Infiltration behaviors of trimethoxysilane derivatives into spin-on-carbon thin films analyzed by TOF SIMS

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Spin-on-carbon (SOC) is a material supporting modern semiconductor nanofabrication and is a liquid formed by dissolving carbon-based polymers in a solvent. After coating, SOC is carbonized via thermal treatment and used as hard mask or gap filler, offering improved overlay control due to transparency, high throughput compared to chemical vapor deposition materials, and high thermal stability compatible with various integrated flows. In nanoimprint lithography, Ito et al. have recently demonstrated that the presence of a SOC layer on silicon wafers enabled rapid disappearance of bubble defects in the resin-filling process [1]. In this study, we investigated the modification of SOC surfaces with adhesion molecules to anchor imprint resin patterns by TOF-SIMS [2]. The presence and absence of modification with 3-acryloyloxypropyltrimethoxysilane (AcPTMS) determines the feasibility of pattern formation.

ODL-301 (Shin-Etsu Chemical) was used as an SOC. A 200 nm-thickness carbonized SOC layer was formed on Si wafers via spin-coating and baking. Chemical vapor surface modification (CVSM) of SOC with AcPTMS was performed at 150°C for 1 h [3]. Using the microprint/nanoimprint method [4], droplets (their volume of approximately 0.3 pL) of UV-curable liquid [5] were placed on SOC surfaces and molded using a modified synthetic quartz plate by UV nanoimprinting. Instead of AcPTMS, trimethoxysilane derivatives (XTMS) with different functional groups were used for the investigation of infiltration into SOC by TOF-SIMS. Their chemical structures are shown in Fig. 1.

Figure 2a and 2b show the depth profiles of Si- secondary ions measured for AcPTMS-modified and unmodified SOC/Si substrates. Compared to Fig. 2b, Fig. 2a indicates that AcPTMS molecules not only existed on the SOC surface but also infiltrated into the inside of the SOC layer. No formation of cured resin patterns was observed on the unmodified SOC surface, whereas resin patterns were left on the AcpTMS-modified SOC surface. To understand the infiltration into the SOC layer, XTMS were investigated by TOF-SIMS. C_3H_7TMS penetrated sufficiently into the SOC. As the alkyl-chain length increased, penetration into the SOC layer was suppressed (Fig. 3). The phenyl group of C_6H_5TMS penetrated more than the cyclohexyl group of C_6H_{11}TMS. $XSi(OCH_3)^{2-}$ ions were detected as secondary ion structures, suggesting that XTMS molecules themselves are trapped within SOC film rather than hydrolyzed molecular species being present.

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[1]T. Ito, W. Zhang, and W. Liu, *Jpn. J. Appl. Phys.* 63, 050804 (2024)
[2]TOF-SIMS: time-of-flight secondary ion mass spectrometry
[3]M. Nakagawa, K. Kawasaki, A. Onuma, and H. Niinomi, *Jpn. J. Appl. Phys.* 62, SG1010 (2023)
[4]M. Nakagawa, *Jpn. J. Appl. Phys.* 61, SD0805 (2022)
[5]N. Takano, H. Niinomi, T. Oshikiri, and M. Nakagawa, *J. Vac. Sci. Technol. B* 42, 042603 (2024)

