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The Superiority of N_2O Plasma Annealing over O_2 Plasma Annealing for Amorphous Tantalum Pentoxide (Ta_2O_5) Films

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As-deposited tantalum pentoxide (Ta_2O_5) films are amorphous. The films will remain amorphous after low-temperature O_2 or N_2O plasma annealing. High-temperature annealing will produce polycrystalline films where grain boundaries can generate leakage current. It was found that N_2O plasma annealing is superior to O_2 plasma annealing in terms of leakage current reduction. This can be easily explained by the lower energy required to break the nitrogen-oxygen bond in a N_2O molecule compared to the energy required to break the O=O bond in an O_2 molecule. We also observed that there is less Si contamination, which may lead to leakage current, in the sample with N_2O plasma annealing compared to the sample with O_2 plasma annealing.

KEYWORDS: tantalum pentoxide (Ta_2O_5), low-pressure metal-organic chemical vapour deposition (LPMOCVD), zero-bias thermally stimulated current (ZBTSC), leakage current, plasma annealing, defect states

1. Introduction

Tantalum pentoxide (Ta_2O_5) films, which have a dielectric constant of 20–25 as compared to a dielectric constant of 3.9 for SiO_2 or 7 for Si_3N_4, have demonstrated potential for use as dielectrics for charge storage in 1 Gb DRAMs.[1] However, Ta_2O_5 tends to leak to a far greater extent than SiO_2 or Si_3N_4. Quite frequently, a post-deposition annealing in an oxidizing ambient is required to reduce the leakage current. Sun and Chen[2–4] demonstrated that Ta_2O_5 films treated by N_2O rapid thermal annealing (RTA) are much less leaky than those treated by conventional O_2 RTA at an annealing temperature of about 800°C. We have confirmed these findings.[5,6] We have also explained the superiority of N_2O compared to O_2 by the lower energy required to break the nitrogen-oxygen bond in a N_2O molecule compared to the energy required to break the O=O bond in an O_2 molecule.[7] Recently, Sun and Chen demonstrated that N_2O furnace annealing is also superior to O_2 furnace annealing.[8] We expect that this finding can also be explained by the same theory. One important mechanism of leakage current is related to grain boundaries. High-temperature annealing tends to cause the as-deposited amorphous Ta_2O_5 film to crystallize into a polycrystalline film, resulting in leakage current due to grain boundaries. For example, Aoyama *et al.* observed that their polycrystalline Ta_2O_5 film after annealing at 700°C was more leaky than their amorphous Ta_2O_5 film after annealing at 650°C.[9] Hence, there is a demand to develop a lower-temperature annealing method in order to decrease the leakage current further. Park *et al.* demonstrated that N_2O plasma annealing is superior to high-temperature O_2 annealing for the reduction of the leakage current of Ta_2O_5 films.[10] Subsequently Kamiyama *et al.* demonstrated that low-temperature O_2 plasma annealing is superior to high-temperature O_2 annealing.[11] However, no comparison between N_2O plasma annealing and O_2 plasma annealing has been made. In this paper, we will demonstrate that N_2O plasma annealing is also superior to O_2 plasma annealing for the reduction of leakage current in Ta_2O_5 films. Previously, we have demonstrated that defect states in Ta_2O_5 can be detected by a novel zero-bias thermally stimulated current (ZBTSC) technique and the leakage current can be reduced by the reduction of defect states detected by ZBTSC.[12,13] A correlation with the defect state density has also been successfully made for N_2O plasma and O_2 plasma annealed samples.

2. Experimental

Ta_2O_5 films were deposited onto n^+–Si wafers by low-pressure metal-organic chemical vapour deposition (LPMOCVD) in a Lam Research DSM9800 system as reported previously.[14] For this study, the film thickness was about 15 nm. The samples were annealed by O_2 or N_2O plasma annealing at 350°C for 30 min. The plasma annealing was performed in a commercial plasma enhanced chemical vapour deposition (PECVD) chamber. The pressure was 0.45 Torr. The RF (13.56 MHz) power used was 100 W. Al dots (200 nm) with a diameter of 1 mm were evaporated through a shadow mask onto Ta_2O_5 inside an electron beam evaporator. With the surface covered by photoresist, the Ta_2O_5 film deposited on the backside of the wafer during the LPMOCVD process was then removed by chemical etching and Al was evaporated to form a back contact. The photoresist on the top surface was removed. Post-metallization annealing at 400°C was performed in a furnace tube for 5 min in pure nitrogen. Please note that previously we used post-metallization annealing at 400°C for 30 min in nitrogen to reduce the leakage current of relatively thick Ta_2O_5 films with a thickness of about 100 nm.[12] For relatively thin Ta_2O_5 films with a thickness of about 15 nm, the annealing time has to be reduced to only 5 min. The leakage current will be significantly higher for a longer annealing time. The defect states in the samples were characterized by ZBTSC technique previously developed by

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us.[12,13)]

