Predicting bandgap in strain-engineered multinary III-V semiconductors

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We are interested in III-V semiconductors. Why III-V? Well, because as we all know, among others, III-V semiconductors are one of the most important material classes in optoelectronic. The applications extends from daily houshold LEDs, laser, solar cell, optical telecommunication to modern advanced technologies such as solar hydrogen production technology. [FORWARD] And **one of the fundamental property** that determines the optical characteristic of these optoelectronic devices is the bandgap: both in terms of it's magnitude and it's nature, whether it is direct or indirect in nature. [FORWARD] And the tuning of this type and size of bandgaps of III-V semiconductors is one of the major goal in optoelectronics-field.

[FORWARD]Varying the relative composition of several III- or V-components in compound semiconductors is one of the major approaches here, the so-called compositional engineering. The vast chemical space of combinations of all group III- and V-elements provide an unique opportunity of bandgap tailoring over a wide range of values, allowing enourmous diversity in device applications. [FORWARD] Alternatively, straining the system can be used to modify the bandgaps, the so-called strain-engineering. For example, here strain in terms of external pressure was applied on a Si-nanomembrane. After certain strain the bandgap in Si-nanomembrane become direct in nature. [FORWARD] In thin-layer heteroepitaxy, choosing the substrate-layer combination with minimum lattice mismatch is often desirable to minimize the strain effect from the substrate. However, in practice, perfect lattice matching is rarely possible. In such cases, not only the composition but the effect of inherent strain from the substrate also substantially affects the active layer's bandgap. Therefore, clearly, by combining these two approaches appropriately, the bandgap engenieering can be enhanced significantly. [FORWARD] Only problem, experiments are generally limited to only a few compositions and strain values because of the experiments like epitaxy are expensive, require to optimize growth condition, lack the required precursors and so on. And thus experimental approaches are often not quite effective for optimizing the best material choices. Additionally, this is very much prone to missing important parts in composition-strain space. [FORWARD]So, we develop a computational approach which is very efficient and accurate to predict the bandgap of strained multinary III-V compounds.

[FORWARD]Quick overview of our approach. We used the density functinal theory. And latter combined it with machine-learning to accelerate the process. For experts in the room, we use vasp with 3d periodic bondary conditions for the density functional theory calculations. Geometry optimizations with PBE-D3(BJ) functional. And the electronic properties calculation with TB09 meta-GGA functional. For binary systems we used primitive cell but for multinary systems, such as ternary, quaternary systems we used 6X6X6 special quasirandom supercell. Regarding the machine learning model we used support vector machine machine learning model in combination with radial basis function kernel. [FORWARD]And the strains were modeled by constraining the lattice parameters in all 3 direction for isotropic, only in in-plane direction for biaxial and in out-of-plane direction for uniaxial strain.

[FORWARD]Let's start with the simplest III-V semiconductor family; the 'binary systems'. [FORWARD] And, here is an example how a strain-bandgap map looks like for GaAs under isotropic strain. In this case, we don't have anything to vary in composition. The positive and negative strains correspond to the tensile and compressive strains, respectively. [FORWARD]
Starting from GaAs at the equilibrium configuration, under compressive strain the bandgap initially increases in magnitude, the trend change its direction, the bandgap starts to decrease then. Under tensile strain however, the bandgap continuously decreased until the bandgap vanishes.
What about the nature of bandgap?[FORWARD]
For that, we simply compared the magnitude of bandgap values with the CB and VB energy difference at the Gamma point. [FORWARD] As long as they overlap that would be the bandgap of direct nature and when they deviate from each other **the bandgap become** indirect. [FORWARD] We find the so-called direct-indirect transition in the nature of bandgap. Let's see what the band structures says? This is the so-

called evolution of bandstructure under strain. [FORWARD] Under tensile strain, the bandgap remained direct at the gamma point throughout and decreases in it's magnitude only. [FORWARD] For compressive strain, however, the direct bandgap GaAs initially increases in magnitude until at about 1.5% of strain when the CBM at the Gamma point transit to the L-point, and ultimately to the X-point; leads to the transition in the in the nature of bandgap: from direct to indirect bandgap transition. [FORWARD]
And we now have a nice systematic computational approach to map this complete strain-bandgap relationship in binary III-V semiconductor materials.[FORWARD] We then extended the analysis to the next higher order ternary systems. [FORWARD] now addition of a 2nd component introduces the concept of composition here. So now we have to map the bandgap w.r.t both strain and composition. Seems simple enough, except a slight problem. [FORWARD] Unlike the binary systems where we could use simple primitive cell for the analysis but now to ensure the ideal admixing among all the components we have to use supercell. Now, the use of this supercell results a well known phenomena, something called 'band-folding'. Due to this 'band-folding' although it is straight forward to get the information about the magnitude of bandgap, but for the nature of bandgap we need to know the nature of specific k-points, if it is gamma, L or X and so on. But because of the bandfolding the k-points get mixed up and thus no longer possible to know its character definitely. [FORWARD] Way out? What if we project our supercell eigenstates on a reference known primitive cell eigenstates and that way determine a weight, Bloch weight, how much of a primitive k-points get mixed up to a supercell state. Using this idea of Bloch weight we can now determine the relative character of a supercell k-points and consequently the nature of bandgap.

