반도체의 P-N 접합과 Scanning Photo Current Microscopy

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도핑에 의한 반도체의 전기전도도 증가
Conductivity of Semiconductor by doping

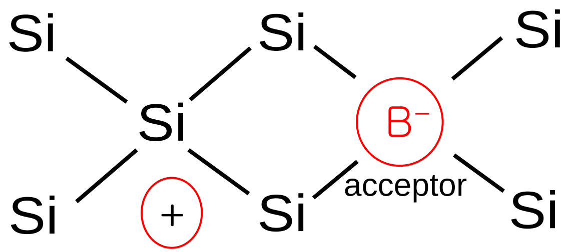
- 불순물 Impurities (or doping) of semiconductor

  → affect the electrical, optical, and magnetic properties
- 도핑 doping (10^5 : 1 , ~10 ppm) increases conductivity by factor of 10^3 (at R.T.)

- Acceptor(3족 원소) : (p-type)

  Si , Ge + B

  (IV) (III)

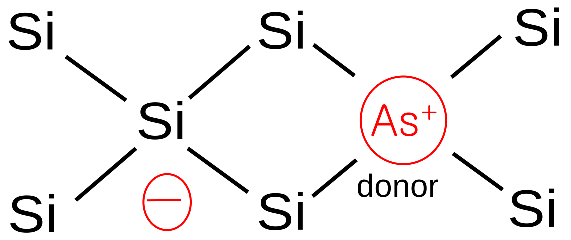


Excess hole

- Donor (5족 원소) : n-type

  Si, Ge + P, As, Sb

  (IV) (V) (arsenic) (antimony)

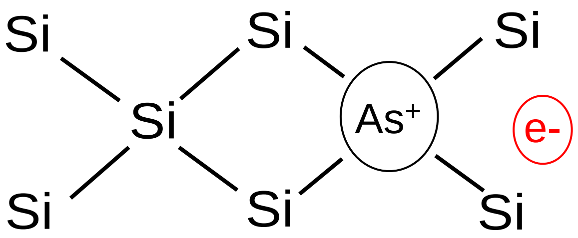


Excess electron from As atom

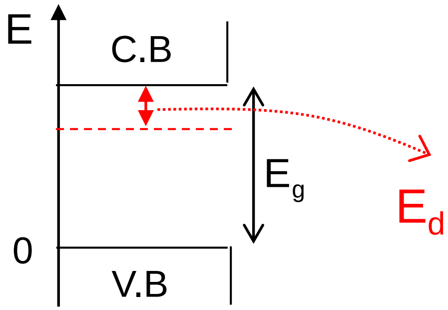
Donor(도너) state

- Donor state: 전도대 근처에서 잉여전자가 유도됨
- Donor electrons move under Coulomb potential $\frac{e}{\varepsilon r}$ between charges in the medium (ε : static dielectric constant)

➔ Energy level of extra electron is modified by donor



- 잉여전자와 3족 이온간의 쿨롱에너지가 추가되어 유전율 ε의 실리콘 결정내에서 에너지 밴드 구조에 에너지 대역이 추가됨.



extra band estimation ➔

E_d (extra band) : donor energy level

Donor energy level

< 보어의 수소원자 모형>
(Bohr hydrogen model)

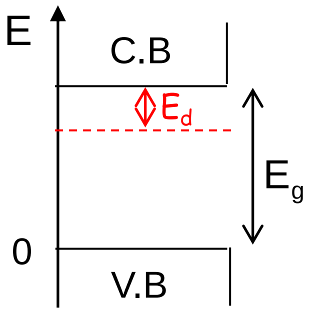
$$-\frac{e^4 m}{2\hbar^2} = -13.6\ \mathrm{eV}$$

수소원자의 이온화 에너지
ionization energy of hydrogen

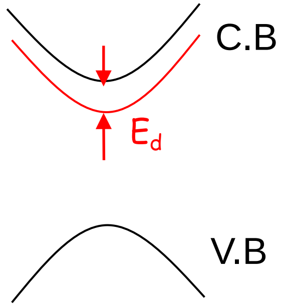
- Extra electron from donor contributes to conduction, as it is ionized
- Donor energy level (≡ E_d) : ionization energy of extra electron in dielectric medium (ε) (Si lattice)
- from Bohr model $e^2 \rightarrow e^2/\varepsilon$; $m \rightarrow m_e$ (effective mass of el.)

