Predictive first-principle bandgap mapping in strain-engineered multinary III-V semiconductors

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Pictorial representation of the summary of our project on "Predictive first-principle bandgap mapping in strain-engineered multinary III-V semiconductors".

[1] Given the extensive diverse applications in our everyday life, the III-V semiconductors family posses a great deal of attention in the scientific community. Since its discovery decades ago, people have learned a lot about its potentials, and eventually developed and mastered different techniques in the goal of fine tune their properties. Composition engineering, i.e., changing the relative composition of group 13 and 15 elements in ternary III-V compounds, is one of the most important approaches to adjusting the bandgap. Systematic application of strain such as mechanical strain (e.g., external pressure, mechanical bending of nanowire) or strain due to lattice mismatch (e.g., core-shell mismatch in nanowires) on a system are alternative strategies to tailor the bandgap. Combining composition and strain engineering, the bandgap can be tuned over a wide range of values, and direct or indirect semiconductors can be designed. 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, one requires a complete knowledge of the material-specific dependence of the bandgap on composition and strain to optimize the proper choice of materials. However, exploring the vast chemical space of all possible combinations of III- and V-elements with variation in composition and strain is experimentally not feasible. Additionally, growing a new material is often challenging because of thermodynamic or kinetic limitations, such as phase separation or surface roughening, in addition to the demanding task of optimizing the growth conditions. This makes an experimental screening approach of vast compound and strain spaces unrealistic. We thus aim to develop a reliable and predictive theoretical approach.

[2] We have established a comparatively computationally cost effective and fairly robust recipe for such analysis using computational tools, modern ab-initio density functional theory (DFT). We have shown that depending on the nature and strength of applied strain in the system the material behavior can change substantially. Namely, a direct bandgap semiconductor can transform to an indirect bandgap semiconductor and vice versa. This ultimately enables us to construct the 'bandgap phase diagram' by mapping the bandgap both in terms of their values and nature with strain and/or composition.

Binary, 1D bandgap phase diagram: [3] Let's start with the simplest, binary III-V semiconductor system. [3a] As an example, in GaAs we have shown that under isotropic compressive strain the nature of the bandgap changes from direct to indirect given by this direct to indirect transition (DIT) point. Under isotropic tensile strain the well know semiconducting GaAs become metal, given by this semiconductor to metal transition (SMT). [3b] As the valence band maxima (VBM) always remain at the Gamma point, therefore, by tracking the evolution of conduction band minima (CBM) under strain enable us to track the nature of bandgap. For example, the CBM starts at the the Gamma point at strain=0, corresponds to a direct bandgap. Then at ~1.56 % strain the CBM shifts to the L point, and the bandgap become indirect in nature; corresponds to the direct to indirect transition. After that CBM consecutively moves from L to Δm to X-point. Following the same principle, the transitions in other commonly used binary III-V semiconductors (including Si) are also analyzed.

Ternary, 2D bandgap phase diagram: [4] Following the great success in binary systems, our next goal was to extend the analyses for higher-order systems. However, in comparison to the binary systems where we could use simple primitive cells for the analysis but in multinary systems, to ensure the ideal admixing among all the components in the composition we had to go for supercell. Unfortunately, the use of this supercell resulted in the well-known 'band folding' phenomena. Due to this band folding, although it was straightforward to get the information about the magnitude of bandgap, but not the nature of bandgap. [4a]

Using the idea of 'Bloch spectral density/weight' we have developed a systematic strategy for the strain-bandgap relationship in the next higher order, ternary systems; by mapping the different direct-indirect transition (DIT) points with composition **and** strain. This is such an example of bandgap phase diagram for GaAsP under biaxial strain. [4b] Finally, based on the bandgap phase diagram, we proposed several design strategies to optimize the selection of material combinations for achieving specific optical applications and new design principles for devices.

Quaternary, quasi-2D bandgap phase diagram: Following the footstep of our previous analyses, we then extended the scope to the next higher order quaternary systems. However, given the huge compositional space, it will be an extremely daunting step to take to cover enough of the vast compositional space in quaternary systems using DFT calculations only. So, we combined our limited DFT capability with the easily extendable ML to cover the composition-strain space efficiently. [5] Here is a snapshot of such a bandgap phase diagram for the quaternary compound, GaAsPSb. [5a] Here, we have used the Support Vector Machine (SVM) supervised machine learning model in combination with Radial Basis Function (RBF) kernel. For the prediction of bandgap nature, we used the classification version of the SVM model, known as Support Vector Classification (SVC) model. [5b] And the regression version of SVM, the Support Vector Regression (SVR) model for the prediction of the bandgap values.

[6] [6a] In conclusion, the best analogy we came up with in this this respect is, 'bandgap phase diagram' is like a navigation map. Similar to a navigation map bandgap phase diagram can help one to chose or determine the best option in configuration (composition and strain) given an application (such as a device) in mind; and vice versa, given a configuration and substrate what can be done with it. [6b] However, one should realize that bandgap phase diagram alone is not enough for this purpose. Alongside electronic properties, the realization of efficient and stable optoelectronics requires smooth transportation of electrons through the system. The presence of any kind of dislocation, heterogeneity in the material composition, or roughness in the heterostructure interfaces can tremendously hinder the electronic mobility and hence, the performance and long-term stability of the devices. Therefore, 'only' in combination with the compositional (thermodynamic) phase diagram, bandgap phase diagram can significantly improve the future development in terms of strategic choice of certain application-oriented most suited material systems or vice versa. Although, we had compositional phase diagram in the picture for quite a long time, but this other one was missing. And now we are giving you the missing piece. We no longer have to rely on our experience or trial and error method but now we have a scientifically consistent systematic way to make our choice superior.

[7] As the extension of this project, among others, few of the most important propositions that we are currently working on are

1. Extension of our bandgap phase transition analysis to the next higher order systems. Given the limitations in visualization we can go up to at least 5 components systems.
2. What about other material systems, for e.g. II-VI or III-VI systems?
3. We have just seen only one of the transition, the direct-indirect transition. But in the similar fashion one can analyze other transitions in indirect region itself such as L-X and so on, given the needs.
4. One can also extend this idea to other contexts. For e.g. using this idea of Bloch weight we aim to map the correlation between bandgap and split-off energy in the direct bandgap regions, which can be used for e.g. in Auger recombination type analyses.
5.

[8] In long term we hope to discover further in this like and would be able to extend the idea in multitude directions.

[9] We have also designed a public website of this whole topic and you can find it here. That includes our results, details of the calculation procedure, latest updates in this regard etc. and so on. Feel free to contact us if you have any further questions, any new ideas from your side. The details you will find there.

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And finally, thank you all for your attention, and being here till the end.