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Toward a microscopic understanding of the calcium–silicate–hydrates/water interface

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ABSTRACT

Calcium–Silicate–Hydrates (C–S–H) are the main binding phases in most concrete which is the primarily used composite construction material in the world. However, a big lack is cleaving between the actual knowledge about C–S–H, compared to what could be reached using state-of-the-art technologies of modern research. In this article, the formation of a C–S–H phase on a native oxide covered silicon wafer is investigated by means of in-situ attenuated total reflection infrared (ATR–IR) and ex-situ surface-enhanced Raman spectroscopy (SERS). The total thickness of the C–S–H phase is determined by X-ray photoelectron spectroscopy (XPS) to be 3 nm. The formation appears to be reversible depending on the environment pH value and can be performed at room temperature. Based on density functional theory (DFT) calculations, it is shown that the C–S–H phase in the presence of water will change its chemical composition in order to reach the thermodynamic ground state of the system. This change is achieved by a metal–proton exchange reaction. The stoichiometry of these metal–proton exchange reactions is nearly independent of the environment pH value. Electrokinetic measurements yield isoelectric points of 2.0 and 2.6 for the native oxide covered silicon wafer (SiO_2) and the C–S–H phase. This is consistent with a predominance of Si–O sites at the C–S–H/water interface.

1. Introduction

Calcium–silicate–hydrates (C–S–H) phases are the basic building blocks of the ordinary Portland cement [1,2]. In general, the microstructure of hydrated cement paste is characterized by two main pore networks. The first one, the space in the cement paste not filled with hydration products is called the capillary pore space. The second pore network is specifically associated with the C–S–H gel phase. Pores contain adsorbed water that plays an important role in drying shrinkage and creep, and they are responsible for the extremely high surface area of C–S–H phases.

Consequently, the interaction of aqueous solutions with mineral surfaces is one of the most important chemical reactions occurring in nature. Such reactions play a major role in dissolution, precipitation, and sorption processes, affecting the composition and quality of natural waters, the formation of soils, the removal of CO_2 from the atmosphere, the uptake and release of plant nutrients, the mobility of heavy metal contaminants, and the global cycling of chemical elements [3–5]. They may also be responsible for the sequestration of water on Mars [6] and the formation of prebiotic molecules early in Earth's history [7]. Interfacial reactions between solid surfaces and aqueous solution are also important in the preparation and performance of metal-on-metal oxide catalysts, metal corrosion and surface passivation [8–13], the cleaning of semiconductor surfaces [14], chemical sensing [15–21], and water treatment [22].

The ability to probe complex mineral–aqueous solution interfaces on an atomic scale has led to detailed insights into how water reacts with mineral surfaces, how heavy metal ions and organic contaminants sorb on and desorb from mineral surfaces, the mechanisms by which mineral surfaces dissolve [23] and grow [24], and the structure and composition of the electrical double layer (EDL) at mineral/water interfaces, including those coated by organic matter or biofilms.

What is not yet known with much certainty are the structure and properties of water at such interfaces. There is experimental evidence that the dielectric constant of water near solid interfaces is an order of magnitude lower than that of bulk water at room temperature. This affects the ability of water molecules to reorient and should influence chemical reactions near interfaces. It has long been

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known that the structure and physical properties of water near mineral surfaces can be substantially different from those of bulk water, that surfaces can perturb the fluid structure and properties up to several molecular diameters from the surface, and that these differences can be key to understanding mineral surface chemistry [1,25–29]. Computational methods are playing an important role in advancing understanding of near-surface water.

The current state of research in the field of mineral/water interfaces is far from being as advanced as in the case of metals and metal oxides/water. This is mainly due to the difficulty of preparing defined substrate surfaces, which do not change their chemical composition and microstructure during the adsorption, permitting the formation of an ordered molecular structure and their spectroscopic characterization. The main purpose of this article is to point one possible way toward a microscopic understanding of the C–S–H/water interface. In this article, the reproducible formation of a C–S–H phase on a native oxide covered silicon wafer is investigated by means of several different surface sensitive spectroscopic techniques. For a deeper understanding, we support our results by ab initio thermodynamic simulations and discuss the formation mechanism of the C–S–H phases.

2. Experimental

2.1. Attenuated total reflection infrared (ATR–IR) spectroscopy

Fourier transform (FT) attenuated total reflection infrared spectra were collected using a Thermo-Nicolet 5700 FT-IR spectrometer with a deuterated triglycine sulfate (DTGS) detector. For the measurements an n-type silicon ATR crystal (27 mm × 20 mm × 3 mm; Tydex, Russia) was used. For each spectrum 1000 interferograms were recorded. To place the ATR crystal under 45° into the beam a four beam condenser (Harrick) was used.