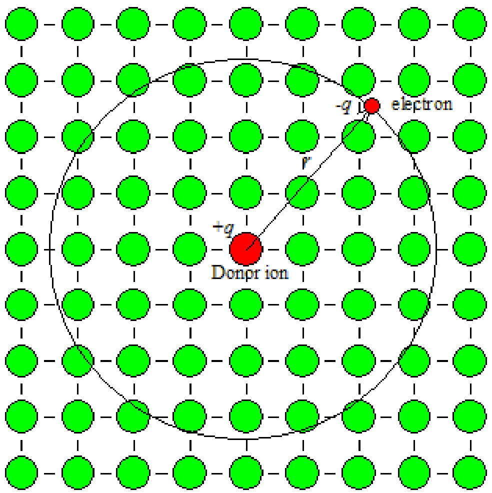
$$\therefore E_d = \frac{e^4 m_e}{2\varepsilon^2 \hbar^2} = \left(\frac{13.6}{\varepsilon^2}\frac{m_e}{m}\right) eV \approx 30\ \mathrm{meV}$$

도너의 이온화 에너지



or





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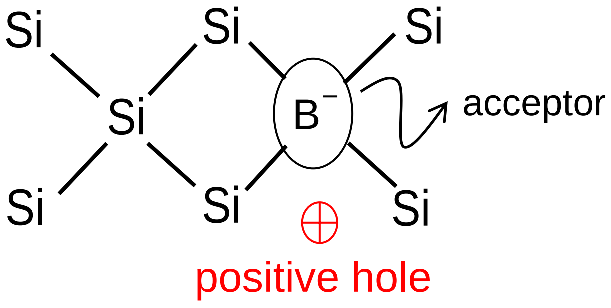
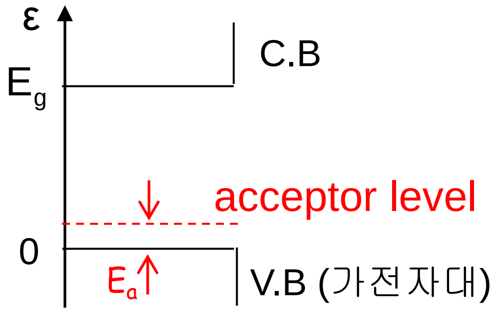
Acceptor(억셉터) States

- Host material : Group 4 (Si, Ge)
  Impurity : group 3 (B, Al, Ga, In)

억셉터: 전자를 받아들일 수 있는 빈 자리 (정공)
"acceptor" : accepts an electron in medium
induces a positive hole 정공





정공과 억셉터 간의 쿨롱 에너지

Acceptor ionization energy ($E_a = \frac{13.6}{\varepsilon^2}\frac{m_h}{m}$) : (10~50 meV)

Si vs Ge ($\varepsilon_{Si}=11.7$, $\varepsilon_{Ge}=15.8$)

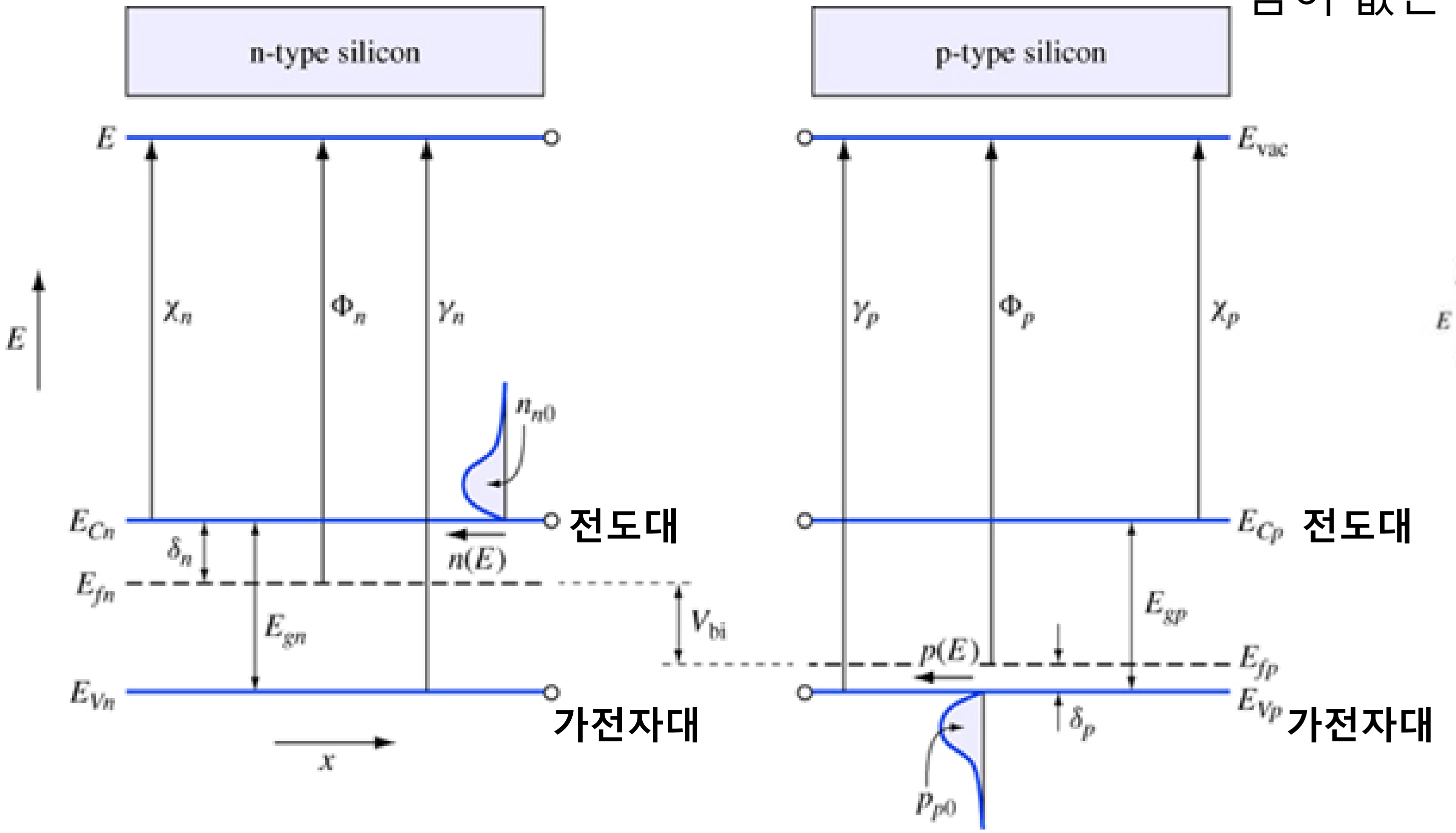
➔상온에서 $k_BT=1.38 \times 10^{-23}$(J/K) x (295K) ~ 26meV

