Control of Si Quantum Dot Nucleation by Remote Plasma Treatment

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1. Research Target

The application of Si quantum dots (Si-QDs) as a floating gate to MOSFETs has been attracting much attention because it will lead us to new functionality such as multivalued memory operations even at room temperature [1] or light emission. The growth control of nanometer-scale silicon dots with an areal density as high as ~ 10^{12} cm^{-2} on an ultrathin SiO_2 layer is a crucial factor for the multivalued capability of the Si dots floating gate MOS devices. In our previous work, we demonstrated the fabrication of nanometer-scale Si dots on ultrathin SiO_2 layers by controlling the early stages of low-pressure chemical vapor deposition (LPCVD) using a SiH_4 gas [2]. Also we reported that the SiO_2 surface treatment with a dilute HF solution is very effective to obtain dot density above ~10^{11} cm^{-2} because Si-OH bonds created on the SiO_2 surface act as reactive sites to precursors such as SiH_2 during LPCVD. In addition, by spatially controlling OH- termination on the SiO_2 surface before LPCVD, the selective growth of Si dots has been demonstrated [3]. In fabricating multiple stacked structures of Si dots in SiO_2, it is very necessary to control Si-OH bonds on the SiO_2 surface by a dry process matching with subsequent LPCVD.

In this work, we demonstrate the feasibility of remote H_2 and/or Ar plasma pretreatment for controlling the areal density of Si-QDs. Hydroxylation of the oxide surface, nucleation density and size distribution of Si-QDs as functions of plasma treatment conditions have been evaluated by Fourier transform infrared attenuated total refection (FT-IR-ATR) measurements and atomic force microscopy (AFM), respectively.

2. Research Results

The 4 nm-thick SiO_2 layer was first grown on n^+ Si(100) at 1000°C in dry O_2. The SiO_2 surface was treated with a remote plasma of pure H_2 and/or pure Ar. The plasma was generated by inductively-coupling external single-turn antenna, that is attached to a 10 cmϕ quartz tube and connected to a 60 MHz generator through a matching box. The substrate was placed on the susceptor at a distance of 32 cm away from the position of the antenna. The VHF power and the flow rate were kept constant at 200 W and 100 sccm, respectively. For the H_2 plasma treatment, the gas pressure was changed in the range of 0.1 - 1.0 Torr and the substrate temperature was varied from 27 to 540°C. The time of H_2 plasma treatment is fixed for 5 sec to avoid the reduction of SiO_2 and to minimize plasma damages. For the remote Ar plasma treatment, the VHF power, the gas pressure and the time of the treatment were kept constant at 100 W, 0.5 Torr and 30 sec, respectively. The formation of Si dots on as-grown and plasma treated SiO_2 was performed by LPCVD using pure monosilane at 540°C. During the deposition, the gas pressure was maintained at 0.2 Torr. AFM observations were carried out in air using a Rh - corted Si_3N_4 probe to assess the dot density and uniformity. The influence of chemical bonding of the oxide surface was examined by FT-IR ATR and XPS measurements.

