Surface structures of thallium on Ge(1 1 1)

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Abstract

The surface structures of thallium on Ge(1 1 1)c(2 × 8) have been investigated by scanning tunneling microscopy (STM), LEED, and Auger electron spectroscopy. The surface phase diagram of Tl on Ge(1 1 1) contains two ordered overlayers, a pseudomorphic (1 × 1)-Tl monolayer surface, obtained by Tl deposition at room temperature, and a Tl-induced (3 × 1) reconstruction; the latter forms at elevated temperature (300–350°C). The pseudomorphic (1 × 1)-Tl structure is interpreted in terms of Tl adatoms replacing the Ge adatoms and adsorbed in on-top Tl-type surface sites of the unreconstructed Ge(1 1 1) surface. The STM data of the (3 × 1) reconstruction are consistent with a modified version of the honeycomb chain-channel model of this structure as proposed in the literature. The Tl induced surface reconstructions on Ge(1 1 1) are discussed in relation to the monovalent chemical character of Tl adatoms. At high coverages the growth of the Tl adlayer is characterised by a Stranski–Krastanov mode with highly mobile adatoms on the first wetting layer. The three-dimensional Tl islands grow epitaxially ordered and rotationally aligned with the substrate. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The surface reconstructions of semiconductor surfaces have fascinated the surface science community for many decades, and their physical origin has become evident in recent studies [1]. It has now become clear that the balance between the minimisation of the electronic bond energy, i.e. the saturation of dangling bonds, and the elastic strain energy determines the lowest energy structure [2–4]. As a result very complicated rearrangements of surface atoms are often encountered both on clean and adsorbate covered semiconductor surfaces, but considerable progress has been achieved in recent years [5]. One of the remaining riddles of surface reconstructions on group IV semiconductor surfaces concerns the apparently simple (3 × 1) structures, which are observed on Si(1 1 1) and Ge(1 1 1) surfaces as a results of the deposition of a variety of metal atoms, such as alkali metal, earth alkali metal, and Ag metal atoms [1,6], but as yet not for group III metals. The similarities between the STM images along with the similar Si2p core level spectra obtained from the different metal-induced (3 × 1) structures suggested that the Si(Ge) arrangement rather than the adatoms determines the

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nature of the reconstructions [6]. Earlier models of the \((3 \times 1)\) structure contained Si( Ge) zig-zag chains along the \((110)\) directions, which are separated by rows of metal atoms, i.e. they represented either variants of the Seiwatz chain model [1,7] or an extension of the Pandey chain model [6,8]. These earlier models were discarded recently on both experimental and theoretical grounds and there seems to be converging opinion towards a model which has been referred to as the “honeycomb chain-channel” model [6,9–11]. The latter involved the unusual formation of a Si double bond in the surface layer [10], which however has been questioned again recently by Willis et al. [12–14], at least for the Ge(111)3 \times 1\) surfaces.

Here we report the observation of a Ge(111)3 \times 1\) structure, which is induced by the deposition of thallium adatoms on the Ge(111)c(2 \times 8) surface. This structure is very unusual for the adsorption of group III metal atoms on Ge(111) or Si(111) surfaces. Ga and In adatoms on Ge(111), for example, form a series of complicated surface structures, which are characterised by discommensurate phases [15–17]. Tl, the heaviest of the group III elements, is however different in its chemistry from the other members of this group in that it can support a monovalent state in its compounds in addition to the more common trivalent chemical state [18]. The stability of the monovalent state of Tl has been associated with the so called “inert pair effect” of the 6s2 electron configuration, that is the reluctance of the 6s electron pair to participate in chemical bonding. This peculiar chemistry, which renders Tl somewhat akin to the alkali metals or to Ag, may be one of the reasons for the formation of the here reported \((3 \times 1)\) surface structure.

We have used scanning tunneling microscopy (STM) in conjunction with LEED and Auger electron spectroscopy (AES) to investigate the surface structures of Tl on the Ge(111)c(2 \times 8) surface. To the best of our knowledge this work is the first study of the adsorption of Tl on Ge surfaces. The structural phase diagram of Tl on Ge(111) has been measured in the temperature range from room temperature (RT) to 400°C, at which temperature the desorption of Tl from Ge(111) is complete. The Tl induced surface structures comprise a \((3 \times 1)\) structure, observed best after annealing at \(\sim 300–350°C\), and a \((1 \times 1)\)-Tl structure at around one monolayer coverage formed in a wider temperature range (RT to \(\sim 300°C\)). At higher coverages the nucleation of large epitaxially-grown three-dimensional (3D) Tl islands is reported.

