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The surface phase transition and low-temperature phase of α-Ga(010) studied by SPA-LEED

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ABSTRACT

The order–disorder phase transition on the α-Ga(010) $(2\sqrt{2}\times\sqrt{2})R45^\circ$ structure was studied by spot-profile analysis low energy electron diffraction (SPA-LEED). A low temperature diffraction pattern reveals a small splitting of the overlayer spots which corresponds to a real-space distance of 81 Å, equivalent to 18 unit cells. The splitting is interpreted as caused by a regular ordering of anti-phase domains of the low-temperature phase. Due to the low symmetry of the surface, the domain boundaries are aligned only in one direction, giving rise to a regular, one-dimensional grid. The temperature dependence of the intensity and width of the reconstruction-induced diffraction spots is also investigated. It suggests that the phase transition takes place at a critical temperature $T_c = 232$ K and that anti-phase boundary proliferation plays a role.

1. Introduction

The (010) surface of α gallium has recently attracted some attention because of two phenomena. The first is the fact that the surface appears to be stable even above the bulk melting point of 303 K [1,2]. The second is a phase transition at about $T_c = 231$ K [3,4] which is accompanied by changes in the surface electronic structure and in the Ga 3*d* core level spectra. The transition also has a pronounced effect on the lifetime of the occupied surface states [4].

The bulk structure of α Gallium shown in Fig. 1a is face-centred orthorhombic with eight atoms per unit cell [5]. Each atom has only one nearest neighbour such that the structure can be viewed as being made of Ga_2 dimers or "molecules". The covalent and localized bonding character of the dimers is also reflected in the electronic structure where it leads to rather flat bands in certain directions of *k*-space [6,7]. Fig. 1b shows that the truncated-bulk structure of the α-Ga(010) surface[1] permits two possible truncated-bulk terminations. In the so-called A termination the Ga_2 dimers are left intact, while in the B termination the surface is cutting through the dimers. X-ray diffraction and low energy electron diffraction (LEED) have shown that the surface structure at room temperature corresponds to the B termination [7,8]. The truncated-bulk surface structure is shown in Fig. 1c. Note that there are two symmetry elements: a mirror plane and a glide plane.

The surface phase transition results in a change of the LEED pattern from a (1×1) structure at room temperature to a $(2\sqrt{2}\times\sqrt{2})R45^\circ$ at temperatures lower than 231 K (see Fig. 2). The (1×1) pattern at room temperature is almost a square, consistent with the geometric structure of the truncated bulk. However, due to the presence of the bulk glide-plane symmetry, which is preserved at the surface, every odd-integer spot along the glide-plane direction is missing [9]. The low-temperature (LT) LEED pattern shows the spots which are missing in the high temperature structure together with new fractional order spots centred in the squares of the (1×1) pattern. Such a pattern would correspond to a $(\sqrt{2}\times\sqrt{2})R45^\circ$ structure, as initially described in the first observation of the phase transition [3]. Later, however, additional spots have been found in the low-temperature LEED pattern [8]. These spots are very weak and detectable only in a small electron kinetic energy range. Therefore the LT LEED pattern actually corresponds to a $(2\sqrt{2}\times\sqrt{2})R45^\circ$ structure. The weak additional spots are hardly visible in Fig. 2.

In this paper we present a spot-profile analysis LEED (SPA-LEED) study of the low-temperature structure and of the $(2\sqrt{2}\times\sqrt{2})R45^\circ$ order–disorder phase transition. Compared to conventional LEED optics, SPA-LEED has the advantage of a considerably

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[1] Note that there are different conventions in use for the crystallographic directions in α-Ga. We and Refs. [3,7] follow the crystallographic convention (*Cmca* symmetry) while Refs. [15,2,16,17] follow the historic (pseudotetragonal) convention. In the latter case the *b* and $\bar{c}$ axes are reversed and the structure has the non-standard *Mbab* symmetry. Our (010) surface corresponds to the (001) surface in this case.

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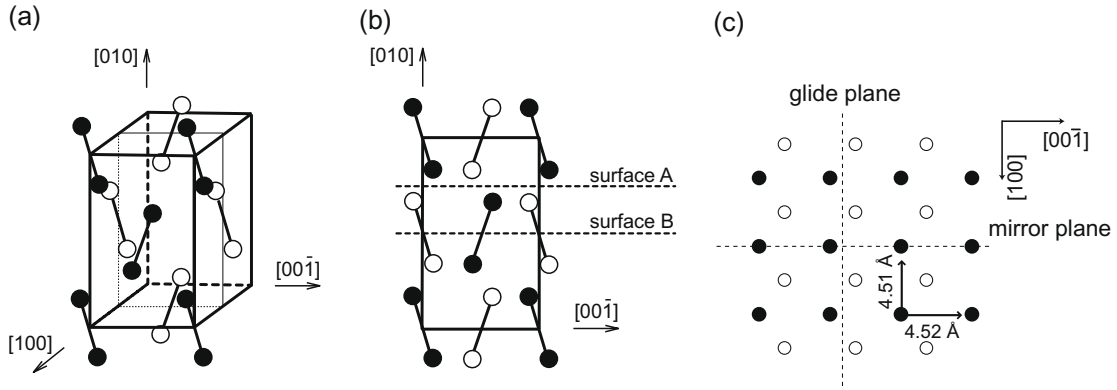

Fig. 1. (a) Bulk structure of α-Ga emphasising the Ga_2 dimers. Dark and light atoms are not in the same plane in the [1 0 0] direction. (b) Side view with an indication of the two possible truncated-bulk surfaces. (a) Top view of α-Ga(0 1 0). Only the first layer is shown.