열적 이온화 "Thermally ionization" of donor or acceptor

→ important for the electrical conductivity

P-N junction band diagram

vacuum level(**진공 준위**)는 전자 또는 정공에 가해지는 힘이 없는 **자유로운 상태**에 해당하는 에너지 준위

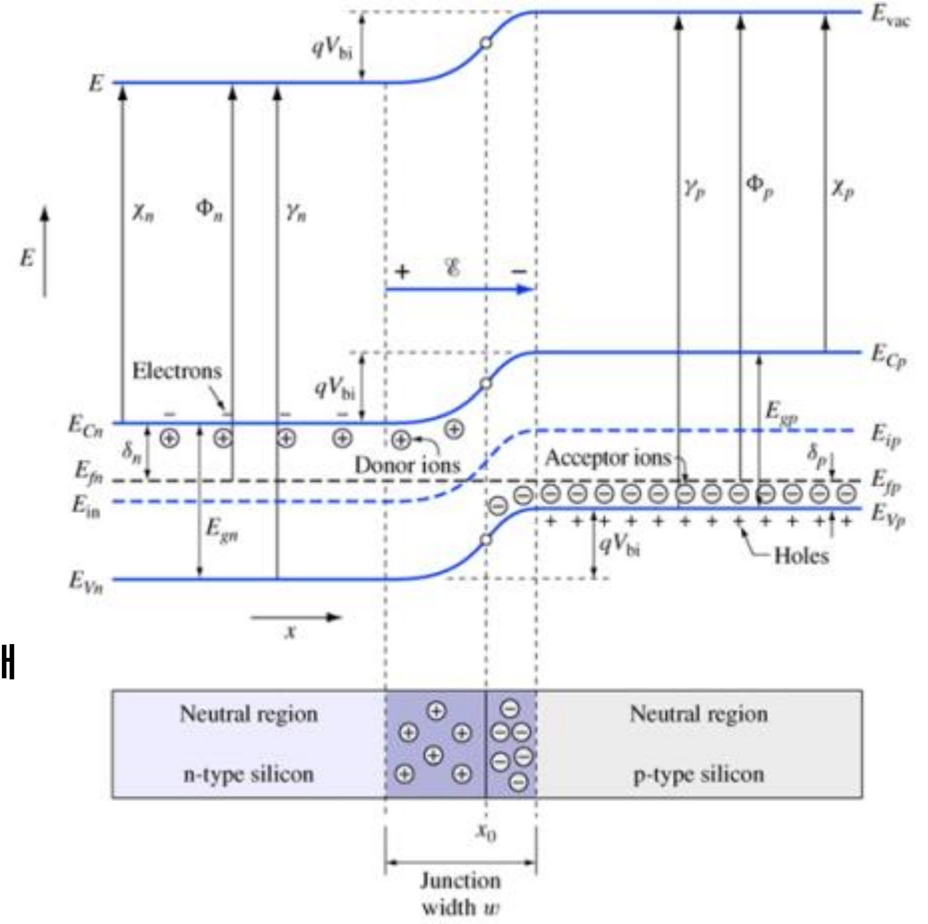


전도대

가전자대

전도대

가전자대

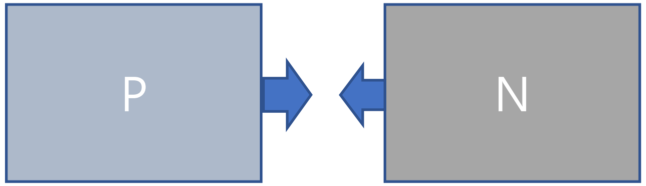


χ (chi, 카이): 전자 친화도 electron affinity

γ: 이온화 에너지 ionization energy

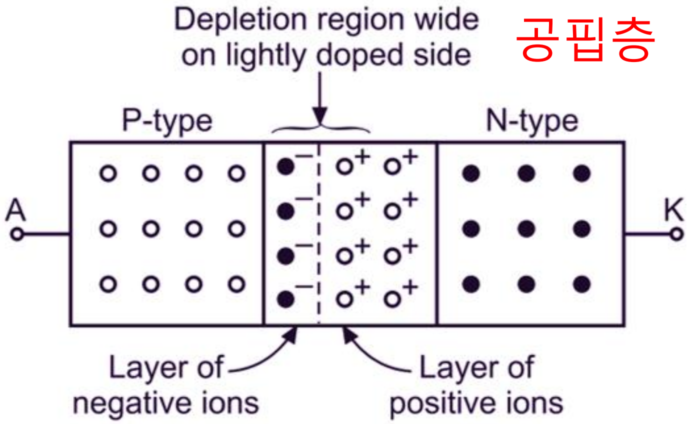
Φ: work function

P-N junction Diode



- P-N junction Diode Equation $I = I_0(e^{\frac{qV}{k_B T}} - 1)$

