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Step structure of arsenic-terminated vicinal Ge (100)

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Germanium (100) crystals, 9° off-axis towards the [011] were exposed to 2.0 Torr of tertiarybutylarsine and 99.0 Torr of hydrogen at 650 °C, then heated to between 450 and 600 °C in vacuum or H_2. The resulting surfaces consist of narrow dimer-terminated terraces, with (1×2) and (2×1) domains, that are separated by steps between one and eight atomic layers in height. The distribution of (1×2) and (2×1) domains changes with temperature, exhibiting a pronounced maximum in the (1×2) fraction at 510 °C. These results suggest that the arsenic passivation of germanium is a critical step in gallium arsenide heteroepitaxy. © *1999 American Institute of Physics.* [S0021-8979(99)01503-0]

High-efficiency solar cells are manufactured by the metalorganic vapor-phase epitaxy (MOVPE) of compound semiconductor thin films on vicinal Ge (100) substrates.[1–3] Germanium is used instead of gallium arsenide because it can be made thinner and lighter without undergoing significant breakage during device processing. The Ge substrates used for heteroepitaxy are miscut at a large angle relative to the [100] axis, usually 9° towards the [011] direction. This surface is chosen based on the assumption that during growth it consists of terraces of one dimer orientation, separated by steps comprising an even number of atomic layers. Such a structure is needed to eliminate defects created by antiphase domains, which arise from the epitaxy of zinc blende on diamond crystal structures.[4–6]

For gallium arsenide heteroepitaxy on silicon and germanium, a crucial step is the passivation of the surface with arsenic prior to growth. By depositing a single monolayer of arsenic on vicinal Si (100) at above 500 °C, a single domain structure can be produced, where all the As dimers on the terraces are oriented parallel to the step edge and all the steps are 2 atomic layers in height.[7,8] However, other studies have shown that the adsorption of arsenic on silicon and germanium surfaces generates a variety of step and terrace structures.[9–13] The latter results suggest that arsenic passivation may not be a straightforward process, and under certain conditions can yield less than optimum results. Additionally, these studies show that both kinetics and energetics should be considered in order to obtain a clear understanding of the step rearrangement induced by arsenic adsorption.

Herein, we report on the arsenic passivation of vicinal Ge (100) substrates in the MOVPE environment. The surface structures following exposure to tertiarybutylarsine and hydrogen have been characterized *in situ* by scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED). We find that the distribution of dimer orientations and the step heights are a sensitive function of the MOVPE process conditions.

The experiments were carried out in an ultrahigh vacuum (UHV) system combined with an MOVPE reactor, as described elsewhere.[14] Vicinal Ge (100) wafers (9° off axis towards the [011] direction) were cleaned in acetone and methanol, rinsed in de-ionized water, and then sequentially dipped in baths of concentrated HF, de-ionized water, and concentrated H_2O_2 for 30 s each. This sequence was repeated three times. After cleaning, the wafers were loaded into the UHV system and transferred to the MOVPE reactor through a vacuum interface. Then they were annealed in 2.0 Torr tertiarybutylarsine (TBAs) and 99.0 Torr H_2 at 650 °C for 30 min. The linear velocity over the sample surfaces was 6 cm/s (relative to 0 °C and 760 Torr).

One set of As-passivated Ge crystals was heated in 20.0 Torr H_2 for 20 min at temperatures between 400 and 600 °C. The gas velocity over the surfaces was 30 cm/s in this case. These crystals were then transferred to the UHV chamber. Conversely, another set of samples was transferred to the UHV system immediately after annealing in TBAs, and heated in vacuum to temperatures between 450 and 600 °C. After the heat treatments, all the germanium wafers were analyzed by XPS, LEED, and STM. The XPS spectra were acquired at a take-off angle of 55° and a pass energy of 23.5 eV. The STM images were recorded at bias voltages between ±2 V and 0.5 nA.

In order to determine the arsenic coverage on the Ge surface, a calibration curve relating the amount of adsorbed arsenic to the As $2p$/Ge $2p$ area ratios in the XPS spectra was obtained. This curve was determined as follows:[15] a specified amount of arsenic was deposited on a flat Ge wafer by heating it above 350 °C under 5×10^{-7} Torr arsine in the UHV chamber. Then XPS spectra and STM images were collected on the same surfaces. The fractional coverage of As was assessed by inspection of the STM images, which show distinctly different topologies for the As- and Ge-terminated regions of the surfaces.

