Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 253 (2007) 3066–3071
applied surface science
www.elsevier.com/locate/apsusc

Adsorption and decomposition of triethylsilane on Si(1 0 0)

J. Lozano [*], A. Brickman, S. Yeninas, D. Early, J.H. Craig Jr.

Department of Physics, Bradley University, 1501 Bradley Ave., Peoria, IL 61625, United States

Received 24 March 2006; accepted 22 June 2006
Available online 28 July 2006

Abstract

The adsorption and decomposition of triethylsilane (TES) on Si(1 0 0) were studied using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), electron stimulated desorption (ESD), and X-ray photoelectron spectroscopy (XPS). TPD and HREELS data indicate that carbon is thermally removed from the TES-dosed Si(1 0 0) surface via a β-hydride elimination process. At high exposures, TPD data shows the presence of physisorbed TES on the surface. These species are characterized by desorption of TES fragments at 160 K. Non-thermal decomposition of TES was studied at 100 K by irradiating the surface with 600 eV electrons. ESD of mass 27 strongly suggests that a β-hydride elimination process is a channel for non-thermal desorption of ethylene. TPD data indicated that electron irradiation of physisorbed TES species resulted in decomposition of the parent molecule and deposition of methyl groups on the surface that desorbed thermally at about 900 K. Without electron irradiation, mass 15 was not detected in the TPD spectra, indicating that the production of methyl groups in the TPD spectra was a direct result of electron irradiation. XPS data also showed that following electron irradiation of TES adsorbed on Si(1 0 0), carbon was deposited on the surface and could not be removed thermally.

PACS: 81.05.Ea; 81.15.Gh; 81.15.Jj

Keywords: Si(1 0 0); Triethylsilane; HREELS; TPD; ESD

1. Introduction

The continuing trend toward smaller feature sizes in microelectronics requires techniques to grow semiconductor materials in a controlled manner. One such technique is atomic layer epitaxy (ALE), in which one atomic layer of material is deposited at a time, providing extreme control over film growth thickness [1–3]. This technique in turn requires the use of suitable precursors for the growth of a given material. Alkylsilanes such as diethylsilane (DES) and trimethylsilane (TMS) have been studied as possible precursors for ALE of silicon [4–9]. In the case of DES/Si(1 0 0), carbon groups are thermally removed from the surface via a β-hydride elimination process that results in desorption of ethylene and hydrogen. A β-hydride elimination process can also be induced at 100 K by electron irradiation of DES/Si(1 0 0); however, this process was only investigated with 600 eV electrons and at this energy, carbon was also deposited on the surface. Adsorption of TMS on silicon results in deposition of carbon that cannot be removed thermally. Irradiation of TMS/Si(1 0 0) with electrons increased the amount of surface carbon dramatically and lead to possible formation of silicon carbide.

It is clear from the previous work mentioned that removal of carbon is possible provided that the precursor alkylsilanes have ethyl groups on them. With this in mind, triethylsilane (TES) was used in this work in an attempt to control the deposition of silicon on Si(1 0 0) both thermally and by electron irradiation at 100 K. The increased number of ethyl groups on TES may present an advantage over DES when irradiating with electrons. The reason for this is that the ethyl groups may screen surface sites that may become available only after irradiating the TES/Si(1 0 0) surface with electrons, thus providing some degree of control over the deposition of silicon and carbon on the surface.

In this work, we used temperature programmed desorption (TPD), electron stimulated desorption (ESD), high resolution electron energy loss spectroscopy (HREELS), and X-ray photoelectron spectroscopy (XPS) to study the adsorption and desorption of TES on Si(1 0 0) and the effects of electron irradiation on the same system.

---

[*] Corresponding author. Tel.: +1 309 677 3822; fax: +1 309 677 2999.
E-mail address: jlozano@bradley.edu (J. Lozano).

0169-4332/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2006.06.051

2. Experimental

The experiments were performed in an ultra-high vacuum (UHV) chamber with a base pressure of 2×10^{-10} Torr. Silicon samples (10 mm × 30 mm) were mounted on a copper sample holder using molybdenum clips. The samples were resistively heated and cooling was achieved by contact with a liquid nitrogen reservoir. A thermocouple was attached to the back of the samples using a silica-based adhesive (Aremco, Ultra-Temp 516) in order to monitor the sample temperature. Temperatures above 500 K were also monitored with an optical pyrometer aimed at the center of the sample through a sapphire window. This configuration was helpful to calibrate the thermocouple readings. Using a Eurotherm 818 PID controller, the sample temperature was increased linearly from 100 K up to 1120 K and cooled down slowly in a controlled manner to allow for surface reconstruction. For TPD experiments, a linear temperature rate of 5 K/s was used. The native oxide layer and ambient contaminants were removed from new samples by annealing the samples to 1120 K. Cleanliness was checked by XPS. A new sample was used for each experimental run.

