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To cite this version:

A. Wierts, J. Ulloa, C. Celebi, P. Koenraad, H. Boukari, et al.. Cross-sectional scanning tunneling microscopy study on II–VI multilayer structures. Applied Physics Letters, 2007, 91 (16), pp.161907. 10.1063/1.2799254 . hal-02547623

HAL Id: hal-02547623

https://hal.science/hal-02547623v1

Submitted on 11 May 2022

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Citation for published version (APA):
Wierts, A., Ulloa Herrero, J. M., Celebi, C., Koenraad, P. M., Boukari, H., Maingault, L., Andre, R., & Mariette, H. (2007). Cross-sectional scanning tunneling microscopy study on II-VI multilayer structures. *Applied Physics Letters*, *91*(16), 161907-1/3. [161907]. https://doi.org/10.1063/1.2799254

DOI:
10.1063/1.2799254

Document status and date:
Published: 01/01/2007

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Cross-sectional scanning tunneling microscopy study on II–VI multilayer structures

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(Received 15 August 2007; accepted 25 September 2007; published online 17 October 2007)

Cross-sectional scanning tunneling microscopy is used to study in the atomic scale the structural properties of ZnSeTe/ZnTe multiple quantum wells and N:ZnTe delta-doped structures. Some peculiar effects are found on the cleaved (110) ZnTe surface plane, which have not been observed in III–V semiconductors. In particular, cleavage induced monatomic wide vacancy chains are always present on the Te sublattice. Furthermore, the semiconductor surface is manipulated when certain positive voltages are applied to the sample. Regarding the heterostructures, the ZnSeTe/ZnTe quantum wells are found to have abrupt interfaces and the Se concentration is determined to be significantly larger than the nominal value. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2799254]

Over the past decades, an increasing amount of research has been performed on II–VI semiconductors. These materials are very interesting for specific optical applications due to their relatively large band gap energy in comparison with the most commonly used III–V semiconductors. For example, the blue/green wavelength region is relatively simple to access with II–VI materials.[1–3] Another interesting property of II–VI compounds is that magnetization can be introduced [by doping with manganese (Mn) for instance] without creating extra charge carriers. With respect to future information technologies, recently, it has been shown that single magnetic atoms can be inserted into self-assembled II–VI quantum dots (QDs).[4,5] This allows the accurate study of the interaction between the injected carriers and the single magnetic atom.[6]

The structural characterization of II–VI semiconductor nanostructures has been mainly performed by transmission electron microscopy. Cross-sectional scanning tunneling microscopy (X-STM) is a unique technique to provide true atomic scale characterization. It has been widely used for nanostructured III–V materials.[7–9] However, in the case of II–VI semiconductors, X-STM has almost never been applied. Limited studies have been done of which the observation of ZnSe/BeTe multiple quantum wells[10,11] (QWs) and a study of wurtzite II–VI compounds[12] are the most important ones. In this article, we present a X-STM analysis of ZnTe based semiconductor heterostructures. Peculiar effects, which hamper scanning of the semiconductor surface and which are not observed in III–V materials, are discussed first. Subsequently, the observation of ZnSeTe/ZnTe quantum wells and nitrogen delta-doped ZnTe (N:ZnTe) structures are discussed.

The samples were grown by molecular beam epitaxy (MBE) on a *p*-type phosphorous doped (100) ZnTe substrate at a temperature of 280 °C. The multiple QW (MQW) structure consists of ten nominally 5 nm thick ZnSeTe QWs with 20 nm thick ZnTe barriers (spacers). The nominal Se content was 5% and the MQW structure was capped with a 100 nm thick intrinsic ZnTe layer. For the N:ZnTe delta-doped structure, the N atoms are introduced by a glow plasma source with a doping concentration of approximately 10^{18} cm^{-3}. The X-STM measurements were performed at room temperature on the (110) surface plane of the *in situ* cleaved sample under ultrahigh vacuum ($p < 4 \times 10^{-11}$ Torr) conditions. Polycrystalline tungsten tips prepared by electrochemical etching were used. The images were obtained in constant current mode during which both topography and current images were recorded simultaneously.

