Microstructure and atomic configuration of the (001)-oriented surface of epitaxial Ni–Mn–Ga thin films

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New Journal of Physics 13 (2011) 033021 (14pp)
Received 16 November 2010
Published 11 March 2011
Online at http://www.njp.org/
doi:10.1088/1367-2630/13/3/033021

Abstract. The (001)-oriented surface of epitaxial off-stoichiometric Ni–Mn–Ga ferromagnetic shape memory alloys was studied in both austenitic and martensitic phases. Scanning tunneling microscopy (STM) imaging of the austenitic surface reveals a well-ordered and reconstruction-free surface exhibiting predominantly Mn–Ga termination. We found that only one of the two atomic species (Ga or Mn) is visible in STM, which is attributed to a pronounced geometric corrugation of the surface layer. After a transformation of the sample from the initial austenitic phase to the martensitic phase upon a high-temperature annealing step, a thorough investigation of the martensitic surface was conducted. On a larger scale, pronounced corrugation lines arise from the macroscopically twinned surface. A second corrugation feature is found on a distinctly smaller scale and is shown to originate from the modulated nature of the martensitic film structure. The irregularly spaced corrugation lines support the model of adaptive martensites.
1. Introduction

The ferromagnetic Ni$_2$MnGa and related alloys have recently attracted considerable interest due to the properties that classify these materials within the group of smart materials, especially due to the magnetic shape memory (MSM) effect [1]. In Ni–Mn–Ga, a magnetic field-induced strain of up to 9.5% associated with the MSM effect has been reported [2], making MSM materials promising candidates for a wide range of applications, such as actuators and sensors [3]–[5].

Stoichiometric Ni$_2$MnGa shows a transition from the austenitic phase to the martensitic phase at $T_M = 202$ K [6]. Whereas the austenitic phase has a cubic symmetry and a fairly simple $L_2_1$ structure, the martensitic phase is complicated due to a variety of different crystallographic structures. The structure in the latter phase depends on the precise stoichiometry and the applied stress [7, 8]. Among the most common, and with respect to magnetic field-induced strain preferential structures in Ni–Mn–Ga, are the modulated martensites (5M, 7M, etc). The crystal structure is approximately described by a tetragonal (5M) or orthorhombical (7M) distorted unit cell. A more precise description has to take the modulation, i.e. the displacement of atomic planes, into account. Several approaches for the specific form of the modulated superstructure are being discussed [8]–[14]. Whereas the modulation approach [8] is based on a static harmonic wave displacing atomic planes in a direction perpendicular to the propagation direction, the stacking approach [9, 11] displaces atomic planes with equal amount in a direction perpendicular to the modulation propagation according to a defined stacking sequence. For 5M and 7M, the stacking sequences $(32)$ and $(52)$, respectively, show good experimental applicability due to the implication of a monoclinic unit cell and they are found to be energetically favorable according to theoretical calculations [15]. Since the modulation and stacking approaches are not clearly distinguishable in diffraction experiments [9], and also the atomic positions from both approaches are very similar [9, 11], their microscopic displacement mechanism was justified due to auxiliary physical arguments. The modulation approach is justified due to the freezing of phonon modes in the premartensitic phase when approaching the martensitic transition temperature, which results in a transverse modulation of the austenitic structure [9, 16]. On the other hand, the stacking approach is justified within the theory of adaptive martensites due to the possibility of constructing the stacking based on microtwinning of non-modulated martensite unit cells on the microscopic scale [14, 17].

In the present work, we address the preparation of high-quality surfaces of epitaxial off-stoichiometric Ni–Mn–Ga films grown on MgO(001) and their microscopic and atomic
structures by scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). Several sputter-annealing preparation cycles with appropriate parameters in ultra-high vacuum (UHV) conditions are necessary in order to obtain a well-ordered surface with only a few defects. Whereas the austenitic film surface shows a highly symmetric surface structure, the martensitic film surface exhibits characteristic corrugations on several distinct scales.