Figure 1 shows three STM images of the germanium surface after heating in vacuum at 475, 510, and 580 °C, respectively. Each surface is composed of terraces that are terminated with dimer rows oriented either perpendicular to the step edge (2×1) or parallel to the step edge (1×2). As an

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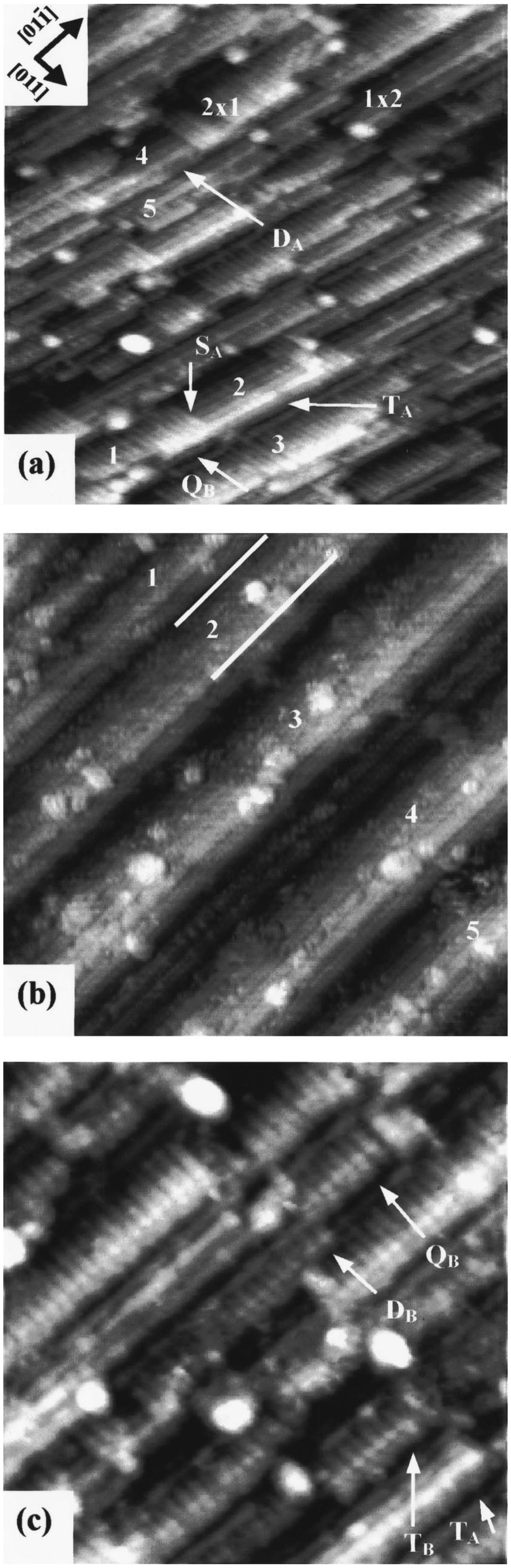

FIG. 1. Scanning tunneling micrographs of the Ge (100) surface after exposure to TBAs at 650 °C and annealing in vacuum at (a) 475 °C, (b) 510 °C, and (c) 580 °C. The image areas are 320×320 Å^2, 340×340 Å^2, and 240×240 Å^2, respectively. The biases voltages are −1.2 V in (a) and (b), and +2 V in (c).

example, two terraces showing a (2×1) and a (1×2) domain are indicated in Fig. 1(a). The width of the terraces varies from image to image and within a given picture. Moreover, the terraces do not extend indefinitely along the $[01\bar{1}]$ direction, but terminate at a step edge. Sometimes one sees steps stacked together, and capped with bright white terrace rows. In addition, round white spots are seen interspersed over the surface. These spots are probably due to clusters of adsorbed atoms (As and/or Ge). Germanium surfaces heated in 20 Torr of hydrogen to the same temperatures exhibit the same structures as those shown here for heating in vacuum.

Further examination of the STM image reveals that the surface structure changes with the annealing temperature. At 475 °C [Fig. 1(a)], approximately equal numbers of (1×2) and (2×1) domains are observed. The As coverage on this surface is 1.0 monolayer (ML). Careful inspection of the image reveals that the surface consists of steps of different heights ranging from 1 to 6 atomic layers. To simplify the following discussion, we labeled some of the terraces with numbers and some of the steps according to their heights: *S* for single, *D* for double, *T* for triple, and *Q* for quadruple. The subscripts *A* and *B* denote steps in which the dimer rows are parallel (*A*) or perpendicular (*B*) to the step edge.[16] Four different step configurations are indicated in Fig. 1(a): S_A, D_A, T_A, and Q_B. These steps occur between terraces 1 and 2, 4 and 5, 2 and 3, and 1 and 3, respectively. Evidently, a random distribution of terrace orientations and step heights is obtained upon heating the As-terminated vicinal Ge (100) surface to 475 °C in either vacuum or hydrogen ambient.

