Ligand Binding energy of CdS/ZnS various interfaces: ab-initio study intimately related with anisotropic CdS/ZnS quantum rod growth

Incheol Jeong

Department of material science & engineering of Chungnam national university, 220 gung-dong, yuseong-gu, Daejeon 305-764, Korea

Email: thegreatestguyiveevermet@gmail.com

The effect of Ligand Binding energy in quantum rod (CdS/ ZnS) plays a critical role in anisotropic growth. As mimicking large chain of ligands and using the head of the chain, I plan to bind the quantum rod and ligands so that it can grow well consequently. So the ultimate goal of this study is on how ligand binding can affect the growth of this quantum rod. There are preferred surfaces between the quantum rod and ligands, and we empirically know that ligands which bind the quantum rod; Phosphoric oxide (PO), Phosphoric acid(PA), Carboxylic acid(CA), Trimethylamine(TMA), have strong tendency to be attached on the surfaces of CdS/ZnS; $(11\bar{2}0)$, $(10\bar{1}0)$, $(000\bar{1})$, (0001). I virtually bond the surface and the ligands, and calculated the ligand binding energy after optimizing their structure, utilizing EDISON simulator. After all, I figured out how they are linked each other and how the quantum rod grows.

INTRODUCTION

When it comes to the fabrication of devices especially photovoltaic cell which has received considerable attention as an alternative energy souce, high sensitivity of the devices (based on nanostructured materials) matters because of their large surface-to-volume ratios with absorbed compounds. CdS/ZnS quantum rod is an important candidate for the assembly of solar cell because it forms the core component of a photovoltaic cell when combined with a p-type semiconductor [1][2] and ZnS/CdS solar cell is one of the most efficient cells. It has been reported that the electrical and optoelectronic performance of CdS/ZnS quantum rod are improved via functionalization with ligands. It was attributed to the passivation of its surface, which prevents that the oxygen in the surrounding environment reacts with point vacancies at the surface. Some compounds have been investigated to determine the most appropriate for the growth of ZnS/CdS quantum rod. Compounds that have been employed as promising ligands include PO, PA, CA, TMA. Even though Fourier-transform infrared (FT-IR) and UV spectroscopy indicated that they are promising ligands, it has been reported that the amount, absorption, and acidity of these ligands also play a role in the binding properties. But recent atomic force microscopy (AFM) measurements have firmed the rightness of these ligands.

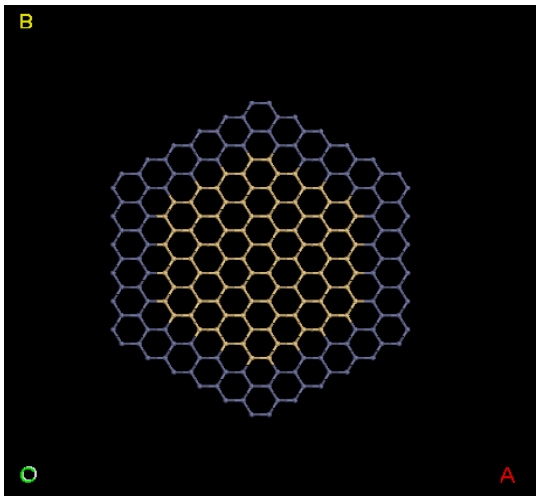

Fig. 1. CdS(core)/ZnS(Shell) quantum rod.

CALCULATION METHODS

Linear combination of atomic orbitals -based-density functional theory (LCAODFT) calculations in EDISON simulator were performed as implemented in the Spanish initiative for electronic simulations with thousands of Atoms (SIESTA). In every calculation, k-sampling were conducted in (20 X 20 X 20) because I found out that 20 points, at least, represent the infinite model considering its stable structure and energy. In determination of the parameters, especially lattice constant and bulk modulus, Python (EOS) were performed.

RESULTS AND DISCUSSION

For determining parameters of CdS & ZnS, Python (EOS) calculations were perfomed and I compared them with experimental values. In both structure, Zinc Blende & Wurtzite, for each materials, calculated values were depicted as approximately as expermental values in Table. 1.

In modeling the bare surface of slabs, triclinic

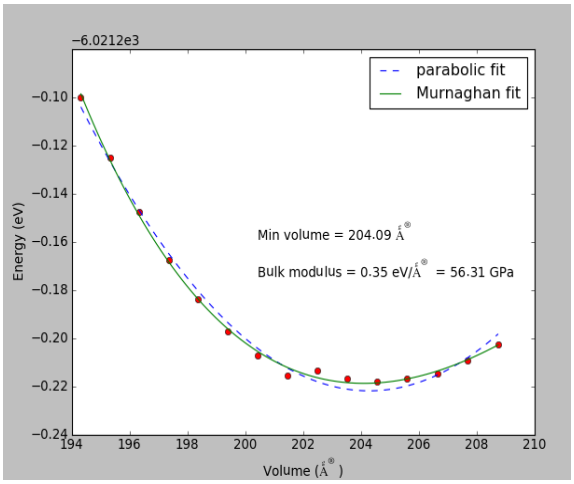

Fig. 2. Python calculation of Zinc Blende structure of CdS.

