Ultra-Thin Zirconium and Hafnium Silicate Films


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Zirconium Silicate films have been shown to be promising candidates for a replacement gate insulator in deep-submicron CMOS technology but a production-worthy deposition technique still needs to be found. One such technique is metal-organic chemical vapour deposition (MOCVD). In this work ultra-thin Zr silicate films were deposited on Si(100) using mixed alkoxide β-diketonate precursors. Zr(O-Pr)2(thd)2 and Si(2-Butyl)2(thd)2 dissolved in octane were introduced into the reactor with a liquid-injection system. O2 or NO were introduced into the chamber separately to reduce C contamination in the films. The C concentration was further reduced by using a “pulse-mode” deposition in which the precursors and the oxidant were introduced during separate steps. Analysis by X-ray Photoelectron Spectroscopy (XPS) has shown that using this pulse-mode technique both NO and O2 reduce the carbon contamination in the films effectively. Fig. 1 shows the XPS Zr3d and C1s spectra for a Zr0.5Si0.5O2 film deposited using NO. No evidence of C-Si, Zr-C and Zr-Si bonds were found in the spectra of the optimized films. HRTEM images show that the as-deposited Zr silicate films and the interface layers are amorphous.

Nitric oxide forms an oxynitride buffer layer which retards oxygen diffusion to the Si interface, thus minimizing the thickness of the interfacial layer. The thinnest interfacial layers for the as-deposited films were 0.6 nm determined by HRTEM (see Fig. 2) or 0.3 nm determined by medium energy ion-scattering (MEIS). After post deposition anneals at 850 °C Zr silicate films with the composition Zr0.5Si0.5O2 and their interfacial layers were still amorphous and no phase separation was observed. The Zr concentration in the interfacial layer was below the sensitivity of the MEIS technique (~ 5 at.%) before and after annealing and this has been confirmed by EELS analysis.

The films were annealed in O2 to remove surface carbon contamination from unreacted precursor on the surface of the film and improve the electrical quality of the interface layer. A “spike anneal in O2 at 850 °C increased the thickness of the interfacial layer.

The Zr silicate films described in this work exhibit promising C-V and J-V characteristics. The hysteresis, fixed charge density and the effective density of trapped charge at the interface were improved significantly by anneals at 850 °C. Most of the frequency-dependent interface states, not passivated by the low temperature FGA, were eliminated after the 60 s nitrogen anneal at 850 °C. After a spike anneal in O2 at 850 °C and an anneal for 60 s in N2 at 850°C, a Zr silicate film with an equivalent oxide thickness (EOT) of 2.3 nm has exhibited a leakage current about 20 times lower than that of a SiO2 film with the same EOT.

In the precursors used for the Zr silicate deposition the Zr and Si are co-ordinated to six O atoms, while only two are required to form the silicates. This leaves 4 oxygen atoms per molecule that may release active oxygen during the decomposition of the precursor. To see if this has an influence on the interface layer thickness nitrogen co-ordinated precursors, [(C2H5)2N]4Hf (TDEAH) and [(CH3)2N]4Si (TDMA) are being tested for the Hf silicate deposition. An interfacial layer was observed for the growth of HfO2 films using TDEAH and O2 at temperatures as low as 375 °C. Preliminary results with Hf silicate layers will be presented.

References

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Fig. 1. XPS spectra with background subtracted showing data (---), fitted peaks (- - -), and sum of fitted peaks (-----) for the as-deposited Zr0.5Si0.5O2 film.

Fig. 2. HRTEM cross section of as-deposited Zr0.5Si0.5O2 film.