2. Experimental details

Epitaxial off-stoichiometric Ni–Mn–Ga film samples were deposited by dc magnetron sputtering on MgO(001) substrates at about 500 °C. At these temperatures, the film grows in the parent austenitic phase with Ni–Mn–Ga(001)[100] || MgO(001)[110] orientation [18, 19] under tensile stress due to a small lattice parameter mismatch of about 1.9% [18].

A sputter chamber with a base pressure of $4.5 \times 10^{-7}$ mbar was used. Films of 150 nm thickness were sputtered from an off-stoichiometric Ni$_{48}$Mn$_{31}$Ga$_{21}$ target with an argon pressure of $3 \times 10^{-3}$ mbar and a sputter rate of 0.26 nm s$^{-1}$. Along with the samples for surface-sensitive experiments, equivalent samples were prepared for general material characterization studies. For the sample series used in this study, energy-dispersive x-ray spectroscopy (EDX) yields the stoichiometry of around Ni$_{49.7}$Mn$_{25.7}$Ga$_{24.6}$. By superconducting quantum interference device (SQUID) magnetometry, a martensite/austenite transition at $T_{M/A} = 263/270$ K was found. Samples are therefore initially in the austenitic state at room temperature. After preparation, samples used for in situ experiments were stored under argon atmosphere and subsequently transferred into a UHV chamber (base pressure $2 \times 10^{-10}$ mbar). Ni–Mn–Ga samples were treated in situ by repeated cycles of Ne$^+$ sputtering (0.5 kV at room temperature for 20–30 min at $5 \times 10^{-6}$ mbar Ne partial pressure) and annealing (30 min at a temperature of 400 °C) in order to produce a well-ordered and contamination-free surface. The preparation cycle consisting of Ne$^+$ sputtering and the subsequent annealing was repeated until the sample surface appeared clean by core level photoemission spectroscopy (XPS) measurements (Mg Kα x-ray source with $h\nu = 1253.6$ eV and an Omicron EA 125 energy analyzer). The clean surface is characterized by unchanged Ni, Mn and Ga core-level intensities and energies after consecutive preparation cycles. One Ne$^+$ sputtering and annealing cycle with the above parameters was repeated after several days in the UHV chamber to remove adsorbed contaminants. Real-space structural investigations were performed with a variable temperature scanning tunneling microscope (Omicron VT AFM/STM) at room temperature with electrochemically etched tungsten tips, which were cleaned in UHV by flash-annealing. The bias voltage of the STM images corresponds to the voltage at the sample. Two STM channels are recorded simultaneously: the z-image (topography) and the i-image (current). Tunneling voltage ($U_T$) and tunneling current ($I_T$) are given separately for every STM image.

3. Experimental results and discussion

3.1. Atomic configuration of Ni–Mn–Ga(001) surfaces in austenitic state

After sputtering and annealing cycles, the surface quality of the Ni–Mn–Ga samples was monitored by LEED at room temperature. Figure 1(a) shows a LEED pattern of the clean Ni–Mn–Ga sample surface in the austenitic state. Sharp spots with a low background are found, confirming good surface quality. The presented LEED image (figure 1(a)) shows a quadratic
pattern with p(1 × 1) symmetry. Ni–Mn–Ga grows epitaxially on MgO in the austenitic phase with 45° rotation between the MgO [110] and Ni–Mn–Ga [100] directions [18, 19]. The orientation of the Ni–Mn–Ga sample corresponding to the LEED pattern in figure 1(a) is depicted in figure 1(b). For indistinguishable atoms with similar atomic radii, we expect the LEED pattern to show the orientation and periodicity of the nearest-neighbor cell (blue dashed square in figure 1(b)). However, this nearest-neighbor cell does not fit to the experimentally obtained LEED images. In order to explain the experimentally observed arrangement of LEED spots, we take into account the surface unit cell (orange dotted square in figure 1(b)), which is rotated by 45° with respect to the main $L_2_1$ directions and is a factor of $\sqrt{2}$ larger than the lattice parameter of the cell for indistinguishable atoms (blue dashed square in figure 1(b)). Since the metallic radii of Ni, Mn and Ga (124, 127 and 135 pm, respectively [20]) do not deviate much, we ascribe our observations to a buckling phenomenon of the surface layer, i.e. the vertical relaxation of one sort of atoms in the surface, as has been suggested earlier for other metallic alloys. Strong buckling is observed in several systems with similar arrangement of two sorts of atoms on the surface, such as the Cu(100)c(2 × 2)Mn surface alloy [21, 22] or the (001)-oriented surface of the half-metallic Heusler alloy NiMnSb [23].

