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Reactions of disilane with the deuterium-terminated Ge(100) 2 × 1 surface

Grant Underwood [a], Lynette Keller Ballast [b], Alan Campion [c,*]

[a] Intel Corporation – SiTD MA Labs, 2501 NW 229 St., Portland, OR 97124, USA
[b] Cerium Labs, 5204 East Ben White Blvd., Austin, TX 78741, USA
[c] Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712, USA

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ABSTRACT

We have studied the reaction of molecular disilane with the germanium monodeuteride surface at 300 K. Temperature-programmed desorption and Raman spectroscopy suggest that the product of the reaction is a GeHD terminated surface. Ion scattering and Auger electron spectroscopies show that silicon does not accumulate on the surface but that it is incorporated into the near-surface (~10 Å) region. We propose a mechanism involving silylene (SiH_2) insertion and subsequent silicon indiffusion. We have also investigated the reactivity of this surface with disilane that has been activated by electron impact, producing a variety of dissociation products that were detected by mass spectrometry. The reactions of these radicals with the surface produced a complex mixture of surface species that included GeH, GeD and SiH_x, as identified by Raman spectroscopy.

1. Introduction

SiGe alloys, strained Si and strained layer superlattices comprise a class of materials and structures with novel electronic and optoelectronic properties that can be tailored for specific applications through band structure engineering [1–3]. Although most of early research in this field used molecular beam epitaxy (MBE) to fabricate the required heteroepitaxial structures, large-scale device fabrication favors chemical vapor deposition (CVD). Consequently there is considerable current interest in the heterogeneous chemistry of silicon and germanium hydrides on their complementary substrates.

Disilane (Si_2H_6) is a promising precursor molecule for atomic layer epitaxial (ALE) growth of silicon on a germanium substrate [4–6]. It decomposes at lower temperatures [7], has a much higher sticking coefficient [8–10] and larger UV [11] and electron impact [12] absorption cross sections than does silane (SiH_4), primarily because the Si–Si bond is weaker and thus more easily broken than the Si–H bond [13]. As these properties are all advantageous for low temperature epitaxy, the reactivity of disilane has been investigated on both silicon and germanium surfaces using a variety of surface analytical techniques. Although there are very interesting differences between these two systems, the overall adsorption and dissociation reactions are similar. It is generally accepted that on the (100) surfaces of both silicon and germanium, disilane dissociatively chemisorbs across surface dimers to form two silyl (SiH_3) radicals which, if neighboring sites are not occupied, further dissociate to form silylene (SiH_2) and surface hydrogen. These adsorption and dissociation processes continue until all the available surface sites have reacted, leaving the surface terminated with a disordered hydride overlayer that is passive to further disilane exposure.

Essentially all of the Si/Ge heteroepitaxy experiments conducted to date have investigated the reactions of the germanium or silicon hydrides with the clean surfaces of the elemental semiconductors. The results of these experiments have been tremendously useful in deciphering the rich chemistry that occurs on the surface during initial uptake and for growth conditions above the hydrogen desorption temperature. As device dimensions continue to shrink, however, thermal budget considerations have stimulated the development of lower temperature growth processes. The growth mechanisms operative under these conditions necessarily involve reactions with the hydride-terminated surface. Although reactions of disilane with the hydrogen-terminated silicon surface with disilane have been studied over a broad temperature range with a variety of techniques [14–17], there is essentially no information about its reactions with the hydrogen-terminated germanium surface.

In this report we present evidence for the surprisingly high reactivity of the "hydrogen-passivated" Ge(100) surface with disilane at room temperature. We also show that dissociating disilane

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* Corresponding author. Tel.: +1 512 471 3012; fax: +1 512 471 8696.
E-mail address: campion@mail.utexas.edu (A. Campion).

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by electron impact produces a number of reactive radicals that react with the surface to give a mixture of GeH, GeD and SiH_x species.

2. Experimental

The experiments were performed in an ultrahigh vacuum (UHV) chamber pumped by a Leybold–Heraeus 360 l/s turbomolecular pump and Varian Multiple Vacion pump system that routinely achieved base pressures of 8×10^{-11} torr. A Stanford Research Systems RGA200 quadrupole mass spectrometer was used for temperature programmed desorption (TPD) experiments, to monitor the purity of species delivered during dosing and to provide residual gas analysis. Initial surface cleanliness was monitored using a PHI cylindrical mirror Auger analyzer. Raman spectroscopy was subsequently used to assess the level of carbon contamination since we have shown that it is much more sensitive that Auger spectroscopy for carbon detection (Raman detection limits >0.1% ML). Ion scattering spectroscopy (ISS) experiments were performed in a second Leybold–Heraeus system equipped with a hemispherical energy analyzer.

Disilane and deuterium exposures are reported in terms of uncorrected gauge pressures achieved by backfilling the chamber. Atomic hydrogen (Scientific Gas Products, Research Grade) and deuterium (Matheson, UHP) were dosed by backfilling the chamber to 10^{-7}–10^{-6} torr molecular hydrogen (deuterium) and then moving the sample to within a few centimeters of a hot, coiled tungsten filament. Disilane was introduced through a pinhole doser assembly placed approximately 1 cm from the sample, so the actual disilane fluence at the sample surface is approximately a factor of 10 or so greater than what would be calculated using the backfilled pressure [18]. The ion gauge filament was only left on for the absolute minimum amount of time necessary to verify dosing pressure (2–3 s) during disilane dosing. This precaution was necessary, as we will demonstrate, because the ion gauge filament efficiently cracks disilane. Dissociated disilane was generated, when desired, by leaving the ion gauge filament on during exposures. All of the exposures, unless specifically stated otherwise, were performed at sample temperatures of 300–310 K.

