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Scanning tunneling microscopy of chemically cleaned germanium (100) surfaces

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Abstract

The effects of HF/H_2O_2 etching, UV/ozone oxidation, and ultrahigh vacuum annealing on the composition and structure of Ge(100) surfaces has been studied by X-ray photoemission and scanning tunneling microscopy. Our results indicate that any carbon impurities left on the surface after the etch and oxidation steps cannot be completely removed by heating in vacuum. On flat Ge(100), carbon pins the steps in place during annealing. Germanium terraces pile up at these locations, producing a mountain-and-valley structure between 20 and 30 atomic layers in height. On Ge(100) 9° off-axis, step pinning by carbon generates a faceted surface covered with V-shaped ridges. © 1998 Published by Elsevier Science B.V.

Keywords: Germanium; Scanning tunneling microscopy; Step-bunching

1. Introduction

The principal commercial use of germanium (100) is as a substrate for the heteroepitaxial growth of III–V compound semiconductor solar cells [1–6]. Owing to the small lattice mismatch between GaAs and Ge, single-crystal films may be deposited without the formation of a large number of strain-relieving defects [7,8]. However, in order to avoid the formation of antiphase domains during the early stages of GaAs growth, a vicinal Ge(100) surface must be used, and this surface must be composed of a regular array of steps two atomic layers in height [8,9]. On such surfaces, all the Ge dimers are oriented in the same direction, providing a suitable template for deposition of GaAs films.

Studies of the adsorption of indium and other elements on Si(100) have shown that impurities can disrupt the normal flow of steps during annealing, causing them to bunch together, and in some instances induce surface faceting [10–13]. We anticipate that impurities on Ge(100) would lead to the same problems. Therefore, the chemical cleaning of germanium substrates must be a crucial step in the heteroepitaxy of compound semiconductor solar cells.

Two methods have been investigated for cleaning Ge(100): HF etching and UV/ozone oxidation [14,15]. It has been reported that these treatments can reduce surface carbon, the most common impurity found on Ge(100), to very low levels. Nevertheless, the impact of these cleaning steps on the atomic structure of the surface was not

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characterized. Herein, we report on a scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) study of chemically cleaned germanium (100). We show that residual carbon contamination exhibits a tremendous influence over the evolution of the surface structure during annealing.

2. Experimental methods

The experiments were conducted in an ultrahigh vacuum chamber (UHV) with a base pressure of 2×10^{-10} Torr. The chamber was equipped with a Physical Electronics X-ray photoelectron spectrometer, a Park Autoprobe scanning tunneling/atomic force microscope, and a Princeton Instruments low energy electron diffractometer [16]. The photoelectron escape angle was 15° with respect to the analyzer axis. Scanning tunneling microscope images were acquired under negative bias in which electrons tunneled out of filled states on the sample surface to the tungsten tip of the scanner. The bias voltage was −2.0 V, and the tunneling current ranged from 0.5 to 1.0 nA. All measurements were made at room temperature.

Flat and 9° off-axis Ge(100) substrates were obtained from Eagle Pitcher Industries. After degreasing a wafer in acetone and methanol, it was rinsed in deionized water, and either etched by a mixture of HF and H_2O_2, or oxidized by ozone produced from a UV lamp. The etching step was carried out two ways: by dipping the Ge(100) in a mixture of HF, H_2O_2 and H_2O, or by sequentially dipping the wafer in baths of concentrated HF, deionized water, and H_2O_2. The latter sequence was usually repeated two or three times. After cleaning, all samples were loaded into the UHV system and annealed in ultrahigh vacuum at temperatures between 400 and 650°C immediately prior to imaging by STM.

3. Results and discussion

Shown in Fig. 1 are spectra of the Ge 3d, C 1s, and O 1s photoemission lines prior to and after sample annealing in ultrahigh vacuum. All these spectra were collected from a Ge(100) 9° off-axis crystal prepared by UV/ozone oxidation. The bottom spectrum in each figure was taken of the fresh sample, while the top one was of the surface after heating up to 650°C. Two peaks are observed in the Ge 3d region for the sample surface prior to annealing (Fig. 1a). These are located at 32.0 and 29.0 eV, and can be assigned to GeO_2 and elemental Ge, respectively [15,17,18]. Since elemental Ge is observed, one may conclude that the oxide coating of the surface is less than the mean free path of escaping photoelectrons at our analysis angle of 15°, or less than about 10 Å. The thickness of oxides is somewhat thinner than that reported