- I_0 : 역방향 포화전류 “reverse bias saturation current",
  the diode leakage current density in the absence of light;
  진성 캐리어 농도의 제곱에 비례함 ($I_0 \propto {n_i}^2$)



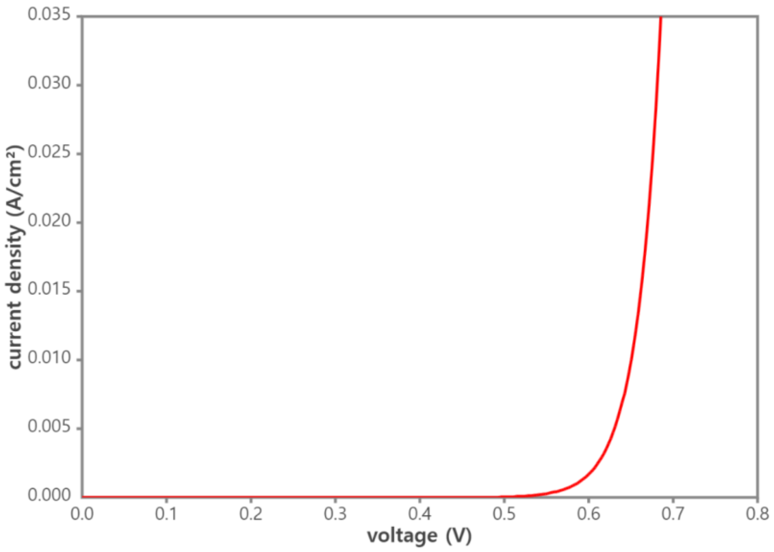
공핍층

- Diode Equation for Non-Ideal Diodes (비이상적인 다이오드)

$$I = I_0(e^{\frac{qV}{nk_B T}} - 1) \qquad \frac{I}{I_0} + 1 = e^{\frac{qV}{nk_B T}}$$

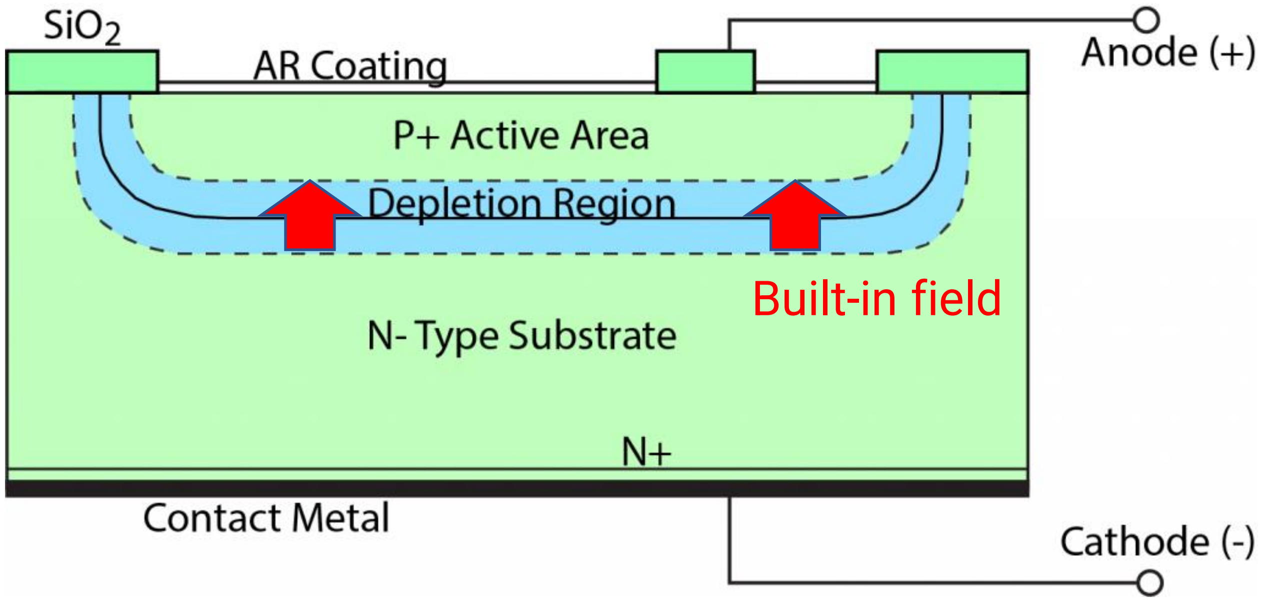
n = ideality factor, a number between 1 and 2 which typically increases as the current decreases

