Surface Science 602 (2008) 2055–2060

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

On the existence of a stable, room temperature dihydride-terminated Ge(100) surface in ultrahigh vacuum

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ARTICLE INFO

Article history:
Received 27 July 2007
Accepted for publication 24 March 2008
Available online 29 March 2008

Keywords:
Germanium
Low index single crystal surfaces
Hydrogen
Adsorption
LEED
Thermal desorption
Raman scattering spectroscopy

ABSTRACT

We present strong evidence, using low energy electron diffraction, temperature programmed desorption and Raman spectroscopy, for the formation of a dihydride-terminated Ge(100) surface phase that is stable in ultrahigh vacuum at room temperature. This phase was prepared by exposing the Ge(100) surface to a large fluence of atomic hydrogen generated by dissociation of molecular hydrogen on a tungsten filament. We observed a strong uptake dependence on filament placement and temperature and propose that the reason a number of previous reports did not observe this phase was an insufficient fluence of atomic hydrogen. Isotopic substitution of deuterium for hydrogen produced identical results and further allowed us to demonstrate that facile hydrogen abstraction may play an important role in the observed differences for hydrogen adsorption on the (100) surfaces of silicon and germanium.

1. Introduction

Over the past decade or so there has been a resurgence of interest in germanium as a microelectronics material due in large part to the demonstration of atomic layer growth [1], and the production of device quality SiGe and $Si_{1-x}Ge_x$ heterostructures [2]. These SiGe systems are of interest because of their unique electronic and optoelectronic [3] characteristics and because they take advantage of existing silicon base technology. Although it is common to grow these structures on silicon substrates there is an increasing interest in film growth on germanium for the investigation of novel devices that take advantage of the smaller band gap, increased dopant solubility and higher hole mobility of germanium [4]. Although these microelectronics applications have provided a new practical motivation for understanding the chemistry of germanium surfaces, the subject is also of fundamental interest.

The surface chemistry of the low index faces of silicon has been extensively explored and the reactions of hydrogen with these surfaces are well understood, especially on the most technologically relevant Si(100) surface. For the purposes of the present contribution it is sufficient to note that the clean Si(100) surface undergoes a 2 × 1 reconstruction in vacuum; exposure to atomic hydrogen produces a monohydride phase that preserves the reconstruction. Additional hydrogen adsorption produces mixed mono- and dihydride phases that eventually saturate to form the 1 × 1 dihydride-terminated surface. More extensive discussions of the adsorption and reactions of hydrogen with silicon surfaces are presented in several reviews [5,6].

The situation for Ge(100) is much less clear, however, despite a number of investigations spanning the past two decades. In 1986, Papagno and coworkers observed a (1 × 1) low energy electron diffraction (LEED) pattern and obtained a vibrational spectrum (using high-resolution electron energy loss spectroscopy (HREELS)) that identified the germanium dihydride scissor vibration [7]. Cohen and coworkers observed a low temperature shoulder in their temperature programmed desorption (TPD) spectra that they attributed to the formation of a germanium dihydride phase [8]. On the other hand, Chabal found no IR spectral evidence of dihydride formation upon exposure to atomic hydrogen and concluded that it was not possible to prepare this phase under ultrahigh vacuum (UHV) conditions [9]. A number of experiments using various combinations of TPD, LEED and STM measurements also concluded that no significant extended dihydride phase results from large exposures to atomic hydrogen under UHV conditions at 300 K [10–14]. There is still considerable current interest in this system as evidenced, for example, by the recent work of Chabal and coworkers, who reported a wet-chemical protocol for preparing a hydrogen-passivated Ge(100) surface that was a mixture of both monohydride and dihydride phases [15]. In an effort to reconcile

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doi:10.1016/j.susc.2008.03.030

the results of the previous UHV investigations, we have used Raman spectroscopy, LEED and TPD to study this system. We report compelling evidence for the existence of a stable dihydride-terminated Ge(1 0 0) surface at 300 K in ultrahigh vacuum and suggest an explanation for the discrepancies observed in the previous studies.

2. Experimental

The experiments were performed using 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 TPD experiments, to monitor the purity of species delivered during dosing and to provide residual gas analysis.

The Ge(1 0 0) single crystal (undoped, Eagle–Picher, 1.1×1.6 cm.) was mounted in tantalum clips and resistively heated by the ‘sandwich’ method previously described by Gillis et al. [16]. The crystal mount, which provides for resistive heating, and cooling to liquid nitrogen temperatures, consists of two electrically isolated OFHC blocks attached to an x,y,z,θ manipulator arm. Although we initially tried to clean the sample using a CO_2 snow nozzle, we found that the resultant temperature gradient caused the formation of visible surface microfractures. We opted, therefore, to mount the sample as received, with no additional cleaning prior to loading into the UHV chamber. Although our as-loaded samples showed a considerable degree of carbon and oxygen contamination, as detected by Auger spectroscopy (PHI cylindrical mirror analyzer), it was easily removed by just a few sputter (600 eV argon, 15–20 $\mu A/cm^2$) and anneal ($\sim$650 °C, 10 min) cycles. In our laboratory, we use Raman spectroscopy to detect surface carbon at levels below the Auger sensitivity limit (which is 0.5%), having shown a number of years ago that the large Raman cross-section for graphitic carbon makes it readily detectable at very low concentrations.

