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Surface structures of Pb on Ge(001) observed by scanning tunneling microscopy

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The different structures of Pb on Ge(001) have been studied as a function of Pb-coverage and annealing temperature. At low coverages a new (2×2) reconstruction was found which is similar to that of several other group-III and group-IV adsorbate structures on Si(001). A structural model for the $c(4 \times 8)$ phase is presented, which explains the appearance of the $c(4 \times 8)$ $c(2 \times 4)$ domain boundaries. Evidence for the existence of a (1×1) layer in the (5×1) reconstruction and of dimer rows in the (2103) reconstruction is given. The incommensurate $(4 \times 1)_i$ phase is shown to consist of distorted $c(4 \times 8)$ unit cells.

1 INTRODUCTION

Metal-semiconductor interfaces continue to be of interest for both fundamental and technological reasons. The closely related systems Pb on Ge and Pb on Si are considered as prototypical examples for metal semiconductor interfaces since they form abrupt junctions with little intermixing at the boundary. Consequently Pb overlayers on the (111) surfaces of the two elemental semiconductors have been studied extensively with a variety of experimental techniques. Surprisingly less work has been done on the technologically more important (001) surfaces.

Using Auger and photoelectron spectroscopy Le Lay et al. found that Pb on Si(001) follows the Stranski-Krastanov growth mode, i.e. after completion of the first layer islands form [1]. With low energy electron diffraction (LEED) Zhao et al. observed five different 2-D superstructures for Pb on Si(001) depending on the coverage and the annealing temperature, namely (2×1) , (2×2) , $c(4 \times 8)$, (4×1) and $c(4 \times 4)$ [2]. Surface X-ray diffraction was used to establish a structural model for the Si(001) (2×1) -Pb reconstruction with three Pb atoms per unit cell [3]. An STM study on Pb on Si(001) revealed similarities to the structures on Sn on Si(001) [4].

Using LEED, Zhang et al. observed five different reconstructions of Pb on Ge(001) namely a $c(2 \times 4)$, $c(4 \times 8)$, (5×1) , $\begin{pmatrix} 2 & 1 \\ 0 & 3 \end{pmatrix}$ (in the following referred to as (2103)) and an incommensurate $(4 \times 1)_i$ phase [5]. Recently some of the reconstructions of Pb on Ge(001) have also been studied with surface X-ray diffraction [6]. This paper gives an overview of the first STM measurements on the various phases of Pb on Ge(001).

2 EXPERIMENTAL

The experiments were performed in an ultra high vacuum (UHV) system (base pressure $< 4 \times 10^{-11}$ mbar) consisting of a molecular beam epitaxy deposition chamber equipped with a RHEED-apparatus, sample heating and a quartz film-thickness monitor, a separate preparation chamber for sputtering and annealing to clean the substrates and an analysis chamber containing a LEED-system and a commercial STM (OMICRON Vakuumphysik GmbH). For the STM measurements we used electrochemically etched tungsten tips, which were formed in situ by scanning at high bias voltage and tunneling current. If not otherwise mentioned all images shown here are unfiltered raw data with a linear background subtracted. Clean reconstructed Ge(001) (2×1) surfaces were prepared by repeated cycles of sputtering with 500 eV Ar^+ ions at a temperature of 500°C and annealing at 650°C until a bright and sharp (2×1) LEED pattern with a low background was observed. The duration and temperature of the annealing process as well as the cooling rate after the anneal do not seem to be particularly critical parameters. Before depositing Pb the quality of the substrates was checked carefully with RHEED, LEED and STM. On well prepared surfaces we observed with STM only a small number density of missing dimers ($\sim 0.1\%$) while the percentage of buckled dimers ($\sim 50\%$) was large compared to typical Si(001) surfaces. Pb was evaporated from an effusion cell with a PBN crucible at a rate of $\sim 5 \times 10^{-3}$ ML/s where one monolayer (1 ML) is equal to 6.25×10^{14} atoms/cm². During deposition the pressure was maintained at less than 1×10^{-10} mbar. We found that samples could be cleaned for reuse either by sputtering and annealing or by simply heating up to 500°C to desorb all of the Pb.

