a fairly uniform size distribution and an areal density as high as ~10^{12} cm^{-2} by exposing ~2 nm thick metal films to remote H_2 plasma at room temperature [6-9].

In this work, to discuss a role of hydrogen radicals on the dot formation from metal films on SiO_2, we have studied the effect of Ar (or He) dilution of H_2 on metal nanodot formation.

2. Experimental

A ~3.8 nm-thick SiO_2 layer was thermally grown on a p-Si(100) substrate and treated with a dilute HF solution to terminate the surface with OH bonds. Approximately 2 nm thick Pt films were deposited on the SiO_2 by Ar sputtering at room temperature. Subsequently, Pt films were exposed to a remote plasma of pure H_2, Ar (or He) and their mixture with various ratios without external heating. The plasma was generated in a quartz tube with a diameter of 10 cm by inductive coupling with an external single-turn antenna connected to a 60 MHz generator through a matching circuit. The substrate was placed on the susceptor at a distance of 23 cm from the antenna to minimize ion damage. During the remote plasma exposure, gas pressure and VHF power were maintained 35 Pa and 350 W, respectively. Dot density and size uniformity were evaluated by AFM. For the evaluation of electrical charged states of prepared Pt dots, electron charging to and discharging from the Pt nanodots were carried out by scanning the sample surface with an electrically biased AFM probe tip in the tapping mode at room temperature in clean room air, where a Rh-coated Si_3N_4 cantilever with a tip apex radius of ~100 nm was used. Before and after the electron charging or discharging, topographic images and their corresponding surface potential images were simultaneously taken with a noncontact Kelvin-probe mode [10].

3. Results and discussion

Fig. 1 shows topographic images taken before and after remote plasma treatment to ~2 nm thick Pt film on the thermally-grown SiO_2 layer. An AFM image of the as-evaporated Pt film shows a fairly smooth surface with a root-mean-square roughness of ~0.16 nm which is almost identical to that of the as-grown SiO_2 surface (Fig. 1 (a)). After exposing the Pt film to remote H_2 plasma, the topographic image shows a significant difference from the results obtained by He plasma and Ar plasma treatments. In the case of H_2 plasma treatment, the formation of well-defined dots with an areal dot density as high as ~3.2×10^{11} cm^{-2} was confirmed. On the other hand, morphological changes induced by He and Ar remote plasma treatments were fairly limited to form smaller dots with a slightly higher dot density, which were not electrically separated from each other as described later. From the analysis of dot size distribution, for the case of

H_2 plasma treatment, the average height of Pt nanodots was larger by a factor of ~4-5 and size distribution was markedly broadened in comparison with the cases of He and Ar plasma treatments. The results suggest that the surface migration and agglomeration of Pt atoms were markedly enhanced by exposing to remote H_2 plasma in comparison to remote He and Ar plasma. Therefore, it is likely that atomic hydrogen on Pt surface plays an important role on the formation of Pt nanodots. Activation energy for surface migration of Pt atoms may also be reduced significantly by atomic hydrogen incident to Pt film surface. Notice that, in each of H_2 and rare gas plasma treatments with and without a metal mesh grid, which was connected to the ground and placed over the sample, almost no changes in the surface morphology and areal dot density were observed as shown in Fig. 2. This result suggests that the influence of ion bombardment on the agglomeration of metal atoms is negligible. To improve the controllability of the Pt nanodots formation, we have investigated the effect of the gas flow ratio between H_2 and He on the formation of Pt dots as shown in Figs. 3 and 4. The pseudo dot density and the size distribution were evaluated from the topographic images. With increasing He dilution, smaller dots with higher areal density were formed. As a result of such a significant increase in the dot density, the dot size uniformity is fairly improved with a shrinkage in the dot size. Also, a similar result was obtained for the case of H_2/Ar plasma. The result indicates that the surface migration of Pt atoms induced by remote H_2 plasma is suppressed with either He or Ar dilution.

