

ADSORBATE REGISTRY AND SUBSURFACE RELAXATION OF THE α -Ge(111) $\sqrt{3} \times \sqrt{3}$ -Sn/Pb RECONSTRUCTIONS

Jan Skov PEDERSEN, Robert FEIDENHANS'L, Mourits NIELSEN,
Kristian KJÆR

Risø National Laboratory, DK-4000 Roskilde, Denmark

Francois GREY and Robert L. JOHNSON

Max-Planck-Institute for Solid State Research, D-7000 Stuttgart 80, Fed. Rep. of Germany

Received 23 March 1987; accepted for publication 15 April 1987

We have performed a surface X-ray diffraction study of submonolayer $\sqrt{3}$ structures of Sn and Pb on Ge(111). The structure factor analysis of fractional-order Bragg reflections shows a significant relaxation in the Ge substrate induced by the Sn/Pb adatoms. The registry of the adatoms is determined from the analysis of the integer-order intensities. The adatoms are situated on top of the second layer of Ge atoms. The intensity profile normal to the surface of a subset of the fractional-order Bragg rods were measured. They display a pronounced intensity variation for both Sn and Pb, which can be explained only by a subsurface relaxation extending at least four atomic layers into the bulk.

1. Introduction

Ultrathin overlayers, chemisorbed on semiconductor surfaces, form a variety of different superstructures. One of the simplest and most common is the α - $\sqrt{3} \times \sqrt{3}$ R30° structure induced by adsorption of 1/3 of a monolayer of group III or IV elements on the Si(111) [1–5] or Ge(111) [6,7] surfaces. In spite of the large effort in recent years, the atomic geometry and chemisorption sites have still not been determined unambiguously [4,5,8–11].

We have studied the $\sqrt{3}$ structure previously for 0.6–1.3 monolayer coverages of Pb on Ge(111) [12]. The results indicated that the chemisorption site of the α -structure is the four-fold coordinated site (T_4) on top of the second layer of Ge (fig. 1). In this paper we report the detailed structure of the Sn and Pb induced α -Ge(111) $\sqrt{3} \times \sqrt{3}$ surface reconstructions (henceforth referred to as Sn and Pb samples) determined by grazing-incidence X-ray scattering. The analysis is performed as follows. First, the projection of the structure on the surface plane is determined from the measured in-plane intensities of the fractional-order Bragg rods. Then the registry is found from the interference of

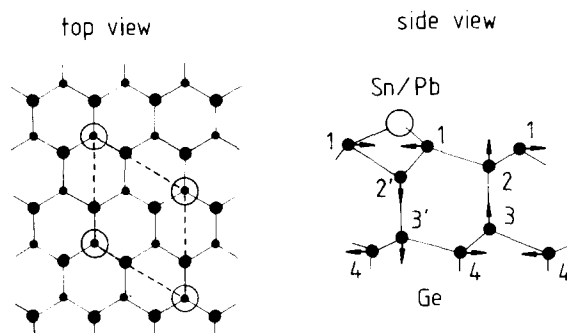


Fig. 1. Left-hand side: top view of the unit cell of the $\alpha\text{-}\sqrt{3} \times \sqrt{3}$ structure. The large and small filled circles indicate the positions of the first and second layer of substrate atoms. Large open circles are adatoms. The registry is T_4 . Right-hand side: side view of the T_4 geometry. The directions of the relaxations are shown by arrows.

the scattering from the surface layers (Bragg rods) and the bulk (crystal truncation rods) at the integer-order reflections [12,13]. Finally, the geometry normal to the surface is deduced from an analysis of the intensity variation along the fractional-order Bragg rods.

2. Experimental

The sample preparation at the Flipper II beamline in HASYLAB and the experimental set-up at the wiggler W1 beamline have been described previously [12,14]. After the preparation and characterization, the sample was transferred to a small portable UHV-cell with a Be-window for X-ray diffraction. The cell was mounted and aligned on the vertical scattering diffractometer at the wiggler W1 beamline. The wavelengths of the X-rays were chosen to be 1.535 and 1.344 Å and the (fixed) angle of incidence was 0.63° and 0.42° , for the Sn and Pb sample, respectively.

The intensities, integrated by scanning the sample azimuthal angle ω , were measured by a detector subtending 2.4° normal to the surface. For a subset of the fractional-order rods intensity profiles (ω -integrated) were recorded up to a momentum transfer of $\sim 1 \text{ Å}^{-1}$ normal to the surface, the upper limit being set by mechanical constraints in the experimental set-up.