3 RESULTS AND DISCUSSION

We begin by presenting our results for low Pb coverages deposited at room temperature. Figure 1 shows an STM image of a Ge(001) sample which is covered with ~ 0.2 ML Pb. The imaged surface area consists of two parts which can be distinguished by their height contrast. The darker domains show dimer rows which are well known from the clean (001) surfaces of Si and Ge and appear either symmetric which results locally in a (2×1) reconstruction or buckled which gives rise to a $c(4 \times 2)$ reconstruction. The domains which appear bright in Fig. 1 exhibit a (2×2) reconstruction. This (2×2) reconstruction has not been reported before for Pb on Ge(001), but reconstructions with a similar appearance in STM have been observed for several group-III and group IV-overlayers on Si(001) [7]. In the case of Si on Si(001) the (2×2) reconstruction has been explained with a diluted dimer model [8]. The (2×2) domains usually have a large aspect ratio ($\sim 10:1$) with their long sides oriented perpendicular to the Ge dimer rows. Remarkably on the short sides of the (2×2) domains we always observe chain-like structures which can be attributed to a $c(4 \times 8)$ reconstruction. On heating up to $\sim 150^\circ\text{C}$ the (2×2) reconstruction vanishes irreversibly. After cooling down we found with STM an increased number of $c(4 \times 8)$ units and lots of substitutional Pb dimers in the Ge dimer rows.

Figure 2(a) shows an STM image of a Ge(001) sample which is covered with ~ 0.5 ML Pb and has been annealed at $\sim 150^\circ\text{C}$ for 5 min. In this image we see two types of reconstructions. In the lower right corner one sees Ge dimer rows which are almost completely buckled and consequently form a $c(4 \times 2)$ reconstruction. Most of the imaged surface area is covered with a chain-like structure with a larger periodicity which can be identified as the $c(4 \times 8)$ reconstruction which we already observed in Fig. 1. It is characteristic of the $c(4 \times 8)$ phase that it exhibits a considerable amount of local disorder. Usually lots of defects and stacking faults can be observed such as half links (see Fig. 2(a) at A) or $1\frac{1}{2}$ chain links (at B).

Similar sorts of chain-like $c(4 \times 8)$ reconstructions have been observed with STM for Sn on Si(001) and Pb on Si(001) [7, 4]. However, two different structural models have been proposed for this type of reconstruction. In both models the $c(4 \times 8)$ reconstruction terminates with a layer of metal dimers.

Figure 1: Filled-state STM image of 0.2 ML Pb on Ge(001) deposited at room temperature. Bright (2×2) reconstructed domains are visible above the (2×1) and $c(2 \times 4)$ reconstructed clean Ge(001).

Figure 2: (a) Filled-state image of 0.5 ML Pb on Ge(001). The upper terrace in the lower right corner shows buckled Ge dimer rows with $c(2 \times 4)$ symmetry while the lower terraces display the chain-like $c(4 \times 8)$ reconstruction. (b) Schematic structural model for the Pb-induced $c(4 \times 8)$ reconstruction and the buckled Ge dimer rows at point C in Fig. 2(a). Only the shaded atoms are visible in the STM image.

