

A Comparison of Defect States in Tantalum Pentoxide (Ta_2O_5) Films after Rapid Thermal Annealing in O_2 or N_2O by Zero-Bias Thermally Stimulated Current Spectroscopy

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The concentration of shallow defect states was found to be greatly reduced if N_2O was used instead of O_2 for post-deposition annealing, resulting in much less leakage current in $\text{Al}/\text{Ta}_2\text{O}_5/\text{Si}$ capacitors. The superiority of N_2O is explained by the formation of a silicon oxy-nitride diffusion barrier, which can reduce Si contamination coming from the Si substrate into the Ta_2O_5 film.

1. Introduction

Tantalum pentoxide (Ta_2O_5) films, which have a higher dielectric constant of 20-25 as compared to a dielectric constant of 3.9 for SiO_2 , have been demonstrated as a promising dielectric for charge storage in 256 Mb DRAMs.¹⁾ However, Ta_2O_5 tends to be much more leaky than SiO_2 . Quite frequently, a post-deposition annealing in an oxidizing ambient after Ta_2O_5 deposition is needed to reduce the leakage current. Pure O_2 is usually the oxidizing ambient used in post-deposition annealing. Recently, Sun and Chen^{2,3)} 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. However, Sun and Chen²⁾ could only speculate the reasons behind the improvement due to the use of N_2O instead of O_2 . They suggested that the improvement due to the use of N_2O may be due to the incorporation of nitrogen into Ta_2O_5 or due to a reduction of oxygen vacancies in Ta_2O_5 . It is expected that defect states in Ta_2O_5 have an important role in its leakage current problem. Hence, it is necessary to conduct a study on the defect states of Ta_2O_5 in order to understand the mechanism behind the superiority of N_2O RTA to O_2 . 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.^{4,5)} In this paper, we will show that there is a defect, defect B, which is produced by the post-deposition annealing process with O_2 and the concentration of this defect is much lower if N_2O is used instead of O_2 , resulting in significantly lower leakage current.

2. Experimental

Ta_2O_5 films were deposited onto (100) p^+ - and n^+ -Si wafers by low pressure metal-organic chemical vapor deposition (LPMOCVD) as reported previously.^{4,5)} For this study, the film thickness was about 98.6 nm. After deposition, the samples were annealed by RTA in O_2 or N_2O at various temperatures and different time durations. Al dots with a diameter of 1 mm were thermally evaporated through a shadow mask onto

Ta_2O_5 . The Ta_2O_5 film deposited on the back side of the wafer during the LPMOCVD process would then be removed by chemical etching and Al was evaporated to form a back contact. The defect states in the samples were characterized by a novel zero-bias thermally stimulated current (ZBTSC) technique.^{3,4)} The purpose of zero-bias is to get rid of a parasitic leakage current that can interfere with the measurement. At zero-bias, the emitted carriers from defect states can still move if there is either a built-in electric field or a temperature gradient across the sample. The sample was mounted in a cryostat. Ultraviolet (UV) light was shone through a UV filter onto the sample at about 95 K for a duration t_{UV} to generate electrons and holes in the Ta_2O_5 film. UV light was used because of the large bandgap of about 5.28 eV for Ta_2O_5 .⁶⁾ Then the UV lamp was turned off and the temperature was ramped up from 100 K towards room temperature or higher. The measured current at zero-bias vs. the temperature was recorded with an X-Y recorder. The heating rate was 0.5 K/s. The UV excitation time t_{UV} was 5-15 min.

3. Results and Discussion

The results, for 850°C RTA for 30 s in O_2 or N_2O , are shown in Fig. 1. In O_2 annealed films, there are two peaks observed, defect B ($E_T = 0.3$ eV approximately) and defect C ($E_T = 0.6$ eV approximately). It has been consistently observed that

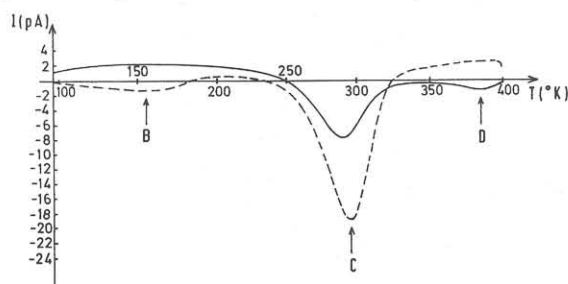


Fig. 1. The ZBTSC spectra of $\text{Al}/\text{Ta}_2\text{O}_5/\text{p}^+$ -Si with O_2 RTA (broken line) and with N_2O RTA (solid line) at 850°C for 30 s. The samples were excited by UV light for 5 min. at 95 K.

