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SiH_4 adsorption on SiGe(001)

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Abstract

The adsorption process of silane (SiH_4) on a SiGe(001) surface has been investigated by using infrared absorption spectroscopy in a multiple internal reflection geometry. We have observed that SiH_4 dissociatively adsorbs on a SiGe(001) surface at room temperature to generate Si and Ge hydrides. The dissociation of Si- and Ge-hydride species is found to strongly depend on the Ge concentration of the SiGe crystal. At a low Ge concentration of 9%, Si monohydride (SiH) and dihydride (SiH_2) are preferentially produced as compared to the higher Si hydride, SiH_3. At higher Ge concentrations of 19%, 36%, on the other hand, monohydrides of SiH and GeH and trihyderide SiH_3 are favorably generated at the initial stage of the adsorption. We interpret that when SiH_4 adsorbs on the SiGe surface, hydrogen atoms released from the SiH_4 molecule stick onto Ge or Si sites to produce Si or Ge monohydrides and the remaining fragments of $-SiH_3$ adsorb both on Si and Ge sites. The SiH_3 species is readily decomposed to lower hydrides of SiH and SiH_2 by releasing H atoms at low Ge concentrations of 0% and 9%, while the decomposition is suppressed by Ge in cases of 19% and 36%.

Keywords: Si; SiGe; SiH_4 adsorption; FTIR; IRAS

1. Introduction

Si/SiGe heterostructures are of great interest because of the applicability in optoelectronic and high-speed electronic devices such as heterojunction-bipolar transistors and modulation-doped field effect transistors [1,2]. Gas-source molecular beam epitaxy (GSMBE) and ultra-high vacuum chemical vapor deposition (UHVCVD) using silane and germane have so far been utilized to fabricate SiGe/Ge heterostructures, because these techniques allow epitaxial film growths at low temperatures with an excellent controllability in the thickness and Ge concentration [3,4].

To achieve the maximum performances in the SiGe/Si hetero devices, we need to control the thicknesses and flatnesses of the grown films with a precision of the atomic scale in the CVD processes. For this purpose, it is necessary to elucidate the adsorption and decomposition of the source-gas molecules on SiGe surfaces. In earlier studies, the mechanisms have been investigated with the analysis on the Arrhenius plot of the growth rate–substrate temperature in the SiGe CVD [3–6]. The SiGe growth on SiGe(001) surfaces is characterized by two major reactions; source-gas adsorption and the surface-hydrogen desorption. The Arrhenius plot is divided into two temperature regions; higher and lower temperature regions. In the higher temperature region, the activation energy of the SiGe growth is almost zero, where the source-gas adsorption process limits the growth. At lower temperatures, the surface hydrogen blocks the adsorption of the source-gas molecules and the activation energy increases to the level as high as 20–40 kcal/mol. In the lower temperature region the addition of Ge enhances the surface-hydrogen desorption and the activation energy decreases. We have investigated the surface Ge concentration dependences of the activation energy and frequency factor in the H desorption by using thermal desorption spectroscopy [7]. We clearly indicated the activation energy gradually decreases with

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increasing the surface Ge concentration. In the higher temperature region, on the other hand, the growth rate behaves very complicatedly. It has been reported that the addition of Ge reduces the growth rate [4,5], although some papers describe an increase of the growth rate [6]. In the case of doping with PH_3 and B_2H_6, Ge enhances the incorporation of the impurity atoms [8], while it suppresses the SiGe growth rate in most cases. It has been speculated that the Ge atoms segregated on the surface affect the adsorption coefficient of the source-gas molecules, but the detailed mechanism has not been elucidated.

So far, the SiH_4 adsorption has been extensively studied on Si surfaces with thermal desorption spectroscopy (TDS), reflection high-energy electron diffraction (RHEED) [9], and infrared adsorption spectroscopy (IRAS) [10]. By using static secondary ion mass spectroscopy, Gates [11] established the following initial step for dissociative SiH_4 adsorption on Si(1 0 0) surfaces,