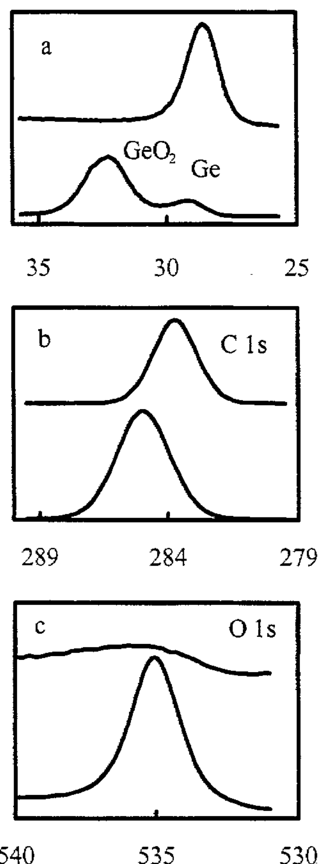

Fig. 1. X-ray photoemission spectra of a Ge(100) 9° off-axis wafer subjected to UV/ozone oxidation and annealed at 650°C for 20 min: (a) Ge 3d, (b) C 1s, and (c) O 1s; upper spectrum after heating, and lower spectrum beforehand.

in prior studies of UV/ozone oxidation of Ge(100) [15].

After heating the wafer to 645°C, the GeO_2 is completely desorbed, as evidenced by the appearance of a single Ge 3d peak at 28.8 eV, and by the disappearance of the O 1s peak at 535.0 eV (Fig. 1c). Heating the crystal also causes the C 1s band to shift from 285.0 to 284.0 eV, and to decrease in intensity by 45% (Fig. 1b). These results may be explained by the desorption of some of the hydrocarbon contaminants during heating, and by the dehydrogenation of other species into an involatile carbon product [15,17].

The surface composition of a Ge(100) substrate cleaned by UV/ozone oxidation is presented in Table 1. Oxygen and carbon are found on this surface. The surface coverages of carbon, oxygen and germanium are calculated from the C 1s, O 1s and Ge 3d peak areas using the atomic sensitivity factors reported in reference [17]. By annealing to 550°C, the oxygen can be eliminated, which is consistent with previous results [15]. However, carbon present on the wafers cannot be completely removed by annealing at any temperature. Moreover, we have found that the amount of carbon left on the wafers varies greatly depending on how these two treatments are performed, and the laboratory conditions under which they are carried out. For example, etching the Ge(100) substrates in a class 1000 clean room yields much lower residual contamination than if they are etched in a laboratory which has no air purification. In addition, a final H_2O_2 rinse guarantees a lower carbon level, because the oxide formed in this step protects the Ge surface from contamination. Carbon deposited on the oxide will desorb along with it when the substrate is heated above 550°C. A final deionized water rinse ought to be avoided, since the protective layer of GeO_2 will dissolve away, leaving the Ge surface susceptible to attack by hydrocarbon vapors in the laboratory [15,18].

Shown in Table 2 are the carbon contamination levels obtained before and after annealing for samples cleaned by different methods. These results illustrate an important point: "The initial amount of carbon on the substrate determines the final amount of carbon on the substrate after heating." No matter how high one heats up the sample, this contamination will remain. Therefore, it is essential that the initial impurity level be reduced below 5% (atoms C)/(atoms Ge) if one wants to achieve "clean" Ge(100) surfaces.

Shown in Fig. 2 are two STM images of a flat Ge(100) surface after HF etching, H_2O_2 oxidation, and annealing in UHV at 650°C. The surface carbon concentration after annealing is about 2.0% (atoms C)/(atoms Ge). A mountain-and-valley structure is evident in the large-scale image of the surface (Fig. 2a). The average height difference from the bottom of a valley to the top of a mountain is approximately 20–30 atomic steps, i.e. 30–40 Å. In addition, protrusions of around 10 Å high are seen in the image. These bright spots are attributed to carbon clusters, since carbon is the

Table 1
The atomic composition of a Ge(100) 9° off-axis wafer cleaned by UV/ozone oxidation and annealed in ultrahigh vacuum at various temperatures

Annealing temperature (K)	Amount on surface (%)		
	Carbon	Oxygen	Germanium
298	6.4	64.3	29.3
373	6.7	65.5	27.8
473	7.9	61.9	30.2
573	7.1	61.9	31.0
673	6.9	60.2	32.9
753	6.1	61.5	32.4
823	13.3	0	86.7
923	13.5	0	86.5
1023	13.2	0	86.8