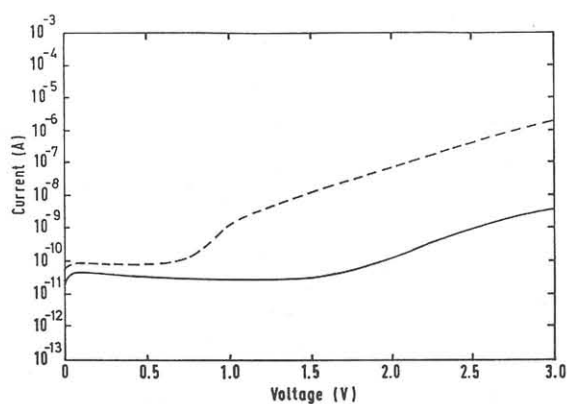


Fig. 2. The I-V characteristics of Al/Ta₂O₅/p⁺-Si with O₂ RTA (broken line) and with N₂O RTA (solid line) at 850°C for 30 s. The polarity of the applied voltage was positive for the top Al contact.

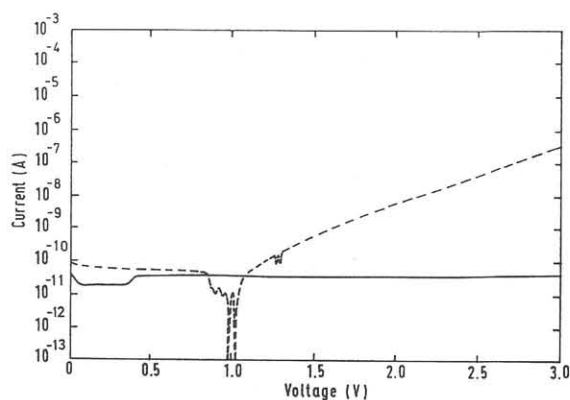


Fig. 3. The I-V characteristics of Al/Ta₂O₅/p⁺-Si with O₂ RTA (broken line) and with N₂O RTA (solid line) at 850°C for 30 s. The polarity of the applied voltage was negative for the top Al contact.

N₂O annealed films have significantly less defects B, as shown in Fig. 1. In addition, the concentration of defect C is also lower for N₂O annealed films. However, a deeper level, defect D ($E_T = 0.8$ eV approximately) was seen in N₂O annealed samples. It is expected that shallower defect states contribute more to leakage current than deeper defect states such that the reduction of defects B and C should outweigh the slight increase in defect D. As shown in Figs. 2&3, the I-V characteristics at room temperature of the samples with O₂ RTA or N₂O RTA at 850°C show clearly that the leakage current of the sample with N₂O is about 2-3 orders of magnitude lower for both polarities of the bias voltage. This reduction of leakage current can be easily correlated with the lower defect B and C density in samples with N₂O RTA. The reduction of defect states and leakage current is true in general for other RTA temperatures, for example, 800°C and 900°C. Thus, the superiority of N₂O RTA over O₂ RTA can be explained by a lower shallow defect states density in Ta₂O₅ films treated by N₂O RTA.

Since defect B is shallower than defect C, defect B is expected to be more important in the cause of leakage current than defect C. We have also put in effort to understand the chemical nature of defect B as follows. The ZBTSC spectra of Al/Ta₂O₅/p⁺-Si capacitors with O₂ RTA at 800°C, 850°C and 900°C are shown in Fig. 4. As shown in Fig. 4, there are two main peaks observed due to defect B and defect C. It can be easily seen that the concentration of defect B increases strongly with the increase in the O₂ RTA temperature, whereas the concentration of defect C is essentially a constant independent of the O₂ RTA temperature. Defect B cannot be due to oxygen vacancy because the concentration of oxygen vacancy is expected to decrease

with the increase in O₂ RTA temperature. Defect B cannot be due to carbon contamination during LPMOCVD because the concentration of carbon is expected to decrease with the increase in O₂ RTA temperature. Hence, we propose that defect B is created by interaction between the Ta₂O₅ film and the Si substrate during the post-deposition annealing step.