We measured 36 fractional and 14 integer-order reflections for the Sn sample and 30 fractional and 10 integer-order for the Pb sample. For both samples the intensity profile of 6 fractional-order reflections were measured. The structure factors were obtained after correcting the integrated intensities for the variation of the Lorentz factor $(\sin 2\theta)^{-1}$ and the effective sample area contributing to the scattering $(\sin 2\theta)^{-1}$.

Table 1

Measured fractional-order structure factor intensities $|F_{hk}^{\text{exp}}|^2$, corresponding uncertainties σ_{hk} and model structure factors intensities $|F_{hk}^{\text{mod}}|^2$; the indices h, k are in units of the in-plane bulk reflections (2/3, 2/3, 4/3) and (2/3, 4/3, 2/3); also displayed are the χ^2 , the displacements a_1 and a_2 , and thermal parameters B from the final fits

h	k	Ge(111)-Sn			Ge(111)-Pb		
		$ F_{hk}^{\text{exp}} ^2$	σ_{hk}	$ F_{hk}^{\text{mod}} ^2$	$ F_{hk}^{\text{exp}} ^2$	σ_{hk}	$ F_{hk}^{\text{mod}} ^2$
1/3	1/3	22.1	1.6	22.6	81.7	9.4	88.1
2/3	2/3	8.9	0.6	9.5	56.4	6.5	48.2
4/3	1/3	15.8	0.7	14.9	45.8	5.3	46.2
5/3	2/3	14.1	0.9	13.5	42.0	4.9	40.5
4/3	4/3	13.4	1.1	14.0	37.3	4.3	40.3
5/3	5/3	2.1	0.3	2.3	7.8	1.0	9.0
7/3	1/3	8.3	0.7	7.5	18.7	2.3	17.3
7/3	4/3	10.4	1.0	11.8	14.9	1.7	14.7
7/3	7/3	5.9	0.5	5.8			
8/3	2/3	10.4	0.8	10.5	18.0	2.1	17.3
8/3	5/3	5.4	0.5	4.9	10.8	1.3	9.8
8/3	8/3				1.3	0.3	1.3
10/3	1/3	6.6	0.5	6.7	12.3	5.0	15.5
10/3	4/3				7.4	0.9	6.9
11/3	2/3	2.3	0.9	2.8	4.2	0.6	3.8
13/3	1/3				4.4	1.7	7.4
		$\chi^2 = 1.0$			$\chi^2 = 0.93$		
		$a_1 = 0.204 \pm 0.015 \text{ \AA}$			$a_1 = 0.158 \pm 0.028 \text{ \AA}$		
		$a_2 = 0.106 \pm 0.010 \text{ \AA}$			$a_2 = 0.070 \pm 0.017 \text{ \AA}$		
		$B(\text{Sn}) = 3.0 \pm 0.5 \text{ \AA}^2$			$B(\text{Pb}) = 3.2 \pm 0.6 \text{ \AA}^2$		
		$B(\text{Ge}) = 0.6 \pm 0.2 \text{ \AA}^2$			$B(\text{Ge}) = 0.7 \pm 0.5 \text{ \AA}^2$		

The extension of the surface reconstruction perpendicular to the surface gives rise to an intensity variation along the rods. As the resolution is relaxed along the rods (2.4°) this intensity variation gives rise to the observation of different intensities for in-plane equivalent reflections. Thus, special attention must be paid to the averaging of in-plane reflections. The resulting independent structure factors, 13 for the Sn sample and 15 for the Pb sample, are listed in table 1. Also displayed are the uncertainties calculated from reproducibility and counting statistics.

3. In-plane structure

In the structure factor analysis, described below, the standard chi-square test was used to evaluate the goodness of a fit [16]:

$$\chi^2 = \frac{1}{N-p} \sum_{hk} \frac{\left(|F_{hk}^{\text{exp}}|^2 - |F_{hk}^{\text{mod}}|^2 \right)^2}{\sigma_{hk}^2}, \quad (1)$$

where N and p are the number of data points and fitting parameters, respectively. A non-linear least-squares fitting procedure was applied and the uncertainties of the fitting parameters were determined according to the standard criterion [16]. First we discuss the Sn sample. A fit of a model with one Sn atom per unit cell gives $\chi^2 = 38$ allowing only a scale factor to vary. An electron density difference contour map [15] suggests that six Ge atoms should be included at positions near the corners of a hexagon with the Sn atom at the center. A model with these atoms with isotropic Debye–Waller (DW) factors for Sn and for Ge, gives $\chi^2 = 1.0$ with three Ge atoms displaced away from their bulk positions towards the Sn atom and three Ge atoms displaced outwards. Including only three Ge atoms increases χ^2 to 16. The corresponding fits for the Pb sample are: one Pb atom plus a DW factor, $\chi^2 = 9.3$; one Pb and three Ge atoms plus two DW factors, $\chi^2 = 3.4$; one Pb and six Ge atoms, $\chi^2 = 0.93$. The fits of the Sn sample were considerably more sensitive than the Pb sample to the inclusion of the Ge atoms due to the different number of electrons.

