Solar Photovoltaics: Fundamental Technology and Applications

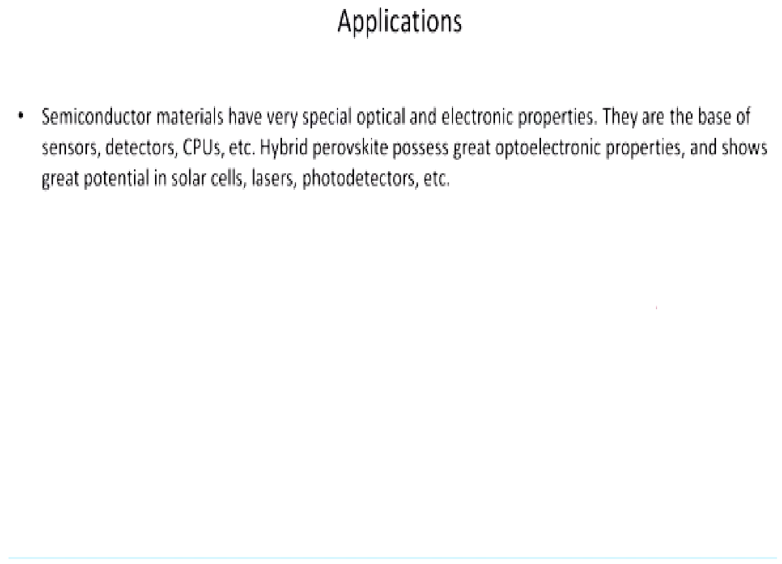
Prof. Soumitra Satapathi
Department of Physics
Indian Institute of Technology – Roorkee

Lecture - 32
Stability in Perovskite Single Crystal Solar Cells

Welcome everyone to our solar photovoltaic course. Today we are having our seventh week lectures on perovskite single crystal. In the last lecture if you remember we have started talking about the perovskite single crystal and what are the advantage of the perovskite single-crystal over their bulk counterpart and we have seen that since the number of trap state or the defect is less in the perovskite single crystal.

So its optical properties and electrical properties are superior than this bulk counterpart and for that reason it is useful for fabricating some solar cell devices, some laser devices as well as some detector based devices. Now in today's lecture we will discuss about the different application of the perovskite single crystal for solar cell, detector and the laser.

(Refer Slide Time: 01:10)

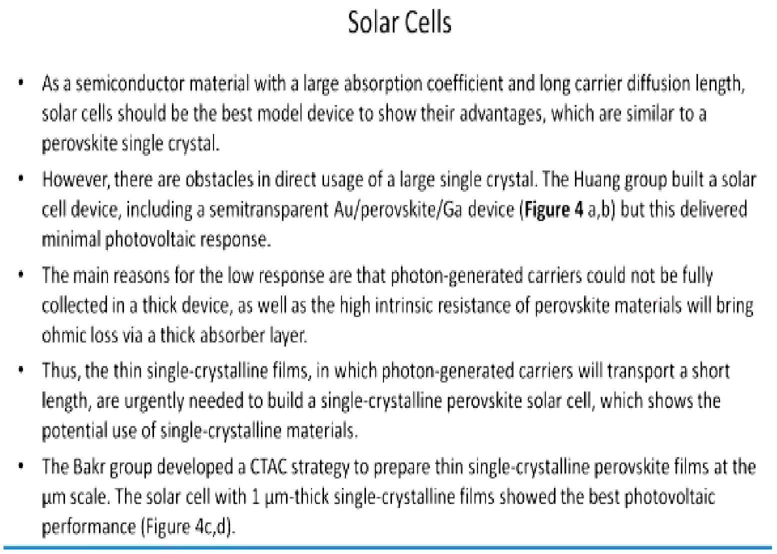


Applications

- Semiconductor materials have very special optical and electronic properties. They are the base of sensors, detectors, CPUs, etc. Hybrid perovskite possess great optoelectronic properties, and shows great potential in solar cells, lasers, photodetectors, etc.

Now some of the applications of the perovskite single crystal are semiconducting materials have very special optical and electronic properties, they are the base of sensor detectors, CPU et cetera. Hybrid perovskite possess great optoelectronic properties and shows great potential in solar cells, laser, photodetectors et cetera. So perovskite single crystal has been used to make light emitting diode and photodetectos and also they have been used in different IC circuits also.

(Refer Slide Time: 01:39)



Solar Cells

- As a semiconductor material with a large absorption coefficient and long carrier diffusion length, solar cells should be the best model device to show their advantages, which are similar to a perovskite single crystal.
- However, there are obstacles in direct usage of a large single crystal. The Huang group built a solar cell device, including a semitransparent Au/perovskite/Ga device (**Figure 4** a,b) but this delivered minimal photovoltaic response.
- The main reasons for the low response are that photon-generated carriers could not be fully collected in a thick device, as well as the high intrinsic resistance of perovskite materials will bring ohmic loss via a thick absorber layer.
- Thus, the thin single-crystalline films, in which photon-generated carriers will transport a short length, are urgently needed to build a single-crystalline perovskite solar cell, which shows the potential use of single-crystalline materials.
- The Bakr group developed a CTAC strategy to prepare thin single-crystalline perovskite films at the µm scale. The solar cell with 1 µm-thick single-crystalline films showed the best photovoltaic performance (Figure 4c,d).

For example, in solar cell semiconducting material with large absorption coefficient and long carrier diffusion link solar cell should be the best model device to show their advantage which are similar to a perovskite single crystal. However, there are obstacles in the direct use of a large single crystal. So one of the research group like Hung's group, they build a solar cell device including a semi-transparent gold perovskite gallium device.

But this delivered minimal photovoltaic response. The main reasons for the low response of the photon-generated carriers could not be fully collected in a thick device as well as the high intrinsic resistance of the perovskite material will bring ohmic loss via thick absorber layer. Thus the thin single crystalline film in which photon-generated careers will transport a short length are urgently needed to build a single crystal perovskite solar cell.

Which shows the potential use of the single crystalline material and the another research group, the Bakr group developed a CTAC strategy to prepare thin single crystalline perovskite film at the micrometre scale. A solar cell with 1 micron thick single crystalline film showed the best photovoltaic performance which we are showing in the next graph.

(Refer Slide Time: 02:43)

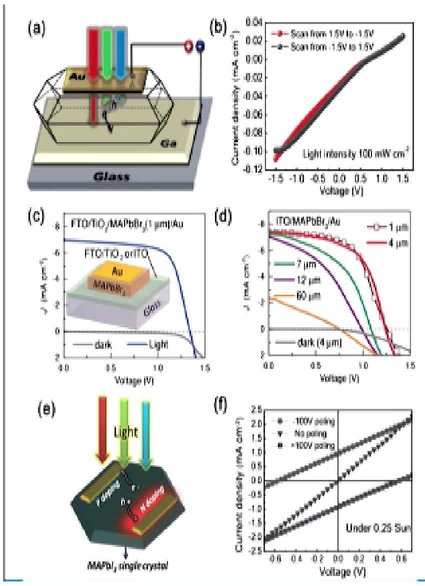


Figure 4. Single-crystalline perovskite-based solar cell devices with different configurations:
a) thick single-crystalline perovskite solar cell with a semitransparent Au electrode as the HTL and Ga electrode as the electron transport layer.
b) J–V curve of the solar cell shown in figure (a);
c) the device structure of a single-crystalline $MAPbBr_3$ film-based solar cell and its photovoltaic performance.
d) Effect of the single-crystalline $MAPbBr_3$ thickness on the photovoltaic performance of single-crystalline solar cells;
e) schematic illustration of a lateral structured single-crystalline perovskite solar cell and its photovoltaic performance f).

You can see that there are different geometry for making the perovskite single crystal as shown in the following figure, here the perovskite single crystal has been sandwich between a gold electrode and a gallium electrode okay and the light falls from the semi-transparent gold electrode and the corresponding structure is showing here, you see that the glass and then there is a perovskite MAPbBr3 which have been sandwich between the gold and the gallium things.

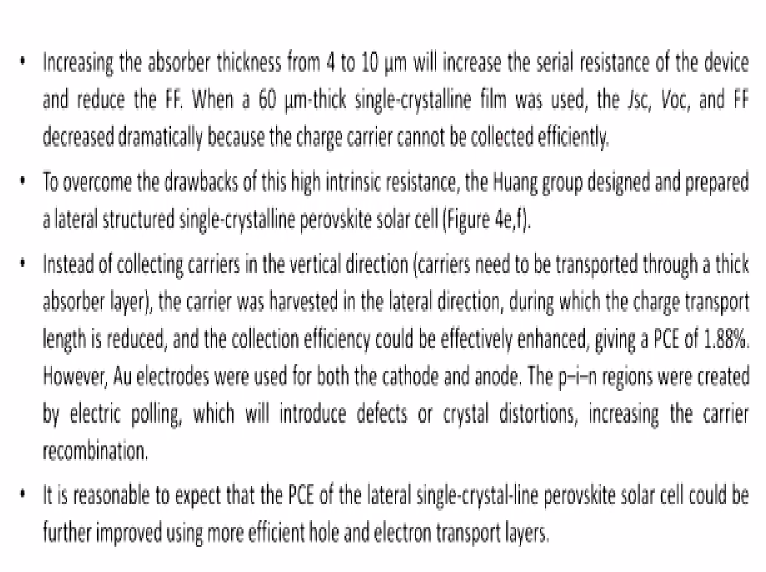
And the corresponding you can also put like if you do not have the gallium you can also use ITO or FTO. So basically FTO, TIO2, MAPbBr3 single crystal 1 micron and the gold and that is the photovoltaic response and MAPbBr3 single crystal also people have done by sequential N doping and P doping and their they got a response like that.