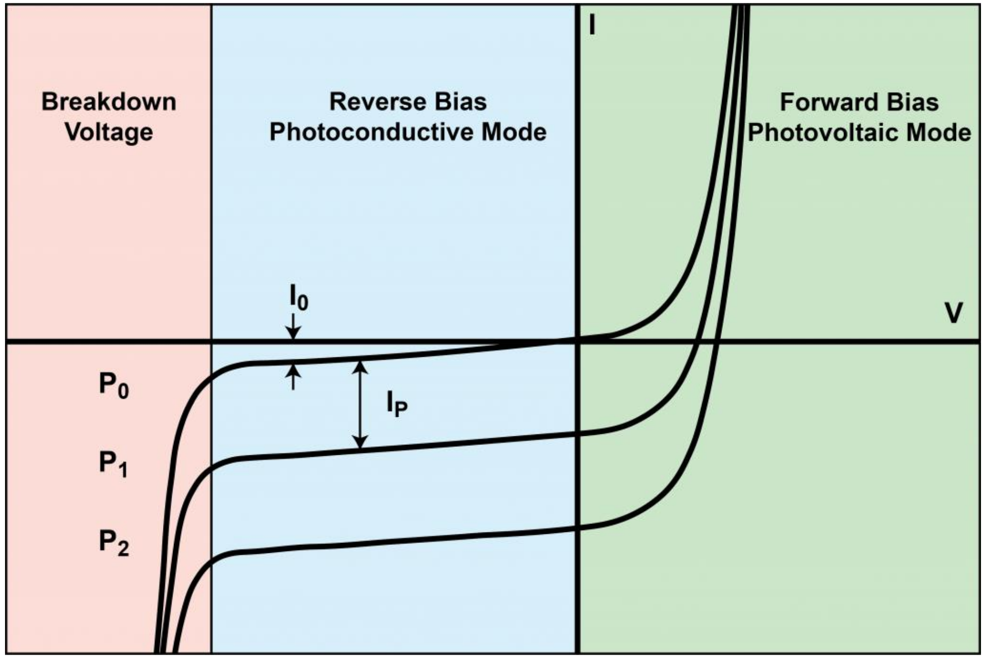
For forward bias, $I \gg I_0$ $\quad \frac{I}{I_0} \cong e^{\frac{qV}{nk_B T}}$



광전류 (photocurrent)

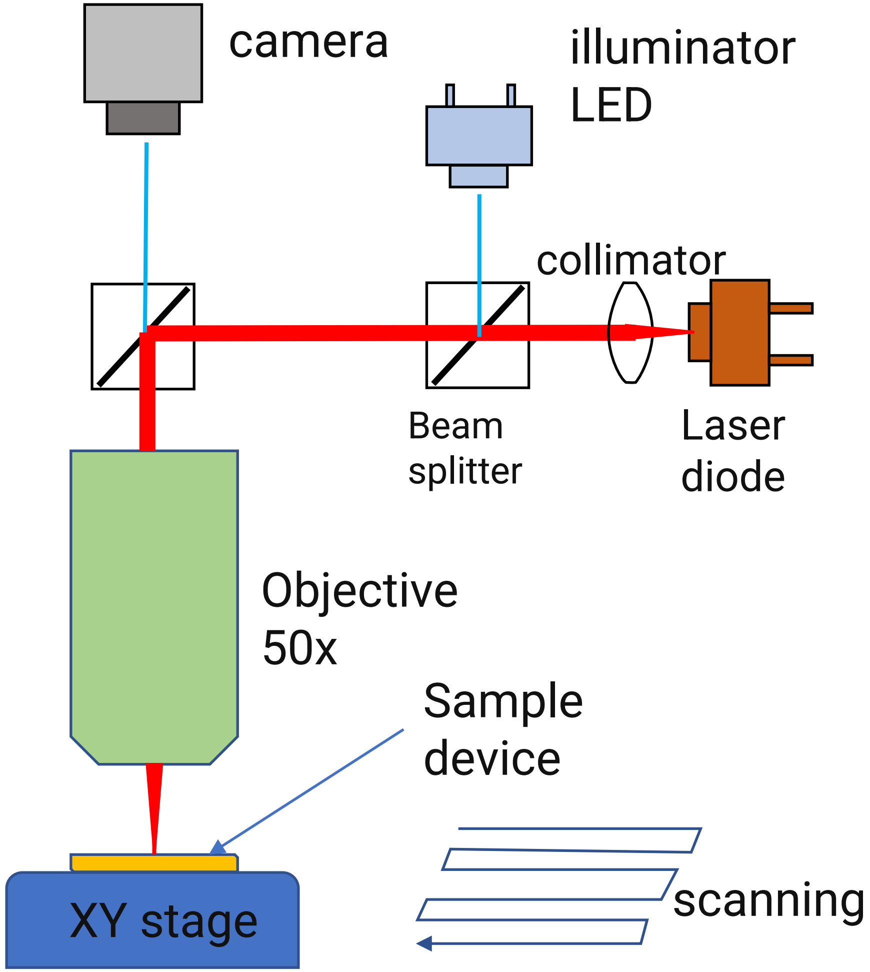
- 밴드갭 에너지 보다 높은 에너지의 광자(빛)이 반도체에 닿으면 전자-정공 쌍이 발생 → 바로 재결합 → 열 발생
- 빛이 공핍층에 닿으면 Built-in 포텐셜에 의해서 서로 반대 방향으로 힘 → 전자-정공 분리 → 광전류





