Single Crystalline Thin-Films as Models for Water Evolution From Mineralogically Relevant Protonated Al-O-Si Sites

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Background

- The existence of water and/or hydroxyl groups at the surface of the Moon is well-established by previous remote spectroscopic observations.[1-4]
- Kinetics simulations using weighted rate constants for H^+ implantation (presumed to govern OH group formation) and subsequent thermal desorption of recombining water molecules as a function of latitude, time, and temperature have been carried out by colleagues within REVEALS to accurately model observed trends in the latitudinal distribution of OH groups across Lunar surface.[5]
- While the previous simulation provides a mechanism by which equatorial OH groups formed by H^+ solar-wind implantation may migrate to cooler polar regions via thermally driven recombinative desorption and subsequent readsorption in the form of condensed water, explicit variations in the extent to which different longitudinal regions containing different mineralogical compositions might contribute to these processes remains an open question.

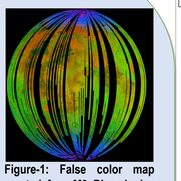


Figure-1: False color map created from M3. Blue shades indicates the presence of OH/H_2O.[4]

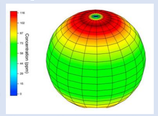


Figure-2: Modeled latitudinal distribution of OH groups at the Lunar surface after simulating 3600 lunar days.[5]

Objective

Single-crystalline $Al_xSi_{(1-x)}O_2$ thin-films will be created and used to explicitly explore surface chemistry associated with deliberately isolated Al-O-Si ternary bridge sites common to feldspar mineralogical frameworks known to be omnipresent within regolith layers present across much of the Lunar surface.

Why Model $Al_xSi_{(1-x)}O_2$ thin-films

- Controllably isolates Si-O-Al bonds in homogenous interface.
- Existence of pre-existing recipes for growth on Ru(0001).[6] (Figure-3)
- Evidence suggesting lower OH thermal stability vs. SiO_2 sites.[7] (Fig-4)

Figure-3: Structure of the two-dimensional model aluminosilicate (Si, Al, and O represented by yellow, grey, and red spheres, respectively).

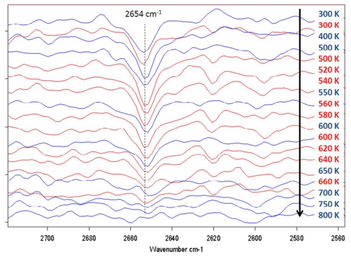


Figure-4: Infrared Reflection Absorption Spectroscopy (IRAS) study shows thermal attenuation of bridging OH groups below ~650K.

Equipment

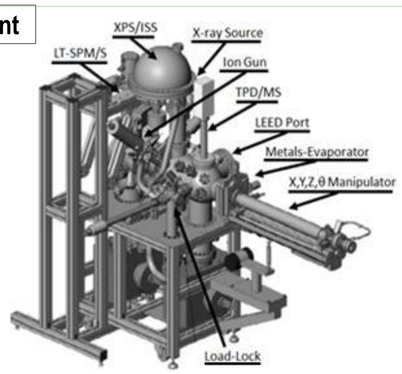


Figure-5: Multi-chambered UHV surface-science apparatus

Experimental Methods

- A Ruthenium (Ru) (0001) single-crystal was cleaned via repeated cycles of Ar^+ sputtering and annealing at 1500 K.
- Following previous recipes, bilayer silica (SiO_2)[8] and aluminosilicate films[6] were prepared via *in situ* physical vapor deposition-controlled growth and characterized with XPS, ISS and LEED.
- Three polymorphically equivalent bilayer films were grown with the following stoichiometries: SiO_2, $Al_{0.42}Si_{0.58}O_2$, and $Al_{0.25}Si_{0.75}O_2$.
- 5L D_2O was directly-dosed on the freshly prepared samples in separate experiments at ca. 130K and then heated to remove contributions from multilayer desorption before collecting TPD spectra from 250-1000K at 10 K/s using a custom designed differentially-pumped mass spectrometer-sample configuration.

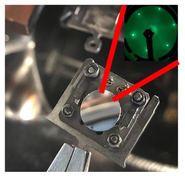


Figure-6: Ru(0001) single crystal mounted within UHV chamber (inset, associated LEED image).