So this figures like you know, figure number a, that is a thick single crystalline perovskite solar cell with semi-transparent gold electrode as the whole transport layer and gallium electrode as the electron transport layer. Now the second graph b, that is the J-V curve of the solar cell which we have fabricated in the a. Now figure number c is the device structure of a single crystal MAPbBr3 film deposited solar cell and its photovoltaic performance.

d is the effect of the single crystal MAPbBr3 thickness on the photovoltaic performance of the single crystal solar cells and finally e is the schematic illustration of a lateral structure single crystalline perovskite solar cell and its photovoltaic performance. So as you can see and if you look at the performance of the pure polycrystalline perovskite film with the perovskite single crystal we can see that still the performance of the film is not as expected as its optical and electrical properties demand it is to be.

And the reason behind it is that it is very difficult to grow the perovskite single crystal uniform film on a substate or in a device geometry, but there are lot of research group which are working on it to make a very uniform and large perovskite single crystal which will be useful for the solar cell device.

(Refer Slide Time: 04:52)



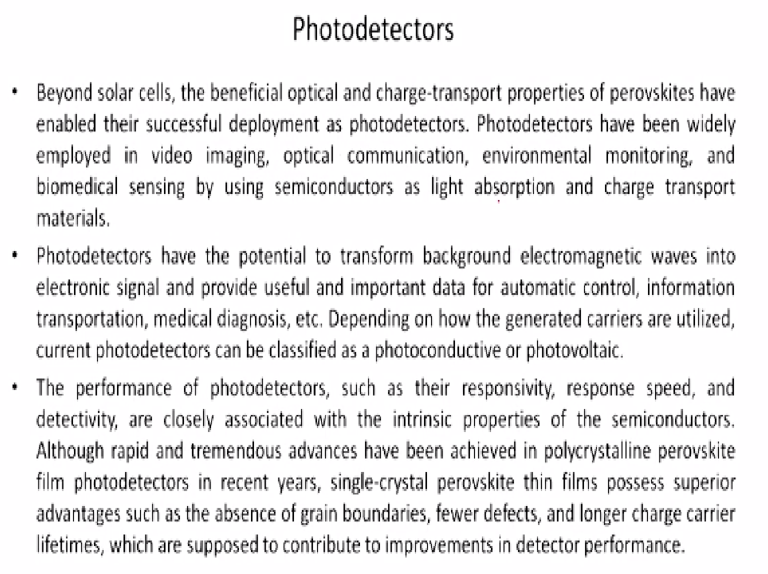
- Increasing the absorber thickness from 4 to 10 μm will increase the serial resistance of the device and reduce the FF. When a 60 μm-thick single-crystalline film was used, the *Jsc*, *Voc*, and FF decreased dramatically because the charge carrier cannot be collected efficiently.
- To overcome the drawbacks of this high intrinsic resistance, the Huang group designed and prepared a lateral structured single-crystalline perovskite solar cell (Figure 4e,f).
- Instead of collecting carriers in the vertical direction (carriers need to be transported through a thick absorber layer), the carrier was harvested in the lateral direction, during which the charge transport length is reduced, and the collection efficiency could be effectively enhanced, giving a PCE of 1.88%. However, Au electrodes were used for both the cathode and anode. The p–i–n regions were created by electric polling, which will introduce defects or crystal distortions, increasing the carrier recombination.
- It is reasonable to expect that the PCE of the lateral single-crystal-line perovskite solar cell could be further improved using more efficient hole and electron transport layers.

Increasing the absorber thickness from 4 to 10 micron will increase the serial resistance of the device and reduce the fill factor. When a 60 micrometre thick single crystalline film was used the Jsc, Voc and fill factor decrease dramatically because the charge carrier cannot be corrected efficiently. To overcome the drawbacks of this high intrinsic resistance, one of the research group, the Hung group designed and prepared a lateral structure single crystalline perovskite solar cell.

Instead of collecting carriers in the vertical direction, carriers need to be transported through a thick absorber layer, the carrier was harvested in the lateral direction during which the charge transport length is reduced and the collection efficiency could be effectively enhanced giving a photovoltaic performance of 1.88%, but you can still say that it is much lower in comparison to the bulk counterpart.

However, the gold electrode were used for both the cathode and anode, the p-i-n regions were created by electric polling which will introduce defects or crystal distortion increasing the career recombination. Now in the both side if we use gold electrode then there is nothing to extract the charge carrier. That is why they have done the electric polling. It is reasonable to expect that the PCE of the lateral single-crystal-line perovskite solar cell could be further improved using more efficient hole and electron transport layer.

(Refer Slide Time: 06:01)



Photodetectors

- Beyond solar cells, the beneficial optical and charge-transport properties of perovskites have enabled their successful deployment as photodetectors. Photodetectors have been widely employed in video imaging, optical communication, environmental monitoring, and biomedical sensing by using semiconductors as light absorption and charge transport materials.
- Photodetectors have the potential to transform background electromagnetic waves into electronic signal and provide useful and important data for automatic control, information transportation, medical diagnosis, etc. Depending on how the generated carriers are utilized, current photodetectors can be classified as a photoconductive or photovoltaic.
- The performance of photodetectors, such as their responsivity, response speed, and detectivity, are closely associated with the intrinsic properties of the semiconductors. Although rapid and tremendous advances have been achieved in polycrystalline perovskite film photodetectors in recent years, single-crystal perovskite thin films possess superior advantages such as the absence of grain boundaries, fewer defects, and longer charge carrier lifetimes, which are supposed to contribute to improvements in detector performance.

Now one of the important application which we will discuss before completing this lecture is the photodetectors. Now beyond solar cell the beneficial optical and charge transport properties of the perovskite have enabled their successful deployment as photodetectors. Now we have all used photodetectors in all kind of optical and electronic circuits.

Whether it is a PMT or whether it is a CCD or whether it is a silicone photo diode we have seen that this photodetectors have been used again and again in various optical and electronic devices. Now this perovskite single crystal can also be useful for making the photodetectors not only in the optical range, but sometimes it can also be extended in the x-ray range also.

Now photodetectors have been widely employed in video imaging, optical communication, environmental monitoring and biomedical sensing by using semiconductors as light absorption and charge transfer materials. Photodetectors have the potential to transfer background electromagnetic waves into the electronic signal and provide useful and important data for automatic control, information transportation, medical diagnosis et cetera.

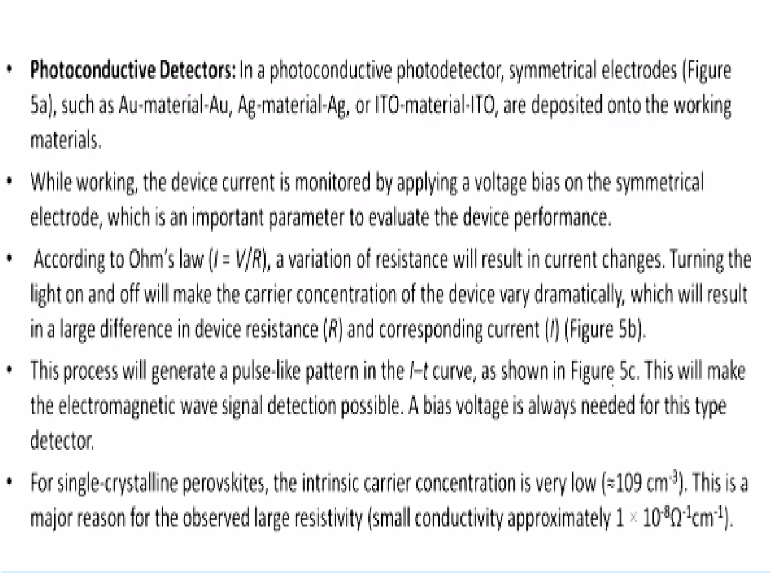
Depending on how the generated carriers are utilised current photodetectors can be classified as a photoconductive or photovoltaic. The performance of photodetectors such as the responsivity, response speed and directivity are closely associated with the intrinsic properties of the semiconductors. All the rapid and tremendous advanced have been achieved in polycrystalline perovskite film photodetectors in recent years.

Single crystal perovskite thin film possess superior advantage such as the absence of grain boundaries, fewer defects and longer charge carrier lifetime which are supposed to contribute to improvements in the detector performance okay. Now whenever we talk about any detector. So what are the properties of a detector we look about.

We look for its responsivity, we look for its response speed, we will look for its detectivity and also some of the intrinsic properties of the semiconductor. Now there are different semiconducting material like silicon, gallium arsenide, these are being used to make photodetectors, but if you use perovskite single crystal as a photodetectors then all of these detection properties like responsivity, response speed and detectivity that changes significantly in comparison to the bulk counterparts.