Scanning photocurrent imaging → local photoelectric effect in air

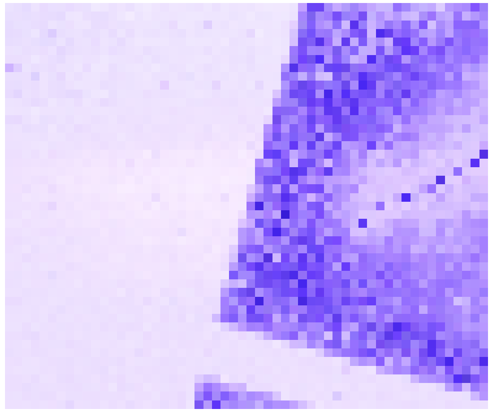
- 빛이 공핍층에 닿으면 전자-정공 쌍이 발생
- Built-in 포텐셜에 의해서 전자-정공 분리 → 광전류
- 광전효과 photoelectric effect : 진공에서 측정
- 실제 소자는 공기중에서 측정: photoelectric effect from pn junction measured by photocurrent mapping
- 용도(usage): 태양광소자, pn-junction 소자, LED, Image sensor, 등 다양한 광전소자 연구 개발
- 제조사(주)세종과학기기, 모델명:SPCM01

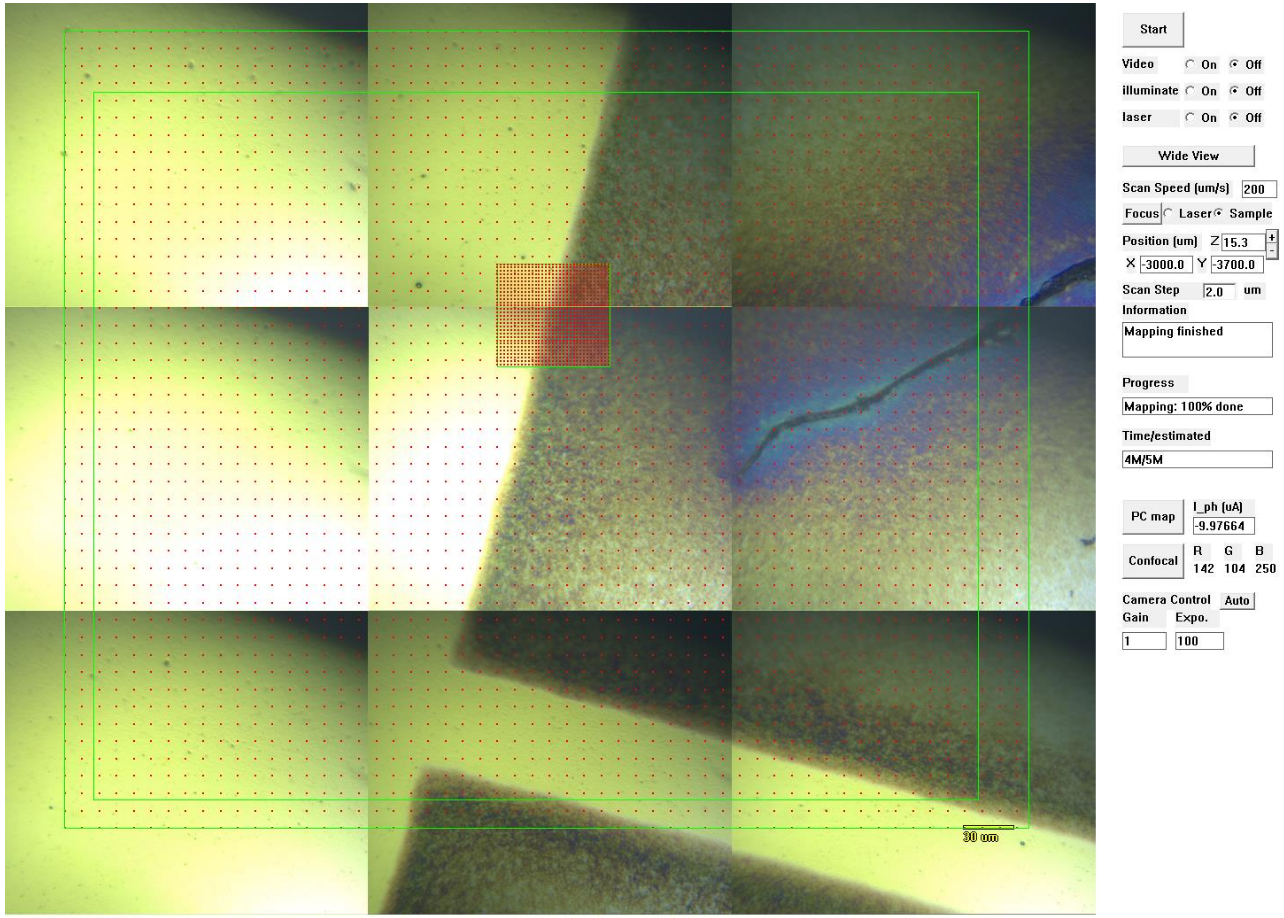


Photocurrent map and confocal image

Photocurrent

confocal





Video ○ On ● Off
illuminate ○ On ● Off
laser ○ On ● Off

Scan Speed (um/s) 200
Focus ○ Laser ● Sample
Position (um) Z 15.3
X -3000.0 Y -3700.0
Scan Step 2.0 um
Information
Mapping finished
Progress
