Assessment of the chemical durability of CVD-amorphous SiO2 thin films

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Abstract

Silicon oxide based films are nowadays of major importance given their implication in many technological fields such as optical coating applications for near UV laser optics, fully dielectric mirrors, beam splitters and devices for non-volatile memories in semiconductor, but also as chemical protective coatings on glass.
CVD processes operating at atmospheric pressure and low temperatures (360 to 650◦C) allow various chemical pathways to be explored, capable of synthesizing this type of materials. Among them, we study the TEOS-O2/O3 gas mixture route, leading to amorphous silica layers with lower content in hydrogen compared to the classical TEOS-O2 route (1,2,3).

In this work in particular, we analyse the long-term chemical durability of this type of material when exposed to aqueous solutions. For this purpose, aging experiments have been carried out by exposing silica films, deposited at different temperatures Td, to a slightly acid aqueous solution (pH=4) under a temperature of 90◦C during 279 days. The goal is to identify the network performances when exposed to chemical alteration, depending on its initial structure quality. The evolution of the structure and elementary composition throughout the alteration process was tracked using a wide range of analytical techniques. More specifically, combination of IBA (Ion Beam Analysis) techniques, namely RBS (Rutherford Backscattering Spectroscopy) and ERDA (Elastic Recoil Detection Analysis), as well as FTIR (Fourier Transform Infrared) spectroscopy and ToF-SIMS (Time of Flight Secondary Ions Mass Spectroscopy) analyses enabled a better comprehension of the hydrolysis mechanism. ERDA and RBS analyses testify to the films loss of thickness. This phenomenon is more pronounced for low Td. A total loss of 41 % is measured for Td=450◦C compared to 17% for 550◦C. The IRTF vibration modes LO3/TO3 ratio has also been used to discuss this loss of thickness. After an initial fast stage of dissolution beetween 12 and 30 nm/day depending on Td, taking place during the first days of alteration, a strong drop is recorded. According to IBA data, independently of the hydrogen content's increase for all the Td values during alteration, the O/Si ratio increases with the alteration treatment for Td=450◦C, whereas it slightly drops for 500 and 550◦C. This behaviour could be associated to the extreme surface densification for highest Td, responsible of the dissolution drop. The evolution of the hydrogen profiles in the coatings has been analysed by ERDA during the treatment and confirm the probable

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implementation of a diffusion barrier at the extreme surface for the highest Td. The network evolution is discussed according to Qn units and hydrated species content thanks to IBA, FTIR and 1H MAS NMR (Magic Angle Spinning, Nuclear Magnetic Resonance) results.

References

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