Reduction of Incubation Period by Employing OH-Terminated Si(001) Substrates in the Atomic Layer Deposition of Al$_2$O$_3$

Sun S. Lee,[†] Jae Y. Baik,[†] Ki-Seok An,[†] Yung D. Suh,[‡] Jin-Ho Oh,[§] and Yunsoo Kim*,[†]

Thin Film Materials Laboratory, Advanced Materials Division, and Precision Chemical Technology Laboratory, Advanced Chemical Technology Division, Korea Research Institute of Chemical Technology, Yuseong P.O. Box 107, Daejeon 305-600, Korea, and Surface Analysis Laboratory, Nano-Surface Group, Korea Research Institute of Standards and Science, Yuseong P.O. Box 102, Daejeon 305-600, Korea

The phenomenon of low initial growth rates in atomic layer deposition (ALD) of various oxides on HF-treated (thus H-terminated) Si(001) substrates, which is termed the incubation effect or incubation period, can be effectively avoided by use of OH-terminated Si(001) substrates. Two ways of preparing OH-terminated Si(001) were devised in this work: one from atomically clean Si(001) and the other from H-terminated Si(001). The effect of reducing the incubation period was confirmed in the ALD process of aluminum oxide (Al$_2$O$_3$) thin films in which trimethylaluminum and water were used as sources of aluminum and oxygen, respectively. The use of OH-terminated Si(001) substrates has another beneficial effect of producing thin films with very smooth surface morphology. We propose the use of OH-terminated Si(001) substrates for growing thin films of many other metal oxides that have shown the incubation period on H-terminated Si(001) substrates.

I. Introduction

In the atomic layer deposition of many oxides on H-terminated silicon substrates, it is often found that the initial growth rates of oxide films, for example Al$_2$O$_3$, ZrO$_2$, or HfO$_2$, are much lower than when the ALD cycles have been executed a few tens of cycles.[1−6] This phenomenon is called the incubation period (effect) or substrate-inhibited growth,[6] and investigators in the field have tried to eliminate or reduce this initial delay in growing oxide films by devising various methods such as formation of a chemical oxide[4−6] by wafer cleaning and excessive use of a metal precursor.[7] The chemical oxide that is formed on a silicon substrate is known to contain many surface hydroxyl species[3−6] and they are responsible for the reduction of incubation period in the case of the ALD of Al$_2$O$_3$ in which trimethylaluminum (Me$_3$Al, TMA) and water were used as sources for aluminum and oxygen, respectively.[1] It is also believed true that the ALD of HfO$_2$ with HfCl$_4$ as the Hf source is initiated by the hydroxyl groups present on the substrate surface.[5,6] Another important aspect of having surface hydroxyl groups on Si substrates is that the film growth becomes more homogeneous[5] than when the Si surfaces are H-terminated, for which island growth is initially prevailing. Using an excessive amount of a metal precursor can be a way of avoiding the incubation period; however, this may not become a viable solution for many practical cases. Although the wafer cleaning method has been improved to such a level that the thickness of the surface oxide formed during the cleaning process is only a few nanometers,[4] it is still desirable not to have this oxide layer

when high-k materials are needed on silicon for the obvious reason of increasing the effective capacitance. One way out of this difficulty would be to hydroxylate the silicon surface to one monolayer thickness only, if possible at all. Preparing surface hydroxyl groups on silicon substrates is not new as it can be found in numerous previous works, especially in relation to chemisorption of water.[8−12] Hydroxyl groups have also been made on a few metal surfaces.[10,12] However, it has not been reported to date that a monolayer of only the hydroxyl groups of reasonably good quality can be prepared on any silicon surfaces. In this work, we report on the preparation of surface hydroxyl groups on Si(001) and the employment of the hydroxylated Si(001) substrates in the ALD of Al$_2$O$_3$.

