

Ion scattering studies of the Pb(110) surface from 160 to 590 K

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Received 26 August 1991; accepted for publication 1 October 1991

The (110) surface of Pb has been the subject of surface structure studies for the reason of surface melting phenomena, i.e. surface melting at $580 \text{ K} < T \leq T_m$ and disordering at $500 \leq T \leq 580 \text{ K}$. Using low-energy ion channeling and neutral impact collision ion scattering spectrometry (NICISS) it is found that the disordering is a rather continuous process starting already at 160 K. Defects are identified as vacancies in the surface chains. Also step formation is an event on the surface observed with increasing temperature. The thermal vibrations of the surface atoms show no deviation from the Debye–Waller behaviour. An anomalous thermal expansion in the $[1\bar{1}0]$ surface chains is found.

1. Introduction

Since the detection of the surface melting of the Pb(110) surface in 1985 [1] this surface has been the subject of numerous studies with all possible surface analytical techniques (for reviews see refs. [2,3]). The experimental findings up to now may be shortly summarized: Below about 450 K the surface behaves like a regular fcc (110) surface showing an enhancement of the amplitudes of the thermal vibrations of the surface atoms [1,2]. Mechanical stress may induce a (2×4) reconstruction [3]. Around 400 K a “roughening” transition is reported, which is understood as the formation of steps along the $[1\bar{1}0]$ surface direction. With increasing temperature the steps decay but more steps are created such that a net increase of (111) facets is suggested [3]. At about 520 K atomic defects are formed accompanied by an increase of the surface diffusion [2,3]. This disordering affects at least two atomic layers. Between 560 and 580 K the number of disordered layers increases, i.e., the thickness of the disordered region increases logarithmically as $-\ln(T_m - T)$ where T_m is the melting temperature. Above 580 K liquid like behaviour is established. The thickness of the liquid layer increases approximately as $(T_m - T)^{1/3}$, as predicted theo-

retically for the solid–liquid and the liquid–vapour interface. The logarithmic behaviour in the disordering regime is hence labelled “pre-melting” [2,3].

In the present study we will describe results from low-energy ion scattering experiments. Since low-energy ion scattering probes the “visible” surface of a solid [4], the results are concerned with the defect formation in or disordering of the two top layers only. We find evidence for point defects at temperatures as low as 160 K, evidence for step formation below 400 K and confirmation of the liquid-like behaviour of the top layer at 580 K.

2. Experiment

The experiments were done in an UHV system equipped with LEED and three ion scattering methods: ISS using a rotatable electrostatic analyser, a time-of-flight (TOF) system at a fixed scattering angle of 165° and a position-sensitive detector for surface channeling experiments [5,6]. A scheme of the ion scattering geometries is partly given in fig. 1. The target is mounted in a Cu-crucible minimizing mechanical stress as far as possible. The target can be rotated around two axes. The target is heated by radiation and/or

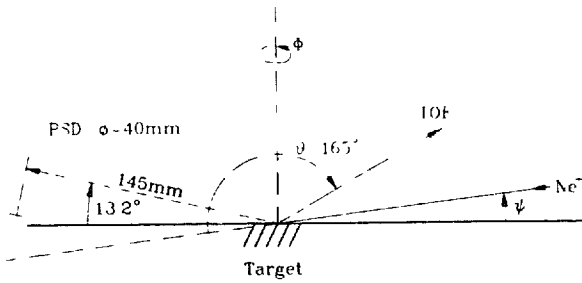


Fig 1. Scheme of the experimental setup, i.e., the scattering geometries used for surface blocking and surface channeling experiments

electron bombardment. The target temperature is measured by a calibrated thermocouple and/or a pyrometer. Long ion bombardment and annealing cycles proved necessary in order to obtain a clean and well-ordered surface in agreement with previous reports [1–3]. Most of the ion bombardment was done with 2 keV Ne^+ incident at a glancing angle below 30° . The target azimuth was continuously varied during the bombardment using a computer-controlled stepping motor.

3. Results

First we present the results using the TOF detector for surface blocking or shadowing experiments. In this mode the ion beam hits the target at a small glancing angle and only particles scattered into a large scattering angle (165°) are detected. When the azimuthal angle is varied structural patterns are measured which show in real space the periodicity of the surface [7]. The minima are due to the surface channeling along major crystallographic directions. The minimum yield is a measure for the “quality” of the surface, i.e., with adatoms and/or steps blocking any surface channels the minimum yield increases [8,9].

