

Surface stoichiometry determination using reflection high-energy electron diffraction and atomic-layer epitaxy: The case of ZnTe(100)

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Using reflection high-energy electron diffraction analysis of the relaxation process in highly strained heterostructures grown by atomic-layer epitaxy, a method is proposed to provide a quantitative determination of the surface stoichiometry. Applying this method to the case of the ZnTe(100) surface, we have found that a $c(2 \times 2)$ Te-rich reconstruction observed below 240°C involves 1.5 ML of Te atoms. Consistent with this result, we also propose a microscopic model for the growth of ZnTe in atomic-layer epitaxy, and we demonstrate the relationship between growth rate and surface reconstruction.

II-VI semiconductors are promising materials in view of optoelectronic applications in the field of light-emitting devices and infrared detectors.^{1,2} High-quality samples required for practical applications are typically grown by molecular-beam epitaxy (MBE) and atomic-layer epitaxy (ALE). Whatever the technique, understanding the growth mechanisms is crucial for achieving well controlled materials and for producing high-quality heterostructures with abrupt interfaces. Atomic-layer epitaxy is very attractive from the latter point of view as it allows precise control of the growth of very thin layers. It is also a very useful technique for attaining a comprehensive view of the growth mechanisms, due to the decomposition of the growth process into discrete steps resulting from the successive deposition of the II and VI elements. As a matter of fact, knowledge of the surface structure is very important for monitoring the growth rate in ALE. Concerning, for instance, the role of the surface stoichiometry, recent work on CdTe has shown that the growth and sublimation processes are closely related to the surface structure.³ In the present work, atomic-layer epitaxy is combined with reflection high-energy electron diffraction (RHEED) to determine both the stoichiometry of the surface and the growth mechanism for the particular case of ZnTe(100).

We have studied in detail the phase diagram of the ZnTe(100) surface under exposure to Zn and Te fluxes. The samples were prepared in a conventional MBE system equipped with CdTe, Cd, Te, and Zn effusion cells. The flux calibration of the effusion cells was achieved *in situ* by Rutherford backscattering spectrometry.⁴ The substrates were $\text{Cd}_{1-x}\text{Zn}_x\text{Te}(100)$ commercial wafers, with $x=0.04$. They were fixed with gallium on a molybdenum sample holder. The temperature was measured with a thermocouple maintained in contact with

the sample holder by means of a spring. Prior to the deposition of ZnTe, a CdTe buffer, about 200 nm thick, was grown in order to improve the surface structure. Then a ZnTe layer about 1 μm thick was grown with a substrate temperature in the 320–360°C range. Under Zn flux, the ZnTe surface is $c(2 \times 2)$ reconstructed [a $c(2 \times 2)\text{Zn}$ surface]. This reconstruction is observed in the whole range of explored temperature, from 180°C up to 450°C. As deduced from RHEED intensity measurements of either the specular beam or of the half-order reconstruction, this surface is stable under vacuum up to 380°C. Above 380°C, which corresponds to the beginning of ZnTe sublimation,⁵ the $c(2 \times 2)\text{Zn}$ surface evolves to a (2×1) surface under vacuum. Under Te flux a $c(2 \times 2)$ surface [called the $c(2 \times 2)\text{Te}$ surface in the following] has been observed in a temperature range between 225 and 250°C, while the surface is $(2 \times 1)\text{Te}$ reconstructed above 270°C. Such a $c(2 \times 2)\text{Te}$ surface was first mentioned by Rajavel *et al.*⁶ Between 250 and 270°C a transitory regime is observed, with a weakening of the $c(2 \times 2)\text{Te}$ reconstruction. The $c(2 \times 2)\text{Te}$ surface evolves to a (2×1) surface under vacuum. As indicated by the stability of the RHEED intensity, the $(2 \times 1)\text{Te}$ surface is stable under vacuum up to 380°C. Above this temperature the surface is still (2×1) reconstructed, but the RHEED intensity level changes due to the beginning of the sublimation process.

In relation to the influence of surface reconstructions on the growth mechanism of ZnTe(100), it is worth mentioning the results of atomic-layer epitaxy, which has been used recently⁷ to grow CdTe/ZnTe heterostructures in a substrate temperature range of 270–290°C. In this temperature range, the growth rate regulates itself to exactly 0.5 ML per reaction cycle (a reaction cycle being the successive exposure to a Zn and a Te flux), which is

consistent with the observed formation of a fully Te saturated (2×1) surface (Te dimers) during the exposure to the Te flux and with the formation of a half-monolayer Zn saturated $c(2 \times 2)$ surface during the exposure to the Zn flux.^{8,9} At lower substrate temperature the growth rate increases to approximately 0.8 monolayers per cycle, but does not reach 1 ML per cycle. As the Zn stabilized surface does not change, a growth rate higher than 0.5 ML per cycle suggests the existence of surfaces that should be Te saturated with more than 1 ML.