The Ge(100) single crystal (undoped, Eagle-Picher, 1.1 cm × 1.6 cm) was mounted in tantalum clips and resistively heated by the "sandwich" method previously described by Gillis et al. [19]. For the TPD experiments, the sample temperature and heating rate were measured with both an infrared pyrometer and a K-type thermocouple attached to one of the tantalum clips near the sample. A computer-controlled temperature ramp produced a constant, stable heating rate of approximately 1.5 $K s^{-1}$, as verified by independent pyrometer and thermocouple measurements.

The Raman spectra were obtained using 514.5 nm radiation from a Coherent Innova-200 argon ion laser. Unless otherwise stated, all spectra were obtained using 1000 s integration times and 300 mW of p-polarized excitation (light polarized in the plane of incidence). Higher laser power caused a slow rise in sample temperature. The scattered light was passed through a holographic notch filter (Kaiser Optical Systems) and dispersed by a Spex HR-320 spectrometer. The detector was a liquid nitrogen cooled Photometrics CH210 charge coupled device and the system resolution was about 1 cm^{-1} per channel.

3. Results

3.1. Undissociated disilane

The initial motivation for the work reported here was to investigate the reaction of photodissociated disilane with deuterium-terminated Ge(100). We conducted baseline experiments for that investigation expecting to find that this surface would be rather passive, by analogy to the hydrogen-terminated Si(100) surface. We were quite surprised to find the rich and interesting chemistry between disilane and the deuterium-terminated Ge(100) surface that we report here.

The deuterium-terminated Ge(100) surface was prepared by exposing the clean, oxide-free, surface to 1000 L of deuterium, some of which had been atomized by exposure to the hot tungsten filament. The surface was then exposed to various amounts of disilane and thermal desorption experiments were performed. A typical TPD spectrum for a disilane exposure of 5000 L is shown in Fig. 1. The *m*/*e* 2, 3, and 4 peaks centered around 300 °C result from H_2, HD, and D_2 desorbing from a germanium surface. The single, rather broad (FWHM ca. 80 K) peak we observe here is quite different from the previous TPD spectra we reported for deuterium desorption from Ge(100), in which we saw two rather sharp peaks (FWHM ca. 30 K) at 260 and 300 °C. Those peaks were assigned to dideuteride and monodeuteride desorption, respectively.

It is well known that the transmission coefficient of quadrupole mass spectrometers is greater for lower mass ions than for higher masses. The exact behavior of this dependence however, is subject to operating conditions and in general must be determined experimentally. To compare the relative coverages of hydrogen and deuterium therefore, it was necessary to determine the relative sensitivity of our mass spectrometer to these two species. We accomplished this calibration by backfilling the chamber to various pressures with hydrogen (deuterium) and recording the resulting *m*/*e* 2 (4) intensity. For our specific spectrometer, under our operating conditions we found the relative sensitivity factor for *m*/*e* 4 to be 0.4 that of *m*/*e* 2. Absolute coverages were determined by correlating plateaus in the TPD spectra with the 2 × 1 and 1 × 1 LEED patterns. [20] For the results reported here, we define monolayer (ML) as the coverage of the saturated 2 × 1 structure.

Applying this mass-dependent throughput factor to our TPD data allowed us to accurately compare the relative amounts of

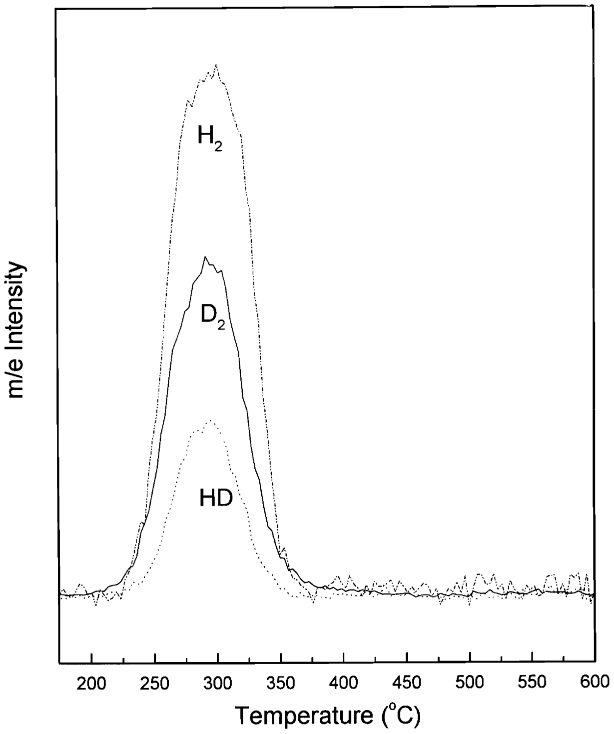

Fig. 1. A typical TPD spectrum for germanium monodeuteride exposed to 5000 L disilane.