In fig 2 I versus ϕ plots of Pb(110) are shown in the temperature range from 160 to 590 K. The structure is like the one of, e.g., Ni(110) [8], however, even at 160 K the minimum yield in the $[1\bar{1}0]$ direction of Pb(110) is higher than that of

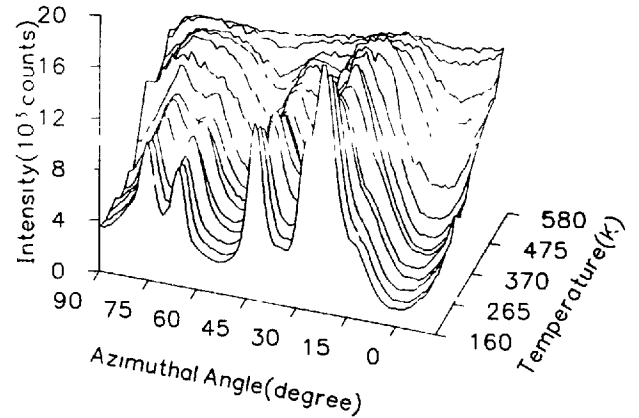


Fig 2. Result of the surface blocking experiment (I versus ϕ) on Pb(110) for temperatures between 160 and 580 K. Ne^+ at 2 keV, angle of incidence 11° , scattering angle 165° .

Ni(110). With increasing temperature the $[1\bar{1}1]$ and $[1\bar{1}4]$ minima are “filled up” first, until at 580 K also the $[1\bar{1}0]$, $[001]$ and $[1\bar{1}2]$ minima merge into the “random” yield ($\phi = 21.7^\circ$). The total flattening of the I versus ϕ plot at 580 K is a very obvious confirmation of the liquid-like structure of the top layer of Pb(110) at this temperature.

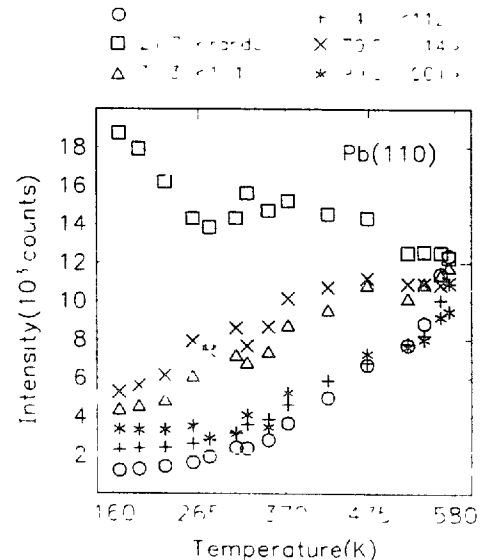


Fig 3 Temperature dependence of the minimum yields of the $[1\bar{1}0]$, $[1\bar{1}1]$, $[1\bar{1}2]$, $[1\bar{1}4]$ and $[001]$ surface channels compared to the intensity for $\phi = 21.7^\circ$ (“random” direction) Scattering conditions as in fig 2

The temperature dependence of the azimuthal minima is compared in fig. 3 with the random intensity. The random intensity decreases with temperature due to the increasing roughness and the increasing thermal vibration amplitudes.

These effects cause a decrease of the reflection probability and an increasing angular width of all backscattered particles, such that a small angle detector "sees" less particles. The different temperature dependence of the minimum yield is the

