Characterization of Advanced Semiconductor Materials by Thermal Desorption Mass Spectrometry with Atmospheric Pressure Ionization

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Thermal desorption spectrometry (TDS) is widely applied in the development of dielectric films in microelectronics providing quantitative and qualitative information about composition, structure, and stability with regards to storage and post-deposition treatments (annealing, etching). With the continuous shrinking of device dimensions new materials are being introduced for interconnects (Cu, low k materials) and for the gate (high-k materials). In this paper the use of TDS in the characterization of new semiconductor materials will be demonstrated through the analysis of low and high k dielectric films. Whereas conventional TDS is performed under vacuum, results presented here come from a set-up operated at atmospheric pressure. The strength and weaknesses of this approach will be discussed in comparison to other analytical techniques.

TDS measurements were carried out at atmospheric pressure on full 8inch wafers in a commercial single-wafer rapid thermal processing tool (RTP, AST SHS2800), connected to an atmospheric pressure ionization mass spectrometer (APIMS, VG Trace+).[1] The wafer temperature was measured and controlled by a thermocouple molded in one of the pins supporting the wafer. Semiconductor-grade nitrogen gas, purified with an active-type purifier, was used as a carrier gas. The ambient gas inside the chamber was sampled and diluted, and then introduced into the APIMS source for analysis in positive-ion mode. The APIMS response was calibrated for H_2O, O_2, CO_2 and CH_4, allowing quantitative analysis of these species.

In the first part of this work, we have analyzed blanket ZIRKON™ LK2000 dielectric films (Zirkon™ LK is a trademark of Shipley Company L.L.C.). This material is a porous organic/inorganic hybrid SiO_xC_y, with an ultra-low dielectric constant (k) of 2.0. Further plasma and Ultra Violet-Ozone (UV-O_3) treatments of the material show an improvement of adhesion and mechanical properties of the films. TDS was used to study the impact of these different treatments on the surface stability and chemical composition, and to evaluate possible moisture uptake. The untreated low k material is hydrophobic. When subjected to different plasma treatments (NH_3, N_2/O_2 and He), the surface of the dielectric layer became hydrophilic, though no penetration of water in the bulk of the material was detected (Fig. 1). Moreover, depending on the chemistry of the plasma used, the surface of the layer was either stabilized or destabilized with respect to the reference surface. The use of a UV-O_3 treatment results in a bulk modification of the layer with the penetration of water into the pores (Fig. 1). Complementary analyses including FTIR and extraction of the corresponding k values using Metal-Insulator-Metal (MIM) capacitors confirmed the TDS results observed for layers subjected to a UV-O_3 treatment. Different residues remaining on the surface after the different treatments were also detected. Their chemical nature depended on the type of treatment used. When an O_2–based plasma was used the surface was strongly oxidized, resulting in the presence of CO_2. In the case of the UV-O_3 treatment, the oxidation of the surface was milder resulting in alcohol, and ether types of residues.

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In the second part of this work, 5 nm thick blanket HfO_2 thin films were deposited by MOCVD on HF-last Si wafers and compared to 5 nm thick dense LPCVD Si_3N_4 films. TDS revealed relatively high concentrations of H_2O in the HfO_2 films, indicating the presence of porosity that was not detected by ellipsometric porosimetry.[2] The apparent total volume of pores decreased at higher deposition temperatures and as a result of post-deposition anneal, in qualitative agreement with film density determined from TEM thickness and RBS Hf dose (Table 1). The discrepancy between volumes of pores and densities partly resulted from desorption of H_2O during chamber pre-purge in TDS. It may also indicate the presence of closed pores in the films. However the relative changes in porosity were in agreement with the changes in density. Organic residues from the metal-organic film precursor $Hf[N(C_2H_5)_2]_4$ were detected mainly as $C_nH_{2n-1}N^+$ ions and were monitored as a function of deposition temperature and anneal conditions. In general organic impurities were detected with higher sensitivity compared to TOF-SIMS analysis.

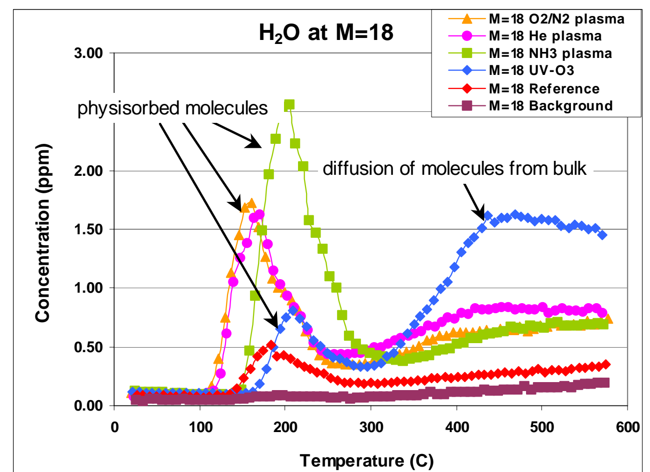

Fig. 1. TDS spectrum of water for Zirkon™ LK2000 dielectric layers subjected to different plasma and UV-O_3 treatments.

Table 1. Comparison of MOCVD HfO_2 film density from TEM and RBS with apparent porosity from TDS for different deposition temperatures and conditions of anneal.

Film condition	Density (% of bulk density)	Porosity (%vol.)
300°C deposition	60 ± 10	3.6 ± 0.1
+ anneal (5min, N_2, 900°C)	76 ± 4	1.9 ± 0.1
+ anneal (spike, O_2, 800°C)	-	1.7 ± 0.1
485°C deposition	83 ± 9	1.7 ± 0.1
+ anneal (5min, N_2, 900°C)	85 ± 7	1.5 ± 0.1
+ anneal (spike, O_2, 800°C)	-	1.3 ± 0.1

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