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Improvement in SiO_2 Film Properties Formed by Sputtering Method at 150 °C

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The quantity of hysteresis phenomena in capacitance response for metal–oxide–semiconductor (MOS) capacitors with 100-nm-thick SiO_2 films formed by the sputtering method was reduced by remote oxygen plasma treatment followed by high-pressure H_2O vapor heat treatment at 150 °C. In order to determine the quantity of hysteresis phenomena in capacitance response, we defined hysteresis charge as the difference in fixed oxide charge density for round bias voltage application. As-fabricated MOS capacitor samples had a high density of hysteresis charges of 1.0×10^{12} cm^{-2}. The density of hysteresis charge was not decreased by 4.7×10^5-Pa-H_2O-vapor heat treatment at 150 °C for 3 h. On the other hand, it was markedly reduced to 1.0×10^{11} cm^{-2} by 13.56-MHz-radio frequency remote oxygen plasma treatment at 300 W and 150 °C followed by 4.7×10^5-Pa-H_2O-vapor heat treatment at 150 °C for 3 h. Hysteresis phenomena are probably caused by a temporal electron charging up of SiO_2 films. [DOI: 10.1143/JJAP.47.8003]

KEYWORDS: MOS capacitor, hysteresis, remote plasma, high-pressure H_2O vapor

1. Introduction

Defect reduction for a SiO_2 gate insulator is important for the low-temperature fabrication of polycrystalline silicon thin-film transistors (poly-Si TFTs) because the characteristics of poly-Si TFTs strongly depend on the properties of the SiO_2 films and SiO_2/Si interfaces.[1–3] Plasma-enhanced chemical vapor deposition (PECVD) using tetraethylorthosilicate (TEOS) and sputtering methods have been developed for the formation of SiO_2 films at low temperatures.[4–7] It is a serious problem that transfer characteristics can depend on gate voltage application rates or gate voltage application directions. Hysteresis phenomena can be observed in transfer characteristics when the gate voltage is round-applied. Threshold voltage can be changed by adjusting the rate of gate voltage application. Those phenomena give a low reliability of electrical circuits formed by poly-Si TFTs. If there is a completely thermal equilibrium condition of electron energy states between gate oxide and silicon channel regions, transfer characteristics do not depend on the rate and direction of gate voltage application. Non-equilibrium charge transfer will give hysteresis phenomena in transfer characteristics. We have developed a high-pressure H_2O vapor heat treatment for reducing densities of defect states in SiO_2 and the SiO_2/Si interface.[8–12] We also previously reported that high-pressure H_2O vapor heat treatment at 260 °C effectively reduces the density of defect states and the quantity of hysteresis phenomena in capacitance response for metal–oxide–semiconductor (MOS) capacitors formed using SiO_2 films prepared by the sputtering method.[13] However, high-pressure H_2O vapor heat treatment has not been effective in reducing the quantity of hysteresis phenomena at a processing temperature lower than 200 °C. In order to solve this problem, we introduce remote oxygen plasma treatment to reduce the density of defect states causing hysteresis phenomena. In this paper, we report reduction of hysteresis phenomena in capacitance response for MOS using SiO_2 films formed by the sputtering method using a combination of remote oxygen plasma treatment with high-pressure-H_2O-vapor heat treatment at 150 °C.

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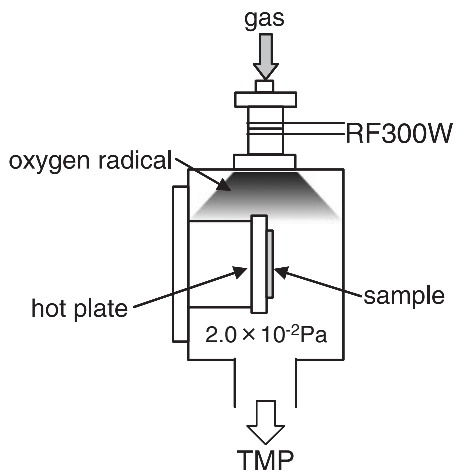

Fig. 1. Schematic apparatus of induction coupled remote plasma equipment.