Previously Bergerson et al.[13] devised a way of making a monolayer of an amine by reacting the amine with a chlorinated Si(001) substrate in a high-vacuum chamber. The amine took the place of chlorine on the surface by removing it as hydrogen chloride, resulting in a self-assembled monolayer. A similar reaction was thought feasible between water and a chlorinated Si(001) substrate. A chlorinated Si(001) surface can be prepared in a high-vacuum chamber by adsorbing chlorine on an atomically clean Si(001) substrate. In the semiconductor industry, however, it is common to use H-terminated Si substrates, and therefore, we designed two kinds of hydroxylation schemes as shown in Figure 1: the first is to start with an atomically clean Si(001) surface to induce chlorine adsorption followed by the reaction with water, and the second is to use a H-terminated Si(001) surface and make a reaction of the surface with chlorine to have chlorine adsorption similar to the first case, followed by subsequent reaction with water. In this paper we describe the realization of the above ideas for the preparation of OH-terminated Si(001) surfaces and their application in the ALD of Al$_2$O$_3$ thin films to reduce the incubation period by the enhanced chemical reactivity due to the presence of the hydroxyl groups.

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* To whom correspondence should be addressed: Tel 82-42-860-7350; fax 82-42-861-4245; e-mail yunsukim@krict.re.kr.

† Thin Film Materials Laboratory, Advanced Materials Division, Korea Research Institute of Chemical Technology.

‡ Precision Chemical Technology Laboratory, Advanced Chemical Technology Division, Korea Research Institute of Chemical Technology.

§ Korea Research Institute of Standards and Science.

Reduced Incubation Period with OH-Terminated Si

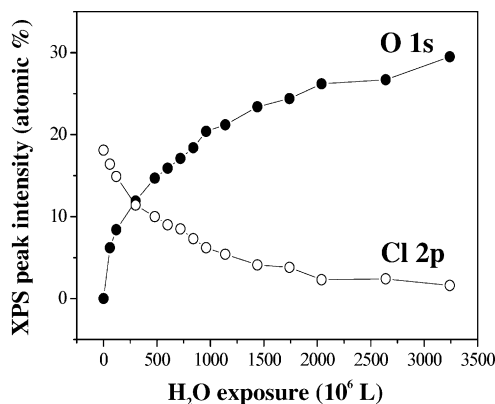*J. Phys. Chem. B, Vol. 108, No. 39, 2004* **15129**
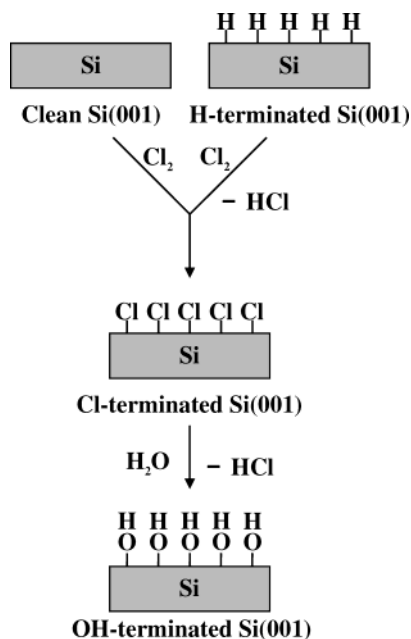
Figure 1. Schemes for hydroxylation of Si(001) surfaces: Hydroxylation can be performed with either a clean Si(001) surface or a H-terminated Si(001) surface.

Figure 2. XP peak intensity variations (in atomic percent) of Cl 2p and O 1s core levels plotted against H_2O exposure in Langmuir.

Water was further purified by several freeze−pump−thaw cycles before use on the clean Si(001)2×1 surface. Dosing of chlorine or water was performed from a backfilled gas line into the appropriate chambers. The exposure was recorded in langmuirs (1 L = 10^{-6} Torr s). The purity of Cl_2 (99.5%, Aldrich) was checked by use of the QMA.

II. Experimental Section

A small reaction chamber attached to the preparation chamber of our ESCALAB MK II (VG Scientific, Ltd.) was employed for chemisorption of chlorine and water and/or ALD experiments. The analysis chamber was equipped with a Mg/Al dual-anode X-ray source, a differentially pumped helium resonance lamp, and a spherical sector electron energy analyzer with a base pressure lower than 1.5×10^{-10} Torr. The preparation chamber (with a base pressure of ∼2.0×10^{-9} Torr), equipped with a quadrupole mass analyzer (QMA), was used for chemisorption of chlorine on clean Si(001). The small reaction chamber, independently pumped by a turbomolecular pump, had dosing lines for Cl_2 and H_2O with a base pressure of ∼1.5×10^{-7} Torr. For the X-ray photoelectron spectroscopy (XPS) measurements, a Mg X-ray ($h\nu$ = 1253.6 eV) was used. A He I line ($h\nu$ = 21.22 eV) was used for angle-integrated ultraviolet photoelectron spectroscopy (UPS) measurements. Synchrotron radiation experiments were conducted at beamline 7 ($h\nu$ = 130 eV) of Hiroshima Synchrotron Radiation Center (HiSOR) at Hiroshima University. Atomic force microscopy (AFM) (Multimode AFM with Nanoscope IV, Veeco Instruments Inc.) was used to investigate surface morphology and roughness. Typical scan condition was 1 Hz scan rate, 200 × 200 nm² scan size in contact mode.

