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Growth of Al_2O_3 thin films using plasma-activated deionized water as a new oxidant in thermal atomic layer deposition process

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Abstract

The atomic layer deposition (ALD) of metallic oxides, mainly alumina (Al_2O_3), when performed in thermal mode uses deionized water (DI) as oxidant source and trimethylaluminum (TMA) as a metal reactant. However, growth per cycle (GPC) of Al_2O_3 thin films for the reactant and co-reactant mentioned above is limited to 0.1 nm/cycle [1]. This barrier in the GPC is overcome by using plasma technology as an oxygen source. This technique is commonly called energy-enhanced ALD because the plasma oxygen source provides tremendous activation energy during the co-reactant step, which allows for greater efficiency in generating active sites on the substrate surface, promoting thus more reactions between the surface and the metal reactant. This process, called plasma-enhanced ALD (PEALD), is commonly used to replace DI water with O_2 plasma as an oxygen source. It is reported in the literature that for the TMA reactant, this replacement of the vapor phase oxygen source (thermal ALD) by a plasma oxygen source (PEALD) generates an increase in the alumina GPC to 0.12 nm/cycle, i.e., a gain of 20% [2]. However, this gain in the GPC has a high cost, as the PEALD uses a sophisticated plasma source. The present work presents a cheap alternative to increase the GPC of alumina by 17%. An atmospheric gliding arc plasma jet and compressed air were used to activate DI water. Plasma-activated water (PAW) was prepared by a forward vortex flow reactor (FVFR) type with air at atmospheric pressure. The activation times were 10, 30, and 60 min, and the following pH of 3.5, 3.0, and 2.5 were obtained. PAWs were characterized by UV-vis spectrophotometry in order to obtain the reactive oxygen and nitrogen species (RONS), namely, H_2O_2, HNO_2, NO_2^-, and NO_3^-. After activation, plasma-activated water (PAW) is carried out into a recipient and introduced in the line of oxygen source in thermal ALD. The ALD pulse times were 0.15-4-0.3-4 s, TMA, N_2 purge, PAW, and another N_2 purge. The number of cycles was fixed at 1000 cycles, and Si(100) was used as substrate. Alumina thin films growth was characterized by *in-situ* mass spectrometry and *ex-situ* by optical profilometry, FT-IR and FEG-SEM. According to the characterizations mentioned above, the existing RONS in PAW probably contributed to the activation of sites in the Si(100) substrate, thus increasing the GPC of the alumina.

References

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