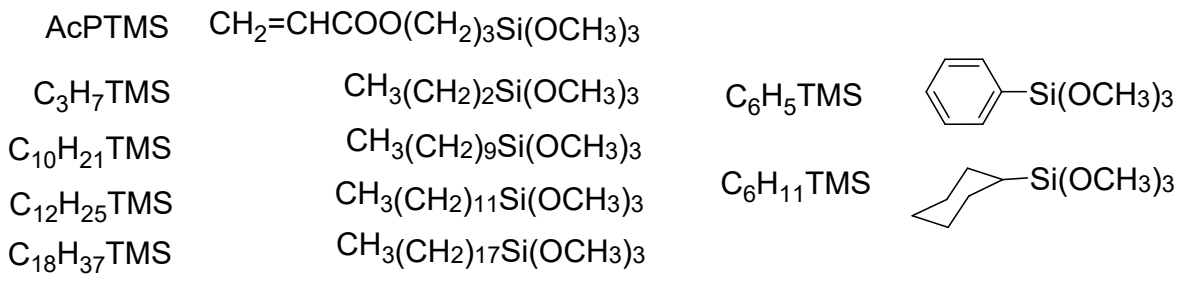

Figure 1: Chemical structures of trimethoxysilane derivatives (XTMS) used for the investigation of infiltration into a 200 nm-thickness spin-on-carbon (SOC) layer on silicon wafers by chemical vapor surface modification (CVSM) at 150°C for 1 h.

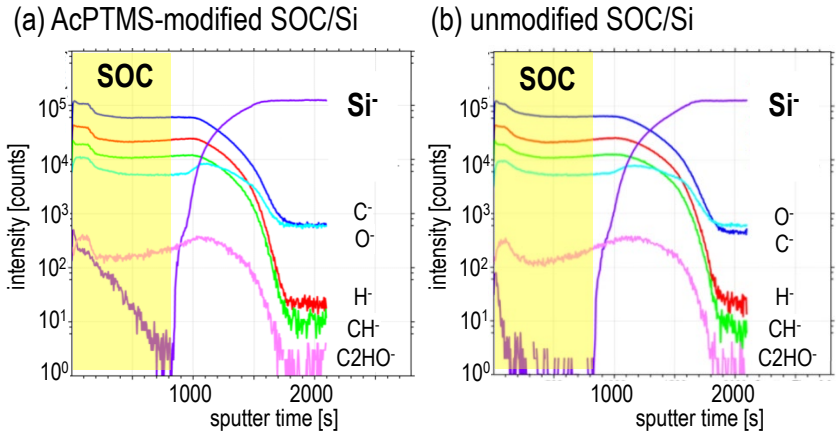

Figure 2: TOF-SIMS depth profiles of Si- secondary ions measured for (a) AcPTMS-modified and (b) unmodified SOC/Si substrates.

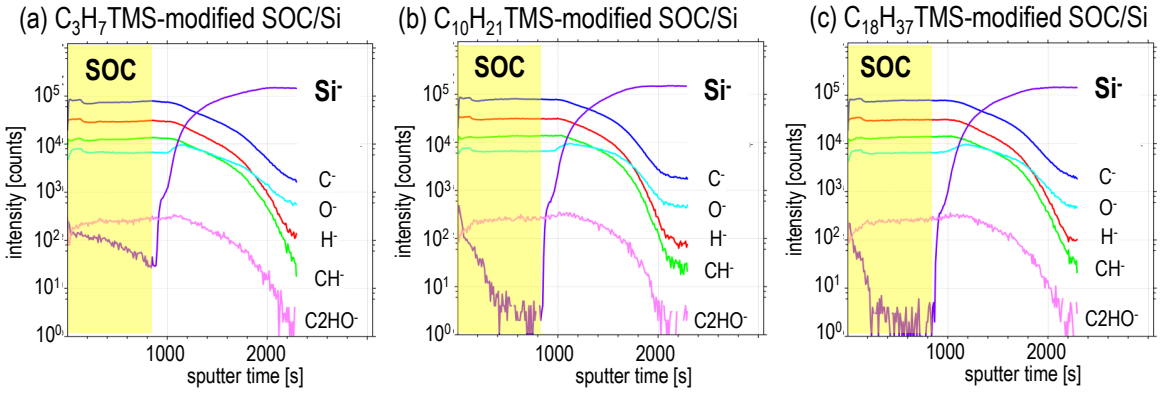

Figure 3: TOF-SIMS depth profiles of Si- secondary ions measured for SOC/Si substrates modified with (a) C_3H_7TMS, (b) $C_{10}H_{21}TMS$, (c) $C_{18}H_{37}TMS$.