So that is why perovskite single crystal has been widely used to fabricate a photodetector material.

(Refer Slide Time: 08:12)



- **Photoconductive Detectors:** In a photoconductive photodetector, symmetrical electrodes (Figure 5a), such as Au-material-Au, Ag-material-Ag, or ITO-material-ITO, are deposited onto the working materials.
- While working, the device current is monitored by applying a voltage bias on the symmetrical electrode, which is an important parameter to evaluate the device performance.
- According to Ohm's law ($I = V/R$), a variation of resistance will result in current changes. Turning the light on and off will make the carrier concentration of the device vary dramatically, which will result in a large difference in device resistance (R) and corresponding current (I) (Figure 5b).
- This process will generate a pulse-like pattern in the I–t curve, as shown in Figure 5c. This will make the electromagnetic wave signal detection possible. A bias voltage is always needed for this type detector.
- For single-crystalline perovskites, the intrinsic carrier concentration is very low (≈109 cm^{-3}). This is a major reason for the observed large resistivity (small conductivity approximately $1 \times 10^{-8} \Omega^{-1} cm^{-1}$).

Photoconductive Detectors: In a photoconductive photodetector symmetrical electrodes such as gold-material-gold, so you see that the material has been sandwiched between the 2 gold electrode or silver-material-silver where the material has been sandwiched between the 2 silver electrode or ITO-material-ITO where the material has been sandwiched between the 2 ITO electrodes are deposited on to the working materials.

While working the device current is monitored by applying a voltage bias on the symmetrical electrode which is an important parameter to evaluate the device performance. According to Ohm's law I = V/R, a variation of resistance will result in current changes. Turning the light on and off will make the carrier concentration of the device very dramatically, which will result in a large difference in device resistance R and corresponding current I.

This process will generate a pulse-like pattern in the I-t curve as shown in the next figure. This will make the electromagnetic wave signal detection possible. If bias voltage is always needed for this type of detector for single crystal perovskite the intrinsic carrier concentration is very low, somewhere around 109 centimetre inverse cube. This is the major reason for the observed large resistivity. Small conductivity approximately 1 * 10 to the power -8 ohm inverse centimetre inverse.

(Refer Slide Time: 09:27)

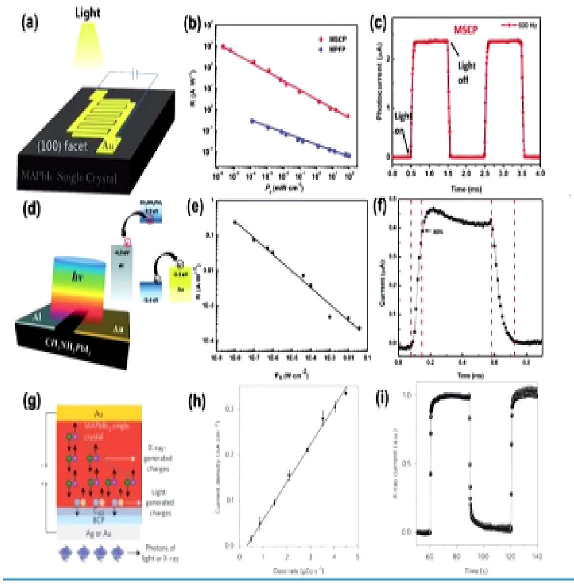
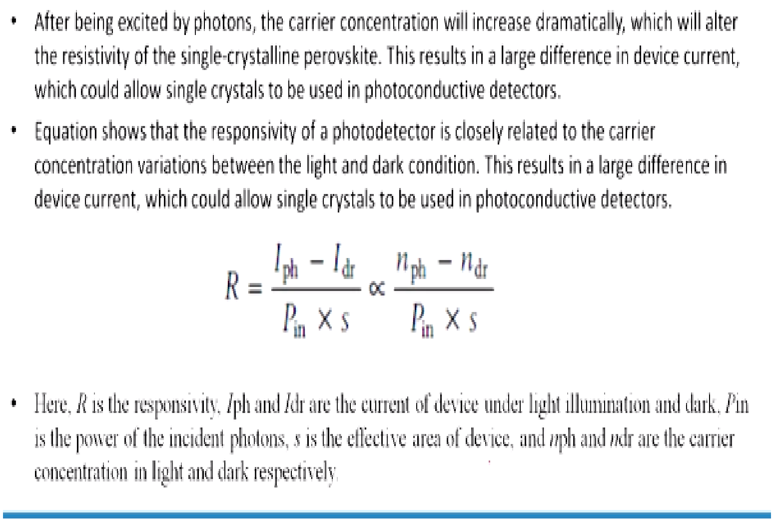


Figure 5. The single-crystalline perovskite-based photodetectors and their performances.

So here we are showing the photoconductive mode single crystal perovskite, as you can see that the photodetectors, this region is the light on and then there is a light off. So there is a sequential things of this. This is the photo current versus time. Similarly, the current versus time has been shown here and then the same photodetectors as I said that it has been used for also the x-ray detection, where the y-axis is the x-ray current, and x-axis is the time.

(Refer Slide Time: 09:52)



- After being excited by photons, the carrier concentration will increase dramatically, which will alter the resistivity of the single-crystalline perovskite. This results in a large difference in device current, which could allow single crystals to be used in photoconductive detectors.
- Equation shows that the responsivity of a photodetector is closely related to the carrier concentration variations between the light and dark condition. This results in a large difference in device current, which could allow single crystals to be used in photoconductive detectors.

$$R = \frac{I_{ph} - I_{dr}}{P_{in} \times s} \propto \frac{n_{ph} - n_{dr}}{P_{in} \times s}$$

- Here, *R* is the responsivity, *I*ph and *I*dr are the current of device under light illumination and dark. *P*in is the power of the incident photons, *s* is the effective area of device, and *n*ph and *n*dr are the carrier concentration in light and dark respectively.

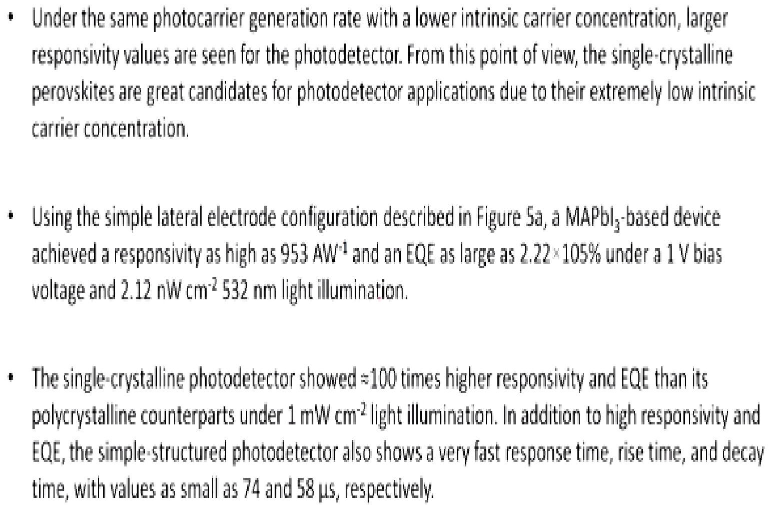
After being excited by photons the carrier concentration will increase dramatically which will alter the resistivity of the single crystalline perovskite. This results in a large difference in device current which could allow single crystal to be used in photoconductive detectors. Equation shows that responsivity of a photodetector is closely related to the carrier concentration variations between the light and dark condition.

This results in a large difference in device current which could allow single crystal to be used in photoconductive detectors. For example, the responsivity, we can write it as IPH, where the I photo current minus I dark current into the power input into the S, the area, that is proportional to the n the number of the photocurrent charge carrier minus number of the dark current into the input power into the area.

Here R is the responsivity, Iph and Idr is the current of the device under light illumination and dark. P input is the power fo the incident photons and s is the effective area of the device. So responsivity of the detector that depends upon the photocurrent, it depends upon the dark current, it depends upon the input power and it depends upon the area of the detector also. So the responsivity is inversely proportional to the input power.

And it is inversely proportional to the area that we expect, if we increase the area responsivity will decrease, if we have a small area then the responsivity will increase and nph and ndr are the current concentration in light and dark respectively.