In figures 2(a) and (b), topographic STM images of the austenitic Ni–Mn–Ga(001) surface are depicted. The surface resembles large atomically flat terraces separated by sharp steps. Additionally, screw dislocations are observed on the sample surface. A few are marked by circles in figure 2(a). Over an area of 500 × 500 nm², we count 18 dislocation sites. These dislocations can be attributed to stress in epitaxial Ni–Mn–Ga films on MgO due to the lattice mismatch and due to growth imperfections during film deposition. In figure 2(d), a height profile along the line scan marked in (b) is plotted. The line profile reveals an average step height of 2.9 ± 0.2 Å, which corresponds to a half of the austenite $L_2_1$ unit cell (see figure 2(c)) with $a = 5.82$ Å [8]. Therefore, steps between two terraces occur between adjacent equivalent atomic layers, e.g. between two neighboring Mn–Ga layers or between two neighboring Ni layers. Atomically resolved STM images in figures 3(a)–(c) give a closer insight into the local termination of terraces. In the STM $i$-image in figure 3(a), the arrangement of bright features in a quadratic lattice is shown. A few dark holes indicate defects, such as missing atoms. The imaged surface atoms are aligned along the [110]- and [110]-directions of the Ni–Mn–Ga $L_2_1$
structure with the nearest-neighbor distance between two atoms being 4.2 ± 0.2 Å. This value agrees well with the Mn–Mn or Ga–Ga interatomic distances of 4.1 Å [8] (compare figures 3(a) and (d)). For Ni termination, an atomic distance of about 2.9 Å and atomic alignment along the [100]- and [010]-directions of the austenite $L_2_1$ unit cell would be expected. Therefore, we conclude that Mn–Ga termination is observed with only one atomic species (Mn or Ga) being imaged by STM. In a recent LEED and photoemission study [24], an Mn–Ga termination of the (001)-oriented Ni–Mn–Ga surface has also been proposed, supporting our real space observations. The specific atomic contrast observed in STM images can be attributed either to electronic effects or to pronounced geometric corrugations (buckling). Based on the element-specific density of states calculations in [15], the contribution of Ga to the density of states around the Fermi level is very small. Thereafter, the total density of states around Fermi level is dominated by the Ni and Mn states. This could explain the observed STM contrast on Mn–Ga terminated surfaces, where only one atomic species is visible. However, no considerable change in the STM contrast was observed for a wide range of tunneling parameters, suggesting that the surface layer exhibits a pronounced topographic corrugation due to the outwards relaxation of one atomic species (Mn or Ga). A buckling phenomenon of the Mn–Ga surface termination has been discussed above in relation to the LEED images and could also explain the STM results based on the protruded position of one sort of atoms. This makes the other sort of atoms merely invisible [23].
Figure 3. (a) STM i-image (8.0 × 3.5 nm²; \(U_T = 0.015\) V, \(I_T = 26.1\) nA) showing a Mn–Ga terminated surface of austenitic Ni–Mn–Ga. (b) Atomically resolved STM i-image (4.0 × 1.8 nm²; \(U_T = 0.002\) V, \(I_T = 71.6\) nA) of a Ni-terminated surface of austenitic Ni–Mn–Ga. (c) STM i-image (8.4 × 3.7 nm²; \(U_T = 0.015\) V, \(I_T = 26.8\) nA) of an incomplete Mn–Ga layer. The defects in the Mn–Ga layer offer a view of the underlying Ni layer in the black box. A Mn–Ga terminated area is marked with a gray box. All images are oriented with the substrate MgO [100]-direction parallel to the image border. (d) The orientation of the different (001) atomic planes in Ni–Mn–Ga including the interatomic distances [8] are depicted.