In scanning the ZnTe semiconductor material, difficulties have come across which were reproducibly observed in all studied samples. One peculiar aspect is the presence of rows of missing atoms on the (110) cleaved surface. A row of missing atoms consists of a monatomic wide chain of vacancies on the Te sublattice. Four of these rows can be observed in the X-STM image in Fig. 1. In this case, the X-STM image was acquired at a bias voltage of −3.5 V, which means that the frame depicts the filled states Te (group VI

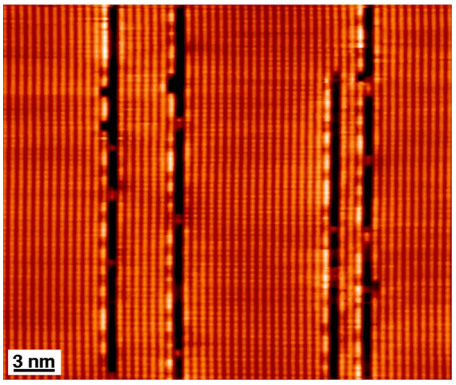

FIG. 1. (Color online) Filled states topography image of the ZnTe substrate (V_{sample}=−3.5 V) showing four monatomic wide vacancy chains on the (110) cleaved surface.

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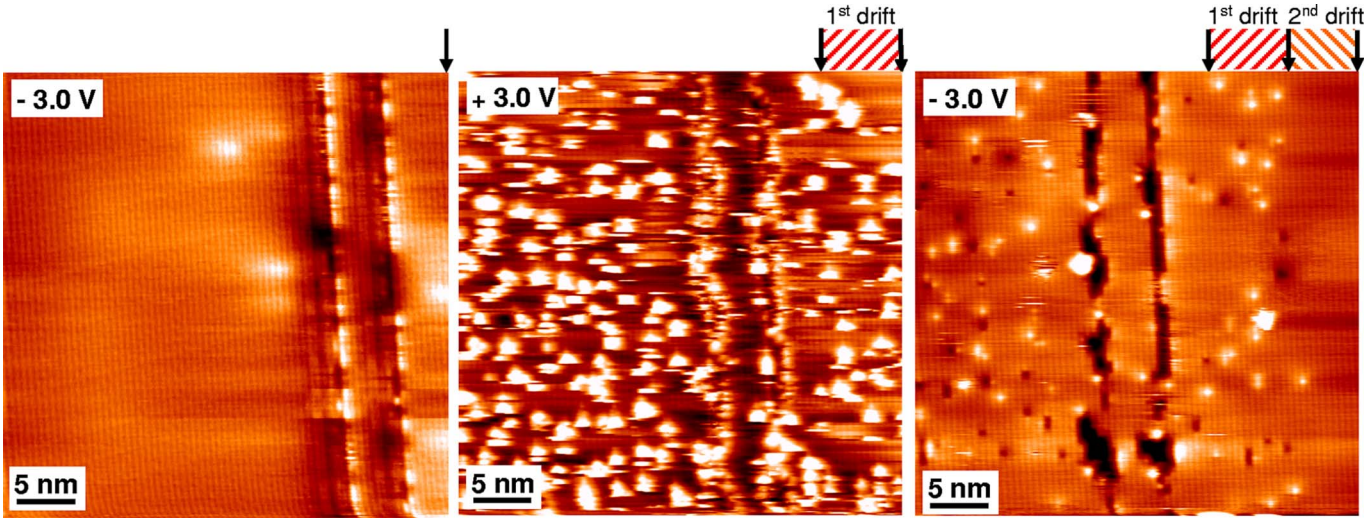

FIG. 2. (Color online) X-STM image sequence in which a specific surface region is scanned at successively negative ($V_{sample}=-3.0$ V), positive ($V_{sample}=+3.0$ V), and negative ($V_{sample}=-3.0$ V) bias voltages. The surface has been manipulated during scanning at positive voltage.