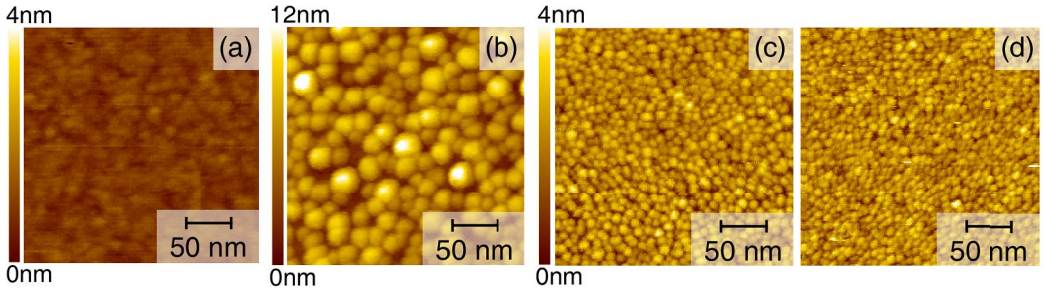

Fig. 1. AFM images of ultrathin Pt film deposited on HF-last SiO_2 (a), after exposed to remote H_2 plasma (b), remote He plasma (c) and remote Ar plasma (d) at VHF power of 350 W. Total gas pressure and substrate temperature were maintained at 35 Pa and RT, respectively.

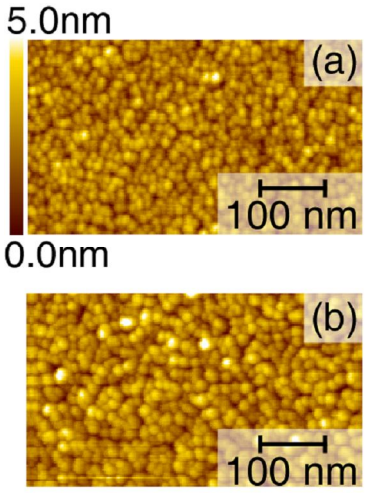

Fig. 2. AFM images of ultrathin Pt film deposited on HF-last SiO_2 after remote H_2 plasma exposure with (a) and without metal mesh grid (b). In this case, initial Pt film thickness was ~3.8 nm. VHF power and total gas pressure were maintained at 100 W and 13.3 Pa, respectively. A stainless mesh grid with 1 mm in gap, which was connected to the ground, was placed onto the sample at a distance of 10 mm away from the sample surface during the plasma treatments.

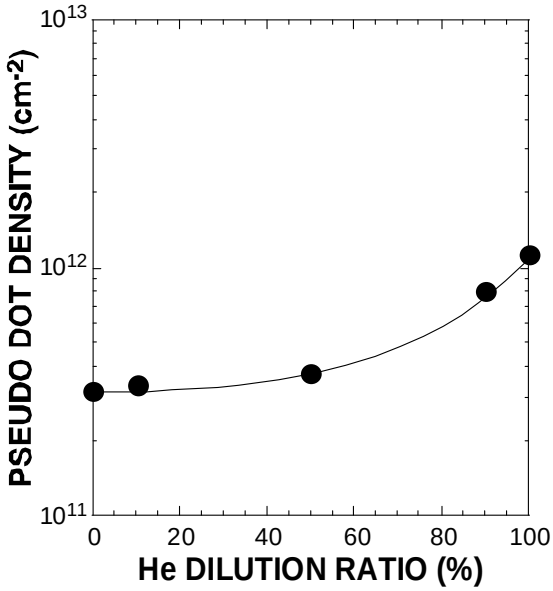

Fig. 3. Areal density of Pt nanodots induced by remote plasma of pure H_2 and He mixture gas at room temperature as a function of He dilution ratio. The VHF power during plasma generation was kept constant at 350 W.

To confirm electrical isolation among Pt nanodots induced by remote He, H_2 and their mixture gases, we investigated the surface potential changes caused by electron injection into the nanodots as shown in Fig. 5. In each case, uniform surface potential images were observed in initial state (Fig. 5 (a)). When the surface was scanned with an AFM tip biased at -2 V with respect to the substrate in the tapping mode, for the case of pure H_2 and the He dilution ratio below 50 %, a distinct decrease in the surface potential of the corresponding area, which is associated with electron injection into each dot, was observed (Fig. 5 (b)). These surface potential changes indicate the migration of Pt atoms in between the dots to reveal the SiO_2 surface. However, for the case of the dilution ratio over 50 % and pure He, no change in the surface potential was observable after the application of any tip biases to the surface, which indicates an electrically-conductive surface (Fig. 5 (c)).

