Part Per Million Water in Gaseous Vapor Streams Dramatically Accelerates Porous Silicon Oxidation

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Abstract

Substantial research has focused on exploiting and understanding porous silicon (pSi) photoluminescence (PL) for applications in areas ranging from chemical sensing to solid-state lighting. At ambient temperature, pure H_2O is well-known to slowly (over a time scale of hours to days) and irreversibly oxidize as-prepared pSi (ap-pSi) to form oxidized pSi (ox-pSi). In this paper, we report that the apparent ap-pSi to ox-pSi oxidation rates can be orders of magnitude faster in the presence of non-aqueous vapor streams that contain just ppm H_2O levels. When H_2O is removed from the non-aqueous vapor stream, ap-pSi oxidation ceases. The non-aqueous analyte vapors serve as a vehicle to transport H_2O directly into the hydrophobic, ap-pSi matrix where the H_2O then oxidizes the ap-pSi leading to ox-pSi, permanently changing the pSi PL and surface chemistry. The ap-pSi oxidation rate is much faster in the presence of non-aqueous vapors because H_2O transport into the pSi matrix is no longer limited by H_2O slowly percolating-oxidizing-percolating through the ap-pSi matrix.

Experimental Data

Figure S1 summarizes the effects of dry air, ambient air, dry T, dry ACN, and dry MeOH vapors, and ambient T, ambient ACN, and ambient MeOH vapors on the ap-pSi surface species (dis)appearance rates. Panel A presents the apparent disappearance (SiH_x (x=1-3)) and growth rates (Si-O-Si, , and O_ySiH (y=1-2)). Small values are indicative of slow rates (growth or disappearance), larger values indicate faster rates. Panel B presents the rate ratio (i.e., $k_i/k_{dry\ air}$) which scales the species rate under each set of conditions to the baseline rate value measured in dry air. A rate ratio greater than unity reflects an increase in rate (growth or disappearance) for a given species under a particular set of conditions in comparison to the corresponding rate measured in dry air.

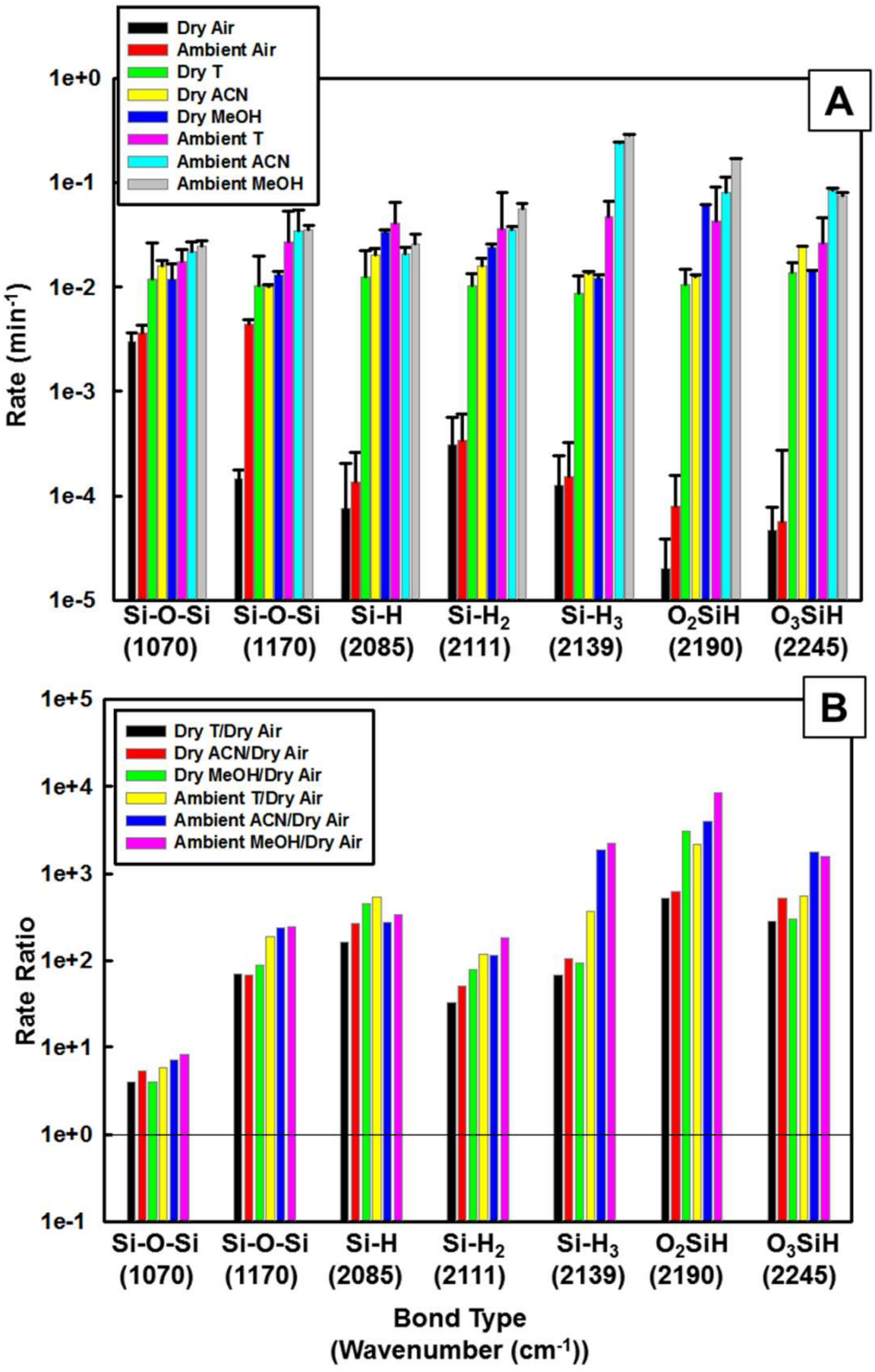
A
Dry Air
Ambient Air
Dry T
Dry ACN
Dry MeOH
Ambient T
Ambient ACN
Ambient MeOH
Rate (min-1)
1e+0
1e-1
1e-2
1e-3
1e-4
1e-5
Si-O-Si (1070)
Si-O-Si (1170)
Si-H (2085)
Si-H2 (2111)
Si-H3 (2139)
O2SiH (2190)
O3SiH (2245)
B
Dry T/Dry Air
Dry ACN/Dry Air
Dry MeOH/Dry Air
Ambient T/Dry Air
Ambient ACN/Dry Air
Ambient MeOH/Dry Air
Rate Ratio
1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
1e-1
Si-O-Si (1070)
Si-O-Si (1170)
Si-H (2085)
Si-H2 (2111)
Si-H3 (2139)
O2SiH (2190)
O3SiH (2245)
Bond Type
(Wavenumber (cm-1))

Figure S1: Recovered oxidation rate data for the Si-O-Si and O_ySiH (y=1-2) growth and SiH_x (x=1-3) disappearance in various vapors. (Panel A) Absolute value of rate changes (0 h - 2 h). (Panel B) Rate ratio (i.e., $k_i/k_{dry\ air}$).

Results and Discussion

The results in Figure S1 show that the oxidation rates (slowest to fastest) exhibit the following general trend ($p < 0.05$): dry air < dry ACN < dry MeOH < ambient T < ambient ACN < ambient MeOH. These results are fully consistent with minute quantities of H_2O in the analyte vapor stream leading to rapid, irreversible ap-pSi oxidation.