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Surface strain during homoepitaxy: growth and ion ablation of CdTe*

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Oscillations of the surface lattice parameter were observed by RHEED during the homoepitaxial growth of (001) CdTe by molecular beam epitaxy (MBE) and atomic layer epitaxy (ALE). The oscillations are associated to a deformation, induced by the surface reconstruction, at the free edges of the small 2D islands formed during the growth. In the same way, a lateral relaxation is measured during the layer by layer "de-growth" of (001) CdTe. Experiments using a CCD X-ray sensitive camera combined with the very bright X-ray beam offered by the European Synchrotron Radiation Facility allowed us to investigate the two layers behaviour of the CdTe surface in real time during the ablation by ion sputtering. The results show a relaxation mechanism, which is effective only when islands are presented on the surface. A correlation has been found between the size the islands, their distribution, and the surface reconstruction. Particularly, a long-distance correlation between islands along the [1-10] direction has been observed.

Keywords: CdTe, homoepitaxial growth, MBE, ALE, sputtering, surface reconstruction

1. Introduction

An oscillatory behaviour of the lattice parameter, with a period equal to the time needed to deposit one monolayer, has been observed during the molecular beam epitaxy (MBE) heteroepitaxial growth of III–V [1] and II–VI [2] strained layers before reaching the critical thickness. This non tetragonal lattice strain relaxation was explained on the basis of an elastic distortion at the free edges of the 2D islands that develop during the growth of a mono-layer. The strain between the epilayer and the substrate was identified as responsible for the lattice distortion, which is maximum at a half of monolayer coverage. Recently, grazing incidence X-ray diffraction (GIXD) studies [3] performed during the ion sputtering of CdTe(001), and RHEED measurements [4] performed during the homoepitaxial growth by MBE and atomic layer epitaxy (ALE) of the same crystal have shown a surface lattice relaxation mechanism strongly anisotropic along the [110] and [1-10] directions. The origins of this relaxation are attributed to the surface reconstruction properties. Here we present a comparative study of these relaxation mechanisms.

2. Epitaxial growth

The evolution of the lattice parameter, measured with a RHEED device operating at 30 keV, was monitored using a high-sensitivity charge-coupled-device camera. A precise determination of the average

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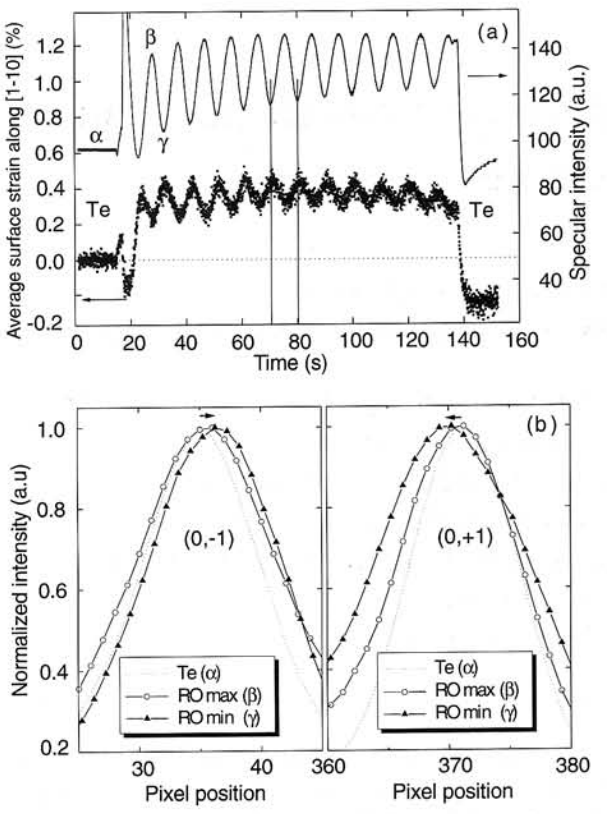

Fig. 1. (a) Oscillations of the RHEED specular spot intensity (solid line) and of the average strain in the [1-10] direction (filled squares) during the homoepitaxial growth of CdTe under Cd excess. (b) Line scans of the (0,-1) and (0,+1) rods during (α) Te interruption (dashes) and at the second maximum (β) and minimum (γ).

in-plane lattice parameter is deduced from the distance between the streaks associated with the (1×1) unit cell by using a dedicated analysis software [1]. In order to enhance the surface contribution, the region of integration along the rods has been chosen to be in anti-Bragg conditions for bulk diffraction.