elements) sublattice. The rows of missing atoms can be distinguished as being the dark straight lines extending preferentially along the $[1-10]$ direction. These vacancy chains were always present from the moment after cleavage and were randomly distributed over the surface. They are cleavage induced and not growth related. Since these X-STM images directly represent the Te atoms, it may appear as if the vacancy chains are rows of missing single Te atoms. However, when removing a row of single Te atoms, adjacent Zn atoms would be left behind with three dangling bonds each, which is energetically unfavorable. Therefore, it is most likely that besides Te atoms, Zn atoms are removed as well in the cleavage process. Since this effect has never been observed for III–V semiconductors, its origin should be related to the structural differences between III–V and II–VI materials. Most probably, it is related to the different hardness and ionicity of both types of semiconductors.[13,14]

Another problem was the difficulty of obtaining empty states X-STM images due to tip induced surface modification when applying positive bias voltages. This effect is illustrated in the image sequence in Fig. 2, where three X-STM images are shown that were obtained successively at negative (−3.0 V), positive (+3.0 V), and negative (−3.0 V) bias voltages. The scanned area was the same in all three cases, except for a small and indicated drift of the tip. As can be seen in the image on the left, the sample surface was originally clean, except for two vacancy chains. However, when a positive bias voltage was applied, a large number of bright spots are observed on the surface. Finally, after having switched back to negative bias voltage in the right image, it can be seen that the semiconductor surface has been strongly modified, showing a lot of vacancies and adsorbents. Apparently, atoms are pulled out of the surface (creating the dark spots) when a positive bias voltage is applied after which they are dragged toward other places where they may be dropped again (bright spots). Due to a drift artifact of the tip, the region that is indicated by second drift is not scanned at positive voltage and is therefore clean. As before, reasons for this surface modification must be sought within structural III–V and II–VI differences. Furthermore, the vacancy chains appear to be preferential sites for this manipulation effect, due to the presence of adjacent atoms with extra dangling bonds. As a result of that, the initial monatomic wide character of the vacancy chains is destroyed in the manipulation process and clusters of missing atoms can be observed on the surface. In addition, some (missing atom) spots of the original vacancy chains are filled with atoms. Apparently, the appliance of positive bias voltages gives rise to a breaking and repairing effect on the vacancy chains. Furthermore, the extent of surface modification is reduced by imaging at higher positive voltages, indicating that this effect is related to the distance between tip and surface.

In spite of these difficulties, X-STM results have been obtained for the $ZnSe_xTe_{1-x}$/ZnTe MQW structure. Two ZnSeTe/ZnTe QWs can be observed in the filled states ($V_{sample}=-3.5$ V) X-STM image in Fig. 3(a). At this high negative voltage, the image is assumed to mainly reflect the topography of the surface.[15] The quantum wells appear as dark layers in which the Se atoms can clearly be resolved as dark spots. The dark contrast in the QWs represents the surface relaxation of the tensile strained ZnSeTe epilayers which is inward since $a_{ZnSeTe} < a_{ZnTe}$ (with a being the lattice constant). The Se atoms are observed as dark spots because of the local dangling bond. It can be seen that the QW interfaces are abrupt and smooth, which means that no segregation was present. The thickness of the QWs is found to be about 5 nm, which is in agreement with the nominal value. Furthermore, Se atoms are observed in the ZnTe material in between the QWs. These Se atoms were most likely residual elements in the MBE chamber that have been incorporated in the material during growth of the ZnTe spacers. Since the X-STM image is atomically resolved, the concentration of Se atoms within the QWs can be deduced by simply counting the dark spots. This was done for both QWs and the resulting Se concentration profile as a function of the distance along the growth direction z can be seen in Fig. 3(b). Again, the abrupt QW interfaces can be traced back from this profile. Furthermore, the concentration of Se atoms within both QWs was deduced to be 17.1% and 17.7%, respectively. This concentration was also determined by using a finite element calculation package to simulate the surface relaxation of the QWs. For this method, continuum elastic theory is used and an isotropic material is assumed. Furthermore, the measured thickness of the QWs is used as an input for the simulation

