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Wetting behavior of aqueous solutions on high aspect ratio nanopillars with hydrophilic surface finish

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In semiconductor manufacturing, potential wetting issues are becoming a concern as feature dimensions are continuously scaled down and novel materials with different wetting properties are introduced in new technology nodes. A recent contact angle (CA) study suggested that partial wetting occurred in nanostructures of different aspect ratios (AR) even for hydrophilic surface terminations (CA < 90˚) [1]. In this work, the characterization of wetting states in nanopillars with different surface modifications is discussed.

Nanopillars of 90 nm pitch, 37 nm diameter and an AR 11 were etched in silicon wafers as described in [2]. Gas disappearance upon wetting was monitored by ATR-FTIR using IR-responsive CO_2 gas as atmosphere in a liquid cell in which the sample was mounted. The samples were made out of wafers with nanopillars, which could be functionalized with SAMs. Among the used SAMs were perfluorodecyltrichlorosilane (FDTS) and phenethyltrichlorosilane (PETS). DIW was saturated with CO_2 to simulate the frequently encountered situation of tools equipped with recirculation tanks under N_2. Also, wetting depths were evidenced by SEM using nanopillars covered with 10 nm steam oxide [3] and HMDS-priming, which were etched in dilute HF solutions.

Figure 1 shows ATR-FTIR spectra of the PETS-functionalized nanopillars. Comparing with the measurements in CO_2 gas atmosphere (dashed curve), the spectra in saturated water environment (solid curve) showed a decrease of the CO_2 gas rotational fine structure peaks and the appearance of a dissolved CO_2 band. As FDTS-functionalized nanopillars showed superhydrophobic properties (CA > 140˚ in Table 1) they were used as a reference to determine the gas volume in-between the pillars (Figure 2). With PETS-functionalized samples, residual gas was detected even after 30 min of wetting time, confirming the occurrence of partial wetting at this contact angle (Figure 1 and 2). Compared with an expected lifetime of about 0.1ms for a 100nm bubble in water, this unexpected long lifetime of the residual gas in-between nanopillars is postulated to be due to the so-called surface nanobubbles [4].

Ellipsometry measurements showed that HMDS priming was not affecting the etching of the steam oxide by dilute HF (Figure 3). Cross-sections of etched structures by SEM gave evidence for laterally non-uniform wetting beside partial wetting (Figure 4).

This study showed that indeed partial wetting can occur with hydrophilic nanostructures, leading to the formation of long-lasting nanobubbles, and that the wetting front is not necessarily uniformly penetrating in-between the structures.

References

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Table 1. Contact angle of DIW on functionalized samples.

Surface treatment	Blanket	Nanopillars
FDTS	109.0	146.3
PETS	80.6	134.5
HMDS	80-81	131-132

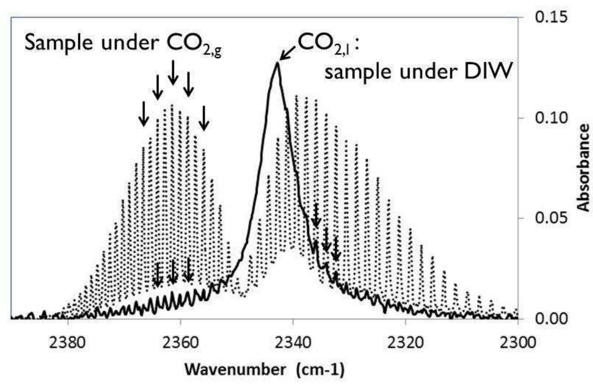

Figure 1. Change in ATR-FTIR spectra of CO_2 after wetting a PETS-functionalized nanopillar sample with DIW saturated with CO_2 (time = 30min; T = 22˚C).

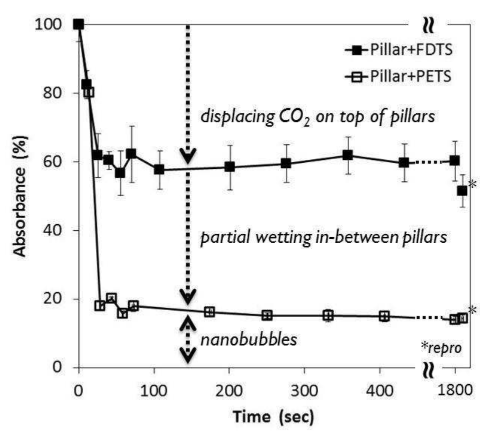

Figure 2. Water wetting kinetics from CO_2 gas absorbance as determined by ATR-FTIR, showing partial wetting and the formation of nanobubbles with PETS-functionalized nanopillars.

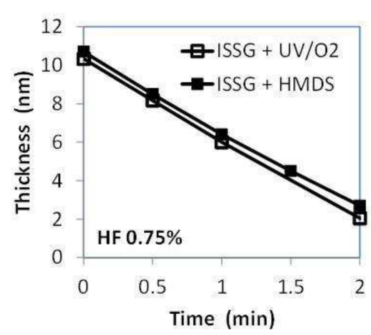

Figure 3. Etching kinetics of HMDS-primed steam oxide compared to as-grown oxide using dilute HF (T = 22˚C).

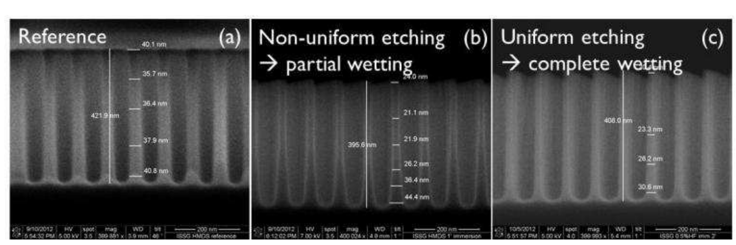

Figure 4. SEM cross-sections of nanopillars covered with HMDS-functionalized steam oxide before (a) and after (b,c) etching by dilute HF (0.75%v, 1min, T = 22˚C).