$$SiH_4 + 2db \rightarrow H(ad) + SiH_3(ad)$$

where db denotes a dangling bond. Niwano et al. [10] have observed the SiH_4 adsorption by IRAS with a multiple internal reflection geometry (MIR) and demonstrated that the SiH_4 molecules dissociatively adsorb on Si(1 0 0) 2×1 to generate SiH_2 at the bridgesite between two adjacent dimers and SiH on unsaturated dangling bonds where they speculated the initial adsorbed SiH_3 is dissociated to SiH_2, furthermore to SiH with dangling bonds. Hamers et al. [12] have also confirmed that SiH_3 produced by an introduction of Si_2H_6 on Si(1 0 0) surfaces spontaneously dissociates into SiH and SiH_2 in several minutes of adsorption with an STM. Although how SiH_4 interacts with pure Si surfaces and how it dissociates have been studied well, investigations on SiH_4 adsorption on SiGe surfaces are few. Cheng et al. [13] have investigated the initial adsorption of SiH_4 and GeH_4 on SiGe(1 0 0) surface by density functional theory (DFT) and demonstrated that the activation energy and reaction coefficient of the adsorption change with a presence of surface Ge, though how further dissociation of the initially adsorbed species progresses on the SiGe surfaces is not still known.

In this study, we have measured Si–H and Ge–H stretching vibration spectra of silane-adsorbed SiGe(0 0 1) surfaces with different Ge concentrations to confirm how the Ge concentration of the SiGe epitaxial layer affects the silane adsorption process at room temperature. IRAS in the MIR geometry [10,14,15] has been utilized to analyze the adsorption state of the semiconductor surface. Especially this allows the detection of hydrogen on Si surfaces with the extremely high sensitivity. We here discuss the adsorption process of SiH_4 on SiGe(0 0 1) surfaces on the basis of the IRAS data we collected in the present investigation.

2. Experimental

SiGe samples were prepared by growing epitaxially SiGe overlayers on the p-type B-doped Si(0 0 1) substrate. The resistivity of the substrate was approximately 10 Ω cm. In gas-source molecular beam epitaxy (GS-MBE) of SiGe on Si(0 0 1), disilane (Si_2H_6) and germane (GeH_4) were utilized as molecular precursors for SiGe epitaxial growth [3]. The Ge content of epitaxial films thus grown was determined by Auger electron spectroscopy. In this study, we have grown SiGe epitaxial films with Ge concentrations of 9%, 19%, and 36%.

The samples were introduced into another ultra-high vacuum (UHV) chamber with facilities for infrared spectroscopy. Before introducing the UHV chamber, each sample is dipped in HF acid, which is effective to remove native oxide on the surface. The chamber schematic has been described in Ref. [10]. The base pressure of the chamber was about 1×10^{-10} Torr. The sample surface was cleaned by resistive heating up to 700 °C for 10 min and then exposed to SiH_4 at room temperature. The SiH_4 exposures are given in units of Langmuir ($1\ L = 10^{-6}$ Torr s), as determined by the product of the pressure of molecular SiH_4, which was monitored with an uncalibrated ionization gauge, and time. The chemical state of the sample surface was monitored by MIR–IRAS in the UHV chamber. This technique is quite surface sensitive and has a high-energy resolution than other spectroscopic tools such as electron energy loss spectroscopy (EELS). The samples used for the MIR–IRAS measurements were $0.5 \times 10 \times 40\ mm^3$ with 45° bevels on each of the short edges. The infrared radiation that exited an interferometer (BOMEM MB-100) was focused at normal incidence onto one of the two bevels of the sample, and propagated through the wafer, internally reflecting about 80 times [10,14,15]. The radiation that exited the other bevel of the sample was focused onto a liquid N_2-cooled InSb detector. The reflection spectra measured for the cleaned surface were used as the background reference spectra.

3. Experimental results

We have measured IRAS spectra of SiH_4-adsorbed SiGe surfaces with different Ge concentrations: [Ge] = 9%, 19%, and 36%. First, we show in Fig. 1 typical IRAS spectra in the Si–H and Ge–H stretching vibration regions of a SiGe(0 0 1) surface with a Ge concentration of 9%. The adsorption was made by exposing the surface to SiH_4 at R.T. These spectra have been collected for a series of SiH_4 exposures ranging from 0.5 to 10^4 L. The salient feature in the spectra is the development of two spectral structures at 2050–2150 cm^{-1}, and 1950–2000 cm^{-1}, which can be attributed to the Si–H and Ge–H stretching vibration modes, respectively. In the Si–H stretching vibration region, four peaks can be observed at 2150, 2137, 2120, and 2094 cm^{-1}. Comparing the obtained spectra with those of the silane-adsorbed Si(0 0 1) surface [10,14,15], we have assigned the peaks at 2094 and 2120 cm^{-1} to the Si–H stretching vibration modes of monohydride Si (SiH) and dihydride Si (SiH_2), respectively. The peaks at 2137 and 2150 cm^{-1} can be attributed to the Si–H stretching