2. Experimental Procedure

100-nm-thick SiO_2 films were formed on p-type single-crystalline silicon substrates by the sputtering method with argon (Ar) and oxygen (O_2) gases at a flow rate of 10 sccm for each gas at a pressure of 1.0 Pa and a 13.56 MHz radio frequency (RF) power of 1.0 kW. The samples were treated with remote oxygen plasma. Figure 1 shows a schematic apparatus of the induction coupled remote plasma equipment. The chamber was evacuated to a pressure of 1.0×10^{-4} Pa. The sample was heated to 150 °C with a hot plate. O_2 gas at a flow rate of 2.0 sccm was introduced. The pressure was 2.0×10^{-2} Pa. The sample was treated with the induction coupled remote oxygen plasma at 300 W of RF power for 30, 90, and 180 min. After the remote oxygen plasma treatment, aluminum electrodes were formed on the SiO_2 films with an area of 0.01 cm^2 in order to fabricate MOS capacitors. The samples were subsequently heated at 150 °C with 4.7×10^5 Pa H_2O vapor for 3 h. Some samples were only annealed with 1.3×10^6 Pa H_2O vapor at 260 °C for 3 h for comparison. Capacitance response at a frequency of 1 MHz (C–V) was measured. In order to investigate hysteresis properties, bias voltage was round-applied between −10 and 1 V with different voltage application durations.

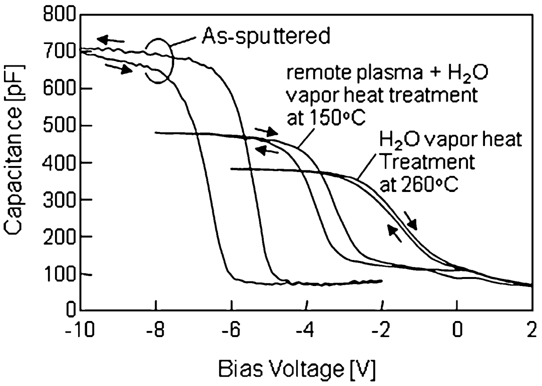

Fig. 2. Capacitance response as a function of bias voltage. The round bias voltage application took 80 s for as-sputtered MOS capacitor, treated with remote oxygen plasma for 180 min followed by high-pressure H_2O vapor heat treatment.

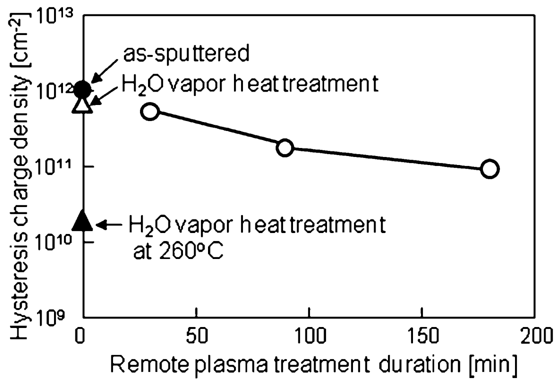

Fig. 3. Hysteresis charge density as a function of remote plasma treatment duration for the C–V measurement in the case of round bias voltage application for 80 s. The solid circle, open triangle and solid triangle present hysteresis charge densities for the as-sputtered sample, high-pressure H_2O vapor heat treatment alone at 150 and 260 °C.