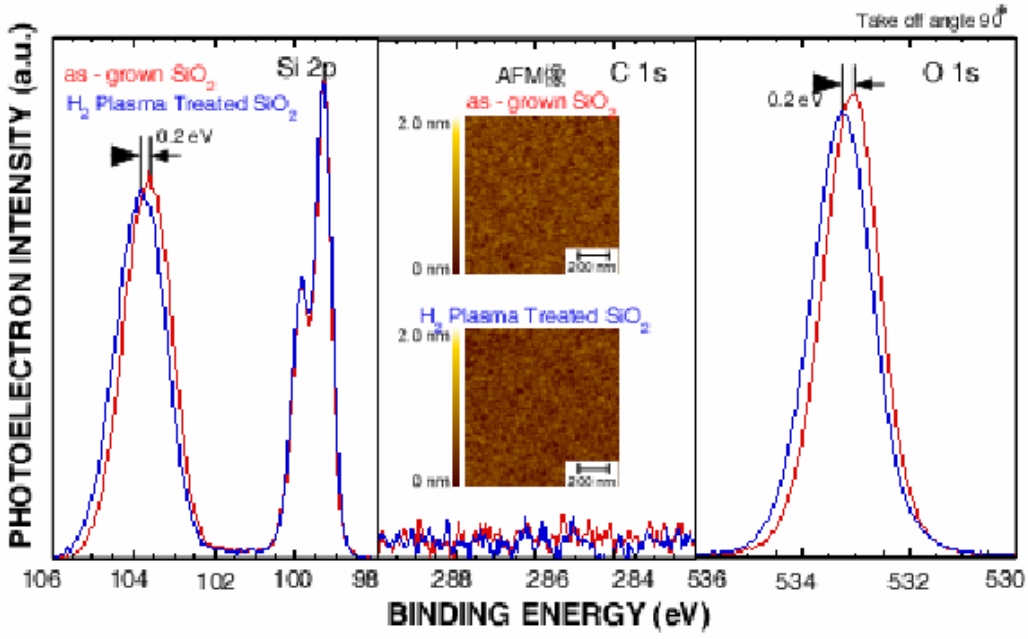

Fig. 1. Si2p, C1s and O1s spectra for the SiO_2 before and after remote H_2 plasma treatment at room temperature for 5 sec, which were taken at photoemission take-off angle of 90°.

Figure.1 shows the Si2p, C1s and O1s spectra for the SiO_2 before and after remote H_2 plasma treatment at room temperature for 5 sec. No significant spectral change in Si2p and O1s spectra and no C1s peak are observed before and after the plasma treatment. These results indicate that the SiO_2 is neither etched by H2 plasma, nor contaminated by carbon. The peak positions of chemically shifted Si2p and O1s signals due to the Si oxidation with respect to metallic Si2p signals from the Si substrate are slightly shifted toward higher biding energy side. This chemical shift can be interpreted as the increase in the component due to OH bonding units by H_2 plasma treatment.

Figure 2 shows AFM images taken after Si dot formation on as-grown SiO_2 and remote plasma treated SiO_2. In the case on as-grown SiO_2, the Si dot density of 6×10^8 cm^{-2} was obtained. When the SiO_2 surface is treated with H_2 plasma prior to LPCVD, the Si dot size is decreased and the density is markedly increased up to 7×10^{10} cm^{-2}. This implies the uniform nucleation of Si-QDs on the SiO_2 surface is enhanced by the remote H_2 plasma treatment. In order to confirm the change in surface bonding states by the plasma treatment, FT-IR-ATR measurement was performed. To avoid the influence of H_2O in the atmosphere, D_2 plasma treatment was used instead of H_2 plasma treatment. The FT-IR-ATR spectrum of the plasma-treated SiO_2 exhibits absorption bands centered at ~2400 and ~2500 cm^{-1}, indicating that the surface is terminated by OD bonds as shown in Fig. 3. From this result, the significant increase in dot density on remote plasma treated SiO_2 surface can be interpreted in terms of the OH termination of

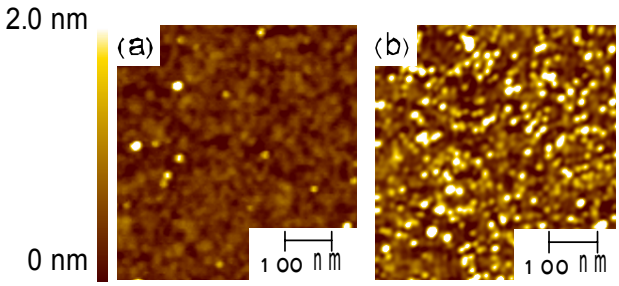

Fig. 2. AFM images of Si dots deposited on (a) as-grown SiO_2 and (b) remote H_2 plasma treated SiO_2.

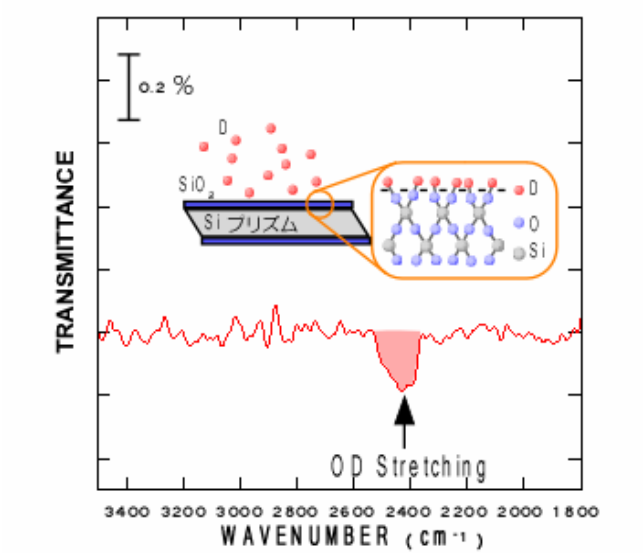

Fig. 3. FTIR-ATR spectrum of D_2 plasma treated SiO_2 on Si(100).