(Refer Slide Time: 11:16)



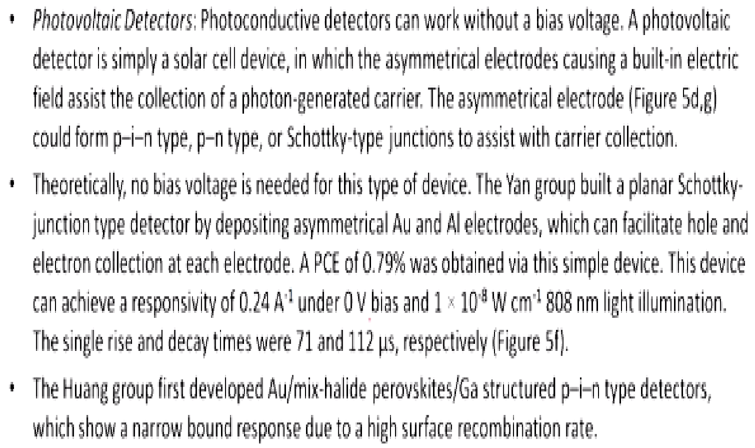
- Under the same photocarrier generation rate with a lower intrinsic carrier concentration, larger responsivity values are seen for the photodetector. From this point of view, the single-crystalline perovskites are great candidates for photodetector applications due to their extremely low intrinsic carrier concentration.
- Using the simple lateral electrode configuration described in Figure 5a, a MAPbI$_3$-based device achieved a responsivity as high as 953 AW^{-1} and an EQE as large as 2.22 × 105% under a 1 V bias voltage and 2.12 nW cm^{-2} 532 nm light illumination.
- The single-crystalline photodetector showed ≈100 times higher responsivity and EQE than its polycrystalline counterparts under 1 mW cm^{-2} light illumination. In addition to high responsivity and EQE, the simple-structured photodetector also shows a very fast response time, rise time, and decay time, with values as small as 74 and 58 μs, respectively.

Under the same photocarrier generation rate with the lower intrinsic carrier concentration, larger responsivity values are seen for the photodetector. From this point of view, the single crystalline perovskite are great candidates for photodetectors application due to their extremely low intrinsic carrier concentration. Using the simple lateral electrode configuration described in the figure MAPbI3 based device achieved resposivity as high as 953 ampere per watt.

And an EQE as large as 2.22 * 105% under a 1 volt bias voltage and 2.12 nanowatts centimetre inverse at 532 nanometre light illumination. The single crystal photodetector showed 100 times higher responsivity and EQ than its polycrystalline counter parts under 1 milliwatt centimetre inverse light illumination. In addition to the high responsivity and EQE the simple structure photodetectors also shows a very fast response time.

Rise time and decay time with values as small as 74 and 58 microsecond respectively. So all the other properties is also useful of the perovskite single crystal as far as the detection is concerned. Now as I said that this perovskite single crystal can also work in a photovoltaic mode. Now what is a photovoltaic detectors?

(Refer Slide Time: 12:27)



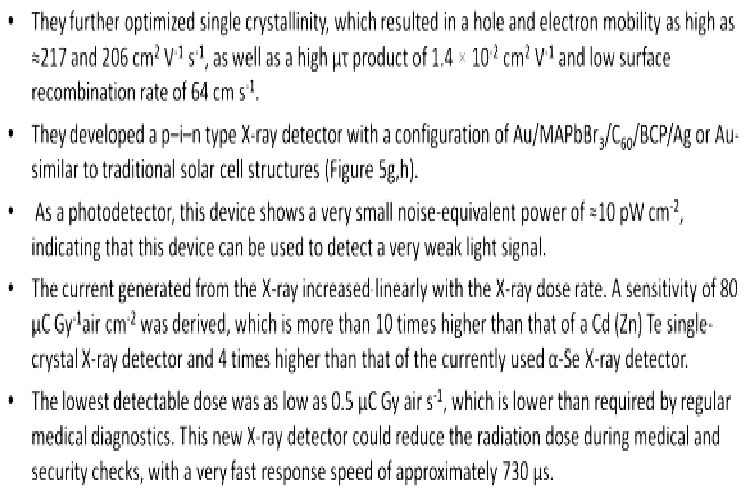
- *Photovoltaic Detectors*: Photoconductive detectors can work without a bias voltage. A photovoltaic detector is simply a solar cell device, in which the asymmetrical electrodes causing a built-in electric field assist the collection of a photon-generated carrier. The asymmetrical electrode (Figure 5d,g) could form p–i–n type, p–n type, or Schottky-type junctions to assist with carrier collection.
- Theoretically, no bias voltage is needed for this type of device. The Yan group built a planar Schottky-junction type detector by depositing asymmetrical Au and Al electrodes, which can facilitate hole and electron collection at each electrode. A PCE of 0.79% was obtained via this simple device. This device can achieve a responsivity of 0.24 A^{-1} under 0 V bias and 1×10^{-8} W cm^{-1} 808 nm light illumination. The single rise and decay times were 71 and 112 µs, respectively (Figure 5f).
- The Huang group first developed Au/mix-halide perovskites/Ga structured p–i–n type detectors, which show a narrow bound response due to a high surface recombination rate.

Photoconductive detectors can work without a bias voltage or a photovoltaic detector is simply a solar cell device. In which the asymmetrical electrode causing a built in electric field assist the collection of a photon-generated-carrier. The asymmetric electrode could form p-i-n type, p-n type or Schottky-type junctions to assist with carrier collection. Theoretically, no bias voltage is needed for this type of device.

The Yan group built a planar Schottky-junction type detector by depositing asymmetrical golden aluminium electrodes which can facilitate hole and electron collection at each electrode. A PCE of 0.79% was obtained by this inbuilt device. This device can achieve a responsivity of 0.24 ampere inverse under 0 voltage bias and 1 * 10 to the power -8 watt per centimetre square at 800 nanometre light illumination.

The single rise and decay times were 71 and 112 microsecond respectively and Huang group first developed gold mix halide perovskite gallium structure p-i-n type detectors which shows a narrow bound response due to a high surface recombination rate.

(Refer Slide Time: 13:27)



- They further optimized single crystallinity, which resulted in a hole and electron mobility as high as ≈217 and 206 cm^2 V^{-1} s^{-1}, as well as a high μτ product of 1.4 × 10^{-2} cm^2 V^{-1} and low surface recombination rate of 64 cm s^{-1}.
- They developed a p–i–n type X-ray detector with a configuration of Au/MAPbBr$_3$/C$_{60}$/BCP/Ag or Au-similar to traditional solar cell structures (Figure 5g,h).
- As a photodetector, this device shows a very small noise-equivalent power of ≈10 pW cm^{-2}, indicating that this device can be used to detect a very weak light signal.
- The current generated from the X-ray increased linearly with the X-ray dose rate. A sensitivity of 80 μC Gy^{-1}air cm^{-2} was derived, which is more than 10 times higher than that of a Cd (Zn) Te single-crystal X-ray detector and 4 times higher than that of the currently used α-Se X-ray detector.
- The lowest detectable dose was as low as 0.5 μC Gy air s^{-1}, which is lower than required by regular medical diagnostics. This new X-ray detector could reduce the radiation dose during medical and security checks, with a very fast response speed of approximately 730 μs.

They further optimize the single crystallinity which resulted in a hole and electron mobility as high as 217 and 206 centimetre inverse per volt inverse per second inverse as well as how the product of the mobility and the tau, the lifetime that is 1.4 * 10 to the power - 2 centimetre square volt inverse and low surface recommendation rate of 64 centimetre per second inverse.

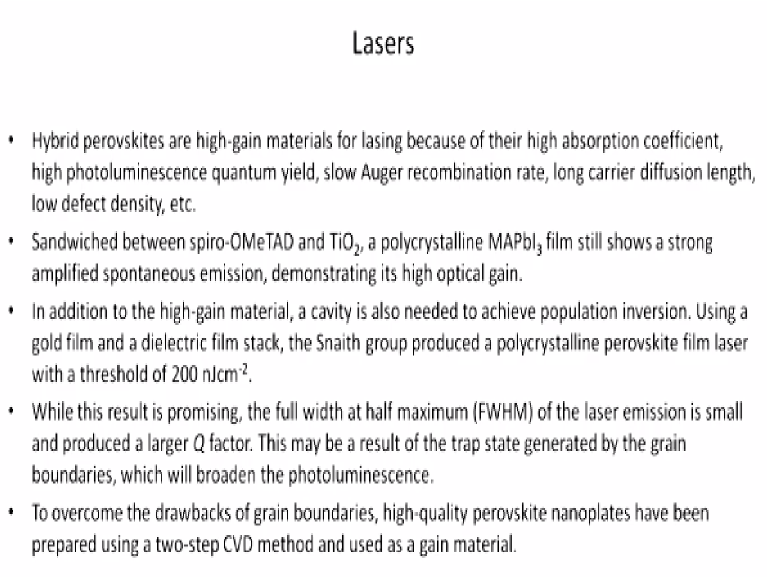
So that means not only the product of the mu and tau increase the surface recombination rate also reduce or the surface recombination rate also reduce because of this perovskite single crystal. They developed p-i-n type x-ray detector also with a configuration of gold MAPbBr3, C60, BCP, Ag or Au similar to traditional solar cell structure. Now in a solar cell structure we use gold and silver.

Like this is an asymmetry between the 2 metal electrodes. So whenever we are talking about the photovoltaic mode we are working in an asymmetric device. So you see that we put gold and silver on the other end right and in between we put the MAPbBr3 and then C60 and BCP. C60 is a small molecule, BCP is another small molecule, but when you work in a photoconductive mode we work in a symmetrical device pattern.

The current generated from the x-ray increased linearly with the x-ray dose rate. A sensitivity of 80 microcoulomb Gy inverse air centimetre -2 was derived which is more than 10 times higher than that of a cadmium or zinc chloride single crystal x-ray detector and four times higher than that of the currently used alpha selenium x-ray detector.

Now in terms of the lasers like perovskite the single crystal has also have been used for fabricating lasers.