3. Results and Discussion

Figure 2 shows capacitance response as a function of bias voltage (C–V curves). It took 80 s for the round bias voltage application. Although there was no change in the thickness of the SiO_2 films after each fabrication process, a high accumulation capacitance was observed for the as-sputtered sample. This result indicates that the as-sputtered sample had a high dielectric-dispersion characteristic in the low-frequency regime compared with the thermally grown SiO_2 film. On the other hand, we measured that the refractive index for the as-sputtered sample was 1.47 in the visible wavelength, which was almost the same as the thermally grown SiO_2 film. The high dielectric-dispersion characteristic would be caused by the no thermal stable state in Si–O bonding networks due to oxygen defects and distortion in SiO_2 film.[9] Accumulation capacitance was reduced by remote oxygen plasma treatment followed by high-pressure H_2O vapor heat treatment at 150 °C or high-pressure H_2O vapor heat treatment at 260 °C alone. This result indicates that the density of defect states in SiO_2 film was reduced by the remote oxygen plasma treatment and high-pressure H_2O vapor heat treatment. Moreover, substantial hysteresis phenomena were observed in capacitance response for the as-sputtered sample. The flat band voltage was −5.1 V for voltage application in the downward direction. It was −6.6 V for bias voltage application in the upward direction. On the other hand, remote oxygen plasma for 180 min followed by high-pressure H_2O vapor heat treatment at 150 °C reduced the quantitiy of hysteresis phenomena, as shown in Fig. 2. The flat band voltage was −3.7 V for voltage application in the downward direction. It was −3.4 V for bias voltage application in the upward direction. A similar result with almost no hysteresis phenomena was observed in the case of high-pressure H_2O vapor heat treatment at 260 °C alone, as shown in Fig. 2. The flat band voltage was −1.7 V in both bias voltage application directions. The charge density N_h causing hysteresis characteristics was estimated from the difference between the densities of the fixed oxide charge obtained by bias voltage application in the upward (↑) and downward (↓) directions as

$$N_h = |N_f(\downarrow) - N_f(\uparrow)| = \frac{C_{max}}{qS}|V_{fb}(\downarrow) - V_{fb}(\uparrow)|, \quad (1)$$

where N_f is the density of the fixed oxide charge, q is the elemental charge, V_{fb} and C_{max} are the flat-band voltage and the maximum capacitance, respectively. S is the area of the Al electrode of 0.01 cm^2. Figure 3 shows hysteresis charge density as a function of remote plasma treatment duration for C–V measurement in the case of round bias voltage application for 80 s. The as-fabricated MOS capacitor had a high hysteresis charge density of 1.0×10^{12} cm^{-2}. High-pressure H_2O vapor heat treatment at 150 °C alone resulted in a high hysteresis charge density of 7.0×10^{11} cm^{-2}. On the other hand, hysteresis charge density was markedly decreased to 9.0×10^{10} cm^{-2} with increasing remote oxygen plasma treatment duration from 30 to 180 min followed by high-pressure H_2O vapor heat treatment. Hysteresis charge density was gradually decreased with increasing remote oxygen plasma treatment duration and became close to that of the samples treated with high-pressure H_2O vapor heat treatment at 260 °C alone, as shown in Fig. 3. From these results, the combination of remote oxygen plasma treatment with high pressure H_2O vapor heat treatment was effective in reducing hysteresis charge density. Moreover we found that hysteresis charge density depends on the duration of round bias voltage application. Figure 4(a) shows hysteresis charge density as a function of round bias voltage application duration for the as-sputtered MOS capacitor, high-pressure H_2O vapor heat treatment and remote oxygen plasma treatment for 180 min followed by high-pressure H_2O vapor heat treatment. The as-sputtered MOS capacitor had a high hysteresis charge density of 1.0×10^{12} cm^{-2} for an 8 s round bias voltage application duration. Its hysteresis charge density hardly depended on round bias voltage application duration up to 400 s. A high hysteresis charge density of 8×10^{11} cm^{-2} appeared for high-pressure H_2O vapor heat treatment at 150 °C alone for an 8 s round bias voltage application duration. It hardly depended on round bias voltage application duration. For the samples treated with remote oxygen plasma followed by high-pressure H_2O vapor heating, the hysteresis phenomenon was observed in C–V characteristics for an 8 s round bias voltage application. The hysteresis charge density was 3.0×10^{11} cm^{-2}. On the other hand, it markedly decreased below 1.0×10^{10} cm^{-2} for the round bias voltage application duration above 400 s, as shown in Fig. 4(a). The remote