The model structure factor intensities and the structural parameters from the best fits are listed in table 1. The parameters a_1 and a_2 are the displacements of the inwards and outwards moving Ge atoms, respectively. a_1 is largest and both displacements are slightly larger for the Sn sample. The B -factor of Sn ($3.0 \pm 0.5 \text{ \AA}^2$) is considerably larger than the bulk values for white tin, $B = 1.07 \text{ \AA}^2$ and grey tin, $B = 0.431 \text{ \AA}^2$ [17]. In contrast the B -factor of Pb ($3.2 \pm 0.6 \text{ \AA}^2$) and Ge are close to the bulk values $B(\text{Pb}) = 2.541 \text{ \AA}^2$ [18] and $B(\text{Ge}) = 0.586 \text{ \AA}^2$ [19].

The measured integer-order structure factor intensities are displayed in table 2. The model structure factors are calculated by adding coherently the contributions from the substrate and the surface layers [12]. When the structure of the surface layers are taken from the fits of the fractional-order

Table 2

Measured integer-order structure factor intensities $|F_{hk}^{\text{exp}}|^2$, uncertainties σ_{hk} and model structure factor intensities $|F_{hk}^{\text{mod}}|^2$

h	k	Ge(111)-Sn				Ge(111)-Pb			
		$ F_{hk}^{\text{exp}} ^2$	σ_{hk}	$ F_{hk}^{\text{mod}} ^2$		$ F_{hk}^{\text{exp}} ^2$	σ_{hk}	$ F_{hk}^{\text{mod}} ^2$	
				$T_4(0^\circ)$	$T_4(180^\circ)$			$T_4(0^\circ)$	$T_4(180^\circ)$
1	2	93.7	20.0	63.5	64.9	176.0	40.0	169.6	171.0
2	0	31.5	12.6	35.0	39.0	136.0	30.0	89.6	93.5
2	1	29.5	1.9	24.7	28.7	72.9	8.4	55.9	60.2
3	1	14.0	0.9	11.1	16.3	32.4	3.7	22.4	27.7
4	0	11.3	0.7	11.4	14.6	24.7	6.0	17.8	21.7
3	2					19.0	5.5	11.8	15.9
				$\chi^2 = 4.3$	$\chi^2 = 5.8$	$\chi^2 = 3.3$ $\chi^2 = 1.2$			

intensities, there are no adjustable parameters in the calculation. For the registries with the adatom on top of the first layer Ge (T_1 site) or second layer Ge (T_4 site), four layers of Ge are included in the surface contribution. For the H_3 site, where the adatom is in the center of the hexagon made up of the first two layers of Ge, only these two layers were included. Finally, we can also turn the substrate 180° with respect to the $\sqrt{3}$ unit cell, giving a total of six possibilities.

In agreement with our conclusions for Ge(111) $\sqrt{3} \times \sqrt{3}$ -Pb [12], it is found that the adatoms are on T_4 sites, but it is not possible to distinguish between the two possible orientations relative to the Ge crystal (table 2): for the Sn sample $\chi^2 = 4.3$ and 5.8 and for the Pb sample $\chi^2 = 1.2$ and 3.3. The other registries give χ^2 in excess of 11.

4. Rodscans and out-of-plane structure

The measured rodscans are shown in fig. 2. The perpendicular momentum l is in units of the reciprocal lattice vector (111). The rodscans display a pronounced and quite similar variation, demonstrating that the atomic geome-

