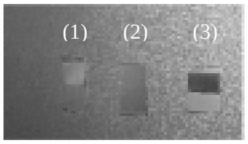

Figure 2. Samples showing successful image reversal with HMDS treatment. White regions: polymer, dark regions: surface of Si wafer. (1) Negative tone, (2) both sides dissolve, (3) positive-tone.

FTIR experiments were performed in transmission mode to probe the chemistry changes associated with silylation. Our interest is mainly to detect the presence of functional groups that indicate resist deprotection and silylation. The commonly observed Si-CH_3 peaks signal the presence of either HMDS or silylated polymers but it is difficult to differentiate one from another. The highly fluorinated polymer (THPMA-F7MA) and TFT solvent peaks densely populate regions where SiO bond peaks commonly occur. Better indicators are the broad carboxylic acid OH stretch that occurrs at 3300–2500 cm^{-} for deprotected polymers and the NH stretch at 3300 – 3030 cm^{-1} for unreacted HMDS present in the film. Additionally, changes in the carbonyl C=O stretch peak(s) at around 1740 cm^{-1} provide insights to whether the resist is protected, deprotected, silylated, or formed anhydrides.

The presence of carboxylic acid side groups may result in anhydride formation during the baking processes. Because anhydride formation is expected to occur at higher temperatures, and since no C=O peaks occur near 1818 cm^{-1} in our IR plots to indicate the presence of noncyclic anhydrirdes, we rule out this reaction.

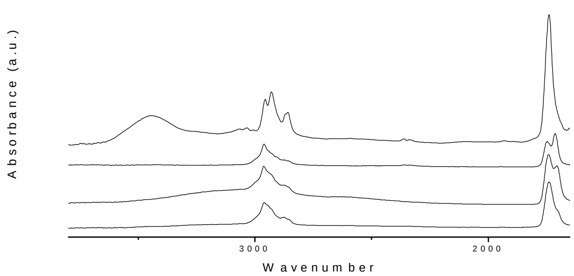

Figure 3. IR plots of different stages of silylating process. Data sets are numbered 1-4 from the bottom up. 1) After PAB, 2) after PEB, 3) silylated, and 4) treated with HMDS but without prior DUV exposure and PEB.

In figure 3, four FTIR plots are shown for the different stages of the silylation process. For ease of reference, the data sets are numbered 1-4, starting with 1 at the lowest position. In the mentioned regions, the first set, from a resist film applied on the NaCl plate and after post apply bake (PAB), shows a small peak around 3500–2500 cm^{-1}, belonging to the OH stretch of the carboxylic acid groups. The single carbonyl C=O stretch peak at 1740 cm^{-1} shows that most of the THP protecting groups are intact, as expected, before exposure to DUV. The carbonyl groups, one from THPMA and the other from the F7MA blocks of the copolymer, appear at a single location since both are from esters of methacrylates.

The second set from the bottom (number 2) is that of the sample after exposure to DUV and PEB step. A large increase in the carboxylic acid OH peak is readily observable after deprotection reactions that removed the THP protecting group. The appearance of a second C=O peak at around 1705 cm^{-1} due to the presence of carboxylic acid indicates the same. The C=O peak from F7MA remains in the same position as in plot 1 since no chemical changes occurred in this block.

Data set number 3 shows FTIR peaks of the sample after silylation for 10 minutes under HMDS vapor at 115 ^{o}C. The disappearance of the carboxylic acid OH peak at 3500–2500 cm^{-1} and a slight shift of the C=O stretch to 1715 cm^{-1} suggest silylation where SiO bonds replace OH bonds of carboxylic acid groups. Surprisingly, the OH peak totally disappears, indicating a nearly 100% reaction where all COOH groups are silylated.

The final data set (topmost) is used to verify the assumptions made above. It is a plot of a THPMA-F7MA polymer sample subjected to HMDS vapor at 115 ^{o}C but without prior exposure to DUV light. A combination of (a) no changes in the C=O stretch at 1740 cm^{-1}, (b) the absence of carboxylic OH peak at 3500–2500 cm^{-1}, and (c) a large NH peak at 3700–3300 cm^{-1} strongly suggests that thermal deprotection did not occur, silylation was absent, and the presence of HMDS in the film is by absorption alone. A comparison of this data set to the first three seems to confirm very well our interpretations of the FTIR plots.

Another analytical method available to investigate diffusion of HMDS or silylating agents into thin polymer films is RBS. With this analytical technique we can probe the diffusion length, depth concentration profile, and density changes in films subjected to silylation. Figure 4 shows an RBS plot comparing Si concentrations in THPMA-F7MA films spincoated on Si wafer, originally and those subjected to HMDS vapor at 115 ^{o}C for 20 and 40 minutes. Spectra for the latter show that Si concentrations in the films vary little between the two silylation times. RUMP simulations indicate that the resist film has a low atomic concentration of Si, ~1 %, in the bulk and up to ~5% in the top 150-250 nm layer. At the time of this writing, more RBS experiments are planned to verify these initial findings.

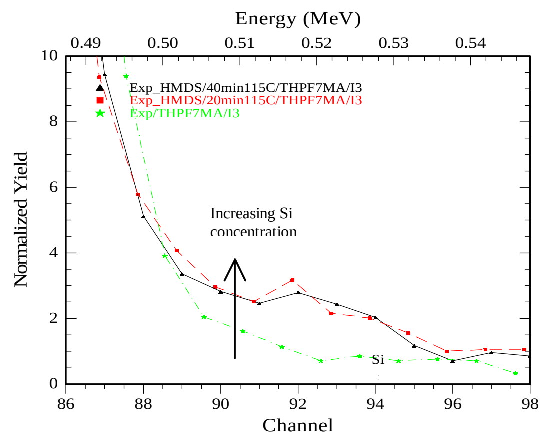

Figure 4. RBS spectra of resist samples. The lower data set is from original resist while the top two are from resist samples after DUV exposure and HMDS/heat treatment.

Conclusions

Our effort at creating a positive-tone CO_2 developable resist has yielded encouraging results. FTIR experiments show that cross-linking due to anhydride formation is unlikely and that silylation does indeed take place when carboxylic acid groups are present when exposed to HMDS vapor at elevated temperatures. With RBS we can begin to understand the diffusion process as well as obtain essential information such as depth concentration profiles of Si-containing molecules. We showed image reversal with large samples. Image reversal at micron and sub-micron length-scales is inherently more challenging since it involves process optimization in a large, multidimensional parameter space. However, the results obtained to date seem to suggest that such is a strong possibility in the foreseeable future.

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