In relation with that puzzling feature, a further clue was the recent theoretical prediction by means of first-principles pseudopotential calculations of a new Se-rich phase of ZnSe(100).¹⁰ This phase is expected to exist for a coverage of 1.5 ML of Se and should be $c(2 \times 2)$ rather than (2×1) reconstructed. However, such a Se-rich surface, which might be present at low temperature, has not been observed yet. We demonstrate in the present work that the stoichiometry of the $c(2 \times 2)$ Te surface observed for ZnTe(100) is identical to that theoretically proposed for ZnSe(100).

Two sets of experiments were carried out for this purpose. First, by measuring the RHEED intensity of the specular beam, we determined the time necessary to obtain a $c(2 \times 2)$ Zn stabilized surface when exposing the sample to a Zn flux, depending on whether the initial surface is the $c(2 \times 2)$ Te surface or the (2×1) Te surface. Second, we measured the number of ALE cycles necessary to reach the critical thickness of ZnTe epitaxially grown on CdTe(100) depending on whether the cycles corresponded to a succession of $c(2 \times 2)$ Te- $c(2 \times 2)$ Zn surfaces or to a succession of (2×1) Te- $c(2 \times 2)$ Zn surfaces. The Zn and Te fluxes used in the present work were about 1.5×10^{14} atoms $\text{cm}^{-2} \text{s}^{-1}$.

In the first set of experiments the surface is exposed to a Te flux. It is $c(2 \times 2)$ Te or (2×1) Te reconstructed depending on the substrate temperature as described previously. In Fig. 1(a), the time necessary to stabilize the RHEED intensity after shuttering of the Te flux and exposure of the surface to a Zn flux is plotted as a function

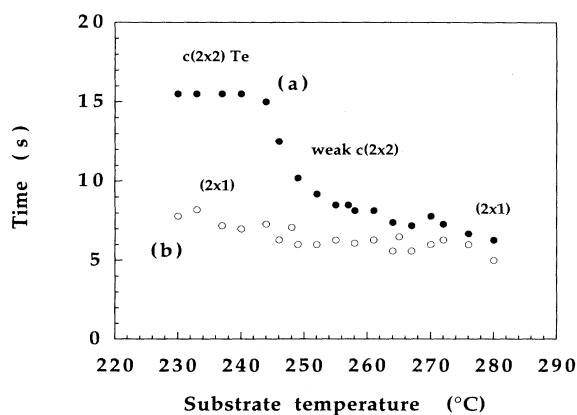


FIG. 1. Adsorption time of Zn on a Te-saturated surface as a function of temperature: (a) without significant dead time between Te shuttering and Zn opening and (b) with a dead time long enough to obtain a stabilized (2×1) surface before Zn opening.

of the temperature. The dead time (between closing the Te cell and opening the Zn cell) is about 0.5 s. It seems reasonable to assume that the sticking coefficient of Zn atoms impinging on the surface before saturation is constant in the 220–280°C temperature range [consistent with a desorption temperature threshold of 380°C for Zn (Ref. 11)]. Provided this assumption is correct, the stabilization time of the RHEED signal when exposing the surface to a Zn flux is directly related to the surface coverage.

Between 225 and 245°C, the time to stabilize the Zn surface does not depend on the temperature (about 15 s). It corresponds to the time necessary to form the $c(2 \times 2)$ Zn surface under Zn flux on a $c(2 \times 2)$ Te surface. Above 245°C the stabilization time decreases and eventually stabilizes at about 7 s above 260°C. Above 260°C the surface stabilized under Te flux is (2×1) Te reconstructed. Then, the stabilization time is the time necessary for evolving from the (2×1) Te surface to the $c(2 \times 2)$ Zn surface. Figure 1(b) is obtained when using a dead time between the Te shuttering and the Zn opening long enough to obtain the transformation of the $c(2 \times 2)$ Te into the (2×1) surface under vacuum. Then the starting surface is (2×1) reconstructed before exposure to the Zn flux whatever the temperature. In this case, only a very small variation of the time necessary to stabilize the $c(2 \times 2)$ Zn reconstruction is observed, namely, 7.5 s at low temperature to 6 s in the high-temperature range. This unambiguously indicates that the (2×1) reconstruction obtained by transformation of the $c(2 \times 2)$ Te surface in the range 225–245°C exhibits the same Te coverage rate as the (2×1) Te surface obtained under Te flux at higher temperature, the adsorbed quantity of Zn being the same in both cases.