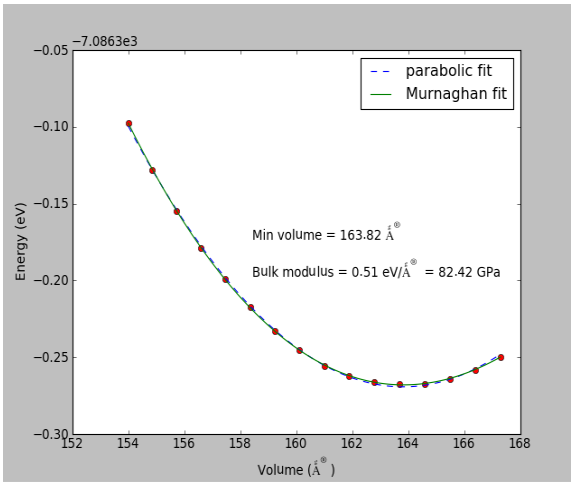

Fig. 3. Python calculation of Zinc Blende structure of ZnS.

supercell consisting of 16 materials (each for CdS and ZnS) were advised to contain two ligand molecules (one at each side of the slab), considering equivalent configurations. Then they were optimized in LCAODFT calculations. After all, the final configurations are Fig. 4, Fig. 5.

Throughout the whole calculation including optimization, it generally appeared that slabs with TMA have the highest energy and the lowest

< Lattice constant >

	Calculated	Experimental
CdS	5.8876	5.8320
ZnS	5.4717	5.420

(unit : Å)

Table. 1. Lattice constants

< Bulk Modulus >

	Calculated	Experimental
CdS	56.31	56.8
ZnS	82.42	83.7

(unit : GPa)

Table. 2. Bulk modulus

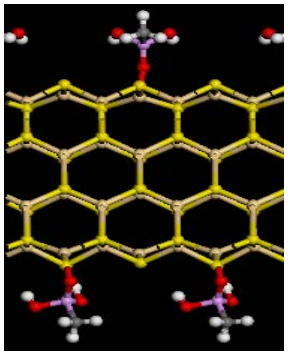

Fig. 4. CdS slab and PA.

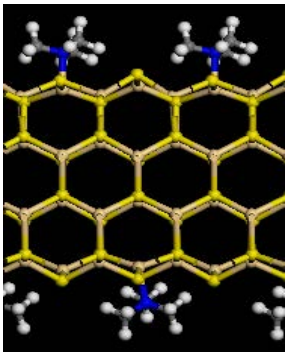

Fig. 5 CdS slab and TMA

	bare surf		Molecule	
	X H atom	H atom		
CdS100	-72548.1	-72803.9	TMA	-877.563
CdS110	-96732.8	-97073	PA	-1716.02
ZnS100	-85342.8	-85599.5	PO	-1221.31
ZnS110	-113792	-114134	CA	-1240.79

Tabel. 3. Bare surface energy.

SYSTEM				
	TMA	PA	PO	CA
CdS100	-73427.3	-74521.9	-74026.9	-74046.2
CdS110	-97611.9	-98791	-98296.2	-98315.1
ZnS100	-86222.1	-87317.5	-86822.6	-86841.8
ZnS110	-115013	-115852	-115357	-115376

Table. 4. System energy.

Binding E				
	TMA	PA	PO	CA
CdS100	-1.58655	-1.97247	-1.68286	-1.55727
CdS110	-1.5442	-1.97305	-1.86564	-1.27861
ZnS100	-1.71847	-1.98544	-1.81012	-1.57218
ZnS110	-1.54891	-2.03507	-1.86231	-1.53882

Table. 5. Binding energy

energy with PA. In the direction of the surfaces, slabs cleaved in $(11\bar{2}0)$ have much stable states than the ones cleaved in $(10\bar{1}0)$

Consequently, slabs cleaved in $(11\bar{2}0)$ with PA or PO should be considered as the most grow-accelerating slabs. Even the one with PO (colored with red above), are not relaxed yet, aim for the next research become certain.

CONCLUSION

It was not simple to apply pseudo-hydrogen in every preferred surfaces of CdS/ZnS wurtzite slabs with EDISON simulator. So I decided to optimize nonpolar slabs without pseudo-Hydrogen and bind them with ligands (PA, PO, CA, TMA) on the preferred surfaces, $(10\bar{1}0)$ & $(11\bar{2}0)$. However, the results from this study provide new insights for improving the properties and surfaces for device application, supporting non-fossil-fuel world.

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