(Refer Slide Time: 15:00)



Lasers

- Hybrid perovskites are high-gain materials for lasing because of their high absorption coefficient, high photoluminescence quantum yield, slow Auger recombination rate, long carrier diffusion length, low defect density, etc.
- Sandwiched between spiro-OMeTAD and TiO_2, a polycrystalline $MAPbI_3$ film still shows a strong amplified spontaneous emission, demonstrating its high optical gain.
- In addition to the high-gain material, a cavity is also needed to achieve population inversion. Using a gold film and a dielectric film stack, the Snaith group produced a polycrystalline perovskite film laser with a threshold of 200 $nJcm^{-2}$.
- While this result is promising, the full width at half maximum (FWHM) of the laser emission is small and produced a larger *Q* factor. This may be a result of the trap state generated by the grain boundaries, which will broaden the photoluminescence.
- To overcome the drawbacks of grain boundaries, high-quality perovskite nanoplates have been prepared using a two-step CVD method and used as a gain material.

Hybrid perovskite are high gain materials for lasing because of their high absorption coefficient, high photoluminescence quantum yield, slow Auger recombination rate, long carrier diffusion length, and low defect density. Now all of this properties we have explained earlier like a high absorption coefficient right. So the perovskite single crystal has a very high absorption coefficient.

And the photoluminescence quantum yield that is the number of photons it can emit per absorbed incident light. So that is also very high. Since the defect states is lower the recombination rate is also very lower and the carrier diffusion length is longer and also the defect density of state is lower. So because of that this perovskite single crystal is also useful for fabricating lasers.

Because for a laser we are mainly looking for 2 properties, one is this photoluminescence quantum yield and another is the defect density. Sandwiched between spiro-OMeTAD and titanium dioxide a polycrystalline MAPbI3 films still shows this strong amplified spontaneous emission demonstrating its high optical again.

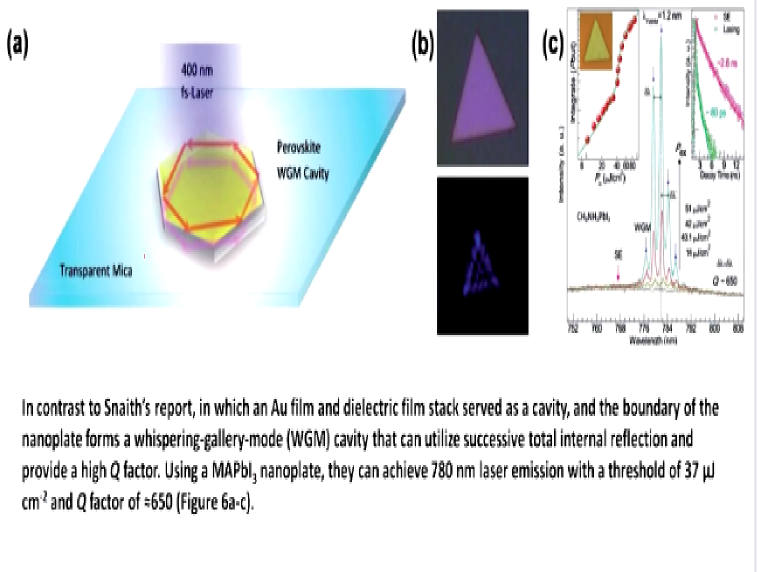
Now if we have done some basic optics we know that usually the number of the charge carriers in the excited state in an equilibrium is less than the number of charge carrier in the ground state that is the normal condition, but for the lasing to happen the number of the electrons or number of the charge carrier or number of the atoms whatever you say in an excited state should be higher than the number of the ground state.

A situation called the population inversion. So now if a population inversion is there in the system then there will be a spontaneous emissions. Now this amplified spontaneous emissions that is possible in a MAPbI3 perovskite single crystal when fabricated along with a small molecule like spiro-OMeTAD and Titanium dioxide.

In addition to high gain material a cavity is also needed to achieve population inversion. Using a gold film and a dielectric film stack, the Snaith group produced a polycrystalline perovskite film laser with a threshold of 200 nano Joule per centimetre square. While this result is promising the full width at half maximum of the laser emission is small and produced larger Q factor.

This maybe a result of the trap state generated by the grain boundaries which will broaden the photoluminescence. To overcome the drawbacks of gain boundaries high quality perovskite nanoplatelets have been prepared using 2 step CVD method and used as a grain material.

(Refer Slide Time: 17:32)

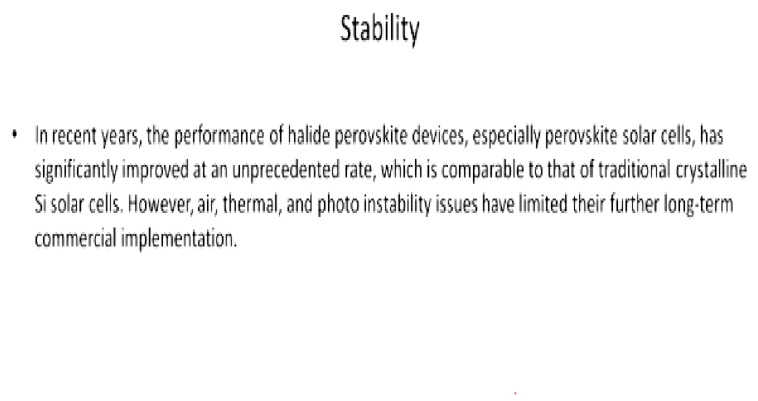


In contrast to Snaith's report, in which an Au film and dielectric film stack served as a cavity, and the boundary of the nanoplate forms a whispering-gallery-mode (WGM) cavity that can utilize successive total internal reflection and provide a high *Q* factor. Using a $MAPbI_3$ nanoplate, they can achieve 780 nm laser emission with a threshold of 37 μJ cm^{-2} and *Q* factor of ≈650 (Figure 6a-c).

Now in contrast to the Snaith's report in which the gold film and the dielectric film stack served as a cavity and the boundary of the nanoplate forms a whispering-gallery-mode cavity that can utilise successful total internal reflection and provide the high Q factor using MAPbI3 nanoplate they can achieve 780 nanometer laser emission with a threshold of 37 micro Joule centimetre -2 and Q factor of 650.

So you see that here the perovskite single crystal is working in a whispering-gallery-mode and here the lasing has been shown and the lasing threshold is happen like in a very small level.

(Refer Slide Time: 18:12)



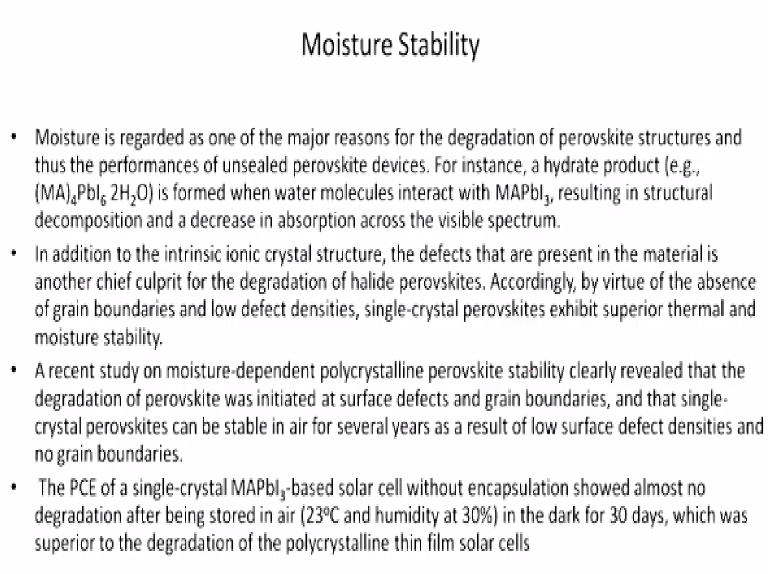
Stability

- In recent years, the performance of halide perovskite devices, especially perovskite solar cells, has significantly improved at an unprecedented rate, which is comparable to that of traditional crystalline Si solar cells. However, air, thermal, and photo instability issues have limited their further long-term commercial implementation.

Now the stability of the perovskite single crystal is also higher than the bulk counterpart. In recent years the performance of halide perovskite devices especially perovskite solar cells have significantly improved at an unprecedented rate which is comparable to that of traditional crystalline silicon solar cells.

However, air, thermal and photo instabilities issues have limited their further long term commercial implementation one of the major problem with the perovskite device.