During the formation of this metal layer the Si dimers in the layer underneath are disrupted. In the model proposed by Baski et al. the metal dimers are oriented perpendicular to the previous top Si dimers while in the model proposed by Itoh et al. the metal dimers are oriented parallel to the previous top Si dimers. The structure visible in the STM image of Fig. 2(a) near (C) allows to decide between these two structural models. Here we see that the chain-like $c(4 \times 8)$ structure is directly connected to the buckled dimer rows of the clean Ge. These dimer rows are separated by a monoatomic step from the topmost Ge layer in the $c(4 \times 8)$ reconstruction. Since this topmost Ge layer is covered by an additional layer of Pb dimers the $c(4 \times 8)$ has the same apparent height as the neighboring Ge dimer rows. The direct connection between the $c(4 \times 8)$ reconstruction and the dimer rows in Fig. 2(a) requires the Pb dimers to be oriented parallel to the Ge dimers in the rows. On clean (001) semiconductor surfaces dimer rows on two terraces which are separated by a monoatomic step are oriented perpendicular to each other. Therefore, we conclude that the metal dimers must be oriented perpendicular to the previous top Ge dimers underneath, which rules out the structural model proposed by Itoh et al. We illustrate our considerations with the schematic model for the atomic arrangement of Fig. 2(a) near (C) shown in Fig. 2(b). On the $c(4 \times 8)$ reconstructed part the Ge is covered by an epitaxial Pb layer. The Pb atoms form buckled dimers similar to the clean Ge(001) surface. Due to the buckling only every second Pb atom is visible in the STM image. The Pb atoms are packed in triple rows with trenches in between. These trenches allow the structure to accommodate the stress which occurs due to the greater covalent radii of the Pb atoms compared to Ge. As one sees in the lower right corner of Fig. 2(b) this atomic model for the $c(4 \times 8)$ reconstruction gives a natural explanation for the connection between the $c(4 \times 8)$ structure and the Ge dimer rows of the next terrace.

Annealing a saturated $c(4 \times 8)$ reconstruction at above 300°C for five minutes leads irreversibly to a new (5×1) reconstruction. A (5×1) structure has also been observed for Sn on Si(001) but not for Pb on Si(001) [7, 4]. In Fig. 3 an STM image of the Ge(001)(5×1)-Pb reconstruction is shown. To remove some noise spikes a (3×3) median filter has been applied to this image. The structure is characterized by a double row of protrusions which are $5a$ apart where a is the surface lattice constant. The distance between the protrusions along the length of the double rows is $1a$. The overall appearance is completely different from the Si(001)(5×1)-Sn structure, which indicates that these two reconstructions have completely different structures.

The double rows in Fig. 3 have two different orientations. The height difference between these two orientations corresponds to a monoatomic step of the Ge substrate. We never observed double rows with two different orientations on a single terrace. Between the double rows of bright protrusions additional small protrusions can be seen. The five protrusions visible at the end of a bright double row (see the arrows in Fig. 3) indicate that the smaller protrusions are possibly related to a (1×1) layer of atoms which is located underneath the bright double rows. Presently a combined X-ray diffraction and STM study is under way to establish a complete structural model for this reconstruction [6].

Adding more lead onto a saturated $c(4 \times 8)$ reconstruction gives rise to the formation of a new (2103) reconstruction which has no counterpart for either Pb or Sn on Si(001). Figure 4 shows two terraces: the upper is covered with the (2103) structure and the lower terrace is covered with (2103) and $c(4 \times 8)$ reconstructions. The $c(4 \times 8)$ has been lifted by about $1.5\text{\AA}$ to be able to display all the different structures within the limited greyscale. The outlined area corresponds to a (2103) unit cell, therefore the pattern of bright protrusions corresponds to one maximum per unit cell. These protrusions are located on bright stripes which are $2a$ apart. Interestingly near step edges or defects some of the bright protrusions are missing. At these locations it is possible to see additional small protrusions with a distance of $1a$ on the stripes. Since the stripes have a (2×1) periodicity and they are oriented in the direction of the original Ge dimer rows they might be related to a dimerized (1×1) layer of Ge or Pb atoms. However, the reason for the occurrence of the (2103) reconstruction remains unclear.

Adding more Pb onto a saturated (2103) surface leads to the incommensurate $(4 \times 1)_i$ reconstruction. STM images of this structure (see Fig. 5) show bright stripes with a spacing of $4a$. On these

Figure 3: Empty-state image of Ge(001)-Pb at a coverage of ~ 1.0 ML showing three terraces of (5×1) phase. The arrows mark five distinct protrusions at the edge of a (5×1) domain. A (5×1) unit cell is also indicated.

Figure 4: Filled-state image of Ge(001)-Pb at a coverage of ~ 1.5 ML Pb. Two terraces covered with the (2103) reconstruction can be seen with one protrusion per unit cell. The $c(4 \times 8)$ region on the lower terrace has been lifted by ~ 1.5 Å to make it more visible.