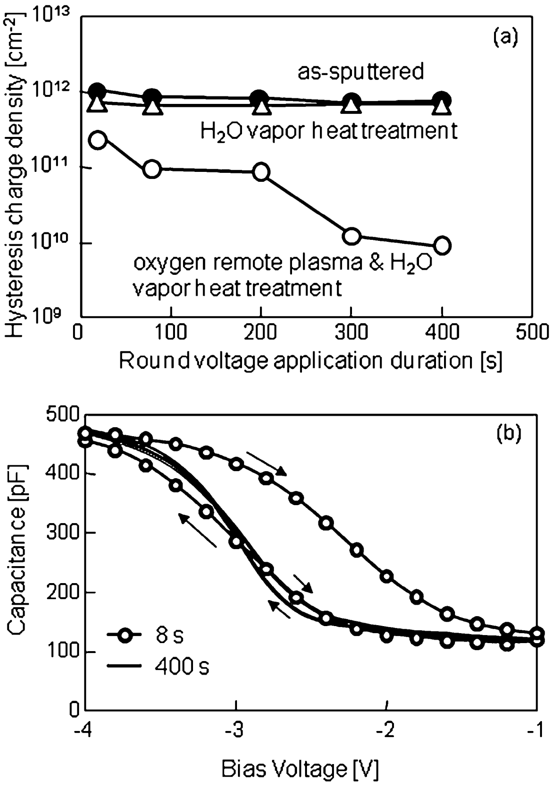

Fig. 4. Hysteresis charge density as a function of round voltage application duration (a) for as-sputtered MOS capacitor, high-pressure H_2O vapor heat treatment and remote plasma treatment for 180 min followed by high-pressure H_2O vapor heat treatment. Capacitance response as a function of bias voltage (b) for remote plasma treatment for 180 min followed by high-pressure H_2O vapor heat treatment for 8 and 400 s round bias voltage application durations.

plasma treatment followed by high pressure H_2O vapor heat treatment markedly reduced the quantity of hysteresis phenomena. Figure 4(b) shows that the *C–V* curves for the samples measured by round bias voltage application for more than 400 s were similar to the *C–V* curves for the samples measured by downward bias voltage application of 8 s bias voltage application duration. The SiO_2 films initially contained defect states trapping positive charges. The *C–V* curves therefore showed a large negative flat-band voltage, when bias voltage was applied downward, as shown in Fig. 4(b). On the other hand, the application of a large negative bias voltage during the *C–V* measurement probably caused electron injection from the Al electrodes. Electrons would be trapped at some trap sites, which are located at Al/SiO_2 interface thereby charging them up. Trapped electrons neutralize positive charged states at the Al/SiO_2 interface. *C–V* curves therefore shifted to the positive direction for upward bias voltage application, as shown in Fig. 4(b). If electron trapping were not stable, trapped electrons would be released with a certain time constant if there is no additional electron injection in the case of the positive bias application. Therefore, hysteresis charge density could change with bias voltage application duration, as shown in Figs. 4(a) and 4(b). We observed that the density of Si–H bonds markedly increased in the case of high-pressure H_2O vapor heat treatment at 150 °C alone using Fourier transform infrared spectroscopy. On the other hand, there is no increase in Si–H bonds in the cases of remote oxygen plasma followed by high-pressure H_2O vapor heat treatment at 150 °C or high pressure H_2O vapor heat treatment at 260 °C alone. We think that the hysteresis phenomena were mainly caused by the lack of oxygen atoms in the case of the as-sputtered sample, and it was caused by the presence of a high density of Si–H bonds in the case of high-pressure H_2O vapor heat treatment at 150 °C alone.