(Refer Slide Time: 18:33)



Moisture Stability

- Moisture is regarded as one of the major reasons for the degradation of perovskite structures and thus the performances of unsealed perovskite devices. For instance, a hydrate product (e.g., $(MA)_4PbI_6\ 2H_2O$) is formed when water molecules interact with $MAPbI_3$, resulting in structural decomposition and a decrease in absorption across the visible spectrum.
- In addition to the intrinsic ionic crystal structure, the defects that are present in the material is another chief culprit for the degradation of halide perovskites. Accordingly, by virtue of the absence of grain boundaries and low defect densities, single-crystal perovskites exhibit superior thermal and moisture stability.
- A recent study on moisture-dependent polycrystalline perovskite stability clearly revealed that the degradation of perovskite was initiated at surface defects and grain boundaries, and that single-crystal perovskites can be stable in air for several years as a result of low surface defect densities and no grain boundaries.
- The PCE of a single-crystal $MAPbI_3$-based solar cell without encapsulation showed almost no degradation after being stored in air (23°C and humidity at 30%) in the dark for 30 days, which was superior to the degradation of the polycrystalline thin film solar cells

Now for example the moisture stability, moisture is regarded as one of the major reasons for the degradation of perovskite structure and thus the performance of unsealed perovskite devices. For instance, a hydrated product for example MA4 PbI6 2H2O is formed when water molecules interact with PbI3 resulting in structural decomposition and decrease in absorption across the visible spectrum.

So if I make a MAPbI3 perovskite film and if we just leave it in the normal environment condition what will happen? Perovskite film will absorb the moisture from the water and they will make a compound, this one MA4 PbI6 2H2O and it will further degrade and basically the crystal structure of the perovskite is lost and its absorptions as well as the charge transport properties will be suffered.

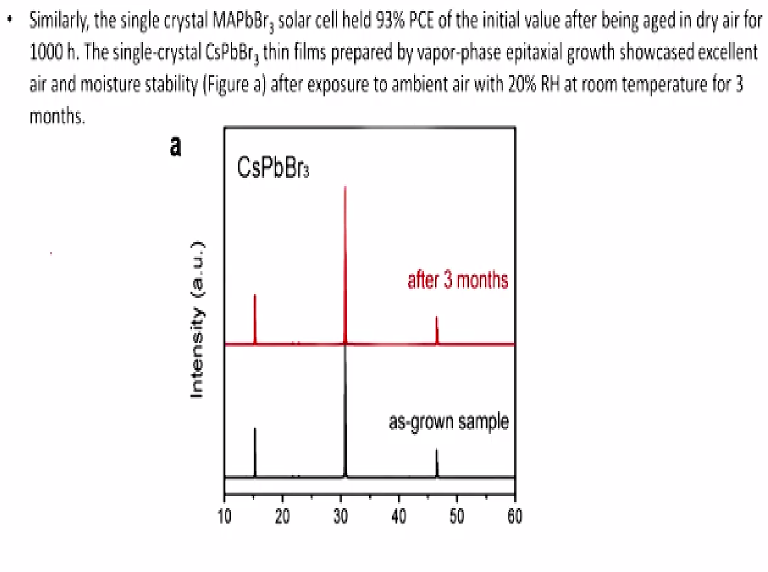
In addition to the intrinsic ionic crystal structure the defects that are present in the material is another cheap problem for the degradation of halide perovskites. Accordingly, by virtue of the absence of grain boundaries and low defect states single crystal perovskites exhibit superior thermal and moisture stability. A result study on moisture dependent polycrystalline perovskite stability clearly reveal that.

The degradation of perovskite was initiated at surface defects and grain boundaries and that single crystal perovskite can be stable in air for several years as a result of low surface defect densities and no grain boundaries. See in perovskite single crystal there is a less number of grain boundaries and there are less number of defect state. So here the thermal stability is also very high in comparison to the polycrystalline film.

The power conversion efficiency or the PC of a single crystal MAPbI3 based solar cell without encapsulation showed almost no degradation after being stored in air at 23 degree Celsius and humidity level of 30% in the dark for 30 days which was superior to the degradation of the polycrystalline thin film solar cells.

So an experiment was performed and polycrystalline perovskite solar cell as well as a single crystal perovskite solar cell was kept in the air and it has been found that the single crystal device is more thermally stable than its polycrystalline counterparts.

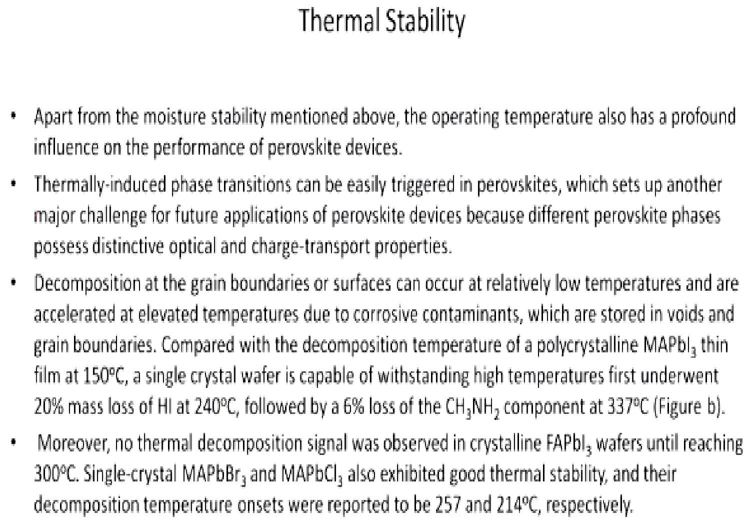
(Refer Slide Time: 20:42)



- Similarly, the single crystal $MAPbBr_3$ solar cell held 93% PCE of the initial value after being aged in dry air for 1000 h. The single-crystal $CsPbBr_3$ thin films prepared by vapor-phase epitaxial growth showcased excellent air and moisture stability (Figure a) after exposure to ambient air with 20% RH at room temperature for 3 months.

Similarly, the single crystal MAPbBr3 solar cell held 93% power conversion efficiency or PCE of the initial value after being aged in dry air for 1000 hour. A single-crystal CsPbBr3 thin films prepared by vapor phase epitaxial growth showcased excellent air and moisture stability after exposure to ambient air with 20% relative humidity RH at room temperature for 3 months.

(Refer Slide Time: 21:06)



Thermal Stability

- Apart from the moisture stability mentioned above, the operating temperature also has a profound influence on the performance of perovskite devices.
- Thermally-induced phase transitions can be easily triggered in perovskites, which sets up another major challenge for future applications of perovskite devices because different perovskite phases possess distinctive optical and charge-transport properties.
- Decomposition at the grain boundaries or surfaces can occur at relatively low temperatures and are accelerated at elevated temperatures due to corrosive contaminants, which are stored in voids and grain boundaries. Compared with the decomposition temperature of a polycrystalline $MAPbI_3$ thin film at 150°C, a single crystal wafer is capable of withstanding high temperatures first underwent 20% mass loss of HI at 240°C, followed by a 6% loss of the CH_3NH_2 component at 337°C (Figure b).
- Moreover, no thermal decomposition signal was observed in crystalline $FAPbI_3$ wafers until reaching 300°C. Single-crystal $MAPbBr_3$ and $MAPbCl_3$ also exhibited good thermal stability, and their decomposition temperature onsets were reported to be 257 and 214°C, respectively.

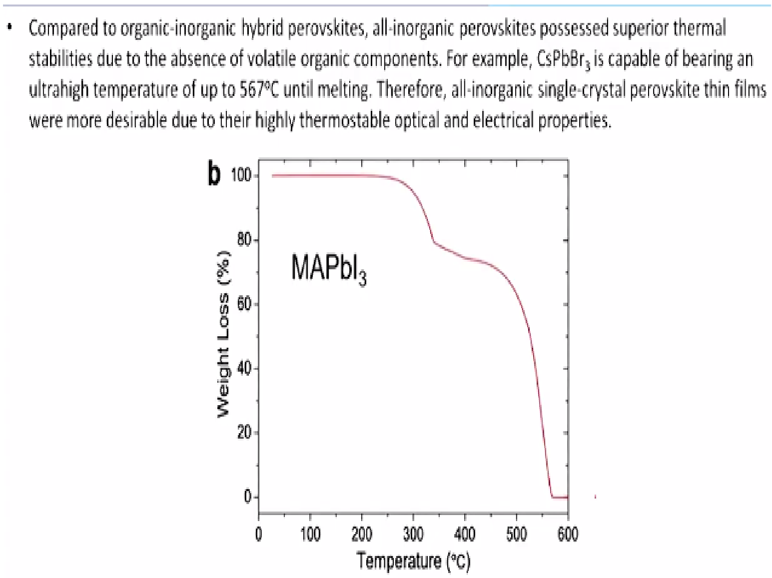
What about the thermal stability? Apart from the moisture stability mentioned above the operating temperature also has a profound influence on the performance of the perovskite device. So we have seen that perovskite shows the temperature dependent crystal structure change. Now if the temperature of the environment changes so then the perovskite crystal structure also changes.

That means the transport properties also changes. Thermally induced phase transitions can be easily triggered in perovskite which sets up another major challenge for further application of perovskite device because different perovskite phases possess distinct optical and charge transport properties. So if I go from orthorhombic to tetragonal phase of the perovskite, the optical properties and the electronic properties and charge transport properties will be way different.

Decomposition at the grain boundary or surface can occur at relatively low temperatures and are accelerated at elevated temperatures due to corrosive contaminants which are stored in voids and grain boundaries. Compared with the decomposition temperature of a polycrystalline MAPbI3 thin film at 150 degree Celsius, a single crystal wafer is capable of withstanding high temperatures first underwent 20% mass loss of HI at 240 degree Celsius followed by 6% loss of CH3NH2 component at 337 degree centigrade.