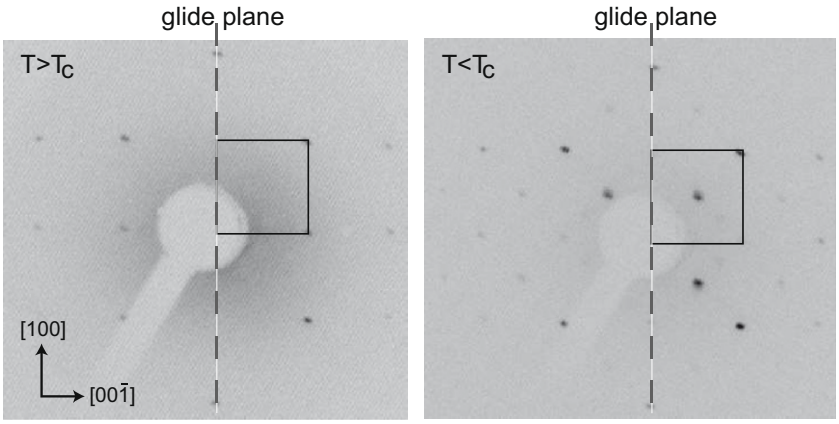

Fig. 2. LEED pattern of α-Ga(0 1 0) above (left) and below (right) the critical temperature T_C of the surface phase transition. The kinetic energy of the electrons is 90 eV. The black rectangle denotes the size of the (1×1) unit cell. The dashed line marks the position of the bulk glide plane.

larger transfer width, resulting in a much higher resolution in *k*-space. This is the crucial point in the present investigation. Indeed our measurements reveal that the low-temperature structure consists of a surprisingly regular array of domains separated by antiphase domain boundaries, whose long periodicity prevents their observation using a conventional LEED optics.

2. Experimental

The α-Ga crystal was mechanically cut from a larger bulk single crystal. The (0 1 0) surface was subsequently polished using diamond paste. The sample, in direct contact with a K-type thermocouple, was inserted into the vacuum system through a load-lock and mounted on a manipulator with cooling (using liquid nitrogen) and heating capabilities (through a filament facing the backside of the sample). The surface was cleaned *in situ* by short cycles of sputtering with 0.5–1.0 keV Ne^+ at 273 K and annealing at the same temperature. At 273 K a sharp (1×1) LEED pattern was observed (see Fig. 2). Surface cleanliness was monitored by X-ray photoelectron spectroscopy. The background pressure was 2×10^{-10} mbar. The SPA-LEED data were taken using an Omicron SPA-LEED with a transfer width of around 2000 Å. The instrument was used to take high-quality reciprocal space maps, i.e. two-dimensional scans, at fixed energies, to measure the spot-profile of specific electron beam reflections. The temperature dependence of the spot lineshape was measured as one-dimensional scans at a constant temperature. The temperature was changed in steps either going up or down through the phase transition. All distances in the SPA-LEED scans are given in units of $Å^{-1}$, as calibrated by using the known surface lattice constant of α-Ga(0 1 0).

3. Results and discussion

Fig. 3 shows a two-dimensional SPA-LEED scan taken at a kinetic energy of 85 eV and a temperature of 155 K. The spots in the image are sharp with a typical spot width of 12–25 $mÅ^{-1}$, corresponding to an average terrace size of several hundred Å. The background intensity is very low and uniform for both phases. The grey scale of the image has been chosen such that many spots are saturated in order to bring out the low-intensity features. The figure shows a small but clear splitting of the (1/2, 1/2) spots in the direction of the glide plane.

Fig. 4 shows a detailed scan across (1,0) and across a (1/2, 1/2) spot, in the direction of the glide plane and perpendicular to it. The splitting of the (1/2, 1/2) spot in the glide-plane direction is 76 ± 1 $mÅ^{-1}$. This corresponds to a real-space distance of 82.6 ± 1.0 Å, consistent with a domain size of 18 times the lattice constant in the direction of the glide plane. This is in the order of a typical transfer width for a standard LEED system and hence the splitting was not observed previously. It has to be noted that we deal with a simple splitting of the spot, no further diffraction maxima in the glide-plane direction are observed. Only the (1/2, 1/2)-type fractional order spots are affected while the (1,0) spot is not influenced. All this points towards a scenario were the