A boron-doped Si(001) wafer (resistivity 5−12 Ω cm; dimensions 5 × 20 × 0.8 mm³) was chemically etched with a 5% aqueous HF solution and rinsed with deionized water before it was loaded into the preparation chamber of the ESCALAB. The wafer was degassed at 800 °C for several hours and repeatedly annealed at 1250 °C by resistive heating to obtain a clean 2×1 surface. Cleanliness of the 2×1 surface was checked by XPS and UPS, which showed no traces of contamination and a high intensity of the surface state (the dimer dangling bond state), respectively. The temperature of the substrate was monitored by infrared and optical pyrometers. Temperatures below 250 °C were estimated by extrapolation of the relationship between the current applied to the substrate and the measured temperature.

III. Results and Discussion

Chemisorption of chlorine on a clean Si(001)2×1 surface was performed at room temperature and the exposure for full saturation was found to be about 5 L of chlorine at 1.0×10^{-8} Torr. For a H-terminated Si(001) surface, chlorination was carried out at 80 °C with chlorine exposure of 6.0×10^8 L (for 10 min at 1.0 Torr). Figure 2 shows the intensity variation of the Cl 2p and O 1s photoelectron peaks starting from a Cl-saturated Si(001)2×1 surface as the exposure to water increased with the substrate temperature kept at ∼230 °C. Water was introduced at ∼1.6 Torr. The peak intensities were calculated in atomic percent from normalized peak areas including that of the Si 2p signal. Similar to the report by Klaus et al.,[14] in which $SiCl_4$ and H_2O were used for the ALD of SiO_2, replacement of surface chlorine atoms with hydroxyl groups by water exposure required more than 10^9 L of H_2O without using a catalyst such as pyridine. Although not shown, the XP survey spectra of a clean Si(001)2×1 surface, its Cl-terminated state, and the final OH-terminated surface revealed that only the relevant peaks of Si, Cl, and O appeared during the process of hydroxylation. Carbon contamination was not detectable within the sensitivity limit of the XPS technique.

In parallel with the XPS experiments, we took angle-integrated ultraviolet photoelectron spectra of the chlorinated Si(001)2×1 surface at increasing water exposures as shown in Figure 3. For comparison, the spectrum of the clean Si(001)-2×1 surface is included (Figure 3a). In the spectrum, the surface state (originated from the dangling bonds) of the clean Si(001)-2×1 is clearly seen at the binding energy of ∼0.8 eV. Upon saturation of the surface with chlorine atoms, the UV spectrum, Figure 3b, changes drastically, showing the appearance of the structures pertaining to chlorine adsorption at 5.8, 6.8, and 8.4 eV below the Fermi level, mainly attributed to the Cl-bonding combinations of Cl−$3p_x$ and Cl−$3p_y$ orbitals, and the Si−$3p_z$−Cl−$3p_z$ orbital, respectively,[15,16] and disappearance of the surface state of the clean Si(001)2×1. From spectra c−g, gradual changes of the peak shapes are seen as water reacted with adsorbed chlorine, removing chlorine as HCl and leaving OH groups on the surface. The structures at the binding energies of 6.9 and ∼8 eV with a broad feature at 11.8 eV develop with decreasing the structures related to the Cl 3p orbitals. The