Atomic hydrogen (Scientific Gas Products, Research Grade) and deuterium (Matheson, UHP) were dosed by backfilling the chamber to 10^{-7}–10^{-6} torr of molecular hydrogen (deuterium) and moving the sample to within a few centimeters of a hot, coiled tungsten filament. The flux of atomic hydrogen was a strong function of both the filament temperature and the distance between the sample and the filament; we discuss these issues later. All doses were performed at a sample temperature of 300–310 K and are expressed as partial pressures (uncorrected for gauge sensitivity) of H_2 or D_2.

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 as verified by independent pyrometer and thermocouple measurements.

Raman spectra were obtained using 514.5 nm radiation from a Coherent Innova-200 argon ion laser. Unless otherwise noted all spectra were obtained using 1000 s integration times with 300 mW of power incident on the surface (higher powers caused a slow rise in sample temperature). The angle of incidence was ca. 70° with respect to the surface normal and the laser radiation was polarized in the plane of incidence (p-polarized). A Navitar f/0.95 camera lens, positioned at 60° from the surface normal in a plane orthogonal to the plane of incidence, was used to collect the scattered radiation. This configuration is the most efficient for surface Raman experiments on highly reflective surfaces [17]. The collected 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

Fig. 1 shows the TPD spectra for D_2 following exposure to various amounts of atomic deuterium. We used deuterium for these experiments to eliminate the interference from background hydrogen in the chamber; the corresponding experiments using hydrogen produced identical results except for a sloping background in the TPD spectra due to the residual hydrogen. For these initial experiments the filament-to-sample distance was set at 4.5–5.5 cm, with a filament temperature of 1700 °C as determined by a pyrometer. The inset in the upper right of Fig. 1 is a standard uptake curve showing TPD peak area as a function of deuterium exposure. The coverage increases rapidly with increasing exposure reaching a plateau at approximately 1000–1500 L. We assume that this plateau represents monolayer coverage of some surface species and set it equal to 1 ML; all other surface concentrations are referenced to this value. At high coverage, a small shoulder begins to appear on the low temperature side of the TPD peak; we originally, and mistakenly, ascribed this feature to contamination or etching.

Fig. 2 shows a typical Raman spectrum of the bare Ge(1 0 0) surface. The intense peak located at 561 cm^{-1} is the second order Ge phonon whereas the smaller peak at 840 cm^{-1} is the third order phonon. The features at 653 and 748 cm^{-1} have not previously been reported but appear to be combinations or overtones of other bulk modes. In the upper trace the spectrum has been expanded approximately five fold to emphasize the less intense peaks. The two broad peaks near 1330 and 1560 cm^{-1} are due to diamond-like

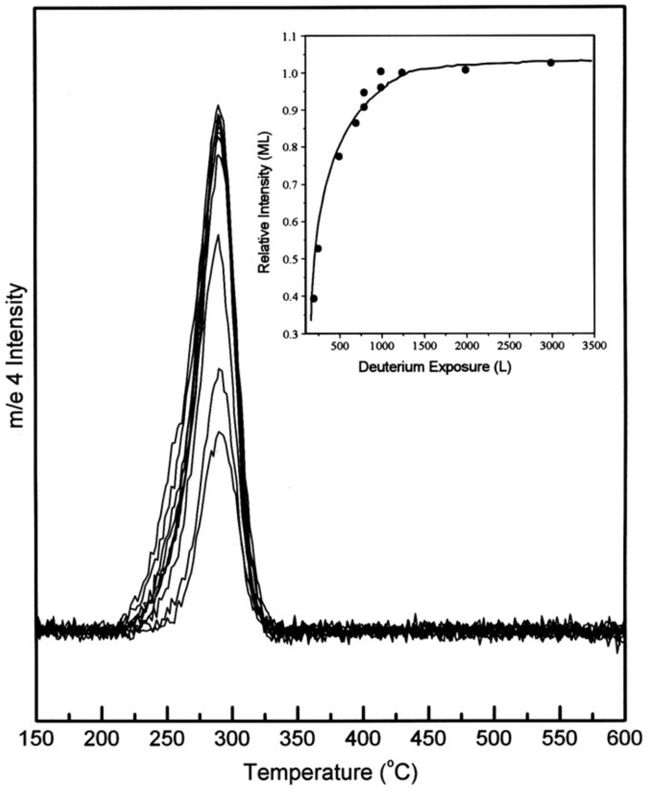

Fig. 1. TPD spectra and uptake curve resulting from relatively small doses of atomic deuterium.