2. Experimental

The experiments were performed in a custom-designed three-chamber UHV system equipped with STM (Omicron micro-STM) and LEED/AES facilities as described previously [19]. The Ge samples were cut from p-doped wafers and attached to Ta sample plates, which could be transferred between manipulators in the different chambers via a magnetically coupled sample transfer rod. The sample plates could be heated indirectly by electron bombardment from the back side and the Ge surface temperatures were estimated by using preset heating powers; the latter were calibrated against a thermocouple reading in a separate experiment (precision is approximately \(\pm 15°C\)). Clean, well-ordered Ge(111)c(2 \times 8) surfaces have been prepared by Ar ion bombardment (0.5 keV) and annealing at 800°C. The surface order and cleanliness of the Ge surfaces were checked by LEED, AES, and STM. Tl was evaporated in the preparation chamber from a boron nitride crucible and the evaporation rate was controlled by a quartz film thickness monitor. The Tl surface coverage, referred to in monolayers (ML) as referenced to the atomic density of the unreconstructed Ge(111)1 \times 1\) surface, has been followed by AES using the Tl \(N_{\text{Te}}\)O\text{O}_{\text{V}}\text{O}_{\text{V}}\ Auger transition at \(\sim 84\) eV. The Tl Auger signal has been approximately calibrated against the STM images for submonolayer coverages and the deposited amount as measured by the film thickness monitor.

3. Results and discussion

3.1. The Tl–Ge(111) surface phase diagram

A first impression of the Tl-on-Ge(111) adsorption system and of the various adsorbate in-
Fig. 1(b) illustrates the temperature stability of the Tl adlayer: the Tl NOO Auger signal is plotted as a function of temperature for 1 ML Tl coverage. The plot indicates that the Tl surface coverage is stable up to ~300°C, but that the desorption of Tl from the Ge(111) surface sets in at $T \approx 300^\circ$C. A considerable amount of Tl has thus desorbed from the monolayer at 350°C, where the $(3 \times 1)$ reconstruction is observed best. At 400°C the desorption of Tl from Ge(111) is complete and the Ge-c(2 × 8) structure is recovered.

At higher coverages (>2–3 ML) the formation of large 3D Tl islands is observed; these islands are epitaxially ordered and rotationally aligned with the substrate as evidenced by the appearance of a LEED pattern which contains the incoherent superposition of reflexes from a $(1 \times 1)$ and a $(0.87 \times 0.87)$ structure (see Fig. 4d). The latter is from the top surfaces of the Tl islands, which have relaxed to their respective bulk lattice constant. In the following we will first describe the results of Tl deposition at RT and then discuss the Tl-induced $(3 \times 1)$ structure in subsection 3.3.

