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Deposition and Determination of Band Alignment of Al₂O₃/Si Gate Stacks by New CVD Chemistry†

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Compared to other precursors, dimethyl aluminum hydride [(CH₃)₂AlH] has high vapor pressure of 2 torr at room temperature and a potential to form alumina films by CVD/ALD with low carbon impurity. Additionally, low deposition temperature of dimethyl aluminum hydride will avoid the formation of low-k interfacial layer during deposition, which is suitable for the MOS device fabrication. In this study, Al₂O₃ thin films have been deposited successfully from dimethyl aluminum hydride and O₂ to investigate the MOCVD behaviour as well as the observation of the band alignment of deposited Al₂O₃/Si gate stacks.

Keywords: High-k gate dielectrics, Band alignment, Precursor, Thermal stability.

INTRODUCTION

Aluminium oxide gate dielectrics have attracted substantial interest as alternatives to SiO₂-based dielectrics due to its suitable valence-band offsets with Si and thermal and chemical stability in direct contact with Si^{1,2}. Conventional CVD uses trimethyl aluminium [(CH₃)₃Al, TMA] and H₂O/H₂O₂/O₃ as precursor and oxidant to deposit Al₂O₃ films. Despite the good quality of the films, potential problems such as higher carbon contamination and a lower refractive index have become the fatal drawbacks. Compared to other precursors, new dimethyl aluminum hydride [(CH₃)₂AlH, DMAH] has high vapor pressure of 2 torr at room temperature and a potential to form alumina films with low carbon impurity and excellent gap-filling property. Additionally, low decomposition and deposition temperature of DMAH, avoiding the formation of low-k interfacial layer during deposition, which is suitable for the MOS device fabrication. By far, although there have been many reports on Al₂O₃ deposition, the fabrication and band alignment of the Al₂O₃ films on Si grown by new CVD chemistry using DMAH and O₂ as a precursor and an oxidant, respectively, have not been thoroughly investigated. A detailed understanding of the growth characteristics of the Al₂O₃ system as well as precise determination of band alignment of Al₂O₃/Si gate stacks is needed. In this study, Al₂O₃ thin films were deposited using DMAH and O₂ to investigate the MOCVD behaviour of this new precursor as well as the observation of the band alignment of Al₂O₃/Si gate stacks.

EXPERIMENTAL

Thick and ultrathin Al₂O₃ films were deposited by MOCVD using DMAH and O₂ as the precursor and the oxidant on Si wafers, respectively. In order to reduce the viscosity of DMAH, 1 % propylamine was added to the precursor. Details of the MOCVD apparatus used here have been described elsewhere³. To investigate the film quality of the new CVD chemistry, dependence of carbon content and refractive index of Al₂O₃ films on growth temperature and partial pressure of oxygen has been analyzed. Since accurate determination of the band alignment is essential prerequisites for device simulations and gives the opportunity to improve material preparation, this necessitates the investigation of band offset for Al₂O₃/Si gate stacks. *Ex situ* O1s energy loss spectra (ELS) and synchrotron radiation X-ray photoemission spectroscopy (SRXPS) were carried out to investigate the band gap and the band alignment of Al₂O₃/Si gate stacks.

RESULTS AND DISCUSSION

As we know, higher residual carbon degrades electrical properties greatly, leading to larger leakage current and small dielectric constant. Temperature dependence of carbon content has been shown in Fig. 1. It is found that that higher deposition temperature leads to significant reduction of carbon content, originating from the reaction of carbon residue with injected oxygen during deposition. Compared to previous reports, the value of the residual carbon content in the Al₂O₃ film deposited

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Fig. 1. Temperature-dependent carbon content of Al_2O_3 films grown on Si substrate

from DMAH is very low ($< 1\%$), which is desirable in the fabrication of CMOS devices. Refractive index is an important parameter to measure the high quality films. Fig. 2(a) and (b) show the variation of the refractive index and the carbon content of the films as a function of deposition temperature and partial pressure of oxygen. It has been seen that the refractive index increases with increasing the temperature and partial pressure of oxygen, which can be attributed to the reduction of the carbon content and formation of dense films. More importantly, the value of the refractive index of our samples is much higher than that reported by other groups. Valence band offset and band gap of $\text{Al}_2\text{O}_3/\text{Si}$ gate stack which are determined by SRXPS and O1s ELS are 3.02 and 7.15 eV, respectively, as shown in Fig. 3. From the viewpoint of energy-band alignment shown in Fig. 4, it can be concluded that the band offset of the $\text{Al}_2\text{O}_3/\text{Si}$ gate stacks is suitable for the fabrication of CMOS devices.

Fig. 2. Temperature and partial pressure of oxygen dependent refractive index of Al_2O_3 films

Fig. 3. Determination of band gap and valence band spectra of $\text{Al}_2\text{O}_3/\text{Si}$ gate stack

Fig. 4. Energy-band alignment of $\text{Al}_2\text{O}_3/\text{Si}$ gate stack

Conclusion

Al_2O_3 has been prepared by new MOCVD chemistry using DMAH and O_2 as the precursor and the oxidant, respectively. Temperature and oxygen partial pressure dependences on carbon content and refractive index of the Al_2O_3 films have revealed that high quality Al_2O_3 films with lower carbon content and increased refractive index have been successfully grown using DMAH and O_2 . Meanwhile, characterization by SRXPS and O1s ELS has confirmed that the band offset of the $\text{Al}_2\text{O}_3/\text{Si}$ gate stacks is suitable for CMOS devices.

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