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Strain engineering in perovskite

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Abstract

Since 2009, halide perovskite which shows excellent semiconductor properties, relatively low cost, and great potential in applications of solar cell start to attract numerous focuses from academia and industry. Up to now the highest PCE could exceed 29% and it is quite close to the theoretical highest efficiency. However, the efficiency of it is still confined by practical obstacles and long-time stability. It shows that train mechanism would be a key factor to improve the performance of halide perovskite devices. In this review, basic principles and factors about strains would be talked about, and some methods to make use of strain materials would be introduced.

Introduction

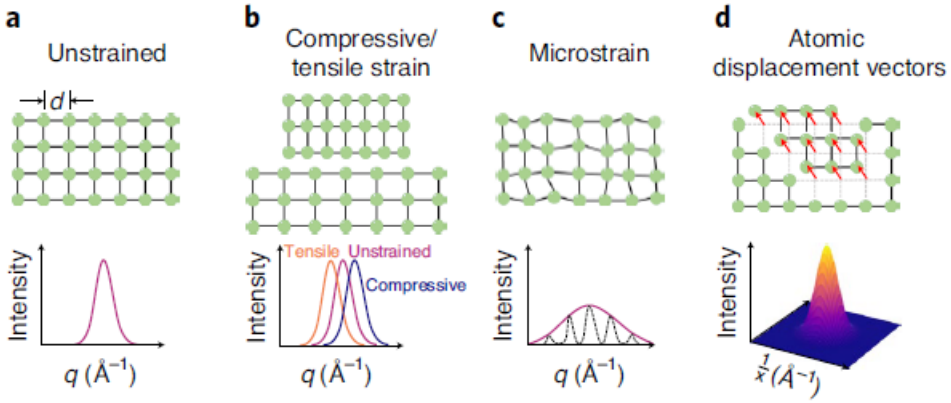
In the field of solar cell, silicon is always be considered as a main material because of its suitable semiconductor properties and decades' development. However, silicon is not a theoretical high-efficiency solar cell material compared to GaAs because of its indirect bond gap so people are dedicating to find new substitutional materials. Since 2009, halide perovskite was found and quickly attracted numerous attentions. It is composed of halide anions, organic cations (usually MA or FA) and Lead cations. Its PCE quickly increased from 3.8% in 2009 to 25.2% in 2019. It has such crazy development because it has some advantages that other semiconductors don't have. It has a direct band gap and its density of state is much larger than that of GaAs so it could show really high light absorption coefficient. Long diffusion time would make it has hundreds of nanoseconds to diffuse but not recombine. Also halide perovskite shows high defect-tolerance because it tend to form shallow traps but not deep traps which means it would have quite high open circuit voltage and relatively low cost to fabricate compared to other solar cell material.

However, stability is a big problem to prevent this promising material from commercializing. Energy loss between layers and degrading of crystal structures are the main factors. Researchers are trying to improve the device stability and performance. They tried several methods, and strain mechanism is a quite good direction to improve. This review will talk about some basic principles and measurements of strain mechanism, and then introduce some factors, including how they affect strains. Finally some methods trying to make use of strains to improve device would be talked.

Basic principles and measurements of strain mechanism in halide pvsk

Strain is defined as a structure deformation when the material is applied with a stress. The stress could derive from external forces or internal forces such as defects, including interstitials and vacancies. Strain could be divided in three kinds. Compressive/tensile strain happened when the crystal is condensed or stretched by external forces and the lattice parameter would be changed. Microstrain happens mostly because of defects and lead to irregular twist inside of structure. Another kind of strain is called atomic displacement vectors.

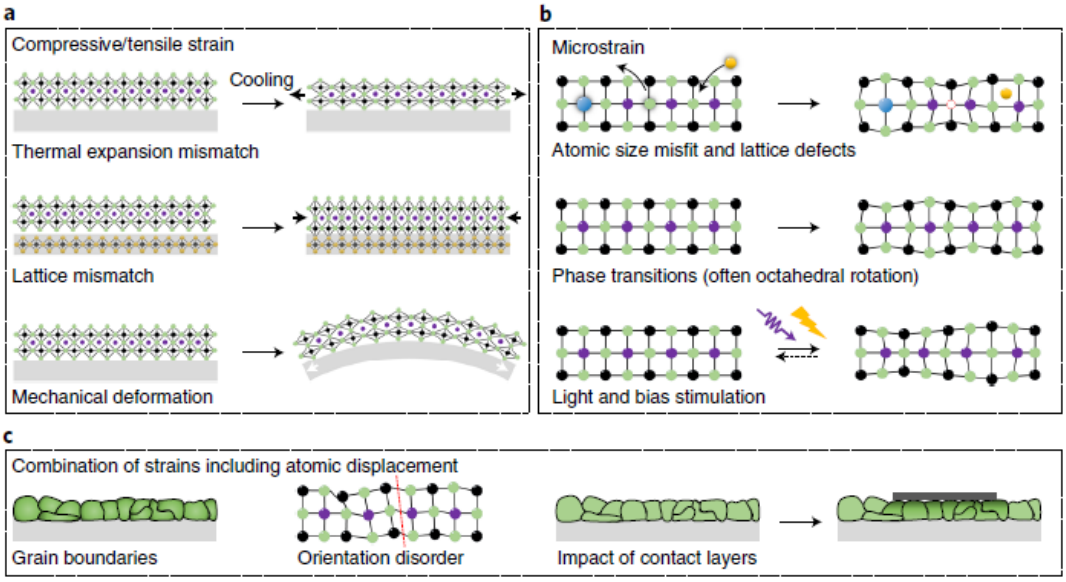
To measure the strain in materials, we need to use XRD and do characterize on materials. In case of compressive and tensile strain, we need to compare the XRD diagram with the standard example to get the difference of interplanar spacing d from Bragg peaks. If it is condensed, the interplanar spacing d would decrease, and if d increases, the material would be stretched. When it comes to microstrain, because of the defects, the peaks are broadening but the interplanar spacing isn't changed too much so we need another method called Williamson-Hall analysis to get the strain. From the XRD diagram, we could get the Full Width Half Maximum (FWHM) and the angels. Then from the formula $FW(S)\times\cos(\theta)=\frac{K\times\lambda}{Size}+4\times Strain\times\sin(\theta)$, we could plot a diagram which shows the linear relationship between FW*cosθ and sinθ, the slope is 4 times of microstrain and the intersection of this line and the y-axis is Kλ/L, L is the crystallite size. However, this method is not perfect. To apply this method, we need to remove the broadening from instruments. There are also many factors inside of materials such as distribution of size and crystallite length would have significant influence on the strain calculation.