More information regarding the nature of defect B can be obtained by comparing the ZBTSC spectra of an Al/Ta₂O₅/p⁺-Si capacitor and an Al/Ta₂O₅/n⁺-Si capacitor with O₂ RTA at 900°C, as shown in Fig. 5. It can be easily seen that the signal due to defect B tends to be stronger for a capacitor fabricated on p⁺-Si substrate than a capacitor fabricated on n⁺-Si substrate, whereas the signal due to defect C is essentially independent of the conductivity type of the Si substrate. This dependence of the ZBTSC signal of defect B on the conductivity type of the substrate was also observed by us previously for samples prepared under slightly different conditions.^{4,5} Our explanation is that defect B is probably a hole trap in Ta₂O₅ because holes can be excited into the Ta₂O₅ film from the valence band of the p⁺-Si substrate during UV excitation for ZBTSC measurement, resulting in more efficient filling up of defect B with holes. Since hole traps tend to be in the lower half of the bandgap close to the top of the valence band E_V . It is very likely that defect B is an acceptor state. As we have discussed above, we believe that defect B comes from reaction between the Si substrate and the Ta₂O₅ film. The valence of Ta is 5, whereas the valence of Si is 4. If Si substitutes for Ta, then it is expected to form an acceptor state. This is in analogy to B forming an acceptor state in Si, which has a valence of 4 while B has a valence of 3. Furthermore, the position of defect B in the bandgap of Ta₂O₅ is

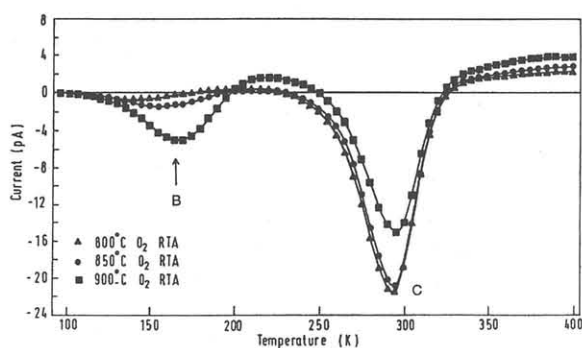


Fig. 4. The ZBTSC spectra of Al/Ta₂O₅/p⁺-Si with O₂ RTA at 800°C, 850°C and 900°C for 30 s. The samples were excited by UV light for 15 min. at 95 K.

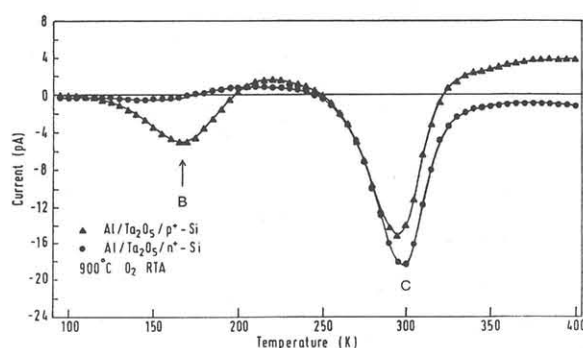


Fig. 5. The ZBTSC spectra of Al/Ta₂O₅/p⁺-Si and Al/Ta₂O₅/n⁺-Si with O₂ RTA at 900°C for 30 s. The samples were excited by UV light for 15 min. at 95 K.

estimated to be $E_V + 0.3$ eV approximately with the help of the equation $E_T = 23kT_m$, where T_m is the peak temperature of a peak in a ZBTSC spectrum.

4. Conclusions

Previously, Sun and Chen^{2,3)} have demonstrated the superiority of N₂O RTA over O₂ RTA for post-deposition annealing of Ta₂O₅ experimentally. However, they did not have a convincing explanation of the physics of the superiority of N₂O RTA. They could only speculate that the nitrogen incorporated during N₂O RTA might help to reduce the leakage current. However, they also pointed out N₂O treated samples might have less oxygen vacancies. In this paper, we clearly demonstrated that the superiority of N₂O RTA over O₂ RTA is due to the smaller quantity of defect states in N₂O RTA samples. Our explanation is as follows. During post-deposition annealing, the Ta₂O₅ film interacts with the silicon substrate such that some silicon atoms diffuse into the film, resulting in defect states. When N₂O is used instead of O₂, a very thin silicon oxy-nitride film is formed at the interface between the Ta₂O₅ film and the silicon substrate. The silicon oxy-nitride can serve as a diffusion barrier for silicon diffusion into the Ta₂O₅ film.

References

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