Table 2
The initial and final amounts of carbon on Ge(100) 9° off-axis surfaces prepared by different cleaning methods

Sample	Procedure	Annealing temperature (K)	Atoms C/atoms Ge (%)
1	HF etching	298	13.5
		923	8.2
2	UV/ozone	298	21.8
		923	15.6
3	UV/ozone + HF etching	298	34.8
		923	29.7

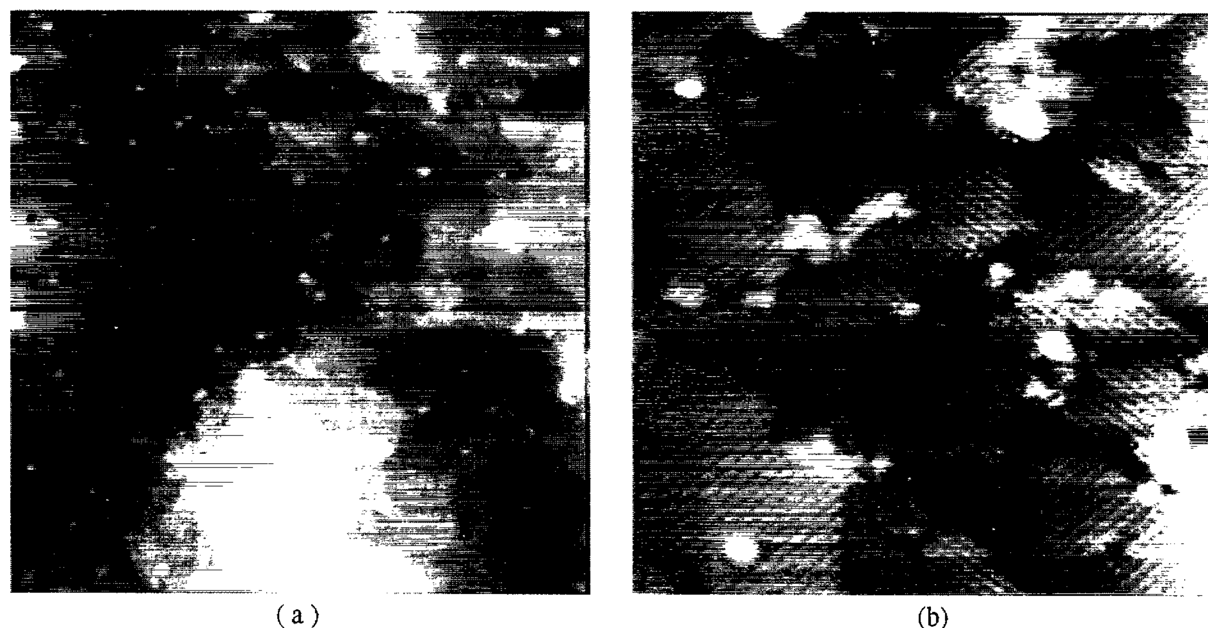

Fig. 2. STM images of a flat Ge(100) wafer etched with HF, oxidized with H_2O_2 and annealed in vacuum at 650°C: (a) 1200×1200 Å^2, and (b) 240×240 Å^2.

only element other than germanium detected on the surface after annealing. It can be seen that these clusters tend to aggregate near the mountain tops. Inspection of the small-scale image (Fig. 2b) reveals that the terraces are composed of well-ordered Ge dimer rows. However, these terraces are relatively small, about 100×100 Å^2. Sprinkled about the edges of these terraces are bright spots averaging 10 Å in diameter which are due to the carbon impurities. Similar images have been obtained on flat Ge(100) wafers after UV/ozone treatment.

We propose that the carbon clusters pin the step movement during high-temperature annealing. Regions containing higher concentrations of carbon particles capture the Ge dimers as they diffuse across the surface, causing material to build up at these sites at the expense of regions which contain fewer impurities. Hence, a mountain and valley structure is observed. As a result of the contamination, annealing does not generate the equilibrium structure of large, equally spaced terraces separated by single-height steps [19].

Shown in Fig. 3 are large- and small-scale STM images of a Ge(100) surface that is 9° off axis towards the nearest (111) plane. This crystal was sequentially etched in HF and oxidized in H_2O_2, and then annealed in vacuum at 650°C. A similar effect of carbon is observed on the structure of the vicinal surface as is observed for the flat one. During heating, Ge builds up at the carbon clusters (bright spots) at the expense of regions that are relatively free of these contaminants. However, instead of a random mountain-and-valley structure, the steps tend to bunch together, forming V-shaped ridges with opposing facets on each side of the ridge. This structure probably results from anisotropic diffusion of Ge brought about by the high density of steps on the vicinal surface.