Whereas the arrangement in figure 3(a) is found to be the one most frequently observed on the film surface, in very rare cases a different surface termination was found. In figure 3(b), the STM i-image shows this second quadratic arrangement of bright features. The rectangular lattice connecting the bright features is rotated by 45° compared to the orientation in figure 3(a). The nearest-neighbor distance between two bright features of 3.0 ± 0.3 Å corresponds to the expected interatomic Ni distance of 2.9 Å according to [8]. The orientation of the quadratic lattice now corresponds to the Ni sublattice. The occurrence of Ni terminated areas implicates the existence of steps between terraces with step height of one quarter of the unit cell apart from the dominating half-lattice parameter step heights. Indeed, steps corresponding to one quarter of the \(L_2_1\) unit cell were found occasionally (not shown). Figure 3(c) shows the STM image of an incomplete Mn–Ga layer where two atomic layers can be seen simultaneously. Within the holes in the terminating Mn–Ga layer, the underlaying Ni plane emerges. The two different orientations of the quadratic arrangements of the bright features are visible and support the assignment of the two different atomic arrangements to the Mn–Ga and Ni sublattices.

3.2. Microstructure of Ni–Mn–Ga film surfaces in martensitic state

The martensitic surface of Ni–Mn–Ga films on MgO(001) was also studied by STM and LEED at room temperature. This was possible after an annealing step, where the temperature
was ramped to roughly 750°C within 40 min and quickly decreased to room temperature by switching off the annealing power. A topographic STM overview image after such a high-temperature annealing step is depicted in figure 4(a). Corrugation lines with a height difference of approximately 1 nm between the minimum and the maximum start to form. The corrugation lines run parallel to the MgO ⟨110⟩ directions. A height profile measured across such a corrugation line is depicted in figure 4(c) and resembles a triangular shape. The height profile clearly shows the surface on both sides of the corrugation line to be flat. The periodicity of the corrugation lines is 38 ± 5 nm on average. The formation of surface corrugations in epitaxial Ni–Mn–Ga films was reported previously [25] and is attributed to the introduction of (101) twin planes upon martensite transformation in order to relax the stress in the martensitic phase. In the martensitic state, the lattice parameters change considerably compared to the austenitic state.
forming a distorted unit cell. Due to the epitaxial growth of the film in austenite, an even higher lattice mismatch arises. The corrugation lines, henceforth referred to as twin lamellae, relax the stress to the substrate by folding the film in zigzag form. Figure 4(b) shows a rendered three-dimensional (3D) topographic STM image of two neighboring twin lamellae. In figure 5(a), a schematic drawing of the twin lamellae is shown. It can be clearly seen how the introduction of twin planes leads to a folding of the film, which is recognized as a corrugation of the surface. According to the model for twinning of constrained films reported in [25], the geometry of the twin lamella is characteristic of the lattice parameters of the two unit cell sides involved in twinning and thus characteristic of the martensite crystal structure. By extraction of the $\epsilon$ angle from STM measurements yielding a value of $3.0 \pm 0.1^\circ$, good agreement with the literature value for $c$–$a$-twinning in 7M martensite of $\epsilon_{c-a}^{7M} = 2.85^\circ$ is found (calculation based on lattice parameters in [8]). The mechanism of $a$–$b$- and $b$–$c$-twinning in 7M martensite, as well as twinning in 5M, can be ruled out since the inclination angle for those twinning types is significantly smaller ($\epsilon_{a-b}^{7M} = 1.6^\circ$, $\epsilon_{b-c}^{7M} = 1.2^\circ$, $\epsilon_{a-b}^{5M} = 1.8^\circ$).