We also investigated other important parameters namely specific dielectric constant, fixed oxide charge density and density of interface traps. As-sputtered MOS capacitors had a high specific dielectric constant of 9.8, a high fixed oxide charge density of $2.8 \times 10^{12}\,cm^{-2}$ and a high density of interface trap of $2.5 \times 10^{12}\,cm^{-2}\,eV^{-1}$. High-pressure H_2O vapor heat treatment at 150 °C respectively reduced them to 4.7, $1.0 \times 10^{12}\,cm^{-2}$, and $2.0 \times 10^{11}\,cm^{-2}\,eV^{-1}$. The combination treatment of remote oxygen plasma for 180 min with high-pressure H_2O vapor heat treatment resulted in 5.1, $9.0 \times 10^{11}\,cm^{-2}$, and $1.8 \times 10^{11}\,cm^{-2}\,eV^{-1}$, respectively. They were similar to those for high-pressure H_2O vapor heat treatment at 150 °C alone. The remote oxygen plasma treatment had no important role in the reduction of specific dielectric constant, fixed oxide charge density or density of interface trap, compared with high-pressure H_2O vapor heat treatment. In addition, we evaluated the tangent theta calculated from the resistance and reactance of *C–V* measurement. The single-crystalline silicon substrate had a resistivity of 20 Ω·cm and a thickness of 525 µm. The tangent theta values in accumulation capacitance were from 66 to 71° for each fabrication process. We also measured current–voltage (*I–V*) characteristic. The as-sputtered MOS capacitor had a leakage current of $7 \times 10^{-7}\,A\,cm^{-2}$ at a bias voltage of 7 V. High-pressure H_2O vapor heat treatment at 150 °C alone reduced $5 \times 10^{-7}\,A\,cm^{-2}$ at 7 V. The combination of remote oxygen plasma treatment for 180 min with high-pressure H_2O vapor heat treatment further reduced this to $1 \times 10^{-8}\,A\,cm^{-2}$ at 7 V. From these results, the combination of remote oxygen plasma treatment with high-pressure H_2O vapor heat treatment is effective in improving SiO_2 films and reducing the leakage current. The present experimental results in Figs. 2–5 and the *I–V* characteristics indicate that there are two kinds of oxide charges in SiO_2 films. One is a fixed positive charge, which gives a negative flat-band voltage. The other one is a temporary charge, which gives a hysteresis phenomenon in *C–V* curves. High-pressure H_2O vapor treatment at 150 °C is not effective in reducing the density of oxide charge trapped states probably because of increase in the density of oxygen vacancies such as Si–H bonds. The present investigation revealed that remote oxygen plasma treatment effectively reduces oxygen defects and makes SiO_2 stable against post H_2O vapor heat treatment.

4. Conclusions

We investigated the improvement in the electrical properties of SiO_2 films at 150 °C. 100-nm-thick SiO_2 films were formed on p-type single crystalline silicon substrates by the sputtering method. The samples were treated with remote oxygen plasma induced by RF induction coupled plasma at 300 W at 2.0×10^{-2} Pa and 150 °C from 30 to 180 min. After the fabrication of MOS capacitors, the samples were subsequently heated at 150 °C with 4.7×10^5 Pa H_2O vapor