Mapping: 100% done
Time/estimated
4M/5M

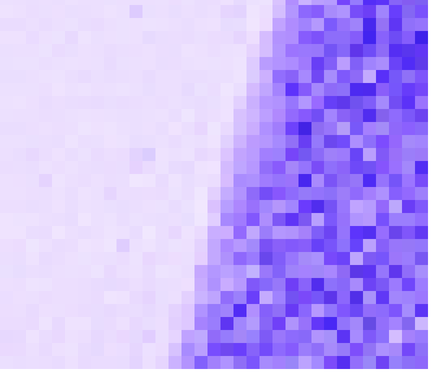
I_ph (uA) -9.97664

R	G	B
142	104	250

Camera Control
Gain 1
Expo. 100

Photocurrent

confocal



Mxene-Si Solar Cell : fabrication process

Bare Si wafer cleaning

1. Acetone, Methanol, IPA, DI 15min (sonication)
2. BOE 5min / DI 5min 2times
3. DI washing many time

Bottom electrode deposition

- Ti / Pd / Ag : 50nm / 50nm / 90nm

Top coating

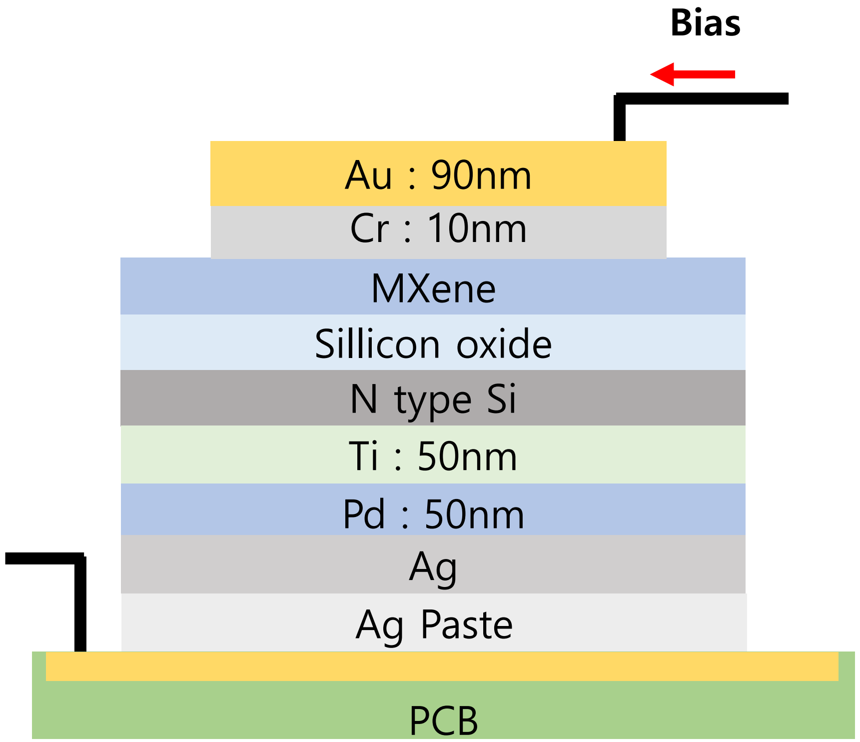
- BOE 5min / 상단 Si의 산화막 제거
- DI water(90℃)내에서 산화막 성장시킴 / 2hr
- UV 경화기 이용, 20분간 O_3 treatment
- Spin coating (1step : 500rpm, 10s / 2step : 2000rpm, 60s)
- Heating 100℃ 10min

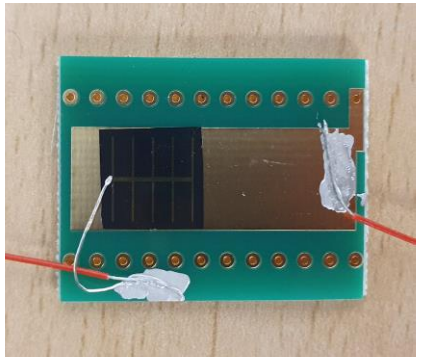
Annealing (tube furnace)