The width of the two side planes forming the twin lamellae (figure 4(a), see also figure 7(b)) differs considerably. In large-scale STM images, we always find a larger area of the image occupied by the same twin variant orientation. We believe that this behavior is related to the lattice parameter mismatch between film and the constraining MgO substrate. Whereas the diagonal distance of a MgO cell is $d_{MgO}^{110} = 5.93$ Å [18], the lattice parameters for bulk 7M martensite deviate strongly ($a_{7M} = 6.12$ Å, $b_{7M} = 5.78$ Å, $c_{7M} = 5.54$ Å [8]). Thus, an interfacial stressed austenitic layer has been proposed and measured experimentally [14]. Due to the smooth match of the austenitic lattice parameter $a_{L2_1} = 5.82$ Å and the martensitic lattice parameter $b_{7M} = 5.78$ Å, stresses in this direction are limited to a minimum. The close match of the $b$-side with the austenitic lattice parameters serves as a precondition for stress reduction based on $c$–$a$-twinning. According to the schematic drawing in figure 5(a), the two twin variant orientations of each twin lamella share different lattice parameters with the interfacial austenitic layer. Based on the similar relative deviation of $a_{7M}$ and $c_{7M}$ compared to $a_{L2_1}$, respectively, we expect no preference of one twin variant over the other. However, our experimental observations show a preference for one twin variant, which we attribute to the deviation of martensitic lattice parameters in films compared to bulk Ni–Mn–Ga, as reported elsewhere [14, 25]. Independent of the preference for one twin variant over the other, the introduction of twin planes is necessary for the relaxation of the large macroscopic strains, which would occur within a single variant martensite configuration.

The observed transformation from austenite to martensite induced by high-temperature annealing was further investigated by SQUID magnetometry. Field cooling and field heating magnetization measurements at an applied magnetic field of 10 mT were carried out before and after the UHV treatment on the sample, which is equivalent to the one used for STM (figure 4(d)). It could be shown that due to the high-temperature treatment, the martensite–austenite transition region is broadened and increased by approximately 30 K to a value slightly above room temperature. We argue that the change in the transition temperatures can be attributed to a slight variation in stoichiometry, although a quantitative change in composition is difficult to detect by XPS or EDX within the certainty of the measurement method. However, a decreasing Mn content was found for samples deposited at elevated temperatures [26, 27]. The annealing step to 750 °C is accompanied by the loss of Mn, which leads to a relative increase in Ni content within the compound. The slightly higher Ni content increases the $e/a$ value (electrons per atom) and thus the martensite transition temperature [7].

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Figure 5. (a) Schematic drawing showing the formation of twin lamellae. After the martensite transformation, the distortion of the unit cell leads to a straining of the film. In order to relax the strain with respect to the constraining of the substrate, two differently oriented twin variants form, separated by a twin plane. This leads to a folding of the film and a corrugation of the surface. The blue surface on twin variants with orientation 2 indicates the small period corrugation feature associated with the modulation of martensites. The magenta lines indicate the displacement of basal planes. (b) The \((5\overline{2}2)\) stacking approach for 7M can explain the origin of the modulation corrugation on the surface of twin variants with orientation 2.

which is likewise observed in our experiment. The recovery of defects might also affect the transition temperature in general, although a considerable change in the number of screw dislocations was not observed, taking into account a number of martensitic STM images. Thus we consider the changes in stoichiometry to be the dominating process affecting the transition temperatures.

In figure 6(a), the LEED pattern of the Ni–Mn–Ga sample surface in the martensitic state is depicted. During the transition from austenite to martensite, the initially sharp austenite
Figure 6. LEED patterns of the sample after transformation to martensite. (a) LEED pattern at 23.3 eV revealing the two characteristic martensitic arrays of spots [(0,1) and (1,1)]. The sample was aligned with the Ni–Mn–Ga[010] direction vertically. (b) Magnification of the (0,1)-type array (23.3 eV). (c) Magnification of the (1,1)-type array (23.3 eV). (d) The (0,0)-type array (9.8 eV) and (e) the (2,2)-type array (38.4 eV). (f) Model of the reciprocal space reproducing the characteristic LEED pattern. The reciprocal lattices for \(a–b\) and \(b–c\) surface cells are taken into account with two simultaneously occurring orientations. The corrugations due to twinning are taken into account by tilting the single reciprocal lattices in the appropriate directions. (g) Possible orientations of the distorted martensite lattice.