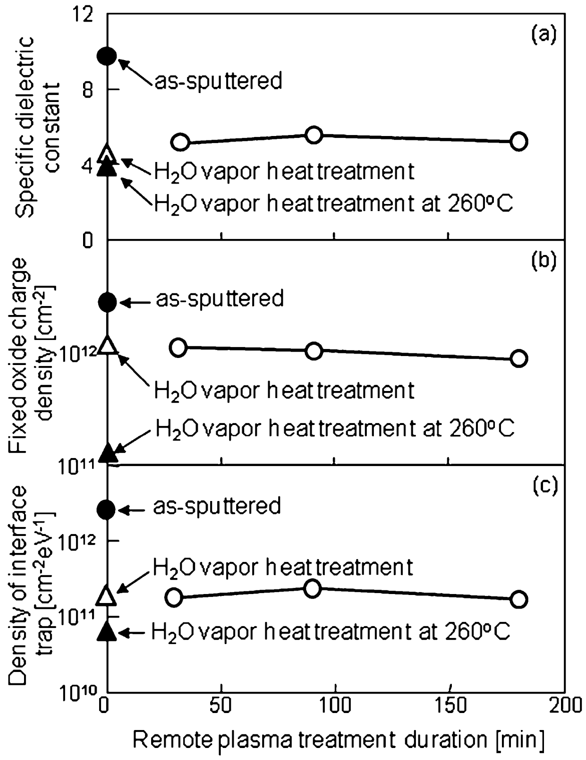

Fig. 5. Specific dielectric constant (a), fixed oxide charge density (b), and the density of interface trap (c) as a function of remote plasma treatment duration. The solid circle, open triangle and solid triangle present those values for the as-sputtered sample, and high-pressure H_2O vapor heat treatment alone at 150 and 260 °C.

for 3 h. *C–V* curves at a frequency of 1 MHz (*C–V*) were measured at a bias voltage between −10 and 1 V. The as-sputtered sample showed hysteresis phenomena, when the bias voltage was round-applied for 80 s and a hysteresis charge density of 1.0×10^{12} cm^{-2}. No reduction in hysteresis charge density was achieved by high-pressure H_2O vapor heat treatment at 150 °C alone. On the other hand, remote oxygen plasma treatment followed by high-pressure H_2O vapor heat treatment at 150 °C effectively reduced the density of hysteresis charges to 9×10^{10} cm^{-2}. A marked change in hysteresis charge density with bias voltage application duration suggests electron charge injection and the temporal trapping of electrons in SiO_2 films. Oxygen defects probably cause temporal electron trapping. Remote oxygen plasma effectively oxidized SiO_2 films and made it stable at 150 °C.

1) S. Higashi, D. Abe, Y. Hiroshima, K. Miyashita, T. Kawamura, S. Inoue, and T. Shimoda: Jpn. J. Appl. Phys. **41** (2002) 3646.
2) A. Kohno, T. Sameshima, N. Sano, M. Sekiya, and M. Hara: IEEE Trans. Electron Devices **42** (1995) 251.
3) K. M. Chang, W. C. Yang, and C. P. Tsai: IEEE Electron Device Lett. **24** (2003) 512.
4) C. S. Pai and C. P. Chang: J. Appl. Phys. **68** (1990) 793.
5) S. Nguyen, D. Dobuzinsky, D. Harmon, R. Gleason, and S. Fridmann: J. Electrochem. Soc. **137** (1990) 2209.
6) Y. Nishi, T. Funai, H. Izawa, T. Fujimoto, H. Morimoto, and M. Ishii: Jpn. J. Appl. Phys. **31** (1992) 4570.
7) J. Chae, E. Kim, Y. Jung, J. Kim, M. Yang, and C. Kim: Jpn. J. Appl. Phys. **43** (2004) 6937.
8) T. Sameshima and M. Satoh: Jpn. J. Appl. Phys. **36** (1997) L687.
9) K. Sakamoto and T. Sameshima: Jpn. J. Appl. Phys. **39** (2000) 2492.
10) T. Sameshima, K. Sakamoto, Y. Tsunoda, and T. Saitoh: Jpn. J. Appl. Phys. **37** (1998) L1452.
11) H. Watakabe and T. Sameshima: Jpn. J. Appl. Phys. **41** (2002) L974.
12) H. Watakabe and T. Sameshima: Proc. 1st Thin Film Materials and Devices Meet., Nara, 2004, p. 183.
13) Y. Urabe, T. Sameshima, K. Motai, and K. Ichimura: to be published in Proc. 4th Thin Film Materials and Devices Meet., Kyoto, 2007.