Results

Surface Characterization:

- XPS (left) and LEED (right) characteristics associated with nominally polymorphically equivalent SiO_2 (brown/upper pattern) and $Al_{0.42}Si_{0.58}O_2$ bilayer films (green/lower pattern) are provided in Fig. 7.
- Both films exhibit similar LEED patterns indicative of equivalent hexagonal lattice parameters (D vs E).
- Al incorporation within the aluminosilicate film is evidenced with XPS by a reduction of Si 2p peak intensity accompanied by an increase in Al 2s peak intensity and broadening of the O 1s peak.[9]

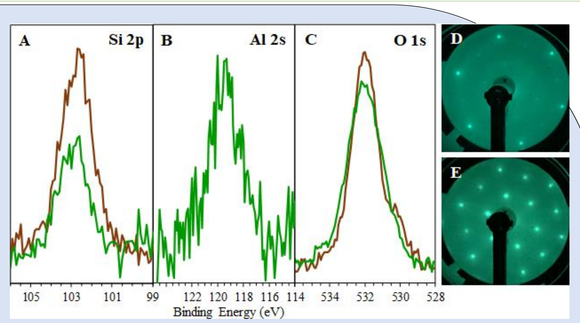


Figure-7: (A-C) Si 2p, Al 2s, and O 1s XPS spectra obtained from bilayer SiO_2 (brown) and $Al_{0.42}Si_{0.58}O_2$ (green) thin-films grown on Ru(0001). (D-E) LEED patterns obtained from bilayer SiO_2/Ru(0001) (D) and $Al_{0.42}Si_{0.58}O_2$/Ru(0001) (E). E_{e^-} = 63 eV in both cases.[9]

D_2O TPD Results:

- D_2O TPD (m/q^+ = 20 AMU) are shown following equivalent procedures using bilayer SiO_2 (brown) and $Al_{0.42}Si_{0.58}O_2$ (green) samples. (Figure-8A)
- To isolate the effect of the Si-OD-Al sites, the spectra have been subtracted to produce the difference spectrum plotted in the lower left panel. (Figure-8B).
- The difference spectrum contains 3 clear desorption components below 700 K.
- Two peaks below ~500K are consistent with the temperature put forward by others for molecular desorption of water from hydrogen bonding arrangements with Si-OH sites.[10]
- The third peak at ~600K (red) fits well with the temperature range for Si-OD-Al attenuation noted in a previous IRAS study (Figure-8C) for nominally identical samples.[7]
- The 4:1 integrated peak intensity ratio found when comparing the lower temperature peaks (blue) to the higher temperature peak (red) is consistent with 2 H-bonded H_2O molecules per every bridging Si-OD-Al site if we presume that the third peak results from recombinative desorption, while the first peaks indicate loss of molecularly bound water. (See Figure-9)
- Presuming a typical recombinative desorption prefactor (10^{13} s^{-1}), we calculate a desorption energy of ~1.6 eV, and can expect that a majority of the sites of these types formed through solar wind implantation on the moon will desorb during each Lunar day at T ≈ 400K.
- A combined TPD/DFT study exploring D_2O interactions at nominally identical films supported on Pd(111) suggested far stabler bridge site protonation, and claimed that ternary OD losses through recombinative desorption were neither expected nor observed below ~1000 K.[11]
- Variation in chemistry correlating with variation in support is postulated to result from differences in the degree of support-film charge-transfer needed to stabilize the deprotonated structures.
- Variation in interstitial cation type/concentration in feldspar structures is postulated to cause qualitatively similar effects on the stability of protonated bridge-sites.
- This is the first report to provide a direct quantification of the concentration of Si-OD-Al sites produced by the aforementioned procedures, which amount to only ~1 OD per every 20 surface layer Al-O-Si sites (~1x10^{13} hydroxyls/cm^2).
  - Through correlation with the known number of silanol groups formed on polymorphically equivalent SiO_2 bilayer films following the same procedure, a defect-mediated dissociative adsorption mechanism has been proposed to explain the limited concentration of OD sites in these experiments.