If the carbon on the surface can be reduced to a low enough level, a single domain (2×1) reconstruction is obtained after annealing the vicinal surface. This structure is presented in Fig. 4. Each terrace is of approximately equal width, and composed of Ge dimer rows oriented perpendicular to the step edge. Two atomic layers separates each terrace. The chemical treatments used to generate the surfaces shown in Figs. 3 and 4 were identical,

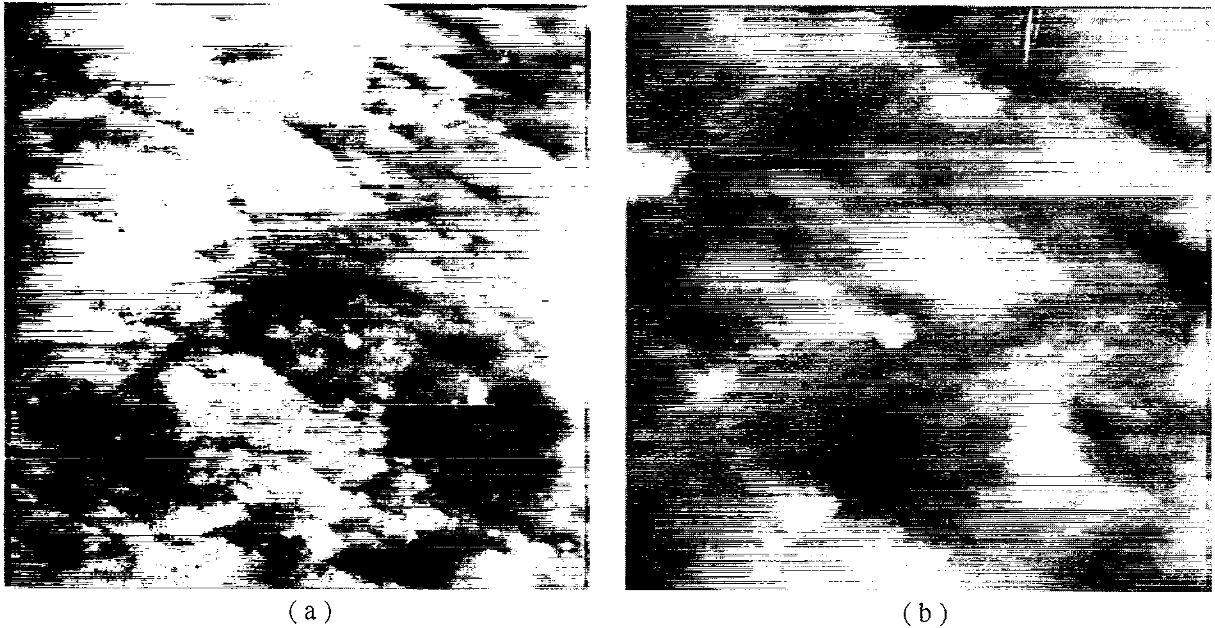

Fig. 3. STM images of vicinal Ge(100) (9° off-axis) etched with HF, oxidized with H_2O_2 and annealed in vacuum at 650°C: (a) 1200 × 1200 Å^2; (b) 160 × 160 Å^2.

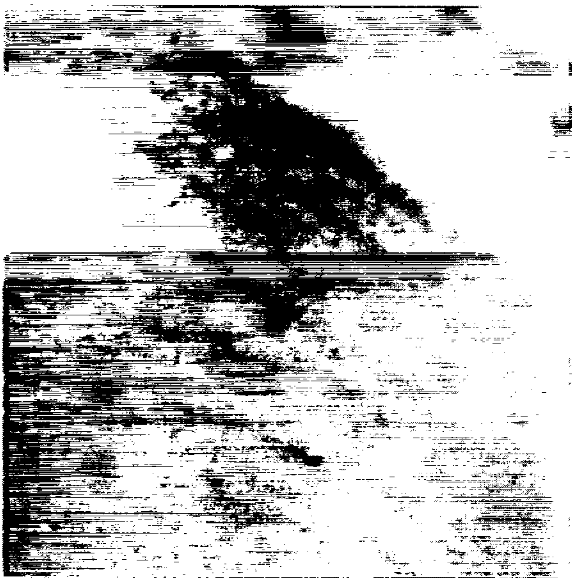

Fig. 4. STM image of vicinal Ge(100) (9° off-axis) etched with HF, oxidized with H_2O_2 and annealed in vacuum at 600°C. The image area is 1200 × 1200 Å^2.

except that in the latter case, more cycles of HF etching and H_2O_2 oxidation were employed to remove all the carbon.