3. Results and Discussion

As previously discussed, the interfacial SiO_x layer between Ta_2O_5 and Si is important because it can lower the capacitance of the Ta_2O_5 capacitor. With the help of cross-sectional transmission electron microscopy (XTEM), the interfacial oxide thickness was found to be about 2.5 nm for an as-deposited sample, a sample with N_2O plasma annealing and a sample with O_2 plasma annealing. No increase in the interfacial thickness due to the plasma annealing has been yet detected. However, a film was observed on top of the Ta_2O_5 film with O_2 plasma annealing. We believe that this film is a SiO_x film based on the experimental evidence discussed below. We observed that the capacitance of the sample with O_2 plasma annealing tends to be lower than that with N_2O plasma annealing by up to 20%. This is contradictory to our experience with high-temperature RTA; a sample with O_2 RTA tends to have higher capacitance compared to that with N_2O RTA.[7)]

The ZBTSC results are shown in Fig. 1. In O_2 plasma annealed films 2 peaks are observed, B and B'. B' is a weak peak and is deeper than B. It is presumed that shallower defect states contribute more to leakage current than deeper defect states so that defect B should be more important than B' for the control of the leakage current. It has been consistently observed that N_2O annealed films have significantly fewer defects B, as shown in Fig. 1. As shown in Figs. 2 and 3, the room temperature I–V characteristics of the samples with O_2 plasma annealing or N_2O plasma annealing show clearly that the leakage current of the sample with N_2O plasma annealing is significantly lower for both polarities of the bias voltage. This reduction of leakage current can be easily correlated with the lower density of B in samples with N_2O plasma annealing. Previously, we pointed out that defect B may be related to Si contamination.[6)] Figure 4 shows the secondary ion mass spectroscopy (SIMS) results for samples treated by O_2 plasma and N_2O plasma, respectively. The N_2O plasma annealed sample shows less Si contamination in the Ta_2O_5 film than the O_2 plasma annealed sample. Thus, the superiority of N_2O plasma annealing over O_2 plasma annealing can be explained by a lower density of shallow defect states related to Si contamination in Ta_2O_5 films treated by N_2O plasma annealing. An alternative explanation based on oxygen vacancies is also possible. Previously, we explained the superiority of N_2O RTA compared to O_2 RTA by the lower energy required to break the nitrogen-oxygen bond in a N_2O molecule compared to the energy required to break the O=O bond in an O_2 molecule.[7)] By the same logic, it is expected that N_2O plasma will have a stronger oxidizing power than O_2 plasma.

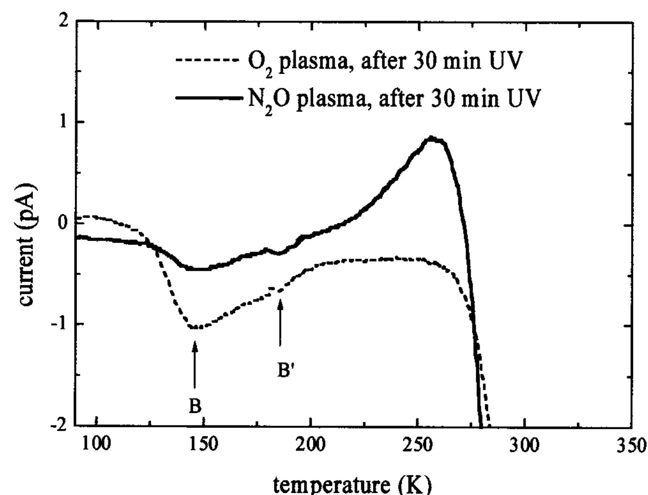

Fig. 1. The ZBTSC spectra of $Al/Ta_2O_5/n^+$–Si with N_2O plasma at 350°C for 30 min (solid line) and O_2 plasma at 350°C for 30 min (broken line). A post-metallization annealing at 400°C was performed in a furnace tube for 5 min in pure nitrogen.

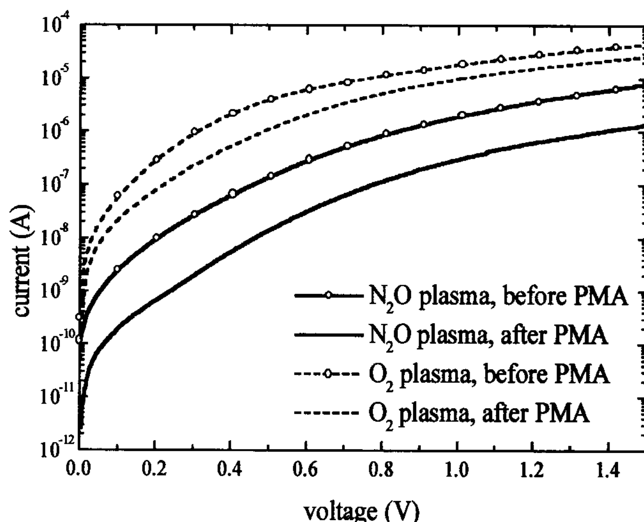

Fig. 2. The I–V characteristics of $Al/Ta_2O_5/n^+$–Si with O_2 plasma before post-metallization annealing (broken line with circle), with N_2O plasma before post-metallization annealing (solid line with circle), with O_2 plasma after post-metallization annealing (broken line), and with N_2O plasma after post-metallization annealing (solid line). Plasma annealing was performed at 350°C for 30 min. Post-metallization annealing at 400°C was performed in a furnace tube for 5 min in pure nitrogen. The polarity of the applied voltage was positive for the top Al contact.