A Dycor Dymaxion quadrupole mass spectrometer was used for TPD and neutral ESD data acquisition. Time-of-flight (TOF) data for electronically desorbed H^+ species was monitored using a UTI-100C quadrupole mass spectrometer. In order to monitor desorption of ethylene, the mass spectrometer was set to detect mass 27 rather than mass 28, to reduce signal interference from other common gases found in UHV systems, such as CO. Enough fragmentation of ethylene occurs in the mass spectrometer ionizer to yield a significant signal of mass 27. All electron irradiation experiments, including ESD, were performed using a Kimball Physics electron gun model EFG-7. A defocused 600 eV electron beam with current density of 2.0 $\mu A/cm^2$, measured using a Faraday cup mounted above the sample, was used for all electron irradiation and ESD experiments. Our measurements indicated a decrease of about 10% in current density at a distance of 1 cm from the center of the beam; considering the dimensions of the samples, the electron beam was fairly uniform over the sample area. Electronically desorbed H^+ species were analyzed using a time-of-flight technique with a flight path of approximately 30 cm. The Kimball electron gun was operated in a pulsed mode, initiating H^+ desorption with a pulse width of approximately 1 μs. The TOF spectra shown were acquired with a multichannel scaling card with a time resolution of 500 ns per channel. XPS data were acquired using a FISONS hemispherical energy analyzer with 0.85 eV full width at half maximum (FWHM) measured on the $Ag3d_{5/2}$ peak. The UHV chamber was equipped with a LK 2000 HREELS instrument with a resolution of 6 meV. The primary beam energy used was 4–6 eV with an elastic peak FWHM of 80 cm^{-1} at over 10^5 counts per second. All HREELS data were acquired along the specular direction.

The dosing temperature for all experiments was 100 K. TES was dosed onto the surface using a leak valve and a stainless steel tube positioned within 20 mm of the silicon surface. The increase in partial pressure of TES in the chamber was recorded and integrated over time to give the TES exposures. For this reason, the actual TES exposures are higher than the reported values by a factor of about 4.

3. Results and discussion

The temperature programmed desorption spectra of hydrogen (mass 2) and ethylene (mass 27) from Si(1 0 0) after various TES exposures are shown in Fig. 1. At the lowest TES exposures, desorption of hydrogen is detected at 815 K. As the TES exposure is increased, a low temperature peak appears at about 160 K. This peak corresponds to desorption of physisorbed TES. Desorption of ethylene from the silicon surface peaks at 750 K. At high TES exposures, a low temperature mass 27 peak appears also at 160 K due to desorption of physisorbed species, and constitutes a fragment of the parent TES dissociated in the QMS ionizer. Desorption of ethylene from silicon occurs at a temperature about 65 K lower than the desorption temperature of hydrogen from silicon. This is highly suggestive of a β-hydride elimination process that has been previously observed on diethylsilane/Si(1 0 0) [6–9] and diethylgermane/Si(1 0 0) [9,10]. In this process, a hydrogen atom in the β-position on the chemisorbed TES molecule migrates to the surface, causing the formation of a carbon double bond. This weakens the Si–C bond of the ethyl moiety causing it to desorb. This takes place at a temperature that is lower than 815 K, which is the desorption temperature of hydrogen from silicon. Thus, desorption of ethylene takes place at a lower temperature than the desorption of hydrogen.

Fig. 2 shows HREELS data after various TES exposures. Loss peaks at 720, 1000, 1225, 1445, 2100, and 2930 cm^{-1} are clearly observed in the spectra. We attribute the 720 cm^{-1} loss

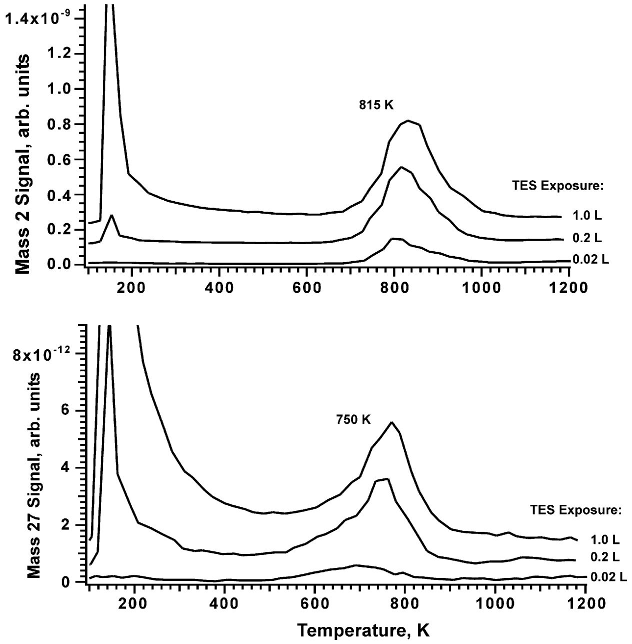

Fig. 1. TPD of hydrogen (top) and ethylene (bottom) from Si(1 0 0) after various TES exposures.