LEED reflexes fade and spread into an array of less intense spots. Two main array types can be identified: the (0,1)-type array of reflexes and the (1,1)-type array of reflexes. The (0,1)-type array resembles a trapezoid with sharp spots at the corners (figure 6(b)). The (1,1)-type array resembles a dagger-shaped arrangement with sharp and bright spots at the corners and faint lines in the horizontal and vertical directions (figure 6(c)). The initial (0,0) spot is split into four single reflexes constituting a square-shaped arrangement (figure 6(d)). The rather complex LEED pattern in the martensitic state can be understood, taking into account the surface topography and surface structure of martensitic films. After the transformation to martensite, several orientations of distorted unit cells are present. On one slope of a twin lamella, the \(a–b\) plane of one twin variant is present whereas on the other slope the \(b–c\) plane of the other twin variant can be
found, given that \( c-a \) twinning is the mechanism involved (figure 6(g)). Since twin lamellae are aligned along two crystallographic directions parallel to \( \text{MgO}[110] \) or parallel to \( \text{MgO}[1\bar{1}0] \), the two reciprocal space lattices of the \( a-b \) and \( b-c \) surfaces occur in two orientations, which are rotated by 90° to each other. In order to reproduce the observed LEED pattern correctly, the tilt angle of both slopes of the twin lamella of roughly 3° has to be taken into account. This leads to a complex arrangement of spots, which form arrays of reflexes (figure 6(f)), reproducing the (0,0)-, (0,1)- and (1,1)-type arrays observed in the experiment.

The reciprocal space model based on the surface topography derived from STM measurements reproduces well the characteristic arrangement of the LEED spots. The sharp spots in the martensitic reflex arrays indicate a narrow distribution of the twinning angle values over the whole sample. The faint lines between the spots of the arrays suggest a narrow deviation in the tilt angle between the substrate and the surface around an average value. Based on the investigation of clean Ni–Mn–Ga surfaces by LEED, a discrimination between the austenite and the martensitic state can be achieved due to the splitting of the initially austenitic reflexes. Moreover, a characteristic array of LEED spots forms due to the twinning, which includes the lattice geometry in an implicit way. For 5M, 7M and NM martensites, the aspect ratios of the \( a-b \) and \( c-b \) surface cells are different and lead to distinctly different arrangements of spots within one array. This difference allows the discrimination between the different martensitic structures by LEED.

### 3.3. Surface modifications in modulated martensitic Ni–Mn–Ga films

In figure 7(a), the detailed topographic STM image of a twin lamella is depicted, revealing additional small-scale corrugation lines. These corrugation lines appear only on one slope of every twin lamella and run in a direction perpendicular to the twin lamellae. The occurrence of small-scale corrugation lines only on one side of the twin lamella becomes especially clear in the \( i \)-image in figure 7(b) or in the enlargements of the \( z \)-image on an area without (figure 7(c)), and with (figure 7(d)) corrugation lines. The corrugation lines exhibit an average distance of 1.93 ± 0.2 nm but appear to be irregularly spaced (figure 7(e)). The origin of this complicated surface structure is found in the superstructure of modulated martensites [8, 9, 11, 14]. Thereafter, modulated martensites imply a displacement of the (110) basal planes in the \( [1\bar{1}0] \) direction of the orthorhombic face centered cell. The period of this modulation is five basal planes for 5M or seven basal planes for 7M martensite. The form of the displacement, either stacking or modulation by harmonic functions, is under discussion, as outlined earlier in the text.