Figure 1(a) shows the variations of the average surface strain in the [1-10] direction and of the related specular spot intensity. The layer is grown at 240°C in Cd rich conditions (CdTe 0.1 ML/s, Cd 0.1 ML/s). The surface is essentially $c(2 \times 2)$ reconstructed. The oscillations of the RHEED specular beam intensity confirm 2D growth mode. The maxima are attributed to the fully covered surfaces. The lattice parameter oscillates with the same frequency as the specular beam intensity. The amplitude of the oscillations decreases from 0.215% to 0.11% as growth proceeds. It is worth noting that the two phases of the oscillations are opposite. We thus conclude to a tensile relaxation of the surface layer being maximum when the surface is half covered. More quantitatively, the lattice parameter oscillates during growth between +0.45% and +0.25%. This indicates a remaining tensile relaxation even when the layer is almost complete.

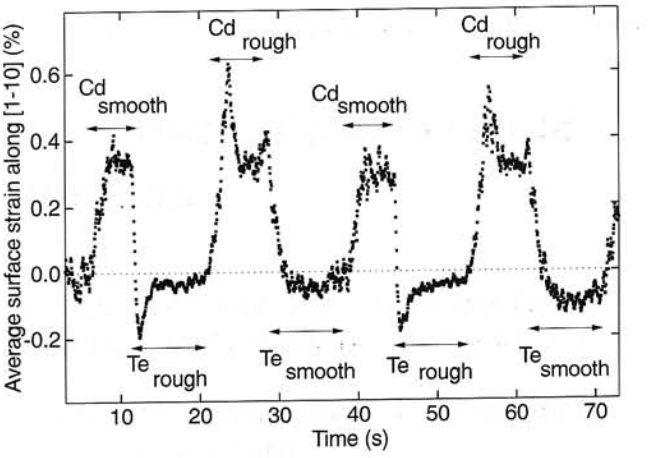

Fig. 2. Variation of the average surface strain in the [1-10] direction during the homoepitaxial growth of CdTe by atomic layer epitaxy.

Figure 2 shows the same surface strain variation in the [1 -10] direction, now for a layer grown at 280°C by ALE. The CdTe flux is 0.15 ML/s, while the excess Cd flux is 0.1 ML/s. The exposure times to Cd and Te fluxes were 5 s and 8 s, respectively, with a dead time of 2 s. In these conditions a self-regulated growth rate of 0.5 ML per ALE cycle (exposure to Cd flux, exposure to Te flux, dead time) is obtained. An increase in the average surface strain between 0.3% and 0.6% is observed during the exposures to Cd fluxes while a decrease below 0% is detected during the Te exposures.

The precise interpretation of the observed variations of the average lattice parameter is not straightforward. Figure 1(b) shows that when switching from the starting smoothed surface [α in Fig. 1(a)] to MBE growth conditions (β and γ) the full widths at half maximum of both (0,-1) and (0,1) rods increase and an inward shift in average of the rods indicating that at least a part of the surface lattice parameter increases. The shift and the broadening are smaller for the rods corresponding to a fully covered layer (β).

