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High resolution electron energy loss spectroscopy study of clean, air-exposed and methanol-dosed Ge(1 0 0) surface

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Abstract

Using high resolution electron energy loss spectroscopy (HREELS), we have characterized the fingerprint spectra of clean, hydrogenated, methanol-dosed and air-exposed *n*-doped Ge(1 0 0). On clean Ge(1 0 0) 2 × 1, we report the observation of a surface phonon peak between ~28–35 meV. The position and shape of this peak is sensitive to the presence of low surface coverage of hydrogen and oxygen. By adsorbing molecular hydrogen on the *n*-doped Ge, this peak shifts towards the elastic peak, and becomes attenuated. The HREELS fingerprint spectrum of air-exposed Ge is similar to that created by dosing Ge with methanol. Methanol undergoes dissociation into methyl radicals and hydroxyl species on Ge surfaces at room temperature and oxidizes the Ge surface readily.

Keywords: Electron energy loss spectroscopy; Vibrations of adsorbed molecules; Germanium; Semiconductor surfaces

1. Introduction

Interests in germanium (Ge) has renewed recently due to the ease of integrating Ge in SiGe alloy for heterobipolar transistors [1]. Other attractive properties such as narrow band gap, high hole mobility and high solubility for *p*-type dopants also makes it a suitable candidate for high performance devices [2]. However, effective utilization of Ge in high speed devices would require the preparation of stable and good quality gate oxide layer [3]. Thus, surface chemistry issues like passivation, cleaning [4], control of oxidation, and how surface adsorbate influences charge density on Ge are critical.

Even though the Ge(1 0 0) 2 × 1 surface is analogous to the Si(1 0 0) 2 × 1, different reactivities may be expected because of the larger degree of surface dimer buckling [5] in Ge. It is well known

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that unlike Si wafer, air-exposed Ge wafer is only covered with a thin GeO_2 layer, which could be readily removed by annealing to 500 °C. While many studies have been carried out on SiO_2, much less is known about the surface chemistry of GeO_2. Using high resolution X-ray photoelectron spectroscopy, Tabet and coworkers [6,7] found an increase in interface electronic state at the germanium/oxide interface and attributed it to the presence of carbidic species.

Our contribution to the surface chemistry of Ge, as reported in this paper here, is twofold. First, the signature of a *clean* Ge surface has been characterized using HREELS. Even though surface phonons on clean silicon were observed as early as 1971 by Ibach [8], it has not been reported on Ge to date. The Ge dimers on the reconstructed 2×1 surface, due to its buckling and polar character [5], are expected to contribute to dipole scattering. Second, when a clean Ge surface is exposed to air for a short period of time, we find that it rapidly develops strong, characteristic HREELS signature peaks, which are not readily attained by *dry* oxidation in vacuum. We have investigated the mechanism for the generation of these peaks by reacting the Ge surface with methanol.

2. Experimental

The experiments took place in a dual–chamber UHV system. The analysis section is equipped with a mu-metal shielded Delta 0.5 high resolution electron energy loss spectrometer (SPECS GmbH) and a reflection high energy electron diffraction (RHEED) system. In the sample preparation section, argon sputtering and gas dosing facilities are available. The base pressure of the system is 1×10^{-10} Torr. The sample used was *n*-doped (5.3×10^{17} Sb) Ge(100) which was subjected to multiple cycles of argon sputtering (600 eV) and flash annealing to 600 °C until a clear 2×1 pattern emerged in the RHEED pattern. For the methanol dosing experiment, the methanol was leaked in through a precision leak valve. The gas dosing lines and the vessel housing the methanol were heated to 100 °C to generate enough vapor pressure for dosing.

In order to assign the vibrational frequencies of the HREELS experimental results, density functional calculations were carried out with Gaussian98 [9]. The clean Ge(100) 2×1 surface is modeled using a Ge_9H_{12} cluster shown in Fig. 1(a). The buckling angle (∼16°) of the dimer for

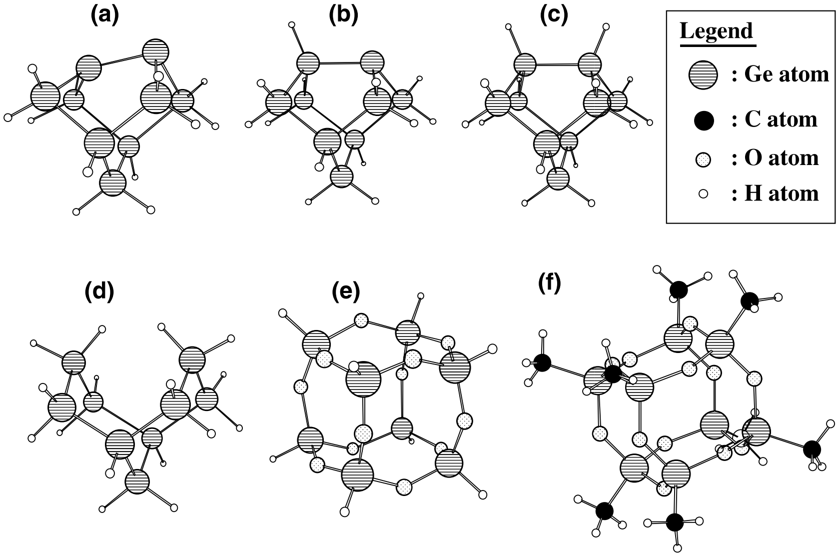

Fig. 1. Models used in theoretical calculations. (a) The Ge_9H_{12} cluster used to model the clean Ge(100) 2×1 surface, (b) a partially saturated monohydride surface, (c) a fully saturated monohydride surface, (d) a dihydride surface (e) a $H_8Ge_8O_{12}$ cluster used to model the GeO_2 layer and (f) a $H_8Ge_8O_{12}$–CH_3 cluster.