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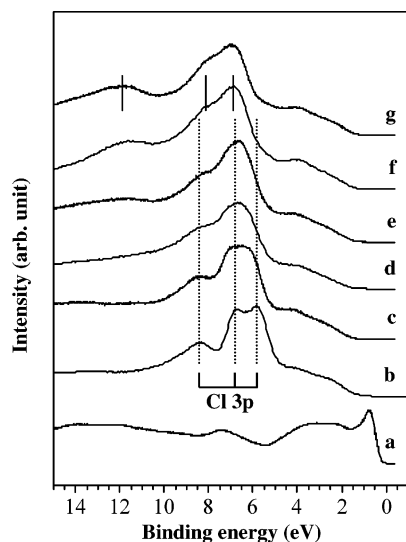
Figure 3. Angle-integrated UP spectra for the process of hydroxylation of a Si(001)2 × 1 surface—(a) clean Si(001)2×1 surface, (b) after its chlorination—and the surfaces obtained by exposing the chlorinated Si(001)2×1 surface to H_2O at ∼230 °C for (c) 2 min, (d) 5 min, (e) 8 min, (f) 15 min, and (g) 25 min at ∼1.6 Torr.

general features of the UV spectra, Figure 3f and g, closely resemble those of water adsorbed on Si(001) reported by other investigators,[17−19] although the spectral interpretations varied. These spectra are not clearly distinguished from those of water adsorbed on the Si(001)2×1 surface. In angle-integrated UPS measurements with the photon source of 21.22 eV, the Si−H bond is not clearly observed because of its relatively small cross-section. However, the difference between the water adsorption on the Cl-terminated Si(001)2×1 surface and that on the clean Si(001)2×1 surface will be clearly shown in the Si 2p core level spectra by SRPES in the following.

Replacement of chlorine adsorbed on the Si(001)2×1 surface by water and subsequent formation of hydroxyl groups on the surface were examined more closely by synchrotron radiation photoemission spectroscopy (SRPES). Figure 4a shows a Si 2p core level spectrum for a clean Si(001)2×1 surface as a reference. In this and subsequent figures (Figure 4b−e), the experimental data are denoted by black dots and the synthesized curves resulting from curve-fitting are denoted by orange-red solid curves running through the black dots. The photon energy and the emission angle were taken at $h\nu$ = 130 eV and 60°, respectively, to obtain surface-sensitive Si 2p spectra. In the figure, the Si 2p components due to the up (U; binding energy shift relative to the bulk component ΔBE = −0.54 eV, in orange) and down (D; ΔBE = +0.06 eV, in olive green) dimer Si atoms having dangling bonds, the Si atoms in the second layer (2nd, ΔBE = +0.25 eV, black solid curve), symmetric dimers and/or defects (C, ΔBE = −0.22 eV, brown solid curve), and the bulk (B, blue solid curve) Si atoms are resolved. The line shape of the spectrum and the fitting results are quite consistent with previous reports.[20,21] The spectrum for a fully chlorine-saturated Si(001)2×1 surface (by 5 L of Cl_2 exposure) is shown in Figure 4b, which is typical of Cl-adsorbed Si(001) as previously reported.[16,22] The complete disappearance of the up and down dimer components and the appearance of a new component (in lime, ΔBE = +0.94 eV) due to chemisorption of chlorine indicate full coverage of the Si(001)2×1 surface by chlorine atoms. Up to this stage, the LEED (low-energy electron diffraction) pattern (not shown) of the Si(001) surface did not show a noticeable change in its 2×1 structure. Exposure of this Cl-covered Si(001)2×1 surface to water vapor (to 2.0
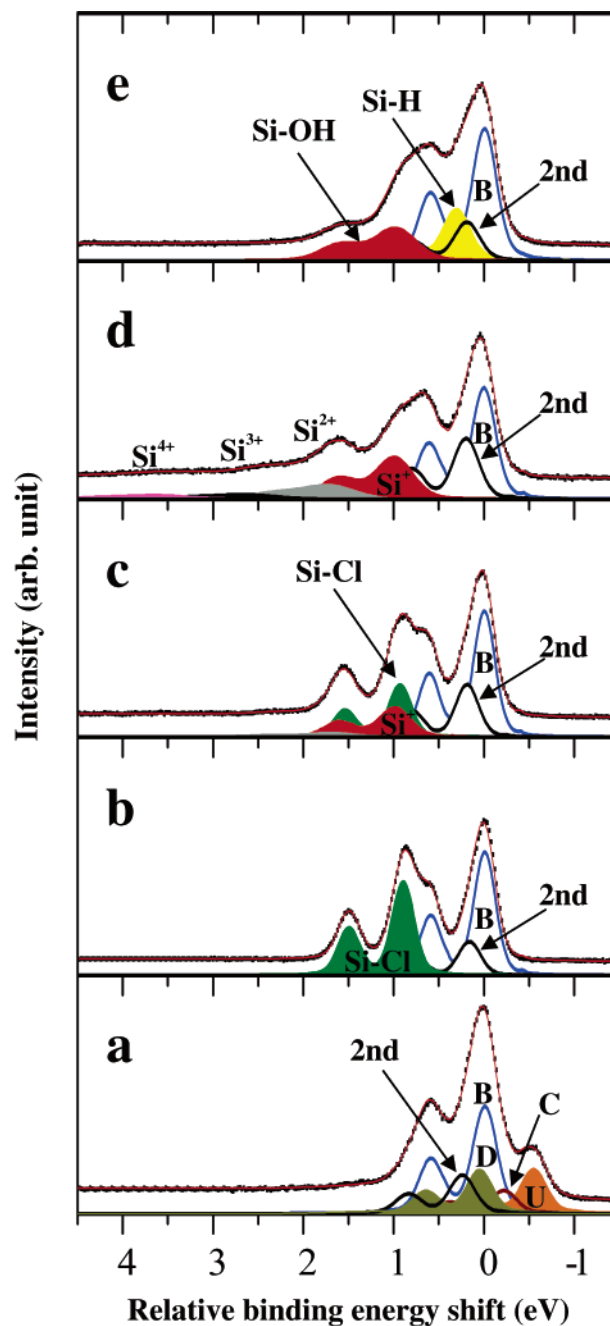
Figure 4. Synchrotron radiation photoemission spectra for the process of hydroxylation of a Si(001)2×1 surface—(a) clean Si(001)2×1 surface, (b) after its chlorination—and the surfaces obtained by exposing the chlorinated Si(001)2×1 surface to H_2O at ∼230 °C for (c) 2.0 × 10^9 L and (d) 7.2 × 10^9 L (complete replacement of Cl). A spectrum for a H_2O-chemisorbed Si(001)2 ×1 surface is given (e) for comparison with the OH-terminated Si(001) surface.