When considering the possible relaxation at the free edges of the islands formed during the growth a relatively large change is expected during MBE growth or from one ALE cycle to an other. For MBE growth, at half monolayer coverage, the average lattice parameter will be shifted towards the value it adopts on top of the islands. For ALE growth it appears that two successive exposures to the same flux are not equivalent. Stronger lattice parameter varia-

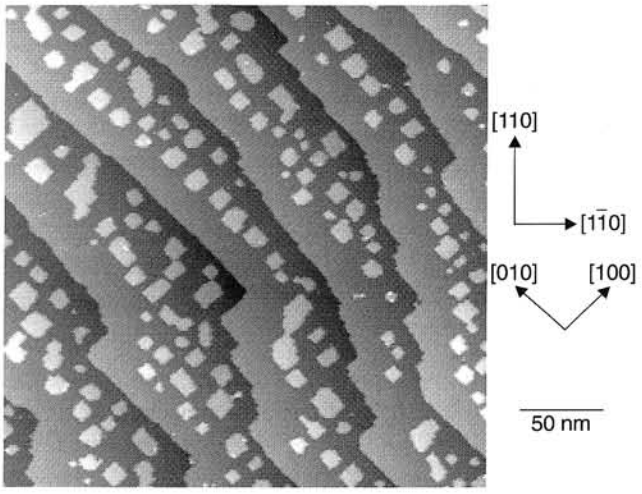

Fig. 3. STM image of a Te terminated (001) CdTe rough surface obtained by ALE.

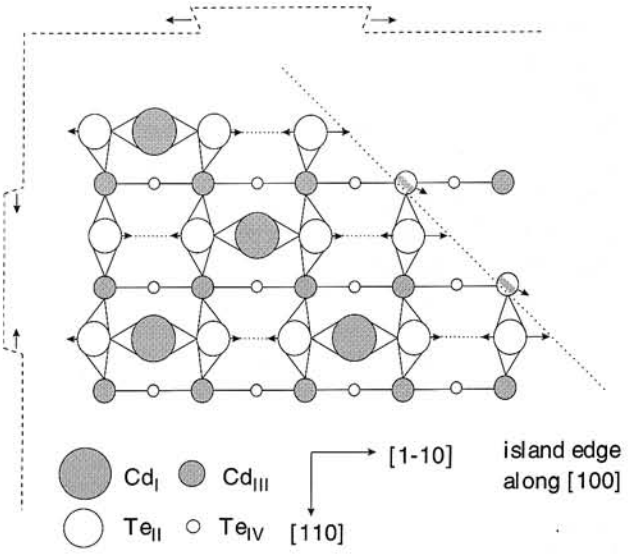

Fig. 4. Top view of the atoms displacements expected from the c(2 × 2) structure.

tions are observed for half of the ALE cycles. These cycles are characterised by a smaller intensity of the specular spot and in the model proposed to explain the self regulated growth rate at 0.5 ML/cycle they correspond to the formation of 2D islands [5]. We therefore conclude that there is a tensile strain for the Cd terminated islands, and a small compressive stress for the Te-terminated ones. The average surface strain measured in ALE upon Cd exposure is very close to the surface strain measured in during the MBE growth under Cd excess, suggesting that the same mechanism is responsible for the tensile relaxation in the [1-10] direction, and is associated to the particular structure of the Cd rich surface.

This surprising relaxation mechanism can be explained as follows. In excess of Cd the growing surface is essentially c(2 × 2) reconstructed. The c(2 × 2) structure was solved on a flat (001)CdTe surface by X-rays [6]. This structure is formed by 0.5 ML of Cd atoms bounded to a full Te layer in such an arrangement that a strong lattice distortion is produced in the CdTe bulk structure down to the 4th atomic layer inwards. In particular, the near surface Te atoms experience a stress in the [1-10] direction. As it can be seen in the STM image in Fig. 3 for a sample grown by ALE, the small islands of CdTe formed during MBE or ALE growth have their free edges running in the [100] directions [7]. Assuming such a shape of islands, the inward relaxation of the Cd atoms would lead to a strong lateral displacement of the Te atoms lying at the free edges of the islands, and finally to an increase in the lattice parameter in the [1-10] direction. This point is illustrated in Fig. 4, which shows the position of atoms in the c(2 × 2) structure as deduced from STM and X-ray Diffraction studies. Thus, the surface lattice relaxation would be a reordening process due to the simultaneous presence of small 2D islands of the surface reconstruction. Following the model, a small compressive strain is expected in the [110] direction. Such a lattice parameter variation was observed during the MBE growth [4].