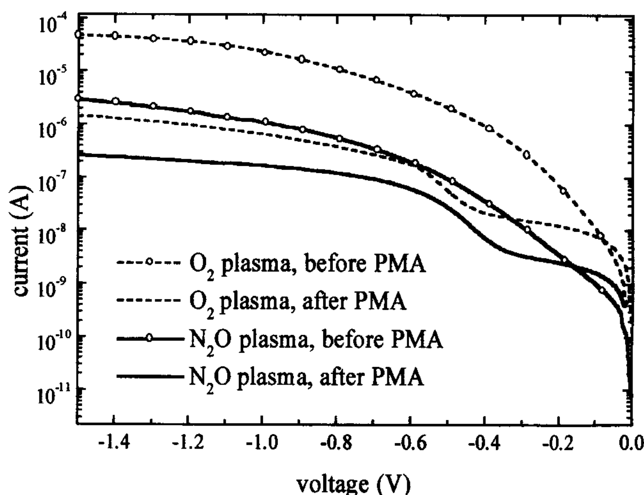

Fig. 3. The I–V characteristics of $Al/Ta_2O_5/n^+$–Si with O_2 plasma before post-metallization annealing (broken line with circle), with N_2O plasma before post-metallization annealing (solid line with circle), with O_2 plasma after post-metallization annealing (broken line), and with N_2O plasma after post-metallization annealing (solid line). Plasma annealing was performed at 350°C for 30 min. Post-metallization annealing at 400°C was performed in a furnace tube for 5 min in pure nitrogen. The polarity of the applied voltage was negative for the top Al contact.

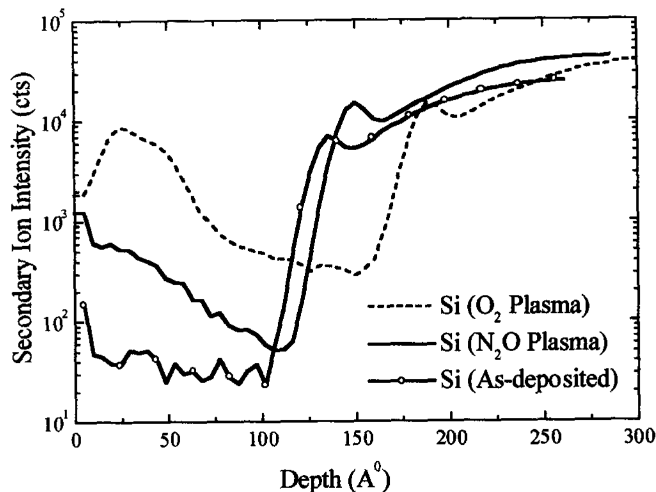

Fig. 4. Secondary ion mass spectroscopy results for Si contamination in N_2O plasma at 350°C for 30 min (solid line), O_2 plasma at 350°C for 30 min (broken line), and as-deposited sample at 350°C for 30 min (solid line with circle). $^{30}Si^+$ ion were monitored during SIMS. Primary ion beam is $O_2{}^+$ and beam energy is 3 keV.

A stronger oxidizing power will reduce the defects related to oxygen deficiency in the film. Previously, Aoyama *et al.* pointed out that insufficiently oxidized Si contamination can cause leakage current.[9] Hence, a stronger oxidizing power and a lower level of Si contamination are two important factors for obtaining a low leakage current.

An interesting point can be observed from the SIMS results displayed in Fig. 4. The Ta_2O_5/Si interface was shifted by about 5 nm for the O_2 plasma annealed sample compared to the as-deposited sample. This shift is almost negligible for the N_2O plasma annealed sample. This indicates that the Ta_2O_5 film is apparently thicker for samples with O_2 plasma annealing. Our explanation is that a SiO_x layer was actually formed on top of the Ta_2O_5 film in the case of O_2 plasma annealing. As shown in Fig. 4, the Si distribution shows a large quantity of Si on the top surface of the Ta_2O_5 film with O_2 plasma annealing. This SiO_x layer was also faintly observed between the glue (used during XTEM characterization) and the Ta_2O_5 film with O_2 plasma annealing. This formation of a SiO_x layer on top of the Ta_2O_5 film was first observed by a Japanese group during UV/O_3 annealing of Ta_2O_5 films at a low-temperature of about or below 400°C.[14–17] This was explained by the oxygen enhanced diffusion of Si into Ta_2O_5 under UV illumination. This effect has, till now, not been observed for samples with N_2O plasma annealing.

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