

Imaging interfaces in artificial semiconductor crystals

Many electronic and optoelectronic devices are fabricated from semiconducting “superlattices”: a sequence of alternating, thin layers of two different semiconducting compounds that have the same crystal structure. A superlattice is like a single crystal, but one that has periodic, abrupt changes of composition at the interfaces between its two constituent compounds. Usually these are compounds of a metal and a nonmetal where only the metal component is modulated (e.g. Gallium Arsenide/ Aluminium Arsenide superlattices, a classic example). We have been studying the interesting case of superlattices where both the metal atoms (the cations) and the non-metal atoms (the anions) are different in the alternate layers. The atomic configurations at the interfaces between two layers is then intrinsically complex, but can be unravelled by ultra-high resolution electron microscopy.

Superlattices built from two compounds with no atom in common exhibit special optical and electronic properties. We have been investigating Zinc Telluride / Cadmium Selenide (ZnTe/CdSe) short-period superlattices, as potentially efficient absorbers of sunlight for solar cells. Our superlattices are alternating thin layers of ZnTe and CdSe with repeat period of order 10 nm. They are grown by Molecular Beam Epitaxy (MBE), the technique of choice to realize semiconductor hetero-structures with flat, sharp interfaces. In this context a precise knowledge of the interfaces is crucial for “engineering” the optical absorption threshold: The short period makes the optical absorption properties very sensitive to the atomic arrangement at the interface.

To take the simplest possibilities, at the interface, do we have Zn atoms bound to Se, or Cd atoms bound to Te? Or more complex configurations? To answer these questions, we used a state-of-the-art Transmission Electron Microscope, located at the Nano-Characterization Platform (PFNC) at CEA-Minatec (Grenoble), whose resolution has been enhanced to better than 0.1 nm by correcting magnetic-lens aberrations. We used a mode where the image contrast is directly related to the number of electrons Z carried by each atom, thus distinguishing different atoms: the higher the number Z , the brighter the image.

High Resolution Transmission Electron Microscopy relies on viewing a very thin slice of the sample precisely parallel to columns of atoms in a chosen direction of the crystal structure. The transmission image shown in Fig. 1 is a view looking parallel to the plane of the CdSe/ZnTe interface. In this projection of the structure, the images of the closest columns of metal and non-metal atoms are only partly resolved; they appear as a pair of unequal dots that blur into each other. But the dots can be clearly identified as two atoms with different values of their electron number Z . The respective brightness of the two dots is inverted on each side of an interface (A or B in Fig.1): In the image, one can differentiate high brightness/low brightness dots for CdSe ($Z_{Cd}=48$, $Z_{Se}=34$) and low brightness/high brightness dots for ZnTe layers ($Z_{Zn}=30$, $Z_{Te}=52$), see the insets at top of Fig. 1.

At the “ZnTe on CdSe” interface A, we see low brightness/ low brightness dots. Their quantitative intensity profile (Fig. 1) is consistent with Zn-Se bonds ($Z_{Se}=34$, $Z_{Zn}=30$). That is, the interface is a very thin slice of a third compound ZnSe, at the atomic scale (Fig. 2). This implies that, when the incident molecular beam is permuted from Cd+Se to Zn+Te during superlattice growth, the change in non-metal species (Te replacing Se) is retarded compared to the change in the metal species (Zn replacing Cd). The “CdSe on ZnTe” interface also appears to consist of a ZnSe-rich layer. High brightness/high brightness dot pairs never appear in the image of the superlattice, ruling out the presence of a CdTe interface layer.

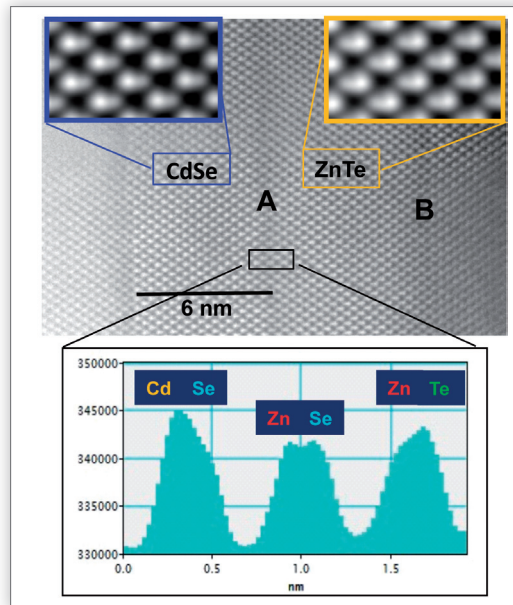


Fig. 1: High resolution electron microscopy image of several layers of a CdSe/ZnTe superlattice. Growth direction is from left to right. Interfaces ZnTe-on-CdSe and CdSe-on-ZnTe are labelled A and B, respectively. Each bright spot represents a close pair of columns in the crystal structure (a column of metal atoms and a non-metal atom column).

The two zooms show that the blurred bright “spots” consist of weak dot/bright dot pairs, corresponding to either (Cd, Se) or (Zn, Te) columns.

At bottom: brightness profile across the interface A showing the Zn-Se bond nature of the interface.

To add additional chemical insight to the image contrast analysis, the samples were investigated by Atom Probe Tomography (APT), another technique available at the Nano-Characterization Platform. A 3-Dimensional chemical mapping of atomic species can be done with (lower) spatial resolution by evaporating, atom by atom, a sharp tip fashioned in the material. ZnSe⁺ molecular ions were detected, originating precisely from all the interfaces, but not CdTe molecular ions.

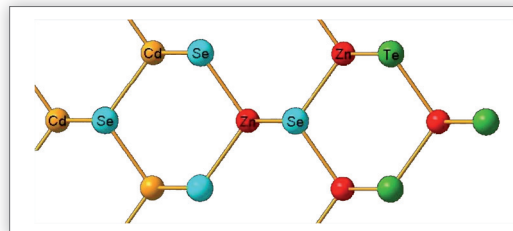


Fig. 2: Atomic structure deduced for the interface between Cadmium Selenide (at left) and Zinc Telluride (at right), showing a Zn-Se bond at the interface. (Colour code: red=Zn, blue=Se, yellow=Cd, green=Te).

The predominant formation of ZnSe bonds at both interfaces proves to be a very robust phenomenon: It persists under a wide range of crystal growth conditions investigated in this study. It is attributed to the difference in cohesive energies between the four possible metal/non-metal couples, which clearly favours ZnSe.

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FURTHER READING

“Atomic arrangement at ZnTe/CdSe interfaces determined by high resolution scanning transmission electron microscopy and atom probe tomography”

B. Bonaf, L. Gérard, J-L. Rouvière, A. Grenier, P-H. Jouneau, E. Bellet-Amalric, H. Mariette, R. André and C. Bougerol
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