Factors lead to strains

Strains would derive from a large range of factors. In a typical process to fabricate halide perovskite, during the film formation, if the substrate has a low coefficient of thermal expansion (CTE), perovskite would form tensile strain because the substrate restrict the contraction of perovskite. In contrast, if the CTE of substrate is higher than the film, it would form compressive strain.

Moreover, just similar with heteroepitaxy, the mismatch between the substrate and the perovskite film would also form strains. Whether the condition would be tensile or compressive depend on the interplanar spacing d of substrate. However, if the difference of d is too large, it will lead to uniformed, distorted interface. When applying this method, researchers should be careful about it.



The above factors will affect the strain pressure of the whole perovskite materials. There are several other factors such as phase transitions, light stimulations, and grain boundaries. When the photovoltaic devices are exposed to light during working, it may generate some microstarin. Although we know perovskite material is high-defect tolerant as a solar cell material, defects would still affect its performance so the microstrain is not people want. Grain boundaries would be another generator of strain inside of material, it come from the different orientation of the same crystal structure. It is proposed that the interfacial strain field between grains lead to the strain.

Impact on device performance and stability

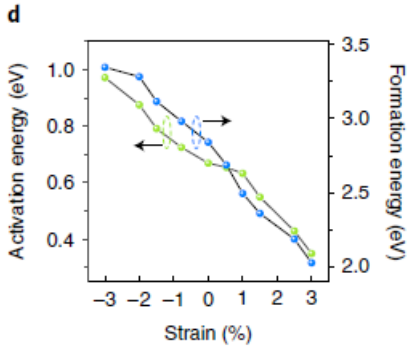
Impact on device performance

To know the influence of strain regarding the semiconductor properties of perovskite, we need to know the composition of the valence band and conduction band of it. The valence band is formed by Pb s orbitals and halide p orbitals. The conduction band is formed by dominant non-bonding overlap between Pb p orbitals, and halide p orbitals slightly contribute to it. Thus, when the material is applied with tensile train, its band gap would increase. In turn, if compressive strain is applied, the band gap would decrease. Although the carrier mobility would decrease because of more dislocations by the higher magnitude of train applied, researchers could try our methods to compensate it like tuning the A ion's stacking pattern. In this way, the interaction between phonons and electrons would be reduced.

Impact on device stability

Halide perovskite has reached impressive performance in terms of semiconductor properties. One of the main reasons to resist it from being commercialized is the stability of device. Ion migration would happen especially for halide ions. Degradation caused by the migration would lead to the short lifetime of device. It is reported that the activation energy of ion migration would increase by the increase of compressive strain. However, according to

Poisson's effect, when the film is applied compressive strain horizontally, it would have tensile strain in perpendicular direction. What's more, it would also lead to cracks and unsmooth texture. These factors should be taken into consideration when applying strain mechanism.



Methods to improve

Annealing-associated modification

Annealing is a routine step when fabricating perovskite solar cells. As mentioned in factors part, mismatch would happen when the coefficient of thermal expansions (CTE) of perovskite and the attached layer are different. One Method to modify is to improve the annealing step, people try to form the perovskite layer on the substrate at room temperature to lower down tensile strain induced by annealing. It is reported that by using amine to help form perovskite film at room temperature and its PCE approaches 23.1%.

Compositional tailoring

Compositional tailoring is introducing other ions (like Cs and Cl) into the crystal structure to reduce the microstrain inside of it. The added ions could be in A position and could also be halide position (X). In this way, from the XRD diagram, the width of Bragg Peak is reduced and the area of it is increased which means there are less microstrains. Although this method could improve the device performance, A site cations would also lower down the stability because their larger or smaller ion sizes. Thus, it is proposed that introducing additive species which crosslink between grains in precursors would enhance the stability.

Interfacial management

As mentioned before, some unwanted strains come from the mismatch induced by the difference of CTE between layers. It is proposed that inserting a layer between the perovskite and substrate would be an approach. However, this method needs to face many problems. Some thin inserting films don't work and some 2D layers, for example, 2D perovskite would be influenced by 3D perovskite because its van der Waals interactions are interrupted. Another way to figure this problem is epitaxy which is a wildly used technique. However, epitaxy is a quite expensive method so this way would annihilate perovskite's low-cost advantage.

Summary

Perovskite is a brand-new and promising semiconductor material. To increase its stability to prompt its commercial application, strain mechanism is a quite good way to improve perovskite's performance because producer only need to apply it when fabricating and it is hard to be influenced by environment once fabricated. By understanding how strains form and how factors affect strains, we could figure out methods to make use of strain to improve device's performance and stability. Although there are many obstacles that prevent researchers from improving it, people could get feedback from several characterization techniques and do some adjustments, finally could find a way to minimize the affect of microstrains and make use of tensile strain and compressive strain.

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