In figure 5(b), an array of unit cells with modulation according to the \((5\bar{2})\) stacking structure is depicted. The displacement of the (110) basal planes in the \([1\bar{1}0]\) direction of two subsequent \((5\bar{2})\) stackings is depicted by the magenta line and yields a slightly monoclinic 14M superstructure cell (gray in figure 5(b)) with length \( b' \). A minimization of energy has been proposed by calculations due to this specific stacking [15]. The connection between the simple orthorhombic unit cell and the slightly deviating atomic positions in the 14M superstructure cell is demonstrated for specific cuts through twin variants with orientation 1 and 2. For the twin variants with orientation 1 (marked orange in figure 5), the unit cell is aligned with the short \( c \)-axis perpendicular to the surface and thus the displacement of the (110) basal planes occurs in the surface plane. For this reason, no substantial height modulation is measured in figure 7(c). For the twin variants with orientation 2 (marked blue in figure 5), the appropriate
Figure 7. (a) Topographic STM image (106 × 106 nm²; \( U_T = 1.0 \) V, \( I_T = 0.3 \) nA) of a twin lamella revealing a second corrugation feature. (b) Current information of the STM topography in panel (a) showing the small period corrugation stripes more clearly. The magnification of an area without (c) and with (d) small period corrugation stripes (51.4 × 11.1 nm²; \( U_T = 1.0 \) V, \( I_T = 0.3 \) nA) clearly shows that the height modulation only appears on one slope of every twin lamella. (e) Line profiles perpendicular to the modulation stripes suggest irregular spacings.

surface cut through the modulated crystal structure along the (100) plane in figure 5(b) reveals a surface corrugation due to the displacement of the basal planes in a direction with out-of-plane component. The distance between two maximum height positions on the surface is approximately \( \lambda_{7M} \approx \frac{1}{2} b' \sqrt{2} \), where the factor \( \sqrt{2} \) accounts for the tilted propagation with respect to the surface (the specific form of the displacement brings about a monoclinic unit cell, which is neglected in this formula). Based on the known supercell length of \( b' = 29.3265 \) Å [15], a distance between two modulation lines of \( \lambda_{7M} = 20.7 \) Å is expected. This corresponds well with the experimentally measured average value for \( \lambda_{7M} \) of 19.3 ± 2 Å. However, the distance of
the modulation corrugation lines appears to be irregular in experiment. This becomes very clear in figure 7(b). Additionally, the height profiles acquired in a direction perpendicular to the stripes in figure 7(e) reveal that two adjacent stripes exhibit various distances and height amplitudes lacking any visible periodicity. Here we would like to note that this irregular configuration dominates, whereas a perfectly periodic sequence of modulation stripes as expected for the 7M martensite is only found in small areas. However, diffraction measurements carried out on the film surface (LEED, not shown) exhibit the characteristic superstructure peaks indicating a periodic modulation with 7M periodicity. Due to the limitations in resolution, we cannot discriminate modulation by stacking or modulation by harmonic displacement waves according to the height profiles. Our measurements suggest microtwinning according to [14] to be the mechanism of the displacement. The irregularly spaced modulation features indicate a non-periodic arrangement, where the completely periodic model of harmonic displacement waves fails, but which is easily described by the model of microtwins within a non-modulated martensitic phase. The irregularities in the (52) stacking sequence are treated by the model of adaptive martensites as stacking faults in order to meet the periodicity requirements, which are not fulfilled by a simple (52) stacking [17]. Similar indications for stacking faults were observed in bulk Ni–Mn–Ga by high-resolution transmission electron microscopy measurements [12].

4. Conclusion

A detailed investigation of well-ordered austenitic and martensitic Ni–Mn–Ga(001) film surfaces was carried out in order to obtain insights into their microscopic structure. In the austenitic state, we observe a reconstruction-free Ni-Mn-Ga(001) surface with predominantly Mn–Ga termination. Our STM data show that only one atomic species (Ga or Mn) is visible, reflecting a pronounced geometric buckling. Upon high-temperature annealing, a transformation of the Ni–Mn–Ga sample from the initial austenitic phase to the martensitic phase was induced. In the martensitic state, corrugation lines are observed that arise from the macroscopically twinned surface. A second corrugation feature on a distinctly smaller scale was identified as an effect of the modulated crystal structure. Whereas both the harmonic wave approach (modulation) and the adaptive martensite approach (stacking) can describe the direction of modulation with respect to twin variant orientation and the periodicity, a direct discrimination between the two models is not possible due to the resolution limitations. However, the irregularity of the corrugation lines supports the adaptive martensites theory.

Acknowledgments

We thank M Laufenberg, E Pagounis, P Ruther and J Stephan for discussions and the Bundesministerium für Bildung und Forschung (BMBF) for funding via project MSM-Sens (13N10061 and 13N10062).

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