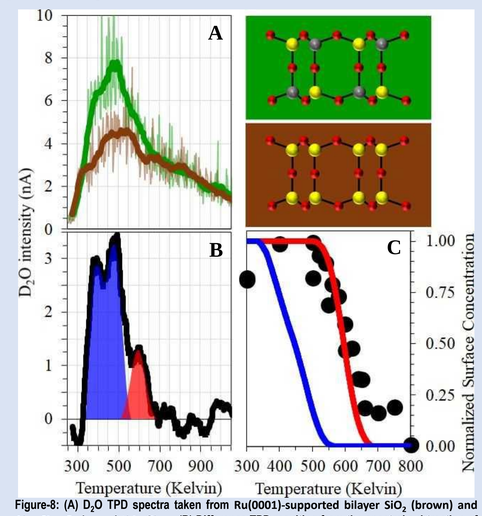


Figure-8: (A) D_2O TPD spectra taken from Ru(0001)-supported bilayer SiO_2 (brown) and $Al_{0.42}Si_{0.58}O_2$ (green) thin-films. (B) Difference TPD resulting from the spectral subtraction of the data provided in panel A. (C) Normalized surface concentrations of bound D_2O desorption precursors associated with the blue and red fits in panel B are plotted as a function of surface temperature (blue and red traces) and compared to Al-OD-Si IRAS peak attenuation data previously reported by others (filled black circles).[9]

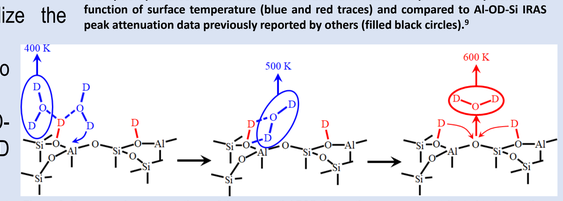
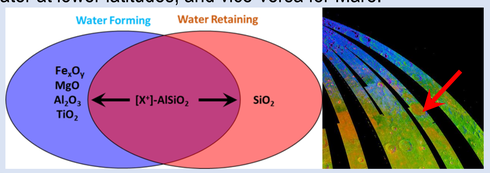


Figure-9: Conceptual representations of the sequential D2O desorption processes attributed to interactions associated with the presence of Al-OD-Si within the $Al_{0.42}$ Si0.58 O2 film. Initially, each protonated bridge site accommodates two hydrogen-bound water molecules, which desorb at different temperatures (~400 and 500 K), with the second desorption channel reflecting molecules that either: (i) bind in more stable initial adsorption configurations (not depicted), or (ii) relax into more stable configurations as a result of the desorption process (as depicted). Following molecular desorption of hydrogen bound water, bridging hydroxyl groups recombine and lead to the desorption of one water molecule for every two protonated bridge sites at ~600 K.[9]

Conclusion

- Relative to simpler binary (Fe, Mg, Al, and Ti) oxides commonly found within Lunar Mare, results from our model $Al_xSi_yO_2$ thin-film experiments suggest stabler hydroxyl group integration following solar-wind H^+ implantation events.
- Since terminal hydroxyl groups provide increased stability to molecular water, feldspar-rich highland regions will tend to retain water at lower latitudes, and vice-versa for Mare.



Future plan

- Ongoing work (occurring this summer) is focused on an analogous TPD investigation of the albite and anorthite end-members of the plagioclase feldspar series to investigate whether our thin-film derived hypothesis may extend to explain different Al-OD-Si site behavior resulting from changes in the nature of the interstitial charge-balancing cations (Mineralogical selections have been aided through collaborative assistance from the CLASS SSERVI site's Exolith laboratory.
- D_2O was used as a proton source based on results from previous work demonstrating evidence of bridge-site protonation using this procedure. Since our results suggest that bridge site protonation may be limited by the number of D atoms created via water cleavage at unrelated defects, we plan to revisit using low-energy D^+ as a protonation source to explore whether higher Si-OD-Al concentrations can be stabilized on the thin-films.
- Follow up investigations intended to provide for more informative comparisons of thin-films and minerals are planned through collaboration with theory.

Reference(s)

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Acknowledgement

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