3.2. Tl adsorption at room temperature

Fig. 2 shows constant-current topographic STM images of submonolayer coverages of Tl deposited onto the Ge(111)c(2 × 8) surface at room temperature. The image 2(a) has been obtained after deposition of ~0.1 ML of Tl. In this empty state image (recorded at positive sample bias, thus electrons are tunneling from the tip into the empty states of the sample) the Ge adatoms of the c(2 × 8) structure are displayed [20]. The c(2 × 8) structure is partly retained at these low Tl coverages, but partial disordering is observed near agglomerations of Tl deposits as seen in the upper and the lower left parts of the image (areas marked A). A number of single somewhat brighter maxima is observed on the intact c(2 × 8) regions (arrows). These are associated with individual Tl adatoms, which appear to be adsorbed on top of the Ge adatoms in the so called Tl positions. From line scans across the Tl adatoms an apparent height difference of 1 ± 0.2 Å with respect to the Ge adatoms is derived, which is a value determined by
mainly electronic effects (note that the radius of Tl atoms is \( \approx 1.7 \) Å). In Fig. 2(b) a filled state image of \( \approx 0.2 \) ML Tl on Ge(1 1 1) is displayed, where the Ge restatoms determine the contrast of the substrate. The striking features of this image are bright-contrast strands of 2–3 lines with Y-shaped ramifications. The distance between the bright lines, which run along the Ge(1 1 1) \((1 \bar{1} 0)\) directions, is \( \approx 11.5 \) Å, which is close to three times the Ge–Ge nearest neighbour distance of \( \approx 4 \) Å. It is therefore tempting to associate these strands with structural elements of a precursor phase to the \((3 \times 1)\) structure. Fig. 2(c) has been recorded after deposition of \( \approx 0.5 \) ML Tl. The area between the bright strands of lines is now filled by a smooth overlayer (medium grey contrast) interrupted by darker defect areas, which reach down to the Ge substrate. In image 2(d), at \( \approx 0.7 \) ML Tl deposition, the flat smooth overlayer areas dominate and the surviving former bright strands form defects, which display an inverted (darker) contrast under the tunneling conditions used for this image. The LEED pattern at this adsorption stage consists of a \((1 \times 1)\) pattern with weak stripes at third order positions.

Fig. 3 shows higher resolution STM images of selected areas of the 0.7 ML Tl-on-Ge(1 1 1) surface. Image 3(a) reveals that the smooth Tl overlayer mentioned above is a regular hexagonal array of unit cells with \( \approx 4 \) Å lattice constant, thus representing a pseudomorphic \((1 \times 1)\) layer. Notice that the STM images of Fig. 3 have been recorded with sample biases of a few tens of millivolts suggesting that the surface is metallic like. Fig. 3(b) shows one of the defect strands in greater detail in a filled state image, which is of interest since it may
constitute a building element of the \((3 \times 1)\) reconstruction. This strand consists of two closely spaced equally bright lines which are flanked by rows of lower-contrast maxima; the latter display atomic-type resolution and are separated by \(\sim 4\) Å along the direction of the strand. The two bright lines are separated by \(\sim 2.5\) Å, which is too close to reflect an interatomic distance on this surface. It is therefore tentatively suggested that the bright lines result from the electronic states of a single line of Tl adatoms. The atomically resolved maxima with the darker contrast, which form a zig-zag line following the strand (as indicated on the image), are associated with Ge substrate atoms. The line scan in Fig. 3(c) gives the distances along A–A' across the strand. The distance between points 1 and 2 of the line scan is \(\sim 12\) Å, which is identical with the longer distance of a \((3 \times 1)\) unit cell; this substantiates the conjecture that the strand is a building element of the \((3 \times 1)\) structure. A \((3 \times 1)\) unit cell is indicated on the image 3(b). The metal atoms in the usual, viz. alkali metal or Ag induced, \((3 \times 1)\) structures are commonly not visible in the filled state images, because of a charge transfer from the metal to the substrate (Si, Ge) atoms [10,12]. This may also partly be the case in the fully developed Tl induced Ge\((3 \times 1)\) structure (see Section 3.3). We presume that the electronic structure of this single strand of the \((3 \times 1)\) structure, which is embedded as a defect in the \((1 \times 1)\) Tl monolayer phase, must be substantially modified as compared with the more extended \((3 \times 1)\) structure.

Fig. 4(a) shows a larger scale STM image of the Ge\((11\overline{1})\) surface covered with one monolayer of Tl. The image displays a smooth overlayer extending over several substrate terraces, which are separated by monoatomic Ge steps. The interesting features in this image are the ragged step edges, which are unlike those of the clean Ge\((11\overline{1})\) surface and appear as a result of the Tl deposition. They indicate that Ge atoms have moved from the terraces to the step edges during the formation process of the pseudomorphic \((1 \times 1)\) Tl monolayer, from which we suggest that the Ge adatoms have been replaced by Tl adatoms. Fig. 4(b) shows an atomically resolved image of the Tl\((1 \times 1)\) phase, where the \(\sim 4\) Å nearest neighbour distance can be readily measured.
Fig. 4. (a) STM image of 1 ML Tl on Ge(111) (2000 × 2000 Å²; 0.23 V, 1.53 nA). (b) Atomically resolved STM image of 1 ML Tl on Ge(111) (100 × 100 Å²; 0.90 V, 0.93 nA). (c) STM image of 5 ML Tl on Ge(111), showing a large Tl island (2000 × 2000 Å²; 0.051 V, 1 nA). (d) LEED pattern of the surface of (c). The arrows denote the Ge(111)1 × 1 reflexes, the outer reflexes are from the Tl island surfaces (0.87 × 0.87 pattern; electron energy 42 V).