Moreover, the key feature clearly shown in Fig. 1 is the 2:1 ratio of the times necessary for the stabilization of the $c(2 \times 2)$ Zn surface, depending on the initial Te-reconstructed surface, that is $c(2 \times 2)$ or (2×1) . X-ray photoelectron spectroscopy (XPS) measurements have furthermore shown that the (2×1) Te surface is fully Te terminated and that the $c(2 \times 2)$ Zn surface consists of undimerized Zn atoms with a coverage of 50%.^{8,9} Note that, in agreement with first-principles calculations,^{10,12} XPS measurements have similarly shown that the (2×1) Se surface of ZnSe (100) consists of fully dimerized Se atoms and the $c(2 \times 2)$ Zn surface of undimerized Zn atoms.¹³

The above statement concerning ZnTe leads us to propose the model shown in Fig. 2(a) for the (2×1) Te surface and allows us to conclude that half a monolayer of Zn atoms is adsorbed on the Te atoms to build the $c(2 \times 2)$ Zn reconstruction from the (2×1) Te reconstruction. Then, the ratio 2:1 suggests that one monolayer of Zn is adsorbed when the initial surface is $c(2 \times 2)$ Te. As a matter of fact, exposing the $c(2 \times 2)$ Te to the Zn flux results also in a $c(2 \times 2)$ Zn reconstructed surface with half a monolayer of Zn atoms on top. This suggests furthermore that the extra Zn atoms (half a monolayer) are incorporated in a complete ZnTe half monolayer grown on the initial surface and located below the Zn terminating atoms. Then, the deposition of 1 ML of Zn atoms is

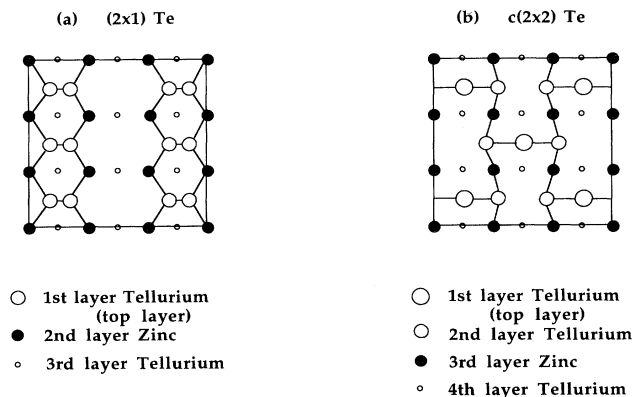


FIG. 2. Top views of Te-saturated reconstructed surfaces: (a) (2×1) reconstruction, (b) $c(2 \times 2)$ Te reconstruction.

only explained with 1.5 ML of Te in the external layers of the $c(2 \times 2)$ Te surface (1 ML under the external Zn atoms and 0.5 ML incorporated in the ZnTe half monolayer). As shown in Fig. 2(b), the model assumed for the $c(2 \times 2)$ Te surface implies the existence of Te trimers on top of the surface, in agreement with the electron counting rule¹⁴ and with the theoretical predictions for ZnSe.¹⁰

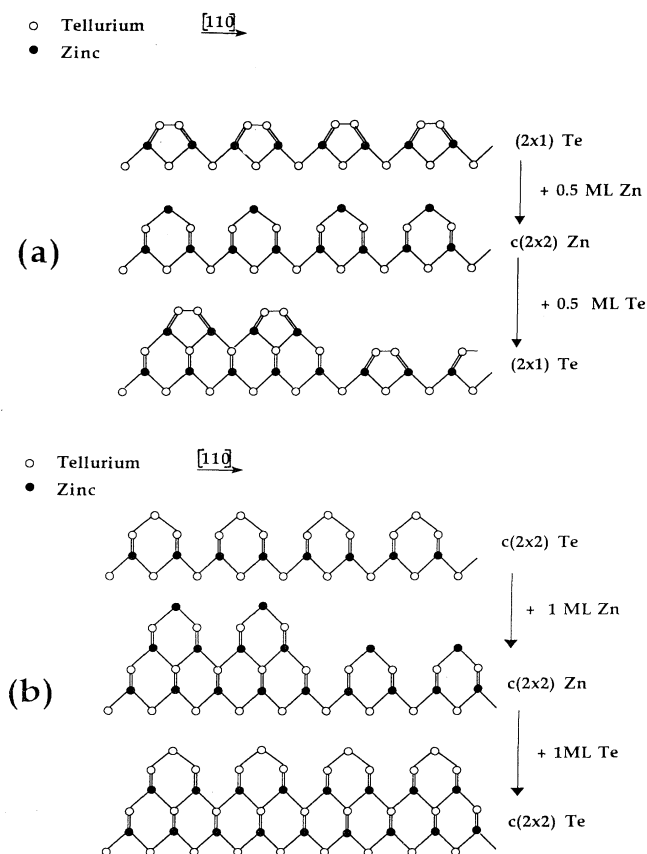


FIG. 3. Models of ALE ZnTe growth. (a) (2×1) Te- $c(2 \times 2)$ Zn- (2×1) Te cycle. The growth rate is 0.5 ML/cycle. (b) $c(2 \times 2)$ Te- $c(2 \times 2)$ Zn- $c(2 \times 2)$ Te cycle. The growth rate is 1 ML/cycle.

