



Vapor-phase adsorption kinetics of 1-decene on hydrogenated Si(1 1 1)

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Abstract

We have investigated in situ and in real time vapor-phase adsorption kinetics of 1-decene on hydrogenated Si(1 1 1), using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIRS). The Si surface is hydrogenated in a NH_4F solution. The p-polarized IR absorbance of Si–H vibrational mode at 2083.7 cm^{-1} and its absence in s-polarized IR absorption spectrum support that the Si(1 1 1) surface is terminated mostly with monohydrides prior to 1-decene exposure. The 1-decene adsorption and simultaneous dehydrogenation result in a decane self-assembled monolayer (SAM). We have employed contact angle goniometry and angle-resolved X-ray photoelectron spectroscopy (AR-XPS) to characterize the decane SAM prepared at substrate temperatures ranging from 30 to 180 °C. Independent of the substrate temperature, the average sessile-drop water contact angle on decane SAM is $102 \pm 2^\circ$, indicative of its hydrophobicity. The constant contact angle suggests that the decane coverage is approximately identical for all SAMs prepared in the above temperature range. The ratio of C(1s) to Si(2p) photoelectron intensities measured by AR-XPS and the integrated CH absorbance upon complete SAM formation measured using ATR-FTIRS further substantiate that the saturation surface coverage of decane is approximately equal for all SAMs. The thickness of the decane SAM and the tilt angle of the alkyl chain, calculated from the C(1s)/Si(2p) intensity ratio, are $13 \pm 2\text{ \AA}$ and $0\text{--}32^\circ$ from the surface normal, respectively. This tilt angle agrees with 27° calculated from the dichroic ratio of polarized IR absorbance of C–H stretching vibrational modes near 2900 cm^{-1} . The polarization measurement additionally provides the twist angle of decane chains at 90° . The fractional surface coverage of decane and hydrogen, calculated from C–H and Si–H stretching vibrational modes, follow a 1st order Langmuir isotherm. The absolute saturation coverage of decane is approximately 4.2×10^{14} molecules/ cm^2 . The isotherms indicate that the adsorption of 1-decene on hydrogenated Si(1 1 1) is a two-step process where fast adsorption precedes slow adsorption. At 80 °C, for instance, the empirical rate constant that governs the 1-decene adsorption is $k'_{2a} = (4.8 \pm 0.1) \times 10^{-2}\text{ min}^{-1}$ for the fast adsorption step and $k'_{2b} = (1.2 \pm 0.1) \times 10^{-2}\text{ min}^{-1}$ for the slow adsorption step. The rate constants measured at different substrate

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temperatures provide the apparent activation energy and pre-exponential factor for the rate-limiting step during fast adsorption: 1.7 ± 0.2 kcal/mol and 0.5 ± 0.1 min⁻¹. The kinetics of decane SAM formation is well described by a chain reaction mechanism, in which alkene desorption is much faster than alkene adsorption and hydrogen abstraction by alkane radical. In this limit, the apparent activation energy for alkane formation is equal to the difference between the intrinsic barriers for hydrogen abstraction and desorption of the adsorbed alkane radical. As an approximation for 1-decene on Si(111), we have performed density functional theory calculations for the 1-hexene adsorption onto a model Si(100) surface and subsequent hydrogen abstraction by the secondary hexane radical to estimate kinetic parameters governing the steps in the chain mechanism. These calculations predict desorption and hydrogen abstraction barriers of 13.8 and 17.6 kcal/mol, respectively, which yield an effective activation energy of 3.8 kcal/mol, in good agreement with the experimentally determined value. The estimated values of the elementary rate constants further support the hypothesis that desorption is much faster than adsorption and hydrogen abstraction. The rate of alkane SAM formation is therefore determined by a kinetic competition between desorption and hydrogen abstraction. Assuming that the desorption-to-hydrogen-abstraction prefactor ratio v_{-1}/v_2 is on the order of 10^3 , the fractional surface coverage of Si dangling bonds (δ) that initiate the 1-decene adsorption is 1×10^{-3} , which translates to 7×10^{11} dangling bonds per cm². Monitoring the decane SAM over a period of 2 months using AR-XPS indicates that Si underneath the monolayer gets oxidized in the ambient air, losing 20% of the initial decane coverage.

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1. Introduction

Self-assembled monolayers (SAMs) of long-chain organic molecules with properly functionalized termini provide a means to modify the characteristics of semiconductor surfaces [1,2]. The modified surfaces prove useful in a variety of applications. For instance, densely packed SAMs on Si can be used for biosensors [3–5], microtribological lubrication [6,7], high-resolution lithography [8–10], and non-linear optics [11,12]. One of the key chemistries [13–17] that couple functionalized alkyl chains to Si is 1-alkene adsorption on hydrogenated Si [13,18,19]. Herein, we focus on understanding the vapor-phase adsorption kinetics of 1-decene on hydrogenated Si(111) and the degradation of decane SAMs for the purpose of reliable and durable surface passivation of Si.

A variety of methods are used to form stable alkyl SAMs on Si surfaces [13,18,20]. In search of a simple vapor-phase process that is highly integratable with conventional Si fabrication processes, we had previously studied the vapor-phase adsorption of 1-decene on hydrogenated Si(100) [21]. The observed Langmuir isotherms of fractional decane and hydride coverages on Si(100) supported that the adsorption mechanism [13,22,23] follows a repeating cycle of (1) H abstraction from Si, form-

ing a Si dangling bond, (2) cleavage of the C=C bond of the 1-alkene by the Si dangling bond, forming a C–Si bond and a secondary C radical on the alkyl chain, and (3) H abstraction by the secondary C radical, forming an alkane adspecies and a Si dangling bond. The isotherms also substantiated that the rate-limiting step is Step 3 where the secondary C radical on the alkyl chain abstracts neighboring H. Since mono-, di-, and trihydrides exist on hydrogenated Si(100) [24–27], and these hydrides may have different reactivities towards the secondary C radical, we reported an empirical rate constant (k'_2) representing an average reactivity of hydrides during the rate-limiting step.

In comparison to Si(100), the Si(111) surface can be terminated preferentially with monohydrides [28], thus providing an ideal surface to determine the rate constant specific to monohydrides. We have employed attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIRS) to monitor both absolute and fractional surface coverages of decane and hydride on Si(111) during 1-decene adsorption. The experimentally observed isotherms of C–H and Si–H surface coverages are used to determine the empirical rate constant for 1-decene adsorption. By measuring the rate constant within a range of substrate

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