Figure 5: Empty-state image of the Ge(001)(4 × 1)_i-Pb reconstruction showing bright parallel stripes separated by four Ge-lattice constants ($a=4.0\text{\AA}$). The arrows indicate the varying periodicity along the stripes. The outlined region corresponds to a $c(4 \times 8)$ unit cell.

stripes additional protrusions can be seen with a distance of either $4a$ or $5a$ along the rows. The additional protrusions between the bright stripes are directly related to the protrusions on the stripes. As can be seen in Fig. 5 a regular distance along the rows of $4a$ corresponds to a $c(4 \times 8)$ pattern. Therefore, the $(4 \times 1)_i$ phase has to be explained in terms of a distorted $c(4 \times 8)$ reconstruction.

Figure 6 gives a schematic overview of the various room temperature 2-D phases of Pb on Ge(001). To prepare the (5×1) phase the sample has to be annealed above $\sim 200^\circ\text{C}$ while all the other phases can be prepared at room temperature. A reason for the coexistence of the (5×1) and the $c(4 \times 8)$ in the same coverage range could be that the Ge dimers persist under the $c(4 \times 8)$ phase and have to be disrupted to form the (5×1) reconstruction. Although the (5×1) has the lower free energy the $c(4 \times 8)$ is favored for samples prepared at room temperature since it has a lower heat of formation. Instead of the (2×2) Zhang et al. observed with LEED a $c(2 \times 4)$ reconstruction at low coverage on annealed samples. We attribute this $c(4 \times 2)$ LEED pattern to the buckled Ge dimer rows since we observed with STM that a small amount of substitutional Pb dimers ($< 0.05\text{ML}$) is sufficient to introduce buckling on most of the surface area.

4 CONCLUSIONS

We have examined the different 2-D structures of Pb on Ge(001) as a function of coverage and annealing temperature. For samples prepared at room temperature four different phases could be observed namely a (2×2) , $c(4 \times 8)$, (2103) and an incommensurate $(4 \times 1)_i$ reconstruction. Annealing of the $c(4 \times 8)$ leads to a (5×1) reconstruction. High resolution STM images could be obtained for all the different phases. The (2×2) is shown to be similar to several other (2×2) reconstructions of group-III or group-IV elements on Si(001). A detailed analysis of domain boundaries between the

Figure 6: Schematic phase diagram of the room temperature phases of Pb on Ge(001).

$c(4 \times 8)$ and dimer rows of the clean Ge allowed the orientation of the Pb dimers in the $c(4 \times 8)$ reconstruction to be determined. We found evidence for the existence of dimer rows in the (2103) reconstruction. The $(4 \times 1)i$ phase is shown to be a distorted new type of $c(4 \times 8)$ reconstruction.

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References

- [1] G. Le Lay, K. Hricovini, and J.E. Bonnet, Phys. Rev. **B39** (1989) 3927.
- [2] R.G. Zhao, J.F. Jia, and W.S. Yang, Surf. Sci. **274** (1992) L519.
- [3] N. Jedrecy, N. Greiser, M. Sauvage-Simkin, R. Pinchaux, J. Massies, and V.H. Edgens, in S.Y. Tong, M.A. Van Hove, K. Takayanagi, and X.D. Xie (eds.) *The Structure of Surfaces III*, Springer Berlin, Heidelberg 1991.
- [4] H. Itoh, H. Tanabe, D. Winau, A.K. Schmid, and T. Ichinokawa, presented at the International Conference on Scanning Tunneling Microscopy, Beijing 1993.
- [5] Y. Zhang, R.G. Zhao, and W.S. Yang, Surf. Sci. **293** (1993) L821.
- [6] V. Jahns et al., in preparation.
- [7] A.A. Baski, C.F. Quate, and J. Nogami, Phys. Rev. **B44** (1991) 11167 and references therein.
- [8] Y.-W. Mo, R. Kariotis, B.S. Swartzentruber, M.B. Webb, and M.G. Lagally, J. Vac. Sci. Technol. **A8** (1990) 201.