Based on the surface reconstruction models proposed above, we suggest the mechanisms illustrated in Fig. 3 for the Zn deposition and, as a consequence, for the ALE growth process of ZnTe(100). Figure 3(a) shows a possible mechanism when the Te surface is (2×1) Te reconstructed. Figure 3(b) shows a possible mechanism when the Te surface is $c(2 \times 2)$ Te reconstructed. In the first case, a growth rate of 0.5 ML of ZnTe per cycle is expected while a growth rate of 1 ML per cycle is expected in the second case.

Another experimental procedure has been explored to confirm the previous growth mechanisms, and incidentally the surface models. This procedure consists of determining the number of ALE cycles necessary to obtain the relaxation of ZnTe grown on CdTe(100). Indeed, due to the high tensile stress (6%), the critical thickness of ZnTe which can be deposited on CdTe(100) before the formation of misfit dislocations is only 4 ML as precisely determined by RHEED analysis during MBE growth, and is correlated with a strong decrease of the RHEED intensity.¹⁵

Based on these observations, we determined the number of ALE cycles occurring before relaxation of the ZnTe layer, depending on which surface is saturated during the Te exposures, i.e., $c(2 \times 2)$ Te or (2×1) Te. Therefore, the specular beam intensity on the RHEED pattern was measured during the deposition, taking advantage of the fact that the critical thickness corresponds to a dramatic decrease of the signal. Figure 4 shows the variations of the RHEED intensity level of the specular beam after saturation for the successive Zn exposures. Clearly, only four Zn exposure cycles are achieved before observing a strong decrease of the intensity, corresponding to the beginning of the relaxation, in the case of $c(2 \times 2)$ Te- $c(2 \times 2)$ Zn- $c(2 \times 2)$ Te sequences. If we recall that the

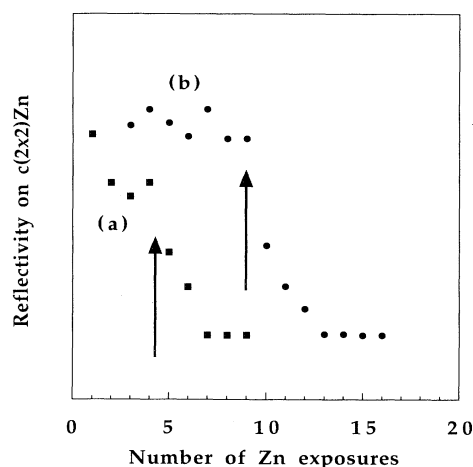


FIG. 4. Reflectivity of the Zn-saturated surface as a function of the number of ALE cycles. (a) The initial Te-saturated surface is $c(2 \times 2)$ Te reconstructed. The deposition temperature is 225 °C. (b) The initial Te-saturated surface is (2×1) Te reconstructed. The deposition temperature is 270 °C. The arrows indicate the occurrence of a surface roughening correlated with the first stage of the relaxation.

critical thickness is 4 ML, this is consistent with a growth rate of 1 ML/cycle. By contrast, eight cycles are achieved in the case of (2×1) - $c(2 \times 2)$ Zn- (2×1) sequences, consistent with a growth rate of 0.5 ML/cycle.^{5,10} These results are in very good agreement with the growth mechanisms reported above in Figs. 3(b) and 3(a) respectively, enforcing the assumption of a $c(2 \times 2)$ Te-terminated surface with 1.5 ML of tellurium on top.

In conclusion, a RHEED analysis of the homoepitaxial growth of the relaxation process in highly strained heterostructure grown by atomic-layer epitaxy has been used as a method to provide an easy quantitative approach to

the surfaces stoichiometry. The results are consistent with the growth rates experimentally measured in atomic-layer epitaxy.

More generally, this method could also be used to study the surface structure and the growth process of other semiconductors. As a further consequence of these results, it appears possible to grow ZnTe by atomic-layer epitaxy at low temperature (225–250°C) with a growth rate of 1 ML/cycle when forming a $c(2 \times 2)$ surface under Te flux. It is worth noting that this growth temperature range is compatible with the growth and doping of CdTe and ZnSe.

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