Extended Abstracts of the 1994 International Conference on Solid State Devices and Materials, Yokohama, 1994, pp. 781-783

The Characterization of Defect States Responsible for Leakage Current in Tantalum Pentoxide Films for Very High Density DRAM Applications

W. S. Lau, T. S. Tan, N. P. Sandler* and B. S. Page*

Department of Electrical Engineering,
National University of Singapore,
10 Kent Ridge Crescent, Singapore 0511,
Republic of Singapore.
*CVD Division, Lam Research Corporation,
49026 Milmont Drive, Fremont, CA 94538, USA.

Defect states in tantalum oxide films grown by low pressure metal-organic chemical vapor deposition on silicon wafers have been studied by zero-bias thermally stimulated current. It was demonstrated that a shallow band of defect states, which are probably hole traps, is responsible for leakage current. The shallow band of defect states can be suppressed by a low temperature post-metallization annealing, resulting in a reduction of leakage current by 2-3 orders of magnitude.

1. Introduction

Tantalum pentoxide (Ta_2O_5) films have been proposed as the dielectric for charge storage in state-of-the-art high density dynamic random access memory (DRAM) devices because of its higher dielectric constant (about 20-25) when compared to that of silicon dioxide (3.9).[1,2] For very high density DRAM structures, the Ta_2O_5 film has to be deposited onto non-flat structures like trenches, etc. Chemical vapor deposition (CVD) is superior to sputtering in terms of step coverage. Recently, the successful demonstration of the application of CVD Ta_2O_5 films in 256 Mb DRAM has confirmed the potential of Ta_2O_5 films for memory applications.[3] The principal problem of this new material is the higher leakage current when compared to silicon dioxide. It is expected that traps or defect states in Ta_2O_5 will play an important role in its leakage current problem through the Poole-Frenkel effect (field assisted ionization of defect states) or trap-assisted tunneling. However, no information on the defect states in CVD Ta_2O_5 films for very high density DRAM applications has ever been published. In this paper, we will report, for the first time, our study on the traps present in CVD Ta_2O_5 films by a novel zero-bias thermally stimulated current technique and the suppression of leakage current by the reduction of those traps, thus providing new insight to the Ta_2O_5 leakage current problem.

2. Experimental

Ta_2O_5 films were deposited onto p^+- and n^+-type silicon wafers by low pressure metal-organic chemical vapor deposition (LPMOCVD) with tantalum penta-ethoxide $Ta(OC_2H_5)_5$ and oxygen as the source materials in a Lam Research Corporation Integrity® LPMOCVD system as reported before.[4] The application of the Lam Research LPMOCVD Ta_2O_5 process to DRAM capacitor structures has been demonstrated before.[5,6] The process parameters are as follows. The flow rate of $Ta(OC_2H_5)_5$ was 0.12 ml/min. The N_2:$Ta(OC_2H_5)_5$ flow ratio was 200:1 and the O_2:$Ta(OC_2H_5)_5$ flow ratio was 100:1. The deposition temperature was 430°C and the pressure was 0.5 Torr. The growth rate was found to be 1.12 nm/min. The Ta:O ratio was found to be 2.5±0.1:1 by Rutherford Backscattering or low-angle X-ray Photoelectron Spectroscopy. For this study, the film thickness was about 98.6 nm. The samples were annealed in oxygen at about 800°C for one hour before metallization. Then Al dots with a diameter of 1 mm were thermally evaporated through a shadow mask onto the front side of the wafer to form an Al/Ta_2O_5/Si capacitor structure. The Ta_2O_5 film deposited on the back side of the wafer was removed by chemical etching and then Al was evaporated to form a back side contact. For one set of samples, a post-metallization annealing in nitrogen at 400°C for 1/2 hour was done. Another set of samples without the post-metallization annealing will serve as control samples.