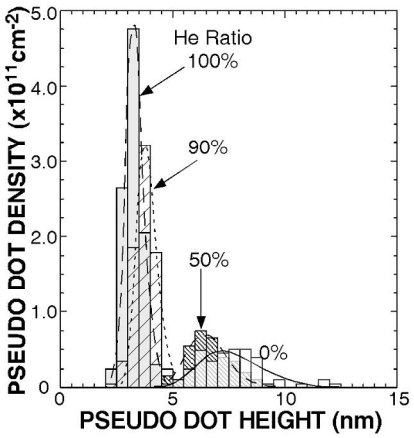

Fig. 4. The size distributions of Pt nanodots formed by remote H_2, Ar and He plasma treatments. The corresponding curves denote the log-normal functions well-fitted to the measured size distribution.

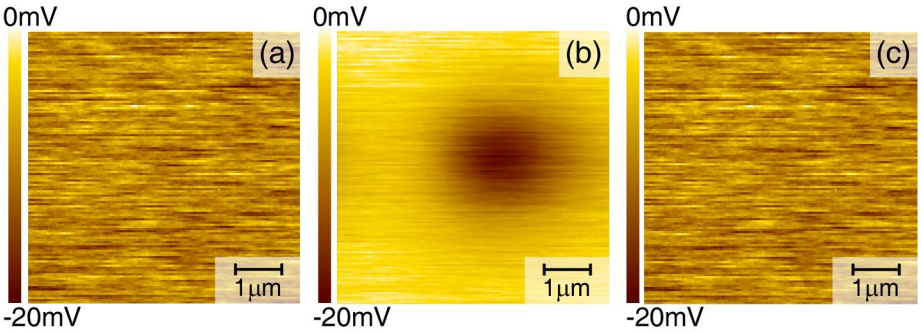

Fig. 5. Surface potential images measured in a Kelvin probe mode before (a) and after electron injection at tip biases of -2.0 V ((b) and (c)). Pt nanodots were induced by remote plasma of H_2 and He mixture gas with dilution ration of 50 % ((a) and (b)) and 90 % (c).

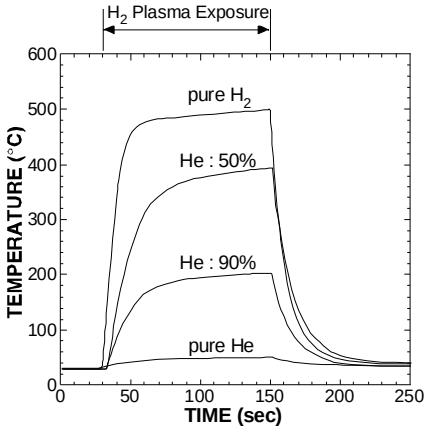

Fig. 6. Temperature changes of Pt foil during remote plasma exposure as a function of He dilution ratio. Temperature during remote plasma exposure was measured with a thermocouple covered with Pt foil.

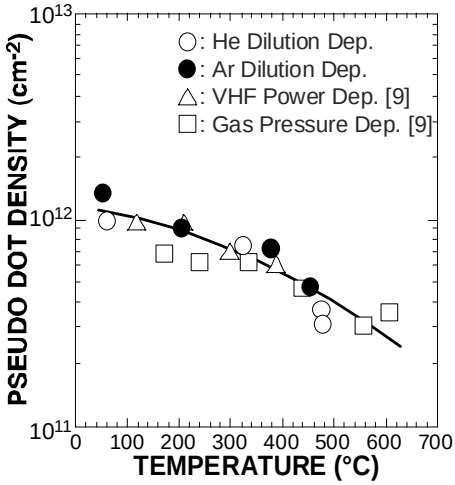

Fig. 7. Areal density of Pt nanodots induced by remote plasma treatment as a function of rare gas dilution ratio, VHF power and Gas pressure dependence during the H_2 plasma exposure [9].