3. Sputtering of (001)CdTe

Using selected conditions of temperature and ion energy, a layer by layer de-growth during ion sputtering was established for Pt(111) and more recently for Si(001) [8] and InSb(110) [9]. Many surface sensitive techniques have been employed to investigate the fundamental driving forces involved during the ion ablation such as STM, electron diffraction techniques (mainly RHEED), He diffraction as well as numerical simulations. The results show that the sputtering process appears as a negative image of the epitaxial growth mechanism: the mobility of vacancies creates vacancy islands in analogy with adatoms and islands in epitaxial growth.

X-ray diffraction was used to investigate *in situ* the Ar^+ ion sputtering of a (001)CdTe surface. The experiments were performed at the surface diffraction beam line of the European Synchrotron Radiation Facility using a monochromatic beam of 16 keV produced by an ondulator. The sample was grown by MBE. A 2 μm thick CdTe layer was deposited on a (001)$Cd_{0.96}Zn_{0.04}Te$ substrate using standard growth conditions. After a subsequent heating at high temperature (340°C) under successive Cd and Te fluxes, the

sample was introduced into the quick-lock chamber under dry nitrogen atmosphere and transferred to the UHV 6-circle diffractometer. Data were collected in the z axis mode while the sample was kept under grazing incidence (0.12°). Ion sputtering was performed *in situ* using ultra high purity Ar gas and ion gun (500 eV) with an incident angle of about 70°. Reflections are indexed in a 1 × 1 surface unit cell with basic vectors related to the cubic axis as follows

$$a_1^s = 1/2[1\ -10]_c;\ a_2^s = 1/2[110]_c;\ a_3^s = [001]_c$$

The quality of the surface was inferred from the widths along the h and k directions of an integer order reflection close to anti-Bragg conditions (at $l \cong 0$). Initially the surface showed an isotropic Gaussian line shape corresponding to a mean domain size L evaluated as $L = a_s/\Delta h(\Delta k)$ of about 600 Å.

Figure 5 shows the evolution of the intensity of the (0,1,0.15) reflection as a function of ablation time. The variation of the intensity is consistent with a layer by layer erosion characterised by a very pronounced intensity minimum around 0.5 ML. At this coverage the roughness of the surface is maximum since a half of the surface is covered by monolayer islands.

The oscillation period is found to be temperature independent in the 170–230°C range. This two layers behaviour suggests that in this range of temperature ion ablation has the effect of removing atoms only from the edges of the topmost terraces [9]. This occurs when vacancies formed within each terrace diffuse to the step edges rather than forming new clusters and when vacancies at the step edges jump from the second to the first layer. The sputtering rate increase observed at 260°C is related with the extra-desorption induced by the surface self-sublimation.

The most surprising results appears in the diffraction profiles performed along the h [1-10] and k [110] directions. Figures 6 and 7 show the diffraction profiles registered after removal of about 0.5 ML of CdTe at different temperatures. A very different behaviour is observed along the h and k directions. Along the [110] direction, beside the main diffraction peak corresponding to the bulk lattice parameter, a broad peak corresponding to surface islands with a surface lattice parameter smaller than the bulk one is observed. Its width is related with the domain size of the islands. The lattice parameter variations are of 4.5, 4.1, 3.3 and 2.9% for temperature ablation of 180, 210, 230, and 260°C, respectively. The domain sizes are of 45, 70, 100 and 130 Å.

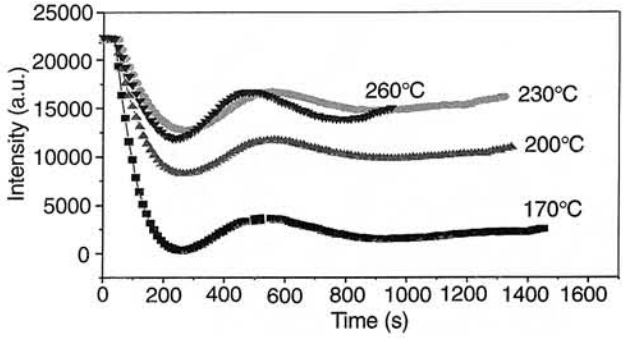

Fig. 5. Intensity evolution of the (0, 1, 0.15) peak during the sputtering of (001) CdTe at different temperatures.