A well-known method to study traps in insulators is the thermally stimulated current (TSC) technique. The traps are filled with carriers by either optical injection or electrical injection at low temperature and then the current due to the emission of carriers from the traps, when the temperature is ramped up, is measured under an applied bias voltage. Seve and Lassabatere[7] used the TSC method to study Ta_2O_5 films prepared by thermal oxidation of sputtered Ta. A shortcoming of the TSC technique is that there is a parasitic current which can bury the signal if the signal is weak and thus limit the sensitivity of the measurement. Recently, it was found that the parasitic current can be greatly reduced when the applied bias voltage is zero.[8,9] The driving force for the transport of carriers can be due to a built-in electric field[9] in the sample or due to a thermal gradient across the sample.[10,11] This technique is known as zero-bias thermally stimulated current (ZBTSC). ZBTSC based on thermal gradient is also known as thermoelectric effect spectroscopy (TEES) and can distinguish electron traps from hole traps, whereas electron traps and hole traps cannot be distinguished in conventional TSC.[10,11]

The sample was mounted in a cryostat. Ultraviolet (UV) light was shone across 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 Ta_2O_5. 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 and t_{UV} was 30 min. for all the ZBTSC measurements reported in this paper.

3. Results and Discussion

If we assume that the leakage comes from the Poole-Frenkel effect, then it is expected that the most energetically shallow defect should deserve more attention. As shown in Fig. 1, a shallow broad band of states was detected at around 100-200 K for samples on both p^+- and n^+-Si substrates. The polarity of the current for that shallow broad band of states is negative independent of the substrate type. The sign convention adopted is that current flowing out of the top contact is considered positive. This indicates that the driving force is probably not due to a built-in electric field, whose polarity is expected to depend on substrate conductivity type. Then the driving force at zero bias is probably due to a temperature gradient across the sample. It is expected that the bottom of the sample was colder than the top at low temperatures because the sample was on the cold finger of the

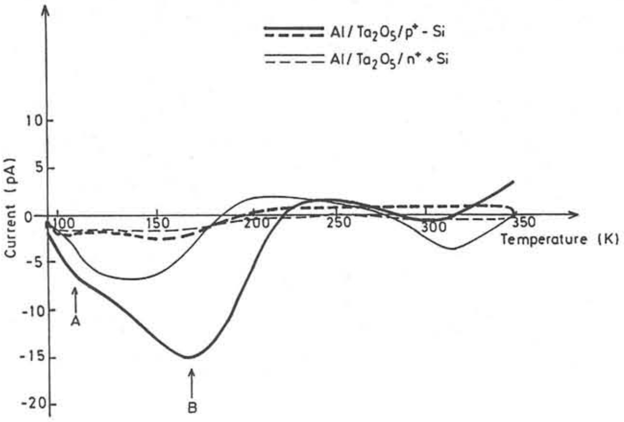

Fig. 1 The ZBTSC spectra of $Al/Ta_2O_5/p^+$-Si and $Al/Ta_2O_5/n^+$-Si structures without (solid line) and with (broken line) post-metallization annealing in nitrogen at 400°C for 1/2 hour. All the samples were excited by UV light for 1/2 hour at 95 K.

cryostat and the top metal contact was contacted by a probe, which was not directly cooled. Then the polarity of the current indicates that the shallow band of states are hole traps. Another evidence that the shallow band of states are hole traps was that the signal tended to be stronger for samples on p^+-Si substrates, as shown in Fig. 1. UV light produces electrons and holes in Ta_2O_5 by across-the-bandgap absorption in Ta_2O_5. Extra electrons can come from the n^+-Si substrate by excitation from the conduction band of silicon into the conduction band of Ta_2O_5. Similarly, extra holes can come from the p^+-Si substrate by excitation from the valence band of silicon into the valence band of Ta_2O_5. Thus, if the shallow band of states are hole traps, the ZBTSC signal will be stronger for samples on p^+-Si substrate. Since the band of defect states is quite broad, most of the established methods of analyzing TSC spectra cannot be applied. However, a rough estimation of the activation energy can be made by

$$E_T = 23\ kT_m \tag{1}$$

where E_T is the activation energy of the defect state, k is the Boltzmann constant, and T_m is the peak temperature corresponding to the defect state.[9] By applying eq. (1), the band of defects can be seen as an overlap of a relatively weak defect band A (E_T = 0.2 eV approximately) and a stronger defect band B (E_T = 0.3 eV approximately). The current-voltage (I-V) characteristics at room temperature were studied to see whether there is a

