## mgr inż. Krzysztof Jankowski

"Silicone oxycarbide dielectric films (a-SiOC:H) produced from organic silicone precursors by CVD method initiated with atomic hydrogen"

## SUMMARY

Amorphous silicon oxycarbide (a-SiOC) thin solid films have broad applications in modern technologies due to their unique properties, such as low dielectric constant, high thermal and chemical stability, and good mechanical properties. They are primarily used in electronics as dielectric materials in integrated circuits and memory devices, in photovoltaics in the production of solar cells as protective and passive coatings, in lithium-ion cells, as ceramic anode materials, and composite nanomaterials in supercapacitors. Additionally, due to the potential for surface functionalization, a-SiOC thin solid films find applications in biomedicine as materials for biocompatible coatings and sensors.

In this study, the feasibility of using a hydrogen plasma-initiated chemical vapor deposition (RHP-CVD) method to produce amorphous silicon oxycarbide (a-SiOC) thin solid films from single-source organosilicon precursors such as dimethoxymethylsilane (DMMS), diethoxymethylsilane (DEMS), and cyclic octamethyl-1,4-dioxane-2,3,5,6-tetrasilacyclohexane ( $^{2}D_{2}$ ) and 1,3,5,7-tetramethylcyclotetrasiloxane ( $D_{4}^{H}$ ) was investigated. The deposition processes were studied as a function of substrate temperature ( $T_{s}$ ), which has a significant impact on the structure of the films and their growth rate.

The properties of a-SiOC thin solid films produced using the RHP-CVD method were investigated through various analyses to assess their physical, chemical, and structural characteristics. The studies included: a) Fourier-transform infrared spectroscopy (FTIR) and b) X-ray photoelectron spectroscopy (XPS) for identifying functional groups in the film structure and evaluating chemical changes related to the elimination of organic groups and the formation of a C-Si-O-Si network; c) <sup>29</sup>Si and <sup>13</sup>C CP/MAS NMR spectroscopy, which allowed for the assignment of the chemical structure of the deposited films at room temperature; d) atomic force microscopy (AFM) for surface morphology analysis including surface roughness and uniformity; e) scanning electron microscopy (SEM) for microstructure and conformality analysis of the surface coverage; f) analysis of changes in density and refractive index as a function of deposition temperature for optical properties; and g) thermogravimetric analysis (TGA) to investigate thermal stability and cross-linking of the films after exposure to high temperatures.

The investigation of each precursor began with characterizing its film-forming properties. It was found that on unheated substrates, the film thickness increased proportionally with deposition time for all precursors. From the slope of the experimental (linear) time dependencies of the evaporated precursor mass, thickness, and mass of the deposited thin solid film product, precursor flow rates (F), thickness growth rate (r<sub>d</sub>), and mass deposition rate (r<sub>m</sub>) were determined. The molecular structure of the precursor affects the rate and efficiency of the RHP-CVD process, with the highest mass deposition rate observed for the cyclic siloxane precursor  $D_4^H$ . Activation plots of the deposition rates for the investigated compounds, obtained from the film deposition kinetics as a function of substrate temperature, indicate that the growth rates (r) and efficiencies (k) are dependent on the substrate temperature and decrease as T<sub>S</sub> increases. This suggests that the rate and efficiency

of the RHP-CVD process are limited by the adsorption of film-forming precursors resulting from monomer decomposition on the growing surface. Exceptions were observed for DMMS and D<sub>4</sub><sup>H</sup> precursors, for which the activation parameters remained practically constant and independent of T<sub>s</sub> at higher temperatures. In view of the Arrhenius plot the rate of film growth rd decreases within the substrate temperature range of 30–350°C in two distinctly separated temperature ranges with the bend point. It means that film growth via the RHP-CVD method is mainly based on two mechanisms with different activation parameters. The transition temperature between these deposition mechanisms depends on the structure of the monomer and is 70°C for DMMS and DEMS, 180°C for <sup>2</sup>D<sub>2</sub>, and 220°C for D<sub>4</sub><sup>H</sup>. Based on FTIR, XPS, and <sup>13</sup>C and <sup>29</sup>Si CP/MAS NMR studies and mechanical property measurements, it was determined that, at low substrate temperatures below the transition temperature, polymeric thin solid films rich in organic CH<sub>x</sub> groups are formed for all the investigated compounds. Increasing the substrate temperature above the transition temperature causes a drastic reduction in the organic group content of the film and the formation of a highly cross-linked silicon oxycarbide material containing siloxane (Si-O) and carbide (Si-C) bonds, with a minor presence of hydrocarbon units. This process results in a significant increase in density and refractive index. The amount of carbide Si-C bonds in the thin film structure depends on the precursor, with the highest amount observed for the cyclic tetrasilacyclohexane <sup>2</sup>D<sub>2</sub>. Based on the structural studies and available literature data, hypothetical mechanisms of the most important chemical reactions for the studied precursors were proposed.

The study demonstrated that the RHP-CVD method can effectively produce amorphous dielectric thin films from precursors containing silicon, oxygen, carbon, and hydrogen. These coatings exhibit excellent uniformity, morphological homogeneity, low surface roughness, controlled density, low refractive index, high conformality, and good mechanical properties, such as high adhesion and hardness.

Keywords: a-SiOC:H thin films, CVD method, remote hydrogen microwave plasma, alkoxymethylsilanes, cyclosiloxanes.