Growth of Al_2O_3 films by Pulsed Injection MOCVD: comparative study of precursor materials

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INTRODUCTION

In the last years, much effort has been made to replace SiO_2 by higher permittivity dielectrics for the applications in dynamic random-access memories and as a transistor gate dielectric in field-effect transistor logic devices (1). A lot of metal oxide materials are actually under investigation as possible candidates for alternative gate dielectric (1), among which Al_2O_3 is considered as one of attractive materials due to its high band gap and thermodynamic stability on Si.

Al oxide films can be deposited by PVD as well as by MOCVD and MOCVD-related techniques (2-10). The goal of this study was to investigate the possibilities of the pulsed liquid injection MOCVD technique for the deposition of thin Al_2O_3 films, including a comparative study of various precursor materials.

EXPERIMENTAL PROCEDURE

Thin films of Al_2O_3 were deposited in a vertical hot-wall pulsed injection MOCVD reactor (11,12). Commercial Si/SiO_2(100 nm) substrates with a thermal oxide (10x10 mm^2) were used for deposition of Al_2O_3 films.

Al isopropoxide ($Al(OPr^i)_3$), Al acetylacetonate ($Al(AcAc)_3$) and Al 2,2,6,6-tetramethyl-3,5-heptandionate ($Al(thd)_3$) were chosen as precursor materials. Monoglyme was used as a solvent for $Al(AcAc)_3$ and $Al(thd)_3$, and toluene for $Al(OPr^i)_3$.

A detailed study of surface quality was performed by AFM operating in Tapping Mode (Multimode SPM, Digital Instruments). Film thickness was determined by profillmetry on the steps formed in the films.

RESULTS

Three series of Al_2O_3 films corresponding to the three different precursors used were deposited. The deposition temperature varied in the range from 300 °C to 700 °C.

The dependencies of the film growth rate on deposition temperature are presented in Fig. 1. The figure demonstrates that among the three precursors studied $Al(OPr^i)_3$ is most unstable, consequently the film growth enters into the diffusion-controlled range at a rather low temperature (~400 °C), while in the case of other two precursors the growth remains limited by the kinetics in the whole range of temperatures studied (350-700 °C). The figure shows that the thermal stability of precursors increases in the range $Al(OPr^i)_3 << Al(AcAc)_3 < Al(tmhd)_3$. An XRD study revealed all deposited films to be amorphous independently of the precursor material and deposition temperature.

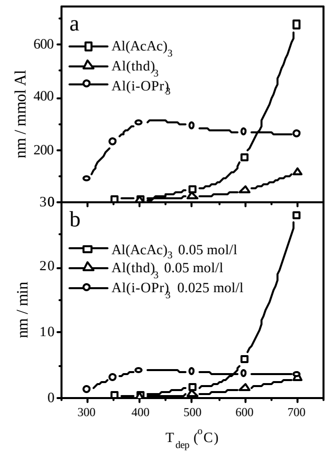

Fig.1. Influence of the deposition temperature on the film growth rate (a - nm/ mmol of injected precursor, b - nm/min).

Comparative study of surface quality for all deposited samples was performed by AFM. All AFM scans were made for a surface window of 2 × 2 μm^2. We calculated the roughness parameter in relation to film thickness (Rms or Ra/thickness, %). The relative film roughness is similar in the case of all three precursors (~1.5 %), when films are deposited at an intermediate temperature (~500 °C). $Al(OPr^i)_3$ gives films with a lower roughness/thickness ratio at lower deposition temperature, while $Al(AcAc)_3$, on the contrary, does it at higher temperatures. The relative roughness of Al_2O_3 films deposited from $Al(thd)_3$ was almost independent of the deposition temperature.

Some deposited films were in-situ or ex-situ annealed at 750 °C for 1-2 hours. No difference was found between the XRD spectra of annealed and non-annealed films. The roughness of annealed films was rather similar to those of non-annealed. This fact suggests that the annealing conditions employed were evidently not sufficient for film crystallisation.

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