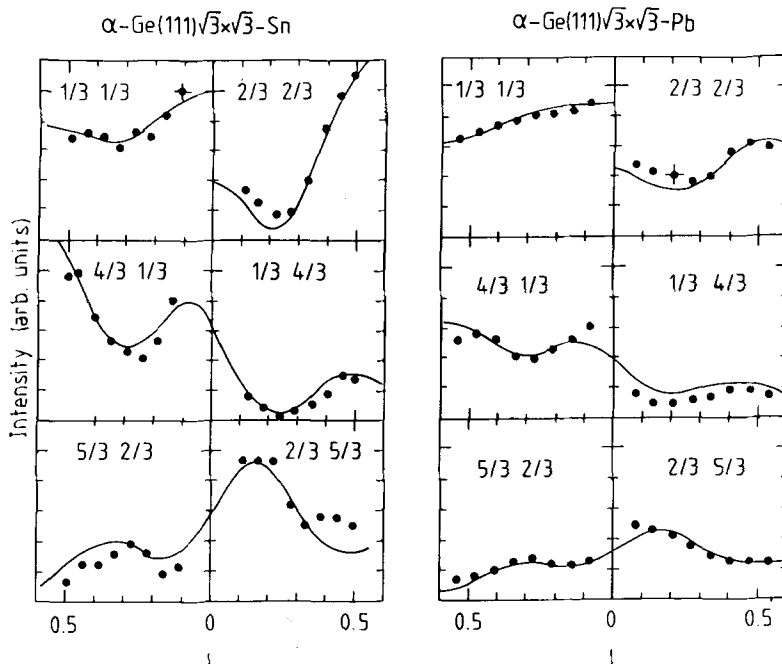


Fig. 2. Measured (points) and calculated (curves) rodscans. l is in units of the (111) reciprocal lattice vector. The details are described in the text.

try is alike for the Sn and Pb reconstructions. However, the variation is weakest for the Pb sample, because of the larger difference in scattering power between Pb and Ge. The period of the variation is approximately 0.5 times the (111) vector indicating an extent of the relaxation of 6.5 Å, i.e. down to the fourth layer of Ge (fig. 1). Horizontal and vertical bars indicate resolution along the rod and experimental uncertainty, respectively. An average value of the in-plane uncertainties is assigned to all points.

A model, including only the adatoms and in-plane relaxed atoms with DW factors and relaxations fixed at in-plane values, gives $\chi^2 = 12.4$ and 1.4 for the Sn and Pb sample, respectively. The perpendicular distance from the adatoms to the inwards displaced Ge atoms is 2.11 ± 0.13 Å for the Sn sample and 1.81 ± 0.23 Å for the Pb sample. The distance from the inwards to the outwards displaced Ge atoms is 4.7 ± 0.7 Å for both samples. Therefore, it is concluded that the inwards displaced Ge atoms belong to the first layer and the outwards displaced Ge atoms to the fourth layer of the substrate.

In the next step the second and third layer of the Ge are also included. In order to reduce the number of free parameters, the distances from atoms 2' to 3' and 2 to 3 (see fig. 1) are constrained to the bulk value 2.450 Å. This is a reasonable simplification, considering the elastic properties of Ge [20]. This 13-atom model gives $\chi^2 = 4.9$ and 1.3 for the Sn and Pb sample, respectively.

Finally, the DW factors are allowed to vary. These seven-parameters fits give $\chi^2 = 4.1$ for the Sn sample and $\chi^2 = 0.8$ for the Pb sample. The calculated rodscans are shown as curves in fig. 2. The B -factors of the Sn sample are $B(\text{Sn}) = 1.4 \pm 0.7$ Å² and $B(\text{Ge}) = 3.8 \pm 1.6$ Å². Those for the Pb sample are $B(\text{Pb}) = 4.9 \pm 0.7$ Å² and $B(\text{Ge}) = 2.0 \pm 1.7$ Å².

The directions of the relaxations are shown by arrows in fig. 1, and can be understood by the relative smaller energy cost for bond-angle changes compared to bond stretching [20]. The bond length between Sn and the Ge atom 2' (fig. 1) is $r_{2'} = 2.67 \pm 0.23$ Å and between Sn and the Ge atom 1 $r_1 = 2.75 \pm 0.08$ Å. These are slightly larger than the sum of the covalent (Pauling) radii [21]

Table 3

Distances normal to the surface found by the rodscan fits; all distances are in Å and the notation from fig. 1 has been used

Distance between	Ge(111)-Sn	Ge(111)-Pb
Adatom-1	1.72 ± 0.13	1.72 ± 0.13
Adatom-2'	2.68 ± 0.23	2.59 ± 0.98
Adatom-3'	5.13 ± 0.23	5.04 ± 0.98
Adatom-2	2.10 ± 0.29	2.44 ± 1.20
Adatom-3	4.55 ± 0.29	4.89 ± 1.20
Adatom-4	6.07 ± 0.28	6.37 ± 0.42
1-4 ^{a)}	4.35 ± 0.31	4.65 ± 0.44

^{a)} Bulk value 4.083 Å.