× 10^9 L at ∼230 °C) changed the spectral shape of the Si 2p peaks as shown in Figure 4c. This change was caused by the partial removal of chlorine atoms from the Si surface and chemisorption of hydroxyl groups in their places as clearly resolved in the figure (lime for Si−Cl and red for Si−OH, with ΔBE = +0.99 eV). When all the chlorine atoms were replaced by hydroxyl groups (at 7.2 × 10^9 L of water), the Si 2p spectrum changed further to that shown in Figure 4d, in which a peak probably due to Si^{2+} species (in gray, ΔBE = +1.71 eV) is resolved together with that due to the hydroxylated Si atoms (Si^+). There also appeared relatively small components corresponding to the Si^{3+} (in black, ΔBE = +2.62 eV) and Si^{4+} (in

purple, $\Delta BE = +3.60$ eV) species[23,24] which indicate partial surface oxidation. The identity of the Si^{2+} species cannot be deciphered at the moment, although it is speculated that it may be due to the oxidized Si species such as partial $2(OH)-Si$ species at the top Si layer with partial breaking of the Si dimer bonds and/or the Si back-bonds between the top and second Si layers, etc. The larger intensity of the final O 1s peak ($\sim$29 at. %) than that of the initial Cl 2p peak ($\sim$18 at. %) shown in Figure 2 may be attributed to partial oxidation of the top and/ or the second layer. Greater attenuation for the Si atoms covered by OH groups than those covered by Cl atoms may also have contributed to the difference in intensities.

To distinguish the OH-terminated Si(001) surface from a H_2O-chemisorbed Si(001) surface, SRPES of the latter was taken (Figure 4e, for 10 L exposure of water at RT) and compared with that of the former given in Figure 4d. In the case of the H_2O-chemisorbed Si(001) surface, the Si 2p component at +0.31 eV due to the Si$-$H bonds (in yellow) contributes much to the intensity in the valley between the bulk Si $2p_{1/2}$ and Si $2p_{3/2}$ peaks[25] whereas for the OH-terminated Si(001), due to the absence of the Si$-$H bonds, the corresponding region shows a decisively deeper valley.

