# UNIVERSITI TEKNOLOGI MARA

# NOVEL SYNTHESIS OF Al<sub>2-x</sub>Hf<sub>x</sub>O<sub>3</sub> MATERIALS AND THE FABRICATION OF GATE DIELECTRIC THIN FILMS FOR METAL OXIDE SEMICONDUCTOR APPLICATIONS

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Thesis submitted in fulfillment of the requirements for the degree of **Doctor of Philosophy** (Science)

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### AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

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#### ABSTRACT

Developments of new materials for MOS applications are important due to the problems of downscaling of SiO<sub>2</sub>. In this work, Hf doped Al<sub>2</sub>O<sub>3</sub> materials were studied as a possible new material for use in metal oxide semiconductor (MOS) application. Novel  $Al_{2-x}Hf_xO_3$  (x = 0.001, 0.002 and 0.003) materials were successfully prepared by a selfpropagating combustion synthesis method. The synthesized materials were characterized by simultaneous thermogravimetric analysis (STA). From the analysis, the synthesis mechanism of the materials were proposed. X-ray diffraction (XRD) results reveal that hafnium doped materials correspond to the hexagonal crystal structure of Al<sub>2</sub>O<sub>3</sub>. Quantitative analysis via Rietveld refinements showed that Hf was successfully substituted in the hexagonal Al<sub>2</sub>O<sub>3</sub> crystal structure. The field emission scanning electron microscope (FESEM) micrographs shown that the Hf doped samples have a quite similar morphology as the pure  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder; however, as the Hf content increases, the small spherical crystallites embedded in the chunks are larger. The Hf content was confirmed, where the synthesized stoichiometry of all materials were perfectly identical to the obtained stoichiometry from energy dispersive X-Ray spectroscopy (EDS). UV-visible spectroscopy showed that Al<sub>2</sub>-Hf<sub>2</sub>O<sub>3</sub> materials exhibited band gap narrowing with respect to pure Al<sub>2</sub>O<sub>3</sub> materials and it is dependent on the Hf content following an exponential function. The optimized Al2O3 and novel Al1.997Hf0.003O3 materials were used as targets in the pulsed laser deposition (PLD) technique for thin film fabrication. By controlling the parameters of PLD technique. high quality ultra-thin Al2O3 and novel Al1997Hf0.003O3 thin films were deposited at various thicknesses. The XRD patterns of thin film samples were obtained via the grazing incidence diffraction (GID) technique. The XRD patterns of thin film samples were indexed to the ICDD reference pattern number 01-088-0826 for Al2O3 hexagonal structure and the crystal growth orientation occurred in the (110) and (024) crystal direction. The RMS surface roughness obtained from the atomic force microscopy (AFM) show that thinner films are smoother compared to thicker ones attributed to the increased crystal defects. The FESEM cross-sections of the thin film samples show very high quality uniform thin films that was very smooth and highly dense. It was found that the band gap energies of the thinner samples have larger band gaps attributable to the quantum confinement effect of low dimensional structures. The MOS capacitor structures were fabricated in order to show the significance and suitability of Al<sub>1,997</sub>Hf<sub>0,003</sub>O<sub>3</sub> gate oxide thin film for the next generation of MOS devices. From the I-V and C-V characteristics, it was observed that Al 1997Hf0 003O3 thin films have lower leakage current, higher capacitance and higher dielectric constant compared to Al2O3 thin films. According to the experimental results, Al 1997Hf0 003O3 thin films were found to be more useful for MOS application compared to Al2O3 thin films.

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