2.62 Å. The same bond lengths for the Pb sample are $r_2 = 2.59 \pm 0.98$ Å and $r_1 = 2.72 \pm 0.08$ Å, compared to the sum of the covalent radii, 2.68 Å. The remaining bond-lengths are close to bulk values with relatively large uncertainties. The perpendicular distances are listed in table 3. The large uncertainties are mainly due to the limited l -range.

5. Discussion and conclusions

All total energy calculations on the α - $\sqrt{3} \times \sqrt{3}$ adatom-induced reconstruction published to date concern Si(111) with relative low Z adsorbates. Adatoms from group III [5,8] and IV [22,23] have been studied, with similar results. When substrate relaxations are allowed the T_4 geometry is preferred. The bonds of the adatom to the substrate atoms are slightly longer than the sum of the covalent radii.

The results of our X-ray study of the α -Ge(111) $\sqrt{3} \times \sqrt{3}$ -Pb/Sn reconstructions are unambiguous experimental evidence for the T_4 chemisorption site of the α - $\sqrt{3} \times \sqrt{3}$ structure and should stimulate theoretical work on the more complicated case of high Z adsorbates. The subsurface relaxations are similar to those found in the theoretical work and indicate the great sensitivity of surface X-ray diffraction to small displacements of atoms from bulk positions. Our results also demonstrate that important information on the atomic geometry normal to the surface can be obtained from measurements of rodscans.

Acknowledgements

The assistance of the HASYLAB staff is gratefully acknowledged. This work was supported by the Danish Natural Science Foundation, the German Federal Minister for Research and Technology and the Max-Planck Society. We have benefitted from discussions with J. Als-Nielsen, J. Bohr and H. Zabel.

References

- [1] P. Chen, D. Bolmont and C. Sébenne, *Solid State Commun.* 44 (1982) 1191.
- [2] P.J. Estrup and J. Morrison, *Surface Sci.* 2 (1964) 465.
- [3] G.V. Hansson, R.Z. Bachrach, R.S. Bauer and P. Chiaradia, *Phys. Rev. Letters* 46 (1981) 1033.
- [4] T. Kinoshita, S. Kono and T. Sagawa, *Phys. Rev.* B34 (1986) 3011.
- [5] J.M. Nicholls, P. Mårtensson, G.V. Hansson and J.E. Northrup, *Phys. Rev.* B32 (1985) 1333.
- [6] T. Ichikawa and S. Ino, *Solid State Commun.* 27 (1978) 483.

- [7] J.J. Métois and G. Le Lay, *Surface Sci.* 133 (1983) 422.
- [8] J.E. Northrup, *Phys. Rev. Letters* 53 (1984) 683.
- [9] T. Kinoshita, S. Kono and T. Sagawa, *Phys. Rev.* B32 (1985) 2714.
- [10] G.V. Hansson, J.M. Nicholls, P. Mårtensson and R.I.G. Uhrberg, *Surface Sci.* 168 (1986) 105.
- [11] M. Saitoh, K. Oura, K. Asana, F. Shoji and T. Hanawa, *Surface Sci.* 154 (1985) 394.
- [12] R. Feidenhans'l, J.S. Pedersen, M. Nielsen, F. Grey and R.L. Johnson, *Surface Sci.* 178 (1986) 927.
- [13] I.K. Robinson, *Phys. Rev.* B33 (1986) 3830.
- [14] T. Ichikawa and S. Ino, *Surface Sci.* 105 (1981) 395.
- [15] J. Bohr, R. Feidenhans'l, M. Nielsen, M. Toney, R.L. Johnson and I.K. Robinson, *Phys. Rev. Letters* 54 (1985) 1275.
- [16] P.R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).
- [17] Calculated with the Debye temperatures from specific heat: J. de Layney, *Solid State Phys.* 2 (1956) 233.
- [18] D.R. Chipman, *J. Appl. Phys.* 32 (1960) 2012.
- [19] B.W. Batterman and D.R. Chipman, *Phys. Rev.* 127 (1962) 690.
- [20] P.N. Keating, *Phys. Rev.* 145 (1966) 637.
- [21] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1948) p. 179.
- [22] S.B. Zhang, M.L. Cohen and J.E. Northrup, *Surface Sci.* 157 (1985) L303.
- [23] J.E. Northrup, *Phys. Rev. Letters* 57 (1986) 154.