Moreover, no thermal decomposition signal was observed in crystalline FAPbL3 wafer until reaching 300 degree Celsius. So instead of MAPbI3 if you make FAPbI3 so then the decreasing temperature increase further. So stability increase further. Single crystal MAPbBr3 and MAPbCl3 also exhibited good thermal stability and the decomposition temperature onsets were reported to be 257 and 214 degree Celsius respectively.

(Refer Slide Time: 22:49)

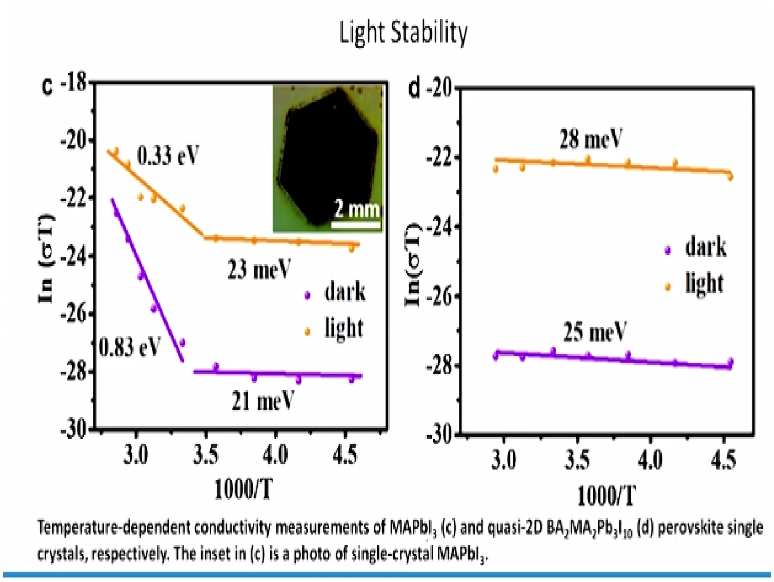


- Compared to organic-inorganic hybrid perovskites, all-inorganic perovskites possessed superior thermal stabilities due to the absence of volatile organic components. For example, $CsPbBr_3$ is capable of bearing an ultrahigh temperature of up to 567°C until melting. Therefore, all-inorganic single-crystal perovskite thin films were more desirable due to their highly thermostable optical and electrical properties.

Compared to the organic-inorganic hybrid perovskite, all inorganic perovskite possessed superior thermal stability due to the absence of the volatile organic components for example CsPbBr3 is cable of bearing an ultrahigh temperature of up to 567 degree Celsius until melting therefore all inorganic single crystal perovskite thin films were more desirable than their organic counterpart.

Because the optical and electrical properties is more stable here. For example, like you know if I make an all inorganic perovskite single crystal CsPbBr3, so it can go until 567 degree before it melts so this data is obtained from the TG data, thermal gravimetric analysis. Now since it can withstand a very high temperature, so that is why this kind of perovskite single crystal is more suitable if you are considering a huge temperature variation.

(Refer Slide Time: 23:39)

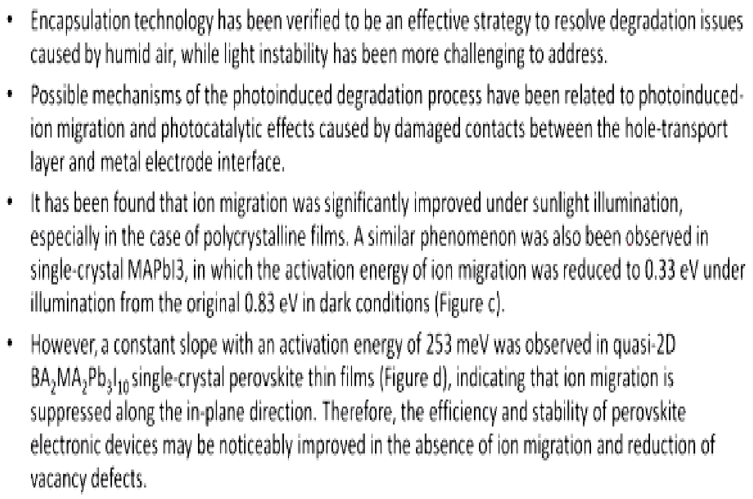

Light Stability

Temperature-dependent conductivity measurements of MAPbI$_3$ (c) and quasi-2D BA$_2$MA$_2$Pb$_3$I$_{10}$ (d) perovskite single crystals, respectively. The inset in (c) is a photo of single-crystal MAPbI$_3$.

The third important factor is the light stability. Now we have mentioned when we have talked about the perovskite solar cell that the ionic part in the perovskite crystal they start diffusing when the light exposed on it. A property commonly known as the ion migration. Now that was the intrinsic instability in the perovskite devices. Now when we make a perovskite single crystal this ion migration property is also reduced.

For example, like you know here the temperature dependent conductivity measurement of MAPbI3 and the quasi-2D BA2 MAPbI3 and perovskite single crystal is shown here. Now in the case of the perovskite single crystal the light stability is higher in comparison to their polycrystalline counterpart.

(Refer Slide Time: 24:19)



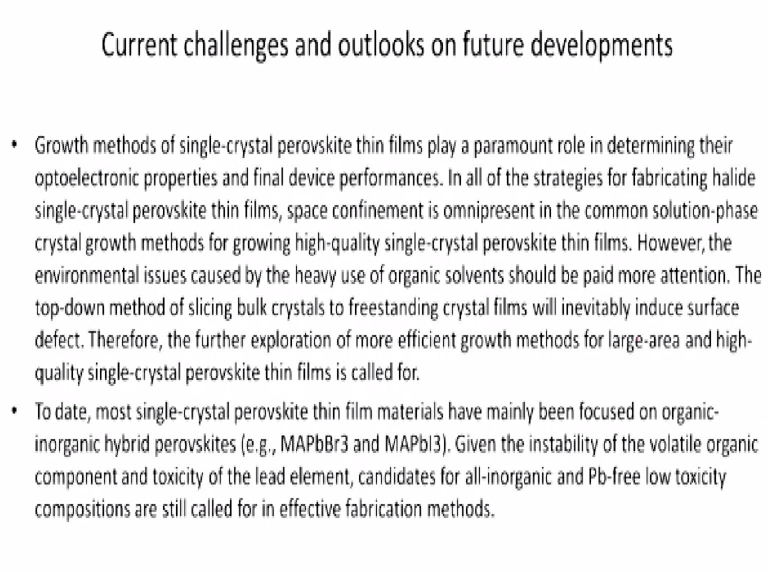
- Encapsulation technology has been verified to be an effective strategy to resolve degradation issues caused by humid air, while light instability has been more challenging to address.
- Possible mechanisms of the photoinduced degradation process have been related to photoinduced-ion migration and photocatalytic effects caused by damaged contacts between the hole-transport layer and metal electrode interface.
- It has been found that ion migration was significantly improved under sunlight illumination, especially in the case of polycrystalline films. A similar phenomenon was also been observed in single-crystal MAPbI3, in which the activation energy of ion migration was reduced to 0.33 eV under illumination from the original 0.83 eV in dark conditions (Figure c).
- However, a constant slope with an activation energy of 253 meV was observed in quasi-2D BA$_2$MA$_2$Pb$_3$I$_{10}$ single-crystal perovskite thin films (Figure d), indicating that ion migration is suppressed along the in-plane direction. Therefore, the efficiency and stability of perovskite electronic devices may be noticeably improved in the absence of ion migration and reduction of vacancy defects.

And finally the encapsulation technology has been verified to be an effective strategy to resolve degradation issues caused by humid air, white light instability has been more challenging to address, possible mechanism of the photo induced degradation process have been related to photo induced ion migration and photocatalytic effects caused by damaged contacts between the whole transport layer and metal electrode interface.

I have been found that ion migration was significantly improved under sunlight illumination especially in the case of polycrystalline film. A similar phenomenon was also been observed in single crystal MAPbI3 in which the activation energy of ion migration was reduced to 0.33 electron volt under the illumination from the original 0.83 electron volt in dark condition. So also in a single crystal MAPbI3 film so what happens the ion migration is observed.

However, a constant slope with an activation energy of 253 millielectron volt was observed in a quasi-2D BA2MA2PbI3 I10 single crystal perovskite thin film indicating that ion migration is suppressed along the in-plane direction. Therefore, the efficiency and stability of perovskite electronic device may be noticeably improved in the absence if ion migration and reduction of the vacancy defects.

(Refer Slide Time: 25:34)



Current challenges and outlooks on future developments

- Growth methods of single-crystal perovskite thin films play a paramount role in determining their optoelectronic properties and final device performances. In all of the strategies for fabricating halide single-crystal perovskite thin films, space confinement is omnipresent in the common solution-phase crystal growth methods for growing high-quality single-crystal perovskite thin films. However, the environmental issues caused by the heavy use of organic solvents should be paid more attention. The top-down method of slicing bulk crystals to freestanding crystal films will inevitably induce surface defect. Therefore, the further exploration of more efficient growth methods for large-area and high-quality single-crystal perovskite thin films is called for.
- To date, most single-crystal perovskite thin film materials have mainly been focused on organic-inorganic hybrid perovskites (e.g., MAPbBr3 and MAPbI3). Given the instability of the volatile organic component and toxicity of the lead element, candidates for all-inorganic and Pb-free low toxicity compositions are still called for in effective fabrication methods.