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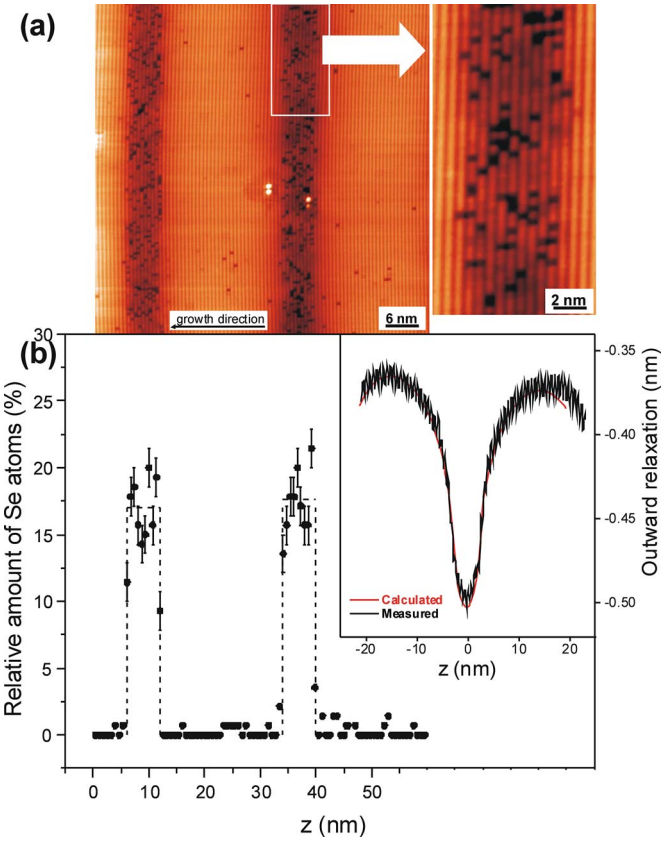

FIG. 3. (Color online) (a) Filled states topography image (V_{sample}=−3.5 V) of the (110) cleavage plane showing two ZnSeTe/ZnTe QWs. The dark spots are individual Se atoms. (b) Profile of the Se concentration within two quantum wells as a function of position along the growth direction z. Inset: measured and calculated outward relaxation profiles across a QW for a Se content of 17%.

and the Se content is changed in order to obtain the best fit to the outward surface relaxation that is directly obtained from the X-STM images. Both measured and simulated outward relaxation profiles are displayed in the inset of Fig. 3(b). The best fit was found for a Se concentration of 17%, which is in very good agreement with the value that was found by directly counting the Se atoms. However, these values are significantly larger than the nominal concentration of 5%, as was intended for the growth of the sample. The main reason for this deviation is that the MBE growth of ZnSeTe materials was probably not properly controlled.

N:ZnTe delta-doped structures were also investigated. The nitrogen incorporation in Te sites allows us to have a *p*-type doping of ZnTe. A filled state X-STM image is shown in Fig. 4, in which the N atoms can clearly be observed as bright circular spots due to the effect of the Coulomb field of the negatively charged impurity (N dopants are in the ionized state).[16] In addition, it can be seen that a significant broadening of the delta-doped layer is present.

In conclusion, ZnSeTe/ZnTe MQW and N:ZnTe delta-doped structures have been studied by X-STM. In doing so,

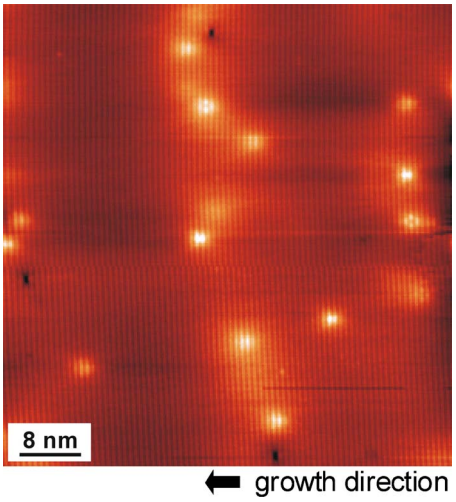

FIG. 4. (Color online) Filled states topography image (V_{sample}=−2.5 V) of a N:ZnTe delta-doped epilayer structure.

difficulties have been encountered which have never been observed before for III–V semiconductors. One peculiar aspect is the observation of monatomic wide vacancy chains on the Te sublattice. Another effect is the manipulation of the semiconductor sample surface when applying positive bias voltages (empty states imaging). Furthermore, ZnSeTe/ZnTe QWs have been observed in which the Se concentration was deduced to be significantly larger than the nominal value.

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