The growth of the Tl adlayer beyond one monolayer coverage follows the typical pattern of a Stranski–Krastanov growth with highly mobile adatoms on the first wetting layer. A small number of large Tl islands is formed as illustrated by the STM image of Fig. 4(c), which has been taken after deposition of ~5 ML Tl at RT. The particular island imaged here is ~25 Å high, about 2000 Å wide and several thousand Å long. Despite the irregular overall shape the island is epitaxially ordered and rotationally aligned with the substrate as confirmed by the LEED pattern of Fig. 4(d), which shows the Ge(1 × 1) pattern (arrows) and reflexes from the Tl island surfaces (the (0.87 × 0.87) pattern). The Tl surface unit cell lattice constant is derived to 3.47 Å, i.e. the Tl islands have relaxed to their respective bulk configuration [21].

3.3. The Ge(111)3 × 1–Tl structure

Annealing of Tl covered Ge(111)c(2 × 8) surfaces to 300–350°C induces the formation of the (3 × 1) structure. The image in Fig. 5(a), for 1 ML Tl deposition at RT followed by annealing to 350°C, shows a well-ordered (3 × 1) overlayer which extends from the lower step edges on to the terraces. Close to the upper step edges narrow strips of bare Ge c(2 × 8) reconstructed areas are recognised, where the Tl adsorbate has desorbed during the annealing step. Three equivalent (3 × 1) domains rotated by 120° are visible in the lower right part of the image. Fig. 5(b) and (c) are dual polarity, i.e. empty and filled state images, respectively, taken from approximately the same area of the surface (as recognised by the specific defect pattern). The stripe pattern of the (3 × 1)
structure appears fairly similar in the STM at the two polarities at this magnification, but the defect regions display a different behaviour with maxima (arrows) in the filled state image (c), which are not seen in the empty state image (b). The defect maxima are offset from the centre line of the stripes, note the thin lines on the image (c), which are drawn to elucidate the offset. In the alkali or Ag derived Si(1 1 1)3 × 1 structures the stripe pattern appeared differently in filled and empty state STM images [22], but in the Ge(1 1 1)3 × 1–Na surface a more similar intensity distribution of filled and empty state images has been observed [13,14]. Here we will argue somewhat speculatively that in the environment of the defects the Tl metal atoms become visible in the filled state image as it has been suggested above in the discussion of Fig. 3(b). The (3 × 1) structure is imaged with atomic resolution in Fig. 6, the double rows correspond to the bright rows in Fig. 5. This filled state image displays the typical zig-zag chain arrangement of the Ge(1 1 1)3 × 1 reconstruction, which is very similar to what has been seen in the case of the Ge-(3 × 1)–Na structure [12–14].