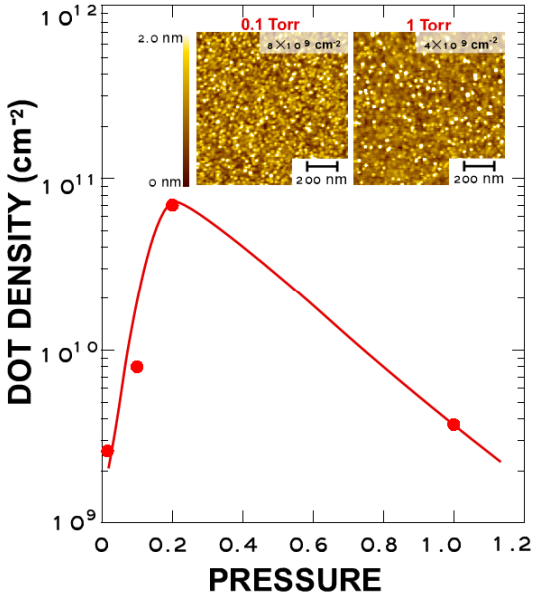

Fig. 4. Si dot density as a function of gas pressure during H_2 plasma treatment.

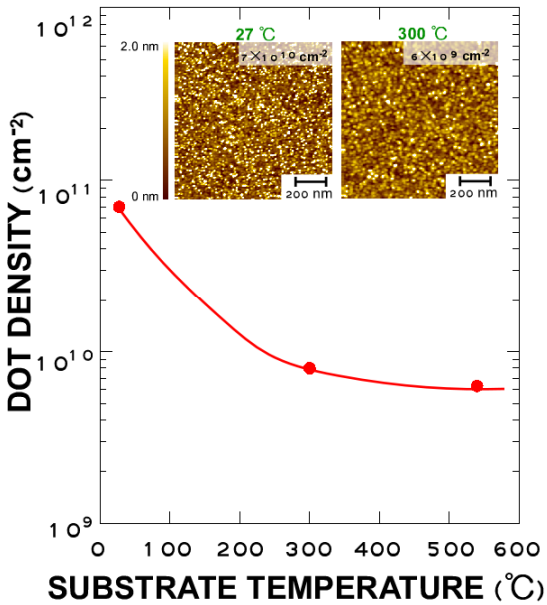

Fig. 5. Si dot density as a function of substrate temperature during H_2 plasma treatment.

the SiO_2 surface and resulting promotion of Si–QDs nucleation.

Then, we investigated the influence of gas pressure during the remote H_2 plasma treatments on Si dots density as shown in Fig. 4. The substrate temperature was kept constant at room temperature. We have observed increasing Si-QDs density with pressure up to 0.2 Torr, then it decreased with pressure. The most likely mechanism is that in the low pressure range, the nucleation is limited by hydrogen radical generation, while in the high pressure range, it is limited by radical diffusion.

Fig.5 shows the influence of substrate temperature during the remote H_2 plasma treatment on the Si-QDs density. The gas pressure was kept constant at 0.2 Torr. Consequently, the Si dots density continually decrease with temperature.

The size distribution of obtained Si dots evaluated from AFM images taken after Si-QDs formation on remote H_2 and/or Ar plasma treated SiO_2 can be fitted to a log-normal function [9] as indicated in Fig. 6. In order to enhance the nucleation density of Si-QDs by remote plasma treatment, Ar plasma, in which ion bombardment may give some effect on the nucleation site formation, was examined in combination with H_2 plasma. In the case of Si-QDs formation on remote Ar plasma treated SiO_2, the Si-QDs density is increased by a factor of 10 compared to the case without the treatment. Note that the H_2 plasma treatment subsequent to the Ar plasma treatment provides a very uniform formation of Si dots with an areal density as high as ~1×10^{11}cm^{-2}. It is likely that weaken bonds and dangling bonds created by Ar plasma exposure react efficiently with radicals, ions and excited molecules generated in H_2 plasma.

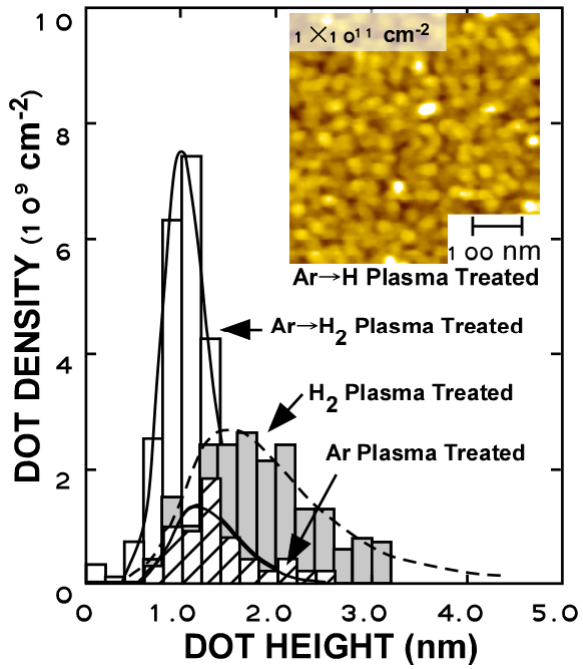

Fig. 5. Distribution of Si-QDs height formed by different pretreatment conditions measured by AFM.