The SRPES experiments demonstrated that we have successfully prepared an OH-terminated Si(001) surface starting from a clean Si(001)2×1 surface. On the other hand, for H-terminated Si(001) surfaces prepared by a wet process, XPS measurements showed similar spectral results except that carbon contamination was always present and the O 1s signals were much larger than those for OH-terminated Si(001) surfaces obtained from clean Si(001)2×1 substrates. This is understandable, for the wet process involves etching, which roughens the surface, and by this process many dihydride species are produced,[26,27] resulting in more chlorine atoms on the Si surface and thus subsequently more hydroxyl groups. It was also noted by XPS that, starting from a H-terminated Si(001) surface obtained by a wet process, the final OH-terminated Si(001) surface was somewhat oxidized judging from the appearance of a Si 2p peak corresponding to the formation of the Si^{4+} species at $\sim$3.6 eV higher binding energy than the bulk Si 2p peak.

To demonstrate the effect of the OH-terminated Si(001) surfaces, which are expected to have enhanced surface reactivity compared to the H-terminated Si(001) surface, ALD of aluminum oxide thin films was performed on two representative Si(001) surfaces: (i) a OH-terminated Si(001) surface obtained from a clean Si(001)2×1 surface and (ii) a H-terminated Si(001) surface. The ALD of Al_2O_3 was carried out with trimethylaluminum and water as sources for aluminum and oxygen, respectively. This ALD reaction has been known to show an incubation period on H-terminated Si(001) or Si(111). To compare the initial growth rates of Al_2O_3 films on these surfaces, only 12 ALD cycles of TMA$-$purge$-H_2O-$purge steps were performed. The substrates were kept at 200 °C for the ALD processes. This deposition temperature was chosen by considering the uses of TMA by other investigators.[28,29] TMA and water were each supplied at 500 mTorr for 40 s. After each ALD cycle was completed, the substrate was transferred to the analysis chamber of the ESCALAB for the measurement of the Al 2p photoelectron peak. The takeoff angle of the photoelectrons was set at 20° to make the measurements more surface-sensitive. Although the intensity of the Al 2p photoelectron peak is not directly proportional to the thickness of a growing film, it can clearly serve as a way of comparing the initial growth rates of the Al_2O_3 films when the films are very thin.
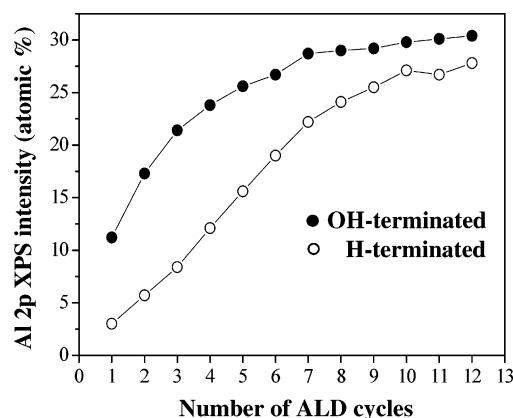
Figure 5. Al 2p XP peak intensities obtained for the OH-terminated Si(001) substrate [prepared by using a clean Si(001)2×1 surface] (●) and the H-terminated Si(001) substrate (○).
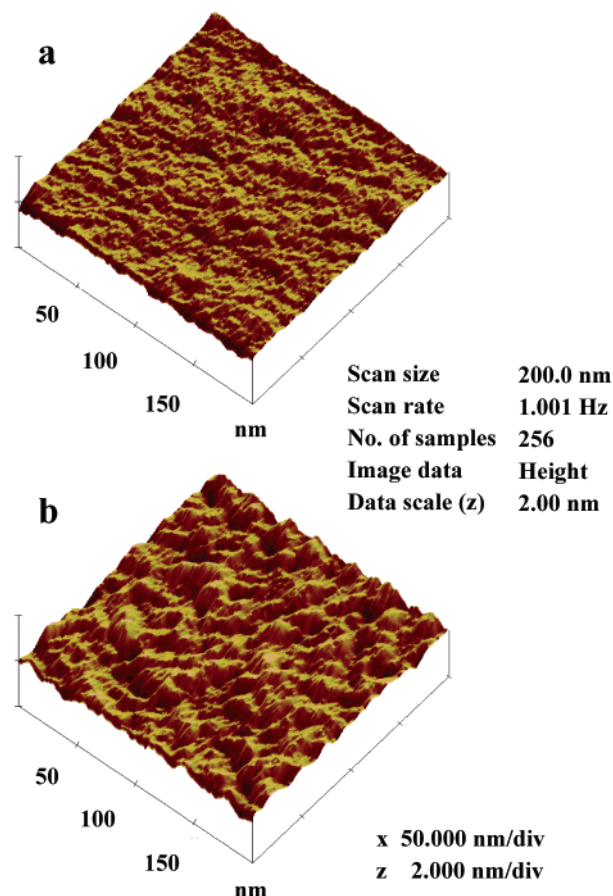
Figure 6. AFM images for Al_2O_3 films deposited on OH-terminated Si(001) (a) and on H-terminated Si(001) (b) with 12 ALD cycles.