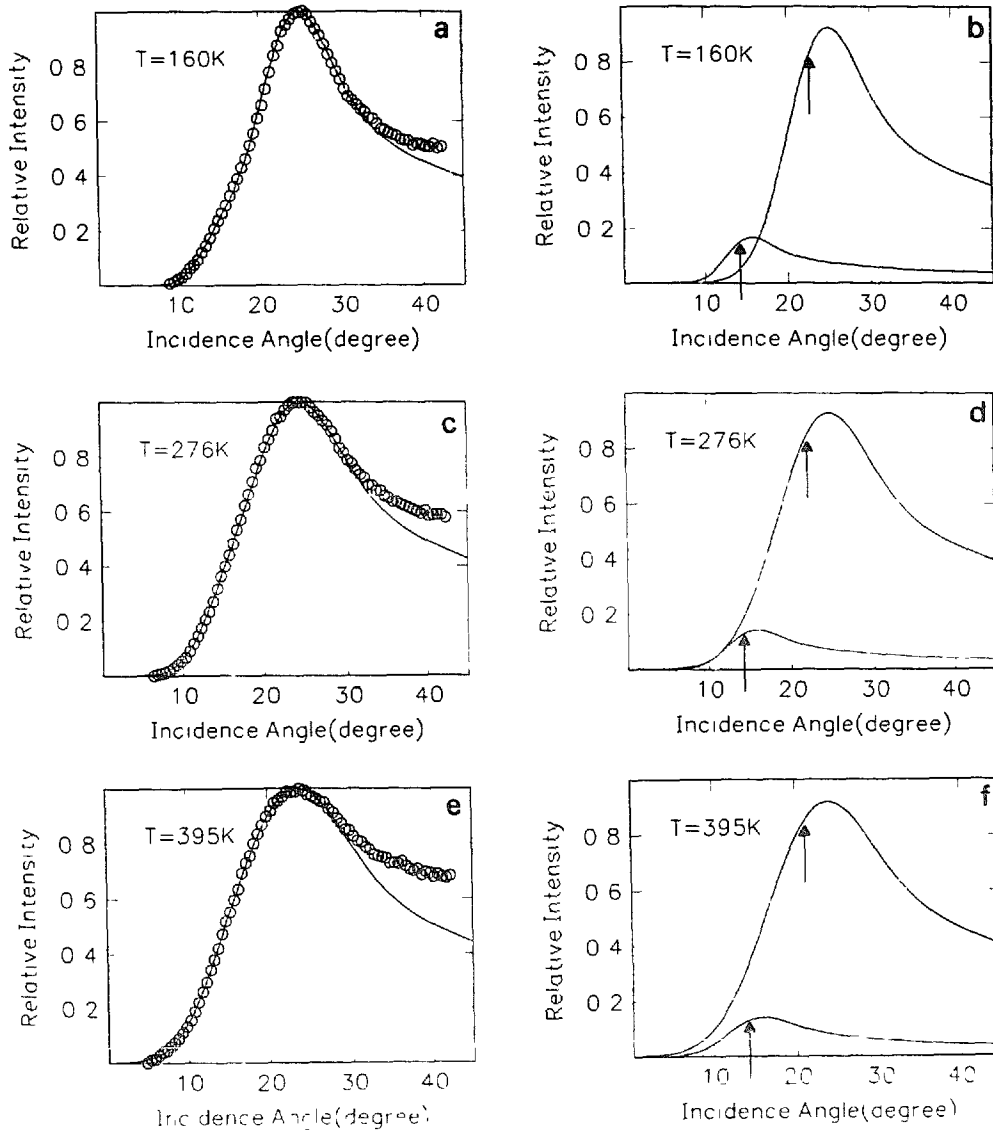


Fig 4 Analysis of the $[1\bar{1}0]$ chain structure Pb(110) by NICISS (I versus ψ). (a), (c) and (e) The circles are the experimental data for 160, 276 and 395 K. The lines are calculated with a two atom scattering model, the Debye model for the surface thermal vibrational amplitudes and an increasing surface lattice constant (table 1), (b), (d) and (f) The large peaks are due to the scattering from the perfect $[1\bar{1}0]$ chains, the small peaks are from the vacancies as calculated from the two-atom model. The lines in (a), (c) and (e) are the sums of these peaks. The arrows mark the critical angles

Table 1

Root mean square thermal displacement amplitudes for Pb atoms in the $[1\bar{1}0]$ chains of the Pb(110) surface, surface lattice constant in $[1\bar{1}0]$ direction and relative number of vacancies (n_v) in the two top layers

Temperature	160	276	395
$\sqrt{\langle X^2 \rangle}$ (Å)	0.207	0.271	0.324
a $[1\bar{1}0]$ (Å)	3.50	3.63	3.82
n_v (%)	13.0	13.1	14.2

$[1\bar{1}1]$ and $[1\bar{1}4]$ channels compared to the $[1\bar{1}0]$, $[001]$ and $[1\bar{1}2]$ channels indicate that not adatoms but steps along $[1\bar{1}0]$ and $[1\bar{1}2]$ are causing the increase of the yield. The minimum yield of $[001]$ is already high at 160 K also indicating steps along $[1\bar{1}0]$ at that temperature. Adatoms would act similarly in all directions. That is, the surface may in fact form “fish-scale” patterns as observed on Au(110) using the STM [10].

The presence of vacancies can be measured directly using the shadow cone effect [11] in the impact collision technique [12,13]. As shown previously for Au(110) [14], vacancies are measured as a doubling of the surface lattice constant in, e.g., the $[1\bar{1}0]$ surface chain (fig. 4). Starting at 160 K we see already a sizeable number of vacancies which increases slightly with temperature. The number of vacancies is of the order of 10% (table 1) relative to the number of Pb atoms in the two top layers of the surface, i.e., the experiment does not discriminate between vacancies in the first and second layer, respectively. Both layers are “visible” to the beam in the $[1\bar{1}0]$ direction. The lines in fig. 4 are calculated on the basis of a two-atom scattering model [14]. At 160 K the agreement between calculation and experiment is very good. The small peak with a critical impact angle of 14.2° is the intensity due to vacancies. We find however that the angle of 14.2° corresponds to an atomic distance of 6.3 \AA instead of 7 \AA expected for a single vacancy. In comparison, the value of 22.7° for the perfect chain agrees very well with 3.5 \AA for the atomic distance in the $[1\bar{1}0]$ chains.