The ATR crystal was chemically cleaned with a 30 min exposure at 80 °C to a 1:3 solution of aqueous H_2O_2: 18 M H_2SO_4 (piranha solution). Afterwards the ATR crystal was rinsed thoroughly with deionized (DI) water with a resistivity of 0.055 μS/cm. Following the cleaning, the ATR crystal was promptly mounted to the ATR assembly and purged with dry N_2. The sample was mounted in a purchased closed fluid cell with tube connections, which were connected with an MDSP3f syringe pump (MMT Micro Mechatronic Technologies GmbH, Siegen) for a continuous fluid exchange, while the flow was adjusted to 500 μL/min. A saturated aqueous solution of $Ca(OH)_2$ was purged with Ar for all measurements to avoid any effects due to CO_2 contamination. All measurements were performed at room temperature 295 K.

2.2. Surface enhanced Raman spectroscopy (SERS)

Raman measurements were done with a SENTERRA dispersive Raman microscope (Bruker). For the investigations a 785 nm laser was used with a power of 50 mW. In order to enhance the Raman intensity of the synthesized C–S–H phase we prepared a film of gold nanoparticles (diameter 40 nm) layer on the sample. This was done by drying one drop of a commercial solution containing the nanoparticles.

2.3. X-ray photoelectron spectroscopy (XPS)

XPS analyses were performed with a Quantum 2000 Scanning ESCA Microprobe (Physical Electronics, USA) spectrometer equipped with a concentric hemispherical analyzer under ultra-high vacuum conditions (10^{-9} mbar) using an Al Kα X-ray source. Spectra were recorded at 45° take-off angle with respect to the surface. A sample area of 100 μm × 100 μm was analyzed with a pass energy of 46.95 eV for survey and 11.75 eV for detailed elemental scans. The spectra obtained were analyzed using the CASA XPS software, and the surface sensitivity factors used to determine the atomic concentrations were taken from the MultiPak Version 6.0 software (supplied by Physical Electronics).

2.4. Electrokinetic measurements

Isoelectric titrations were performed between pH values 2 and 12 (Malvern ZetaSizer Nano ZS, 633 nm, $f(\kappa) = 1.5$). The titrations were conducted at room temperature using hydrochloric acid (1 M) and potassium hydroxide (1 M) solutions.

2.5. Spectroscopic ellipsometry

Spectroscopic ellipsometry measurements were performed on a Jobin-Yvon UVISEL ellipsometer, in the range of 0.6–6 eV, to verify the thickness of the surface layer.

2.6. Atomic force microscopy (AFM)

The AFM images are recorded with a Veeco Digital Instrument Nanoscope Dimension 3100 in ambient atmosphere. The tool is disposed on a free-vibration table and enclosed inside a free-acoustic cover during the measurement. All the measurements are done in tapping mode with a resolution of 512 points per line.

2.7. Scanning electron microscopy (SEM)

SEM images were recorded by means of a NEON 40 FE–SEM (Carl Zeiss SMT AG, Germany). The imaging was performed using acceleration voltages between 1.5 and 10.0 kV.

2.8. Computational methods

The total-energy and ground-state structure calculations in the present work were performed using density functional theory (DFT) as implemented in the Vienna ab initio simulation program (VASP) [30]. The electron–ion interaction is treated within the projector-augmented wave (PAW) method [31]. The valence electron wave functions are expanded into plane waves up to the kinetic energy cutoff of 360 eV. This energy cutoff was found to yield converged structural parameters for bulk $Ca_3Si_3O_9$. The Brillouin zone sampling was performed with 2 × 2 × 2 and 2 × 2 × 1 mesh of Monkhorst–Pack *k*-points [32] for the $Ca_3Si_3O_9$ bulk and surface calculations, respectively. This was found to ensure an energy convergence better than 0.05 eV. The electron–electron exchange and correlation (XC) energy is approximated within the generalized-gradient approximation (GGA), using the XC potential developed by Perdew et al. [33]. The PW91 functional has been found to describe reliably the structure and energetics of hydrogen bonded water molecules [34–36].

The optimization of the atomic coordinates (and unit cell size/shape for the bulk materials) was performed via a conjugate gradients technique which utilizes the total energy and the Hellmann Feynman forces on the atoms (and stresses on the unit cell).

We used the usual approach for modeling the surfaces using three-dimensional periodic boundary conditions (PBC) by considering slabs of $Ca_3Si_3O_9$. In addition to the *k*-point density and E_{cut} discussed above, the convergence in surface calculations is also dependent on the thickness of the slab of material and the width of the vacuum layer between the slabs. Again we checked convergence by running a series of test calculations with different slab thicknesses and gap widths. Following these test calculations the $Ca_3Si_3O_9$ (0 0 1) supercell used in the calculations contained two layers of $Ca_3Si_3O_9$ units. The simulation cells were constructed so