It is common practice prior to the metalorganic chemical vapor deposition (MOCVD) of GaAs on Ge(100) to anneal the sample under a flux of arsine, or some other arsenic source. Therefore, we imaged the surface of several wafers after annealing them in tertiarybutylarsine and hydrogen in an MOCVD reactor. We have found that this procedure shows promise for reducing carbon contamination, and for producing a highly ordered single-domain structure. Further research is under way to resolve the structure of the As-passivated vicinal Ge(100) surface. This will be reported on in a later publication [20].

In conclusion, we have discovered that residual impurities on the Ge(100) wafers have a profound influence on its surface structure. Pinning of the step movement by carbon clusters produces a mountain-and-valley structure on flat Ge(100), and a faceted structure with V-shaped ridges on vicinal Ge(100) (9° off-axis). The final amount of

carbon on the surface is determined by the initial amount of carbon present on the substrate after cleaning. Etching the wafer sequentially with HF and H_2O_2 appears to be the most efficient method of removing carbon and other surface contaminants, provided that the treatment is carried out in a clean room, and the last step is an H_2O_2 dip.

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References

[1] P.A. Iles, F. Ho, M. Yeh, G. Datum, Proc. 24th Intersoc. Energy Conv. Eng. Conf., IECEC-89, IEEE, New York, 1989, p. 791.
[2] J.A. Gonzalez del Amo, Proc. ESA Electron. Comp. Conf. (ESA SP-313), ESA, 1991, p. 21.
[3] C. Flores, B. Bollani, R. Campesato, in: K.E. Singer (Ed.), Proc. 17th Int. Symp. Gallium Arsenide and Related Compounds, IOP, Bristol, UK, 1990, p. 591.
[4] J.C. Chen, M.L. Ristow, J.I. Cubbage, J.G. Werthen, Conf. Record 22nd IEEE Photovoltaic Specialists Conf., 1991, vol. 1., IEEE, New York, 1991, p. 133.
[5] C. Flores, D. Passoni, G. Smekens, G.L. Timo, Proc. European Space Power Conf. (ESA SP-369), vol. 2, ESA, 1995, p. 351.
[6] C. Flores, B. Bollani, R. Campesato, D. Passoni, Microelectron. Engr. 18 (1992) 175.
[7] Y. Shinoda, Y. Ohmachi, Mater. Res. Soc. Symp. Proc. 67 (1986) 65.
[8] K. Mizuguchi, N. Hayafuji, S. Ochi, K. Mitsui, in: M. Fujimoto, M. Bristol (Eds.), Gallium Arsenide and Related Compounds 1985, Proc. 12th Int. Symp., Adam Hilger, New York, 1986, p. 139.
[9] D. Bringans, Crit. Rev. Solid State Mater. Sci. 17 (1992) 353.
[10] Y. Yang, E.D. Williams, Surf. Sci. 215 (1989) 102.
[11] T.R. Ohno, E.D. Williams, J. Vac. Sci. Technol. B 8 (1990) 874.
[12] E.D. Williams, N.C. Bartelt, Science 251 (1991) 393.
[13] L. Li, Y. Wei, I.S.T. Tsong, Surf. Sci. 304 (1993) 1.
[14] K. Prabhakarana, T. Ogino, R. Hull, J.C. Bean, Surf. Sci. 316 (1994) L1031.
[15] X.-J. Zhang, G. Xue, A. Agarwal, R. Tsu, J. Vac. Sci. Technol. A 11 (1993) 2553.
[16] H. Qi, P.E. Gee, T. Nguyen, R.F. Hicks, Surf. Sci. 323 (1995) 6.
[17] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer, Physical Electronics Division, Eden Prairie, MN, 1979.
[18] K. Prabhakaran, T. Ogino, Surf. Sci. 325 (1995) 263.
[19] D.J. Chadi, Phys. Rev. Lett. 59 (1987) 1691.
[20] S. Gan, L. Li, B.K. Han, R.F. Hicks, to be published.