The reduction of the distance for the vacancy

indicates an actual relaxation or anharmonic potential for the atoms neighbouring the vacancy. The positional shift of these atoms, i.e., 0.3 \AA , is of the same order of magnitude as the root mean square thermal displacements $\sqrt{\langle x^2 \rangle}$ used in the two-atom scattering model (table 1).

In figs. 4a, 4c and 4e the experimental data are compared with the calculated results from the two atom scattering model. The agreement is satisfactory. In figs. 4b, 4d and 4f the contribution from the perfect chain (large peak) and the vacancies (small peak) are shown separately. We note a shift of the critical angle of the perfect chain which corresponds to an increase of the surface lattice constant in the $[1\bar{1}0]$ direction. The increase at 395 K is 0.32 \AA or 8.6% compared to the expected normal thermal expansion of 0.7% between 160 and 400 K.

4. Discussion

In relation to previous results [1–3] we confirm the formation of the quasi-liquid layer at 580 K on Pb(110). Obviously (fig. 2) even the near order structure is destroyed. This can be learned from comparison, e.g., with the Au(110) surface above 650 K [8]. There the (1×2) structure is destroyed but the atoms of the top layer remain on lattice sites. The lattice site occupation is randomized. Furthermore calculations made for the Pb case agree with the assumption of an “amorphous” top layer [15]. With respect to the disorder or melting of deeper layers low energy ion scattering in the modes used here cannot contribute.

For the disordering or premelting the situation is less clear, simply because medium-energy ion scattering (MEIS) [1,2] and the other techniques discussed, mainly LEED, do not necessarily probe the same quantities [3]. Our results support the model that at around 400 K the step formation in the $[1\bar{1}0]$ and $[1\bar{1}2]$ directions is saturated (fig 3). The step formation along $[1\bar{1}2]$ has not been suggested previously. Above 400 K the steps may decay and more adatoms are formed in the $[1\bar{1}0]$ surface channels which cause the increasing

blocking (intensity increase) with T in these directions.

The step formation is preceded or caused by vacancy formation in the $[1\bar{1}0]$ chains (fig. 4). The vacancies are already detected at 160 K. Their number increases slightly with increasing temperature. This finding is qualitatively comparable to the situation on Au(110) where below the order-disorder transition at 650 K the first detectable defects are vacancies followed probably by the buildup of steps [14]. For Au(110) the disorder and roughening accompanying the order-disorder transition has been predicted [16–18]. In general, e.g. also Pb(110), the fcc (110) surfaces are expected to disorder and/or to form steps around 0.5 to 0.6 T_m ($T_m = 600.7$ K in case of Pb) [19]. Our results, i.e., the blocking in the $[1\bar{1}1]$, $[1\bar{1}4]$ and $[001]$ directions (fig. 3), indicate that the step formation along $[1\bar{1}0]$ and $[1\bar{1}2]$ occurs between 270 and 400 K. The I versus ψ results (fig. 4) on the other hand show quite clearly that the “quality” of the $[1\bar{1}0]$ chains is rather poor, i.e., the chain lengths are short and vacancies in the chains are numerous. Again these data may be compared to results from Au(110) [14], Pt(110) [13], Ir(110) [9], or Cu[110] [21] which show good chain structures at room temperature. The point defect formation at temperatures well below $0.5T_m$ has not been predicted theoretically (to our knowledge). In point of view of the surface annealing behaviour of metal surfaces, e.g., after moderate ion bombardment, which require activation energies of 0.2 to 1.5 eV and occurs at about $0.3T_m$, [22,23] the results reported here for Pb(110) are in a reasonable range.

The anomalous thermal expansion of the $[1\bar{1}0]$ surface chains has not been reported previously. It may be related to the anisotropic behaviour found in LEED, XPD and MEIS studies [24–26]. The anisotropy of disorder is observed at lower temperatures along $[1\bar{1}0]$ compared to $[001]$ as predicted by theory [27,28]. Our results show an anisotropy in the step formation behaviour (fig 3). An anomalous thermal expansion of the order of 5 to 15% was found previously for the distance between the first and second layer between 29 and 485 K [29,30]. The reduced lattice distance for the vacancy may be related to the expanded

lattice constant, i.e., with increasing temperature not only the edge atoms but also larger sections of the chains may relax towards the vacancy

Acknowledgements

We thank J.W.M. Frenken for helpful discussions. Financial support by the DFG is gratefully acknowledged.

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