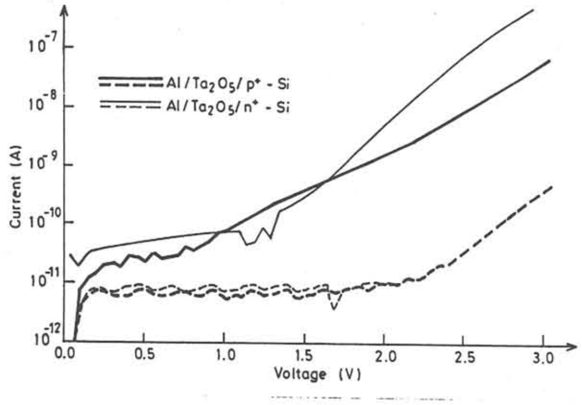

Fig. 2 The I-V characteristics of $Al/Ta_2O_5/p^+$-Si and $Al/Ta_2O_5/n^+$-Si structures without (solid line) and with (broken line) post-metallization annealing in nitrogen at 400°C for 1/2 hour. The polarity of the applied voltage was positive for the top aluminum contact for all samples.

reduction of leakage current corresponding to the reduction of defect states measured by ZBTSC in samples with post-metallization annealing. As shown in Fig. 2, it can be seen that the leakage current is reduced by 2-3 orders of magnitude by the post-metallization annealing step for both samples prepared on p^+- and n^+-Si substrates. Thus the correlation of leakage current with the shallow broad band of states detected by ZBTSC is confirmed.

4. Conclusions

In conclusion, a broad band of states responsible for leakage current was detected by ZBTSC in LPMOCVD Ta_2O_5. The broad band of states can be suppressed by a low temperature post-metallization annealing in nitrogen. It is striking to note that this suppression of defects occur at a relatively low temperature of 400°C and the post-metallization annealing was done after an annealing step in oxygen at a much higher temperature of 800°C. The reader should also note that the metallization method was conventional thermal evaporation, not electron-beam evaporation or sputtering, otherwise a significant improvement in electrical properties by a post-metallization step is expected. Our tentative explanation for this unexpected improvement by a low temperature post-metallization annealing step is that the aluminum may help to getter some impurities in the LPMOCVD Ta_2O_5 films. It will not be possible to separate this effect from the annealing of ion damage produced by sputtering, if sputtering is used for metallization instead of thermal evaporation. The reader should also note that the reduction of leakage current in LPMOCVD Ta_2O_5 films by post-metallization annealing reported here is contrary to the observation by other workers[12,13] that the insulating property tends to degrade after post-metallization annealing for Ta_2O_5 films prepared by thermal oxidation of electron-beam evaporated tantalum or by reactive sputtering. Further study is therefore necessary to understand the difference between LPMOCVD Ta_2O_5 films in this work and Ta_2O_5 films prepared by other methods.

References

1) K. Ohta, K. Yamada, R. Shimizu and Y. Tarui: IEEE Trans. Electron Devices **ED-29** (1982) 368.
2) H. Shinriki, T. Kisu, S.-I. Kimura, Y. Nishioka, Y. Kawamoto and K. Mukai: IEEE Trans. Electron Devices **37** (1990) 1939.
3) K. Sagara, T. Kure, S. Shukuri, J. Yugami, N. Hasegawa, H. Goto and H. Yamashita: IEICE Trans. Electron. **E75-C** (1992) 1313.
4) W. Kern, A. Chen and N. Sandler: J. de Physique IV, Colloque C2, supp. au J. de Physique II **1** (1991) 311.
5) P. C. Fazan, V. K. Mathews, N. Sandler, G. Q. Lo and D. L. Kwong: IEDM Tech. Dig., 1992, p. 263.
6) G. Q. Lo, D. L. Kwong, P. C. Fazan, V. K. Mathews and N. Sandler: IEEE Electron Dev. Lett. **14** (1993) 216.
7) G. Seve and L. Lassabatere: Thin Solid Films **21** (1974) 19.
8) D. K. Chen and M. B. Das: IEEE Trans. Eletron Devices **ED-32** (1983) 2506.
9) W. S. Lau, T. C. Chong, L. S. Tan, C. H. Goo and K. S. Goh: Jap. J. Appl. Phys. **30** (1991) L1843.
10) B. Santic and U. V. Desnica: Appl. Phys. Lett. **56** (1990) 2636.
11) Z. C. Huang, K. Xie and C. R. Wie: Rev. Sci. Instrum. **62** (1991) 1951.
12) G. S. Oehrlein and A. Reisman: J. Appl. Phys. **54** (1983) 6502.
13) J.-G. Hwu and S.-T. Lin: IEE Proc. part G **137** (1990) 390.