[FORWARD]For example this is such a map how it looks like for GaAsP under isotropic strain. This is your composition axis now. You have the strain here. The colors are the magnitude of bandgaps.
[FORWARD] And then, if you map the nature of the bandgaps as well, you can construct such a separation line that separates the nature of bandgaps of different kinds. Anything in this region will have bandgap direct in nature and anything in this region will be indirect bandgap. This so-called 'direct-indirect' transition line as if separates the band gaps into 2 phases. Due to the similarity with commonly used phase diagrams, we call this representation a "bandgap phase diagram". [FORWARD]

You can do the same for other kind of strain as well. For example this is how the similar picture looks like for Biaxial strain, GaAsP. This is again the 'direct-indirect transition' line that separates the two region.
What special about this biaxial strain is that, we can model the 'epitaxy' in terms of this type strain. [FORWARD] If we assume the source of the biaxial strain as the substrate effect from epitaxial growth, then you can add the different substrates here like this. These lines corresponds to how much strain will be there if you grow let say these compositions on this substrate. [FORWARD] What can we do with it? This can guide you to spot the most suitable choice depending on your need. Based on the bandgap phase diagram, we propose several design strategies to optimize the selection of material combinations for achieving specific optical applications and even new design principles for new devices. For e.g. here is an example let say you want to grow a quantum-well heterostructure (QWH) composed of biaxially strained GaAsP on GaAs substrate. The bandgap phase diagram shows the areas in compositional phase space a direct bandgap in GaAs1−x Px can be achieved. The bandgaps in this region are indirect and hence, are inappropriate for the heterostructure. Additionally, as the QW layers here are made out of a single material with varied composition only, the epitaxial growth could be performed efficiently. [FORWARD] This again shows an efficient approach for the monolithic integration of multiple QWH to construct multi-junction photovoltaics. In this case, the QWHs are separated by thin indirect bandgap layers of the same material as QWH but only with a different composition. This would make the integration approach efficient, as no sample transfer is required during growth. [FORWARD] Here is another idea. Close to the direct-indirect transition region as you move along this line, you can grow a GaAsP epitaxial layer on GaP with P-concentration continuously changing from direct to indirect bandgap region or vice versa. This way, changes in the bandgap magnitude, as well as the nature of the bandgap, are possible. You can implement this in both the horizontal and vertical directions.
[FORWARD] You can also make the epitaxial layer either direct or indirect depending on your choice of your substrate, GaAs or Si. You can optimize the choice the substrate-layer pair.

Essentially this way one can choose or determine the best option. Best option in materials combination given an application in mind or vice versa, given a materials combination what can be done with it. **This is completely predictive.**
[FORWARD]
So far, we used the so called direct computational approach to construct the bandgap phase diagram.
Unfortunately, as you go further to the higher order systems such as quaternary system increase in one more degrees of freedom almost exponentially increases the compositional space. Just as an hand waiving estimation: from ternary to quaternary such a direct approach would increase the number of DFT calculation needed, to approx 2 order in magnitude. Therefore, it will be a close to impossible approach to take to cover enough of this vast composition-strain space using DFT calculations only. So, we go for machine learning. [FORWARD]

Using Support Vector Machine in combination with Radial basis function kernel, we established a machine learning model to constructed the bandgap phase diagram for quaternary system. The feature space of our ML model consists only composition and strain values, no complecated features. And we want to predict the bandgap both magnitude and nature. [FORWARD] This is a strain snap shot of bandgap phase diagram for Ga(AsPSb) biaxial strain. And then you scan over strains. [FORWARD] With only about 4000 DFT calculations training set using our machine learning model we reached an excellent prediction accuracy, RMSE in bandgap magnitudes prediction is 46 meV, accuracy in bandgap nature prediction is 94%. Notice how the transition lines are moving. Starting with the compressive strain somewhere here as we go towards the unstrained struture the line move this way and come back as we go to the more and more tensile strain region. [FORWARD] So, now if you collect and plot all these transition lines together then you can see something interesting. [FORWARD] Within plus-minus 5% strain in this region you can have direct-indirect transition under both compressive and tensile strain. [FORWARD] In this region you can reach to direct-indirect transition only under tensile strain and [FORWARD] in these two regions you can not make any direct-indirect transition within 5% strain. [FORWARD] In the similar spirit like previous ternary system, here also you can analyse the effect of specific substrate under ‚epitaxial-growth' model. For example this is how it would look like. Left plot is how much the in-plane biaxial strain will be there when you grow these compositions on Si-substrate and right plot is the corresponding bandgaps, magnitude and nature.[FORWARD]

To summarize;I showed you straining the system not only change the bandgap in terms of its magnitude but it also affect the nature of bandgap itself. Under strain a direct bandgap semiconductor can transform to an indirect bandgap semiconductor and vice-versa. Using density functional theory and the concept of band unfolding, we developed a predictive first-principle computational protocol for the comprehensive mapping of the bandgap magnitude and type over a wide range of composition and strain values for multinary III-V semiconductors, the so-called bandgap phase diagram. Further, by combinning first-principles calculations with machine learning we developed an efficient DFT-ML hybrid computational approach for an accelerated mapping the bandgap phase diagram for multinary III-V semiconductors. The rapid estimation of bandgaps for a large number of composition and strain values using this approach will be extremely useful for screening of multinary III-V materials, which otherwise would be impossible to cover with first- pricple calculations only. Finally, I showed you that this way of mapping the effect of strain can be used to choose application-specific best-suited material systems and hence would be highly beneficial to device design.
Hopefully, I was able to convince you the **great benefit and predictive power** of this new mapping in semiconductors. Just as a final note: for convenience I have presented here only selected choice of the systems as examples. We also did for other systems and details you will find here. [FORWARD]

With this, I am at the end. I would like to thank my supervisor Prof. Ralf Tonner-Zech and our collaborators. Many thanks to all of our collaborative supercomputer centers. And finally, thank you for your attention.

We now know what to do, how to do, and how to do it efficiently?