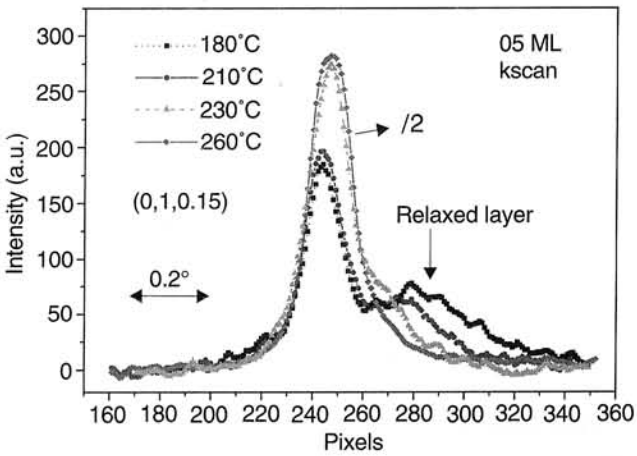

Fig. 6. Peak profile of the (0,1,0.15) reflection along [110] direction for 0.5 ML sputtered at different temperatures.

Along the [1-10] direction a completely different behaviour is observed: two symmetric satellite peaks can be seen on each side of the main peak. These satellites are characteristic for a regular distribution of islands along this direction. From their position, an

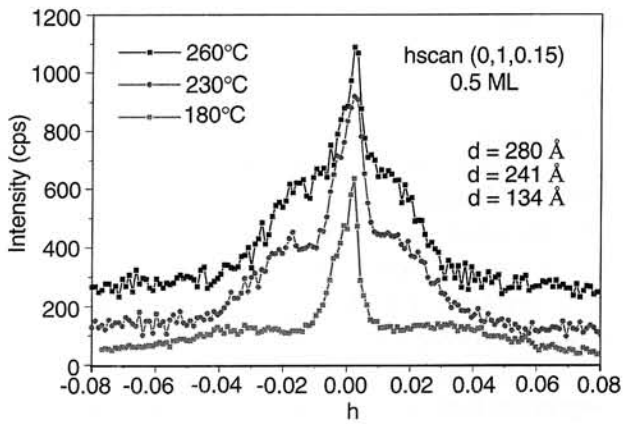

Fig. 7. Peak profile of the (0, 1, 0.15) reflection along the [1-10] direction for 0.5 ML sputterd at different temperatures.

average island distance from 130 Å at 180°C to 280 Å at 260°C is determined.

To understand these findings and in particular the broad peak in the k scans, it is necessary to take into account the surface energy minimisation during the sputtering and to consider the microscopic structure of the (001) CdTe surface. One interesting result is the surface reconstruction change during sputtering. Figure 8 shows evolution of the surface reconstruction with sputtering time at 200°C. The surface reconstruction is initially c(2 × 2) corresponding to the Cd-stabilised surface mentioned above. It changes quickly to a (2 × 1) one after the sputtering starts. This reconstruction is associated with the surface lattice relaxation observed along the [110] direction. The arrows indicate the end of the sputtering after removal of about 1 ML of CdTe. Stopping the ion ablation leads first to an enhancement of the (2 × 1) order peak but after few minutes (not shown here) the c(2 × 2) surface is eventually recovered. As no desorption of Te or Cd is expected at 200°C, we conclude that the (2 × 1) surface observed during the ablation presents the same stoichiometry as the c(2 × 2) surface.