References

[1] A. Kohno, H. Murakami, M. Ikeda, S. Miyazaki and M. Hirose, Jpn. J. Appl. Phys. 40 (2001) 721.

[2] S. Miyazaki, Y. Hamamoto, E. Yoshida, M. Ikeda and M. Hirose, Thin Solid Films 369 (2000) 55.

[3] S. Miyazaki, M. Ikeda, E. Yoshida, N. Shimizu and M. Hirose, Proc. of 25th Int. Conf. on.Phys. of Semicond, (Osaka, 2000) 373.

[4] R. R. Irani and C. F. Callis in Particle Size Measurement: Interpretation and Application, (Wiley, New York, 1963)

3. Summary

We demonstrated the control of the nucleation density of Si-QDs by remote H_2 and/or Ar plasma treatment. The density of Si dots was controlled from 6×10^9 to 7×10^{10} cm^{-2} by changing the substrate temperature and pressure at the remote H_2 plasma process. The combination of remote Ar plasma and subsequent H_2 plasma treatments is very effective to achieve a uniform size distribution of Si dots with an areal density of the order of 10^{11} cm^{-2}. These results imply control of Si-QDs nucleation sites utilizing remote plasma treatment is very promising for fabrication of multiple stacked dot structure of Si-QDs.

4. Future Research Plan

In order to realize stack structure of Si quantum dots, process technologies for not only dot formation, but also oxidation of dot surface at low temperature have to be developed. The final goal is to integrate these process technologies into the conventional MOSFETs fabrication and to demonstrate the new functionality in Si-QDs MOSFETs.

5. Published Papers and Patents

① Published Papers

1. K. Makihara Y. Okamoto, H. Nakagawa, H. Murakami, S. Higashi and S. Miyazaki, "Electrical characterization of Ge microcrystallites by atomic force microscopy using a conducting probe": Thin Solid Films 457 (2004)103-108.

② Proceedings

1. K. Makihara, Y. Okamoto, H. Nakagawa, H. Murakami, S. Higashi and S. Miyazaki, "Electrical Characterization of Ge Microcrystallites by Atomic Force Microscopy Using a Conducting Probe" SPSM-16. (2003.) B6-3, p115
2. K. Makihara, Y. Okamoto, H. Nakagawa, M. Ikeda, H. Murakami and S. Miyazaki "Local characterization of electronic transport in microcrystalline germanium thin films by atomic force microscopy using a conducting probe" AWAD2003. (2003). p37
3. K.Makihara, H.Deki, H. Murakami, S.Higasi and S.Miyazaki "Control of the Nucleation Density of Si Quantum Dots by Remote Hydrogen Plasma Treatment" ICSFS to be published.

4. K.Makihara, Y.Okamoto, H. Murakami, S.Higasi and S.Miyazaki “Characterization of germanium nanocrystallites grown on quartz by a conductive AFM probe technique” AWAD 2004 to be published.

③ Patents

1. S. Miyazaki and S. Higashi, Japan Patent Application Number: 2004-091328, “Quantum Dot MOSFET, Memory Device, Photo-Sensor and Their Integrated Circuits”.

④ Other Publications

1. K. Makihara, K. Takeuchi, M. Ikeda, H. Murakami and S. Miyazaki, The 20h Symposium on Plasma Processing p. 321.
2. K. Makihara, K. Takeuchi, M. Ikeda, H. Murakami and S. Miyazaki, The Japan Society of Applied Physics (The 50th spring meeting, 2003) No2, p975
3. K. Makihara, Y. Okamoto, H. Murakami, S. Higashi and S. Miyazaki, The Japan Society of Applied Physics (The 64th Autumn meeting, 2003) No2, p402
4. K. Makihara, T. Sibaguchi, H. Murakami, S. Higashi and S. Miyazaki, The Japan Society of Applied Physics (The 51st spring meeting, 2004) No2, p839
5. K. Makihara, H. Deki, H. Murakami, S. Higashi and S. Miyazaki, The Japan Society of Applied Physics (The 51st spring meeting, 2004) No2, p853