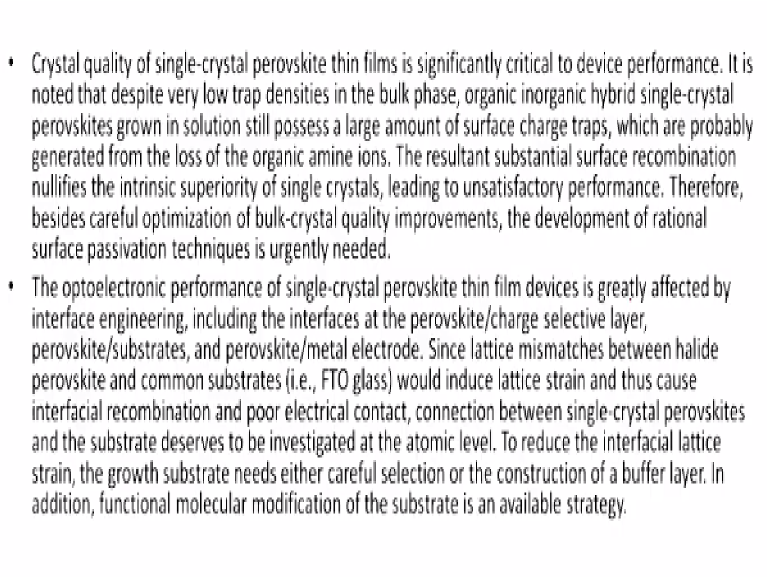
So what are the current challenges and outlooks on future developments? Growth methods of the single crystal perovskite thin film play a paramount role in determining their optoelectronic properties and final device performance. Now the perovskite single crystal can grow in several different methods. We have discussed all these method.

Now this growth method can influence their morphology, can influence their photo physical properties that is why the optoelectronic properties especially the device properties can heavily depend on the growth method. In all of the strategies for fabricating halide single-crystal perovskite thin-film space confinement is only present in the common solution phase crystal growth method for growing high quality single crystal perovskite thin films.

However, the environmental issues caused by the heavy use of organic solvents should be paid more attention. The top down method of slicing bulb crystal to freestanding crystal films will inevitably induce surface defect. Therefore, the further expression of more efficient growth methods for large area and high quality single perovskite thin films is called for. To date, most single crystal perovskite thin film materials have mainly been focused on organic inorganic hybrid perovskite as per example MAPbBr3 and MAPbI3.

Given the instability of the volatile organic component and toxicity of the lead element candidates for all inorganic and lead free low toxicity compositions are still called for in effective fabrication methods.

(Refer Slide Time: 26:56)



- Crystal quality of single-crystal perovskite thin films is significantly critical to device performance. It is noted that despite very low trap densities in the bulk phase, organic inorganic hybrid single-crystal perovskites grown in solution still possess a large amount of surface charge traps, which are probably generated from the loss of the organic amine ions. The resultant substantial surface recombination nullifies the intrinsic superiority of single crystals, leading to unsatisfactory performance. Therefore, besides careful optimization of bulk-crystal quality improvements, the development of rational surface passivation techniques is urgently needed.
- The optoelectronic performance of single-crystal perovskite thin film devices is greatly affected by interface engineering, including the interfaces at the perovskite/charge selective layer, perovskite/substrates, and perovskite/metal electrode. Since lattice mismatches between halide perovskite and common substrates (i.e., FTO glass) would induce lattice strain and thus cause interfacial recombination and poor electrical contact, connection between single-crystal perovskites and the substrate deserves to be investigated at the atomic level. To reduce the interfacial lattice strain, the growth substrate needs either careful selection or the construction of a buffer layer. In addition, functional molecular modification of the substrate is an available strategy.

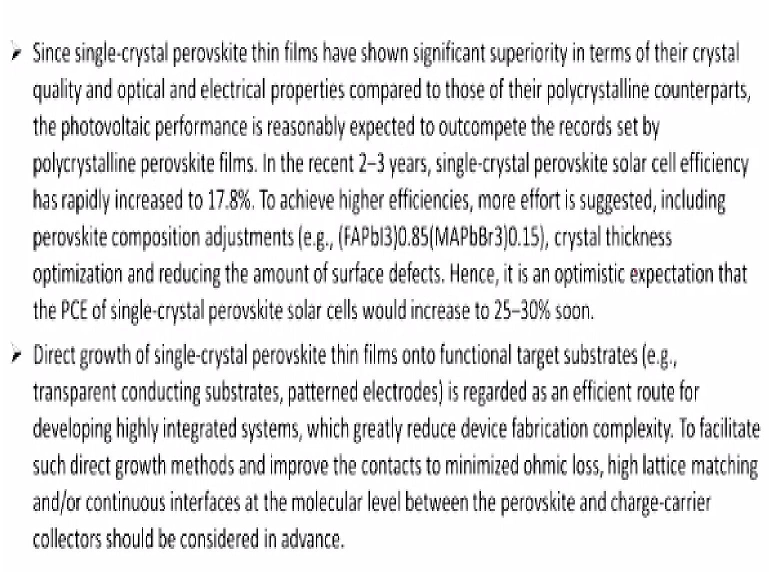
So crystal quality of the single crystal perovskite thin film is significantly critical to device performance. It is noted that despite very low trap density in the bulk phase organic inorganic hybrid single crystal perovskite grown in solution still possess a large number of surface charge traps which are probably generated from the loss of the organic amine ions. So although the volume defect density is less the surface trap density or the surface charge density still exist due to the loss of the amine group.

The resultant substantial surface recombination nullifies the intrinsic superiority of the single crystal leading to unsatisfactory performance. Therefore, besides careful optimisation of the bulk crystal quality improvements the development of rational surface passivation techniques is urgently needed. The optoelectronic performance of single crystal perovskite thin film device is greatly affected by interface engineering.

Including the interface at the perovskite charge selective layer. Perovskite substrate and perovskite metal electrode. Since lattice mismatch between halide perovskite and common substrate for example FTO glass would induce lattice strain and thus cause interfacial recombination and poor electrical contract connection between single crystal perovskite and the substrate deserves to be investigated at the atomic level.

To reduce the interfacial lattice strain, the growth substrate needs either careful selection or the construction of a buffer layer. In addition, functional molecular modification of the substrate is an available strategy.

(Refer Slide Time: 28:21)



- Since single-crystal perovskite thin films have shown significant superiority in terms of their crystal quality and optical and electrical properties compared to those of their polycrystalline counterparts, the photovoltaic performance is reasonably expected to outcompete the records set by polycrystalline perovskite films. In the recent 2–3 years, single-crystal perovskite solar cell efficiency has rapidly increased to 17.8%. To achieve higher efficiencies, more effort is suggested, including perovskite composition adjustments (e.g., $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$), crystal thickness optimization and reducing the amount of surface defects. Hence, it is an optimistic expectation that the PCE of single-crystal perovskite solar cells would increase to 25–30% soon.
- Direct growth of single-crystal perovskite thin films onto functional target substrates (e.g., transparent conducting substrates, patterned electrodes) is regarded as an efficient route for developing highly integrated systems, which greatly reduce device fabrication complexity. To facilitate such direct growth methods and improve the contacts to minimized ohmic loss, high lattice matching and/or continuous interfaces at the molecular level between the perovskite and charge-carrier collectors should be considered in advance.

Single-crystal perovskite thin films have shown significant superiority in terms of their crystal quality and optical and electrical properties that we have already discussed compared to those of their polycrystalline counterparts. The photovoltaic performance is reasonably expected to outcome the record set by polycrystalline perovskite film in the recent 2-3 years single crystal perovskite solar cell efficiency has rapidly increased to 17.8%.

To achieve higher efficiency more effort is suggested including perovskite composition adjustment, crystal thickness optimisation and reducing the amount of surface defects. So these are the 3 challenge. One is the perovskite composition adjustment, another is the surface passivation and another is the crystal thickness. Hence it is optimistic expectation that the PCE of the single crystal perovskite solar cell would increase to 25% to 30% soon.

So we know that the quasi circular limit, the thermodynamic limit for a single crystal or for a single junction solar cell is 32%. Now those days are not very far when by doing all of this optimisation the perovskite single crystal will touch the number or very close to that number. Direct growth of single crystal perovskite thin film on to functional target substrate as for example transparent conductive substrate, pattern electrodes is regarded as an efficient route for developing highly integrated system while greatly reduced device application complexity.

To facilities such direct growth methods and improve the context to minimized ohmic loss, high lattice matching and/or continuous interface at the molecular level between the perovskite and the charge carrier collectors should be considered in advance. So what we have learned that there are lot of advantage of using perovskite single crystal like for application in solar cell, application detectors, application in lasers.

But there are also still some challenges. Challenges like compositional mapping, challenges like surface defects and all of these things. So once a optimised method for the crystal growth, a large uniform crystal growth has developed then it is possible to still improve the efficiency parameters or the efficiency of a solar cell made from the single crystal perovskite films. Thank you.