Thermal Desorption Spectrometry as a Method of Analysis for Advanced Interconnect Materials

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Introduction

In semiconductor manufacturing, the increasing demand for smaller, faster, and more powerful devices requires the introduction of novel materials for the fabrication of interconnects. In particular, the thermal stability of such materials and their chemical interaction with various processing conditions must be well understood to achieve a successful integration scheme. Thermal desorption spectrometry (TDS) is a powerful technique that provides quantitative and qualitative information on composition, structure, stability with regard to processing, storage and post-deposition treatments such as annealing and plasma etching [1–3].

Carbon-based aromatic polymers are promising as low–k interlayer dielectrics (ILD) [4]. However, such materials have weak mechanical properties, which can give rise to delamination during the chemical mechanical polishing (CMP) step. Also, due to the porous structure of the material, chemical species such as cleaning agents and metal diffusion barrier precursors may penetrate into the material during processing [5]. One possible solution is the creation of a dense surface sealing layer to improve the adhesion properties of the film and prevent the penetration of contaminants and moisture into the film [5].

Self-assembled monolayers (SAMs) are nanometer-scale organic films that have potentially various applications in very advanced BEoL integration schemes. Thiolate SAMs can be used as effective corrosion inhibitors of copper surfaces for applications such as wafer level packaging and wire bonding [6]. Silane SAMs could be used either to promote adhesion of diffusion barriers onto ILD materials [7] or used as diffusion barriers themselves [8].

In this short review the use of TDS for the characterization of new semiconductor materials for advanced BEoL technologies will be illustrated. Important integration issues such as the hydrophobic/hydrophilic character and surface sealing of low-k ILD materials modified by plasma treatments, the thermal stability of thiolate SAMs on Cu surfaces used as corrosion inhibitors, and the chemical labeling of silane SAMs for process monitoring will be discussed in this paper.

Experimental Set-up

Thermal desorption spectrometry (TDS) measurements were carried out at atmospheric pressure on full 200-mm wafers in a single-wafer rapid thermal processing
(RTP, AST SHS 2800) system, connected to an atmospheric pressure ionization mass spectrometer (APIMS, VG Trace+) (see Figure 1) [9]. The RTP system comprises a single-wafer quartz tube in which the wafers are directly loaded from the cleanroom. The chamber was purged typically for 4–6 min in order to reduce the background levels of impurities, and the TDS heating program was started [10]. The wafer was heated with lamps and the temperature was measured and controlled by a thermocouple molded in one of the pins supporting the wafer. The temperature was ramped up from room temperature to the temperature required with a constant heating rate. Semiconductor-grade nitrogen gas, purified with an active-type purifier (SAES MonoTorr), was used as the carrier gas. The ambient gas inside the chamber was sampled, diluted, and introduced into the APIMS source for analysis in the positive-ion mode, as described elsewhere [9]. The APIMS typically scans over a mass range extending from m/e = 11 to 100, with an integration time of 0.1 s per scanned mass. APIMS is the most sensitive gas analysis technique for bulk gases used in the semiconductor industry (trace gaseous impurities detection on the ppt scale) [9].

Impurities are ionized predominantly by charge transfer from the primary ions of the carrier gas molecules created at atmospheric pressure in a corona discharge. Whereas ionization mechanisms only produce mono-charged ions, cluster ions are readily formed. The APIMS response was calibrated using a non-linear method for H₂O, O₂, CO, and CH₄, allowing for a quantitative analysis of these species in the 0.1–1000 ppb range [11]. Before carrying out TDS measurements, the background of residual impurities in the RTP chamber needs to be measured using bare Si₃N₄/Si wafers. This is especially important after the tool has been inactive for a few hours (time of the purge of the quartz line going to the APIMS before starting a run of experiments). The most common impurities include O₂ giving a peak at

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**Figure 1.** Scheme of the TDS-APIMS set-up.