Figure 5 shows the intensities of the Al 2p photoelectron peaks taken for the two substrates, plotted against the number of ALD cycles. After the first ALD cycles, it is obvious that the Al 2p intensity is much greater for the OH-terminated Si(001) substrate than for the H-terminated Si(001) substrate. As the number of ALD cycles is increased, the peak intensity of the OH-terminated Si(001) substrate consistently shows greater values than the H-terminated Si(001) substrate. The differences would have been more striking had we used a much shorter water supply time as in an actual ALD situation,[4] because a longer water supply tends to produce more surface active sites. The OH-terminated Si(001) substrate made from a H-terminated Si(001) surface and the SiO_2-formed Si(001) substrate showed

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Al 2p signal intensities comparable to that of the OH-terminated Si(001) substrate made from a clean Si(001)2×1 surface. Their Al 2p intensities are not shown in Figure 5 for clarity. It was noted that the OH-terminated Si(001) substrate made from a H-terminated Si(001) surface showed highest reactivity toward the ALD of Al_2O_3. Thus, the in situ ALD experiment clearly demonstrated that hydroxylation of Si(001) surfaces has the effect of reducing the incubation period in the initial growth of Al_2O_3 films.

The Al_2O_3 thin films were then examined by atomic force microscopy as shown in Figure 6. It is clearly seen that the film (Figure 6a) deposited on the OH-terminated Si(001) substrate has much smoother surface morphology than the film (Figure 6b) deposited on the H-terminated Si(001) substrate. The root-mean-square surface roughness values were measured to be 0.070 and 0.135 nm, respectively, for the Al_2O_3/OH/Si(001) and Al_2O_3/H/Si(001). This is a good indication that the OH-terminated Si(001) surface helps the Al_2O_3 film grow homogeneously on the substrate surface as well as eliminating the incubation period.

IV. Summary

The OH-terminated Si(001) surfaces have been prepared from both a clean Si(001)2×1 surface and a H-terminated Si(001) surface obtained by a wet process. An OH-terminated Si(001) surface was compared with a H_2O-chemisorbed Si(001) surface by SRPES in which the state of the surface OH species was clearly distinguished from the mixed state of H and OH species of H_2O-chemisorbed Si(001). The OH-terminated Si(001) surfaces have been found to show the effect of reducing the incubation period in the initial stage of the ALD of Al_2O_3 thin films. It has also been found that the Al_2O_3 films grown on OH-terminated Si(001) are much smoother than those grown on H-terminated Si(001). The method of preparing OH-terminated Si(001) surfaces described in this paper may have general applicability for hydroxylation of other semiconductors such as Ge[30] and GaAs[31] and such metals as Ru,[32] Rh,[33] and Pt[34,35] and many other materials[10,12] that have been reported to show dissociative chemisorption of water, for the purpose of surface functionalization, including self-assembled monolayers.[36,37] Presently, we are investigating the possibility of reducing the incubation period for the $HfCl_4$−H_2O ALD system for producing HfO_2 thin films.

Supporting Information Available: (1) Hydroxylation of a clean Si(001)2×1 surface, (2) LEED pattern of a Cl-terminated Si(001)2×1 surface, (3) hydroxylation of a H-terminated Si-(001) surface, (4) comparison of Si 2p photoelectron peaks of OH-terminated Si surfaces made in 1 and 3, (5) Comparison of O 1s photoelectron peaks of OH-terminated Si surfaces made in 1 and 3, and (6) XP survey spectra for different OH/Si(001) surfaces (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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