By contrast annealing the crystal at 510 °C produces a single domain (1×2) as seen in Fig. 1(b). The As coverage on this surface is 0.9 ML. In Fig. 1, the terraces are labeled 1–5, and the beginning and the end of terrace 2 is highlighted by two white lines. It is evident that all the dimer rows run parallel to the $[01\bar{1}]$ direction such that the steps are exclusively *A* type. Inspection of many regions of the sample surface reveals that the terraces contain on average four dimer rows, or are 32 Å across. The image shows terraces containing between three and six dimer rows. Also, a step 8 atomic layers in height is seen between terraces 3 and 4, while the other steps are 4 atomic layers in height.

Figure 1(c) shows an STM image of an As:Ge (100) surface after heating to 580 °C. The As coverage on this surface is 0.6 ML. In this case, a mixture containing 75% (2×1) and 25% (1×2) domains is obtained. Several types of steps are indicated with arrows in the figure. They range from 2 atomic layers in height D_B to 4 atomic layers in height (Q_B).

Figure 2 shows the dependence of the arsenic coverage on the temperature of annealing the crystal in hydrogen. Also shown in the figure is the effect of temperature on the fraction of the Ge surface that is covered with (2×1) domains. These data were obtained from analysis of the STM images. As the temperature is raised from 450 to 600 °C, the arsenic coverage gradually falls from 1.0 to 0.4 ML. At the same time, the fraction of (2×1) domains first decreases from 0.5 at 475 °C to ~0.1 at 510 °C, then increases to 0.9 at 600 °C.

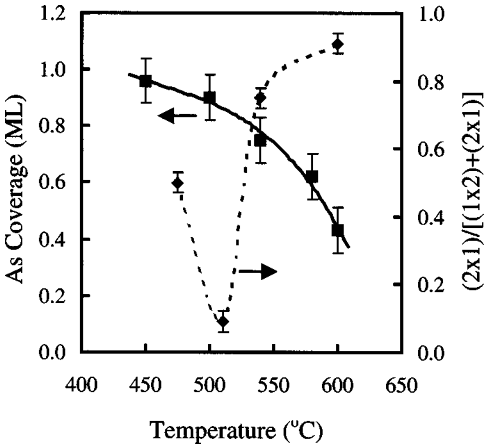

FIG. 2. The effect of the hydrogen annealing temperature on the arsenic coverage and the percentage of the terraces covered by (2×1) unit cells.

The change in the surface structure with temperature is not completely understood at this time. Previous studies of arsenic passivation of vicinal Si (100) have shown that at 1 ML coverage, the surface exhibits the (1×2) phase with *A*-type steps.[17,18] These results are consistent with the structure observed at 510 °C [Fig. 1(b)] but not the one at 475 °C [Fig. 1(a)]. We do not believe that the latter structure is due to kinetic limitations, such as too low a diffusivity of the As and Ge atoms. This does not seem likely because the terrace and step structure is well developed, and the terraces themselves show a high degree of ordering. Therefore, these results suggest that the energetics of forming *A* and *B* steps are approximately the same at 475 °C. Arsenic is known to adsorb two ways onto Si (100) surfaces, by adsorbing on top of the silicon dimers, or by replacing them in the top layer.[19] If these processes occur simultaneously at low temperature, then a mixed domain structure will be generated. At 580 °C, the mixed domain structure most likely results from the decrease in the arsenic coverage, since (1×2) terraces with *B*-type steps are preferred on the Ge-terminated surface.[20] At 600 °C, over 90% of the surface is covered by (2×1) terraces, which are due to Ge–Ge dimers. The (1×2) domains contain Ge–Ge, As–As, or Ge–As dimers, as revealed by line scan measurements.[15]

The results presented above demonstrate that the arsenic passivation step prior to gallium arsenide heteroepitaxy strongly affects the initial structure of the growth surface. It is evident that the single domain (1×2) obtained at 510 °C is desirable for depositing GaAs without antiphase domains. In summary, our results show that a substrate is not a static template where film growth takes place, but that the surface reorganizes into a structure that is in equilibrium with the MOVPE growth environment.

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