



TiO₂ chemical vapor deposition on Si(111) in ultrahigh vacuum: Transition from interfacial phase to crystalline phase in the reaction limited regime

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ABSTRACT

The interaction between the metal organic precursor molecule titanium(IV) isopropoxide (TTIP) and three different surfaces has been studied: Si(111)-(7×7), SiO_x/Si(111) and TiO₂. These surfaces represent the different surface compositions encountered during TTIP mediated TiO₂ chemical vapor deposition on Si(111). The surface chemistry of the titanium(IV) isopropoxide precursor and the film growth have been explored by core level photoelectron spectroscopy and x-ray absorption spectroscopy using synchrotron radiation. The resulting film morphology has been imaged with scanning tunneling microscopy. The growth rate depends on both surface temperature and surface composition. The behavior can be rationalized in terms of the surface stability of isopropoxy and isopropyl groups, confirming that growth at 573 K is a reaction limited process.

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1. Introduction

The term chemical vapor deposition (CVD) refers to a process where gaseous precursor compounds chemically react on a heated substrate surface. Single crystalline materials can for example be built by using this method. CVD can also be used to manufacture a layer of well-defined material on top of another material. By selecting the right deposition conditions, highly pure, stoichiometric and structurally controlled materials can be deposited with atomic layer precision of the thickness. Other advantages are uniform thickness over large areas and excellent conformal coverage of structured surfaces [1,2]. CVD, and in particular metal organic CVD (MOCVD), can often be performed at low processing temperatures, making the method economically viable.

The CVD process involves as a critical step the adsorption and reaction of precursors on the surface. This leads to changes of the properties of the substrate surface atoms, which often entails the formation of an extended interfacial region between the substrate and the deposited material. In addition, the precursor reactions can result in various decomposition fragments located on the surface or

confined within the film. Consequently, in the initial stages of the growth the chemical composition of the surface may vary, which is likely to have an effect on the subsequent deposition in a progressive manner. Studies of the surface and interface during the initial stages before steady-state growth are thus necessary for the understanding of the properties of the resulting thin film.

MOCVD of TiO₂ on silicon using titanium(IV) isopropoxide (TTIP) as precursor has been studied by numerous techniques [3–8]. A schematic figure of TTIP is shown in Fig. 1. It has been found that deposition of TiO₂ can be performed without either carrier gas or additional oxidant. TTIP is therefore an excellent choice when addressing fundamental properties of MOCVD of metal oxides on silicon substrates.

Taylor et al. [3] have identified three growth regimes as a function of substrate temperature for the TTIP precursor: reaction-limited growth (<700 K), flux-limited growth (700–1000 K) and desorption-limited growth (>1000 K). It has furthermore been found that the microstructure of the TiO₂ film depends on the growth temperature. The work by Taylor et al. [3] includes a very detailed discussion on the precursor reaction chemistry and the importance of precursor surface coverage and diffusion. It is suggested that the reaction-limited growth regime is particularly interesting because the microstructure and properties of the TiO₂ film in this growth regime are dependent on the structure of the molecular precursor.

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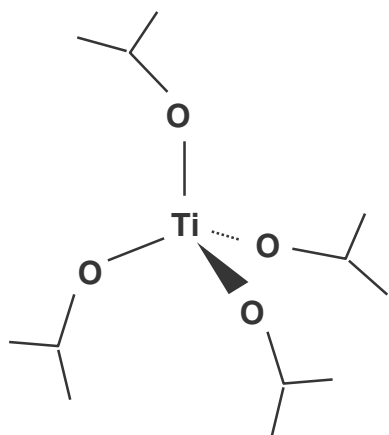


Fig. 1. Schematic illustration of the titanium(IV) tetraisopropoxide molecule.

Wu et al. [8] have studied reaction pathways of the TTIP molecule on TiO_2 using temperature-programmed reaction spectroscopy (TPRS) and reactive scattering measurements. Cho et al. [8] have used TPRS to study the reaction of TTIP on $\text{Si}(100)$. In both of these TPRS studies the desorbed fragments are identified as hydrogen, propene, acetone and isopropanol. However, the TPRS results from these studies differ as a function of temperature, which indicates that the reaction pathway of the TTIP molecule depends on the surface properties.

Photoelectron spectroscopy (PES) of core levels is a non-destructive technique that offers an atom-specific analysis of the chemical and physical properties of surfaces, adsorbates and interfaces. Monitoring film growth with PES is strongly facilitated by the variable photon energy, the high photon energy resolution and the high photon flux provided at a synchrotron radiation source. X-ray absorption spectroscopy (XAS) is a most valuable complement to core level PES. The technique is based on the excitation of a core electron into unoccupied states. The spectrum is sensitive to changes in both the electronic and the geometric structures. Thereby the method enables the identification of different polymorphs.

We have previously demonstrated that the core level PES-XAS combination is powerful for studies of deposited metal oxides. Detailed information on the thickness and chemical composition of the interface formed upon TiO_2 growth on $\text{Si}(111)$ using TTIP has been presented [6]. It has also been shown that the interfacial properties can be altered upon pre-oxidation of the silicon surface prior to TTIP exposure [7]. In these previous studies the silicon substrates were kept at 773 K during TTIP exposure.