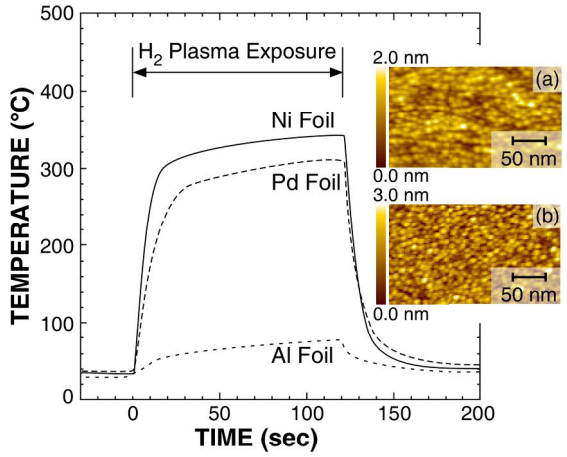

Fig. 8. Temperature changes of Ni, Pd and Al foils with remote H_2 plasma exposure. Insets show AFM images of Ni (a) and Pd nanodots (b) induced by remote H_2 plasma exposure at the same plasma condition. Areal dot densities of Ni and Pd nanodots are ~6.7×10^{11} and ~6.5×10^{11} cm^{-2}, respectively.

To get an insight into the surface migration of metal atoms enhanced by remote plasma exposure, a raise in the surface temperature was monitored during remote plasma exposure by using thermocouple covered with a Pt foil, 0.1 mm in thickness and 1x1 cm^2 in size, as shown in Fig. 6. By exposing the Pt foil to remote plasma of pure H_2, the surface temperature was increased up to ~500 ^oC. With increasing He dilution, the surface temperature rise was markedly decreased and, in pure He plasma, was ~50 ^oC at most. Since, in 500 ^oC annealing without plasma, the nanodot formation from 2nm-thick Pt film does not occur, it is likely that the migration of Pt atoms is driven by local heating caused by the efficient recombination of atomic hydrogen on pure Pt surface. Notice that a thermocouple covered with an Al foil with native oxide showed a surface temperature rise as low as ~50 ^oC during pure H_2 exposure with the same conditions. In addition, no changes in the surface micro roughness of Al film before and after remote H_2 plasma exposure were confirmed. When Pt nanodot densities are summarized as a function of the maximum temperature measured on the Pt foil during remote plasma treatment, it was found that the dot density depends only on the surface temperature as shown in Fig. 7. In Fig. 7, the results of ref. [9] were also included, where Pt dots were formed by remote pure H_2 plasma treatment with various gas pressure and VHF power at constant VHF power and gas pressure, respectively. With increasing the surface temperature from 50 to 500 $^\circ C$, Pt nanodots density was decreased gradually. Notice that, in H_2 plasma conditions where the surface temperatures raises higher than 350 $^\circ C$, the formation of electrically isolated Pt nanodots was confirmed. Considering these results, the observed dependence of the dot density on the temperature during the remote plasma exposure is determined by the fluence of atomic hydrogen on Pt surface. For the Ni and Pd foils with almost no native oxide, the temperature was increased up to ~350 $^\circ C$ as shown in Fig. 8. We also confirmed formation of Ni and Pd nanodots, which were electrically isolated, induced by remote H_2 plasma at the same plasma conditions as shown in inset of Fig. 8. This result indicates that the heat energy generated by surface recombination of atomic hydrogen incident on the clean meal surfaces play a role on the surface migration.

4. Conclusions

We have demonstrated a new technique to form high areal density metal nanodots on SiO_2, in which ultrathin metal films deposition on SiO_2 were exposed to remote H_2 plasma, and studied the effect of remote H_2 plasma on the metal nanodot formation and the influence of dilution of the plasma with rare gases. Topographic AFM images taken after the H_2 plasma treatment show a significant difference from the results obtained by Ar plasma and He plasma treatments. The temperature of the thermocouple covered with a Pt foil was markedly increased during remote H_2 plasma exposure in comparison with He and Ar plasma exposures. The result suggests that the local heating caused by surface recombination of atomic hydrogen incident on the clean meal surfaces plays a role on the surface migration.

Acknowledgements

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*Corresponding author: semicon@hiroshima-u.ac.jp