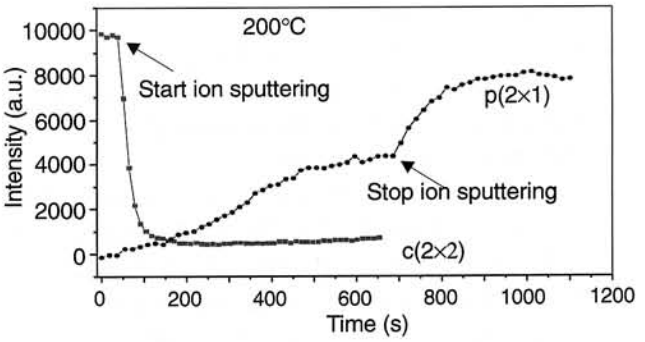

Fig. 8. Evolution of the c(2 × 2) and (2 × 1) structures as a function of the sputtering time.

As mentioned above, the c(2 × 2) structure is formed by 0.5 ML of Cd atoms bounded to a full Te layer in such an arrangement that a strong lattice distortion is produced in the CdTe bulk structure down to the 4th atomic layer inwards. The (2 × 1) surface observed during ion ablation is supposed to present the same atomic pattern as the c(2 × 2). However the strain can no longer be transferred deeply towards the bulk: the (2 × 1) symmetry does not allow the bond rotation around the Cd atoms in the third layer which is in the c(2 × 2) structure which is essential for propagation of the strain. An alternate possibility to release the strain along the [110] direction is to allow a surface lattice contraction. The deformation produced in the tetrahedron by the inward relaxation of the surface Cd atoms can be compensated by the lateral contraction of the lattice in the [110] direction. However, the domains along the [110] direction cannot be much extended. Thus, the (2 × 1) structure requires the surface coverage to be lower than one in order to enable the formation of regular atomic faults which are responsible for the lattice relaxation. Sputtering reduces the surface coverage and consequently promote the one-dimensional relaxation. The surface lattice parameter along [110] can then be relaxed, thus allowing the surface energy to be reduced by a phase transition from the c(2 × 2) to a (2 × 1) structure. Such a transition was observed by STM [10] on a smooth (001)CdTe surface. The transformation between the two different unit cells, probably due to the creation of Cd vacancies by the tip of the STM, was assumed to be mediated by the collective shift of a complete row of Cd atoms. The fact that the c(2 × 2) surface is eventually retrieved a few minutes after sputtering is stopped is probably due to the minimisation of the electrostatic energy in this strongly ionic material and might be also correlated to the coalescence of the 2D islands. To summarise the sputtering process: the first few atoms removed in the beginning produce Cd rows shift in the [110] direction and the surface can re-order to a (2 × 1) structure. The relaxed surface layer gives the broad peak, which is visible in the k scans. For example, after removal of half a monolayer, the system is constituted of a regular distribution of 2D islands of 100 × 240 Å 2 at 230°C.

4. Conclusions

Surface strain has been observed during growth and ablation of homoepitaxial CdTe. The lattice pa-

Table. 1. The lattice parameter variations tendencies during growth and ablation of homoepitaxial CdTe.

	MBE growth	ALE growth	ALE growth	Sputtering
Dominant reconstruction	c(2 × 2) Cd terminated	c(2 × 2) Cd terminated	(2 × 1) Te rich	(2 × 1) Cd terminated
1 -1 0	Large expansion	Large expansion	Small contraction	Ordained islands
1 1 0	Small contraction	Small contraction	Small expansion	Large contraction

rameter variations tendencies measured during MBE and ALE growth and during sputtering are summarised in Table 1.

Oscillations of the lattice parameter have been observed during the homoepitaxial growth, either by MBE or by ALE of (001)CdTe. The variations of the average lattice parameter are attributed to a relaxation at the free edges of small, one monolayer thick islands formed during the growth. An anisotropic relaxation of the islands is observed when the growth occurs under Cd-rich conditions. A mechanism of the relaxation based on the surface reconstruction stabilised during the epitaxy is proposed.

In the same way, an anisotropic relaxation of the surface lattice parameter and a long-distance correlation between islands along the [1-10] direction were observed during sputtering of (001) CdTe. In the [110] direction, a correlation has been found between the relaxation and the size of the islands, and the surface reconstruction.

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