Application of XRF Spectrometry in Characterization of High-k Ultra-Thin Films

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XRF is a fast, cheap and nondestructive technique suitable to the chemical analysis of thin films. Another advantage of using XRF lies in the possibility of detection of Al-containing thin layers on Si-wafers. With Rutherford Backscattering, Al peak can not be separated from that of Si substrate. One challenge for XRF of ultra-thin layers is the sensitivity. In this work, the feasibility of using a wavelength dispersive XRF to study the nanometer thick high-k oxide layers is proven.

ZrO_2, HfO_2, Al_2O_3 and Zr- and Hf-aluminates were deposited by ALCVD in a Pulsar 2000 ALCVD reactor attached to an ASM P8200 Polygon cluster tool. Philips PW 2400 wavelength dispersive XRF spectrometer has been used. Si K_α, Al K_α, Zr $L_{\alpha1}$ and Zr $L_{\beta2}$, and Hf $L_{\alpha1}$ and Hf $L_{\beta2}$ have been chosen for the detection of Si, Al, Zr, Hf.

Growth curves measured by XRF agree well with those from RBS (for ZrO_2 and HfO_2) and ICP-OES (for Al_2O_3). As an example, Fig. 1 shows the growth curves of ZrO_2 layers by XRF and RBS. The agreement confirms the calibration procedure and thus guaranties the reliability of the measurement.

It is found that there is an incubation period for ALCVD of HfO_2, ZrO_2 and Al_2O_3 (Fig.2). The growth rate (Fig.3) on HF-last surface changes with the increase of the cycle number. The incubation can be explained with the growth model shown in Fig.4. The 1st period of the incubation, A-B, corresponds to nucleation and island growth. At point B, the highest growth rate is reached, corresponding to the largest surface area. At B, the layer starts to flatten. At C, a flat surface of the layer forms, corresponding to a constant growth rate in the following deposition. The incubation depends on material and surface passivation. ZrO_2 and HfO_2 have much longer incubation than Al_2O_3. On HF-last surfaces, the incubation is significant. On Si-nitride layer, it is less important. On chemical oxide, there is almost no incubation.

The compositions of Hf- and Zr-aluminate layers can be determined by XRF. From Fig. 5, we can see that the composition of the aluminates can be controlled, by using different ALCVD recipes of deposition cycle numbers of the components. It is proven that there is no matrix effect (interaction) between Al & Hf, or Al & Zr in the XRF measurement.

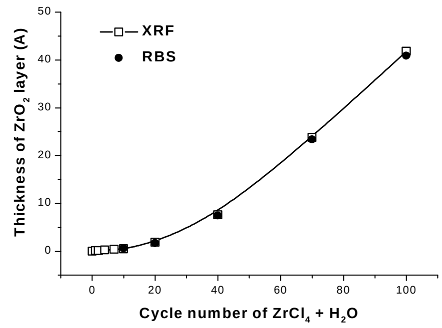

Fig.1 Growth curves of ZrO_2 by XRF and RBS.

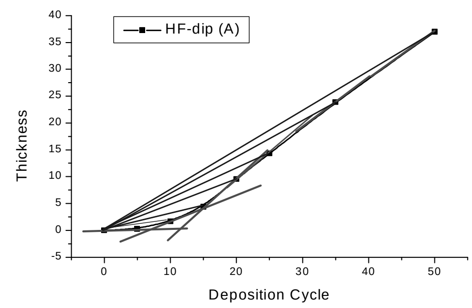

Fig.2 Incubation in growth of Al_2O_3 on HF-last surface.

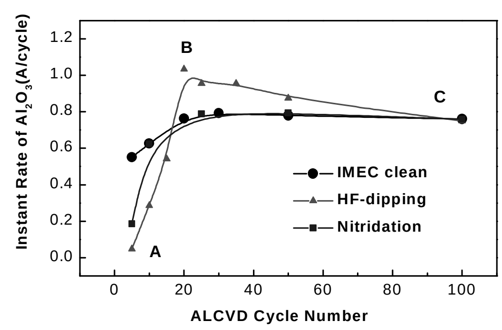

Fig.3 Growth curves of Al_2O_3 layer on different surfaces.

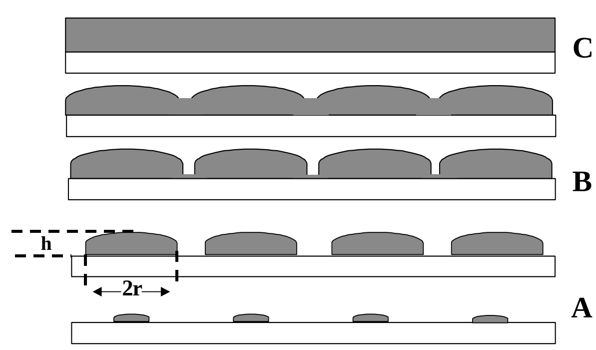

Fig.4 Growth model of ALCVD, showing a process of nucleation, island growth and flattening.

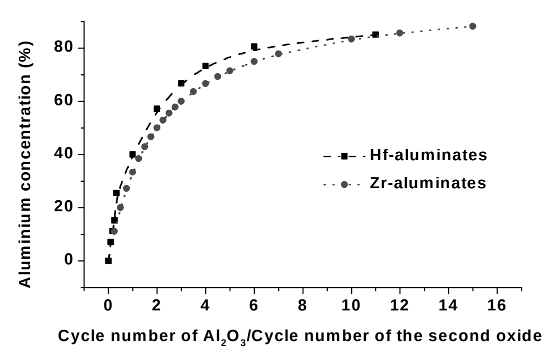

Fig.5 Composition control of the aluminate layers.