Deposition results in an interface with mixed composition. This has a strong implication for the initial stages of growth. In the following, we study the TTIP interaction with the three main components involved in the growth on $\text{Si}(111)$: the clean (7×7) surface, SiO_x and TiO_2 . We first study the precursor decomposition pathway by progressive annealing of a cold layer. Next, we study the growth at 573 K and compare it to the growth at 773 K. That is, growth at a temperature associated with a reaction-limited process is compared to growth at a temperature associated with a flux-limited process.

2. Experimental

Core-level photoemission spectra were recorded at beamline D1011 at the Swedish National Synchrotron Radiation Facility MAX II [9]. The end station comprises a 200 mm radius hemispherical electron energy analyzer of Scienta type for photoemission measurements and a multichannel plate for recording of XAS spectra by collection of Auger electrons. The base pressure was in the low 10^{-10} Torr range or better. The photoemission spectra were all recorded at normal emission and

the binding energy scales are referenced to the Fermi level of a sample holder clip. The XAS spectra were calibrated by using first- and second-order light from the monochromator.

The PES and XAS measurements were performed on four different occasions. Flux monitor reading, synchrotron ring current and measured PES signal intensity have an approximately linear relationship after a specific injection of the synchrotron storage ring. We therefore normalize our spectra with the synchrotron ring current or flux monitor reading. Measuring the integrated signal intensity of a core line from the same sample before and after a new injection of the synchrotron storage ring can however give different results even after normalization. The signal to background ratio can change. The problem is not as simple as saturation of the detector and empirical knowledge from numerous injections, samples and spectra has therefore been used to correct for this non-linear effect. The quality of using the damping of the substrate signal as a measurement for the overlayer thickness is obviously reduced in such cases.

The STM images were acquired with a commercial UHV microscope [10]. The images presented here are unprocessed, except that a best-fit plane has been subtracted from the data. The transfer of the sample to the STM chamber involved exposure to air. The sample was therefore heated in-situ to about 150 °C prior to imaging to remove volatile contaminants from the surface.

The n-doped (P) $\text{Si}(111)$ wafers (Virginia Semiconductors, resistivity $0.1\text{--}1.0 \Omega \square \text{cm}^{-1}$) were first cleaned *ex situ* with a wet etching method followed by repeated 5–10 second heating to 1400–1500 K *in situ* at a pressure below 2×10^{-9} Torr during the flashes. This method gives a sharp (7×7) low-energy electron diffraction pattern. A pyrometer was used to check the temperatures of the surfaces.

Titanium(IV) isopropoxide, TTIP (Aldrich, purity 99.999%) was dosed using a stainless-steel tube positioned a few millimetres from the sample. The dose was controlled by a leak valve and measured as the background pressure in the preparation chamber during dosing multiplied by the time of exposure ($1 \text{ L} = 1 \text{ Langmuir} = 1 \times 10^{-6} \text{ Torr} \cdot \text{s}$). Both the high vacuum side and the UHV side were thoroughly passivated with TTIP prior to sample exposure.

Experiments with the aim to study the decomposition pathways for the TTIP molecule were performed as follows: TTIP was dosed onto a cooled surface which was kept between 120 and 197 K as measured by a thermocouple mounted some distance from the silicon sample. Heating to 300 K was accomplished by radiative heating of the whole sample holder by two filaments. Heating to 573 K and higher was performed by direct current and the temperature was now checked by the pyrometer. Each heating cycle lasted for 30 s. In each case, the sample was allowed to cool down before each measurement. In the first temperature series a clean $\text{Si}(111)\text{--}(7 \times 7)$ surface kept at 120 K was exposed to 6 L of TTIP. From the survey spectra measured using 758 eV photons the intensity of the total silicon signal after the exposure is reduced to 78% of that recorded for the clean $\text{Si}(111)\text{--}(7 \times 7)$ surface. Hence, a very thin layer (4–5 Å) has been adsorbed. In the next experiment a silicon surface was pre-oxidized by exposing the $\text{Si}(111)\text{--}(7 \times 7)$ surface to 300 L of oxygen while the sample was kept at 773 K. The $\text{SiO}_x/\text{Si}(111)$ surface was subsequently cooled down to 197 K and exposed to 2 L of TTIP. The survey spectra measured using 758 eV photons show that the intensity of the bulk silicon signal is reduced after the exposure. The Si 2p bulk signal is 67% of that of the $\text{SiO}_x/\text{Si}(111)$ surface. The adsorbed film is thus somewhat thicker compared to the previous experiment. Finally, a TiO_2 film was grown by exposing a pre-oxidized $\text{Si}(111)$ surface to 50 L of TTIP molecules while the sample was kept at 773 K. This treatment produced a well-defined TiO_2 anatase film. The sample was thereafter cooled down to 193 K before the surface was exposed to an additional 2 L of TTIP.

CVD of TiO_2 using the TTIP precursor was performed in three different series: growth at 573 K starting from clean a $\text{Si}(111)\text{--}(7 \times 7)$ surface, growth at 573 K starting from a pre-oxidized $\text{Si}(111)$ surface ($\text{SiO}_x/\text{Si}(111)$) and growth at 773 K starting from $\text{SiO}_x/\text{Si}(111)$. Most of

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