The Ge-(3 × 1)–Na reconstruction has been interpreted recently by Willis et al. [12–14] in terms of a slightly modified, “honeycomb chain-channel” (HCC) model, in which the originally claimed
Si–Si (or Ge–Ge) double bond [10] is relaxed to a single bond (between 2–3 in Fig. 7). Apart from a charge transfer from metal atoms to Ge atoms 1, a transfer of charge is postulated to occur between Ge atoms 3 and 4, i.e. within the first Ge layer only (also denoted by + and − in Fig. 7), whereas in contrast some charge transfer between second and first layer substrate atoms was originally invoked by Erwin and Weitinger [10]. The interpretation of the filled state STM images in terms of zig-zag chains of negatively polarised Ge atoms (1 and 4 in Fig. 7) and invisible metal atoms in the rows in between the Ge chains is very similar in both structure models and this interpretation is presumably also valid for the Ge-(3 × 1)–Tl structure. It is not completely clear why we are unable to detect the Tl atoms in the filled state images of the extended (3 × 1) structure. A possible reason could be that the Tl adatoms transfer their 6p electron charge to the Ge atoms 1 as suggested in the HCC model (and as it is also believed e.g. for the 5s charge of Ag) and that the Tl6s2 electron configuration is unable to take part in the tunneling process. The empty state images of Ge-(3 × 1)–Na, which also display a zig-zag chain arrangement [14], have been associated within the modified HCC model with the positively polarised Ge surface atoms 2 and with positive Na atoms (+ in Fig. 7). Unfortunately, we were unable to obtain atomically resolved empty state images of the (3 × 1)–Tl structure, however the similarity of the (low resolution) images Fig. 5(b) and (c) leads us to conjecture that the empty state rows in Fig. 5(b) are made up by empty Ge and Tl states. It is interesting to speculate in this context on the nature of the point-type defect maxima in the extended (3 × 1) structure (Fig. 5(c), filled states) and of the bright lines in the (3 × 1) strand-like defects observed in the pseudomorphic (1 × 1)-Tl monolayer (Fig. 3(b)). We propose tentatively that the maxima in the filled state images involve filled states of Tl adatoms, in which the Tl–Ge charge transfer, that stabilises the extended (3 × 1) structure, is suppressed by the different bonding situation in the defect region. The shift of the maxima in the defect regions from the centre of the (3 × 1) rows into the dark channels as seen in Fig. 5(c) is supportive of this interpretation.
4. Conclusions

The surface structures of Ti on Ge(1 1 1)c(2 × 8) and on Si(1 1 1)7 × 7 surfaces, the latter have been investigated previously in our group, show common trends but also some significant differences. On both substrate surfaces a pseudomorphic (1 × 1)-Ti monolayer structure is observed, but the Ge–(1 × 1)-Ti structure is formed at room temperature whereas the corresponding Si structure requires elevated temperature (>250°C) for activation [4,23,24]. This presumably reflects the greater stability of the Si–(7 × 7) reconstruction as compared to the Ge-c(2 × 8) structure.

At low coverages the Ti adatoms are adsorbed on top of Ge adatoms of the (2 × 8) structure. With increasing coverage the Ti adatoms replace the Ge adatoms, which diffuse to the step edges, and the Ge-c(2 × 8) structure de-reconstructs, giving way to the (1 × 1)-Ti structure. It has been argued that the Si–(1 × 1)-Ti surface is the result of monovalent Ti adatoms in on-top T1 positions on an unreconstructed Si(1 1 1) surface [24]. Accordingly, each Ti p$_z$ adatom orbital saturates via covalent bonding one Si surface dangling bond state, leaving the completely filled Ti 6s$^2$ configuration in a non-bonding band. It has been proposed that the unoccupied Ti 6p$_{x,y}$ band is separated from the full 6s band by a measured surface band gap of ~0.5 eV, because the Si–(1 × 1)-Ti surface is semiconducting. Interestingly, the Ge–(1 × 1)-Ti surface appears to be metallic-like or has a very small surface state band gap, if at all. The similarity of the electronic structures of Si and Ge suggest that a similar bonding mechanism is operative in the two (1 × 1) structures. Using simple tight binding ideas it is conceivable that the weaker Ti–Ge interaction leads to a smaller separation of bonding, anti-bonding, and non-bonding states and thus to a closing or the absence of a surface band gap.

The observation of the Ge(1 1 1)3 × 1–Ti reconstruction at elevated temperature may be connected with the monovalent chemical character of Ti, but a (3 × 1) structure has not been observed on the Si(1 1 1)–Ti system [23]. The reason for this different behaviour of Si and Ge towards Ti is unclear at present. The STM results of the Ge–(3 × 1)–Ti structure are consistent with a modified version of the honeycomb chain-channel model as proposed in the literature [12–14], but the detailed adsorbate configuration and the bonding mechanism of the Ti adatoms in the channels of the (3 × 1) reconstruction remain unclear.

At higher coverages the Ti adlayer follows the Stranski–Krastanov growth mechanism with large epitaxial islands growing on top of the first pseudomorphic (1 × 1) wetting layer. This growth pattern is similar to the growth of In [25] and Ti [4] layers on Si(1 1 1) and it is characteristic of a very high adatom mobility on the (1 × 1)-Ti monolayer.

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References