- At 300℃ 1hr / Ar = 50 [sccm]

Top electrode deposition

- Cr / Au : 10nm / 90nm





MXene synthesis by Etching MAX

알미늄 식각

	Condition
MAX	Ti_3AlC_2 1g
Etchant	HCl 30ml + LiF 1.98g
Etching time	24hour
Temperature	70℃
Etch RPM	300 rpm

중화과정 (ph=7)

No	Centrifuge RPM	Time
1	3500rpm	5min
2	3500rpm	5min
3	3500rpm	5min

Mxene 층분리과정

No	Process	Time
4	Sonication	1hr

식각 부산물 제거

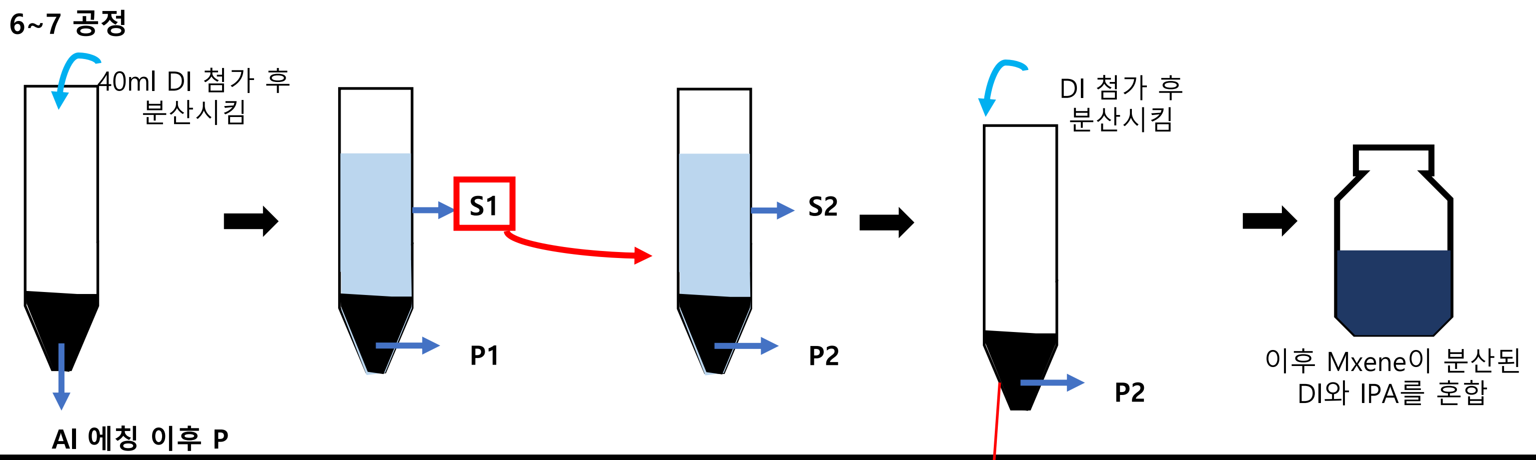
No	Centrifuge RPM	Time
5	3500rpm	1hr

Mxene Solution 제작과정

No	**Centrifuge RPM**	**Time**
6	3500rpm	10min
7	10000rpm	10min

P : Precipitate
S : Supernatant

6~7 공정



40ml DI 첨가 후
분산시킴

Al 에칭 이후 P

S1

P1

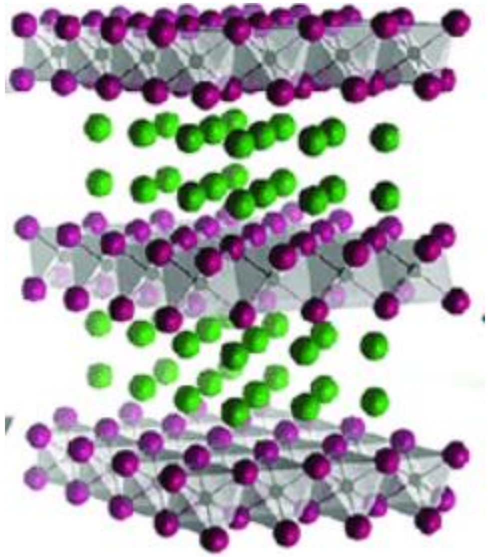
S2

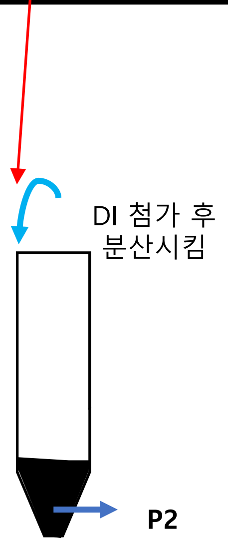
P2

DI 첨가 후
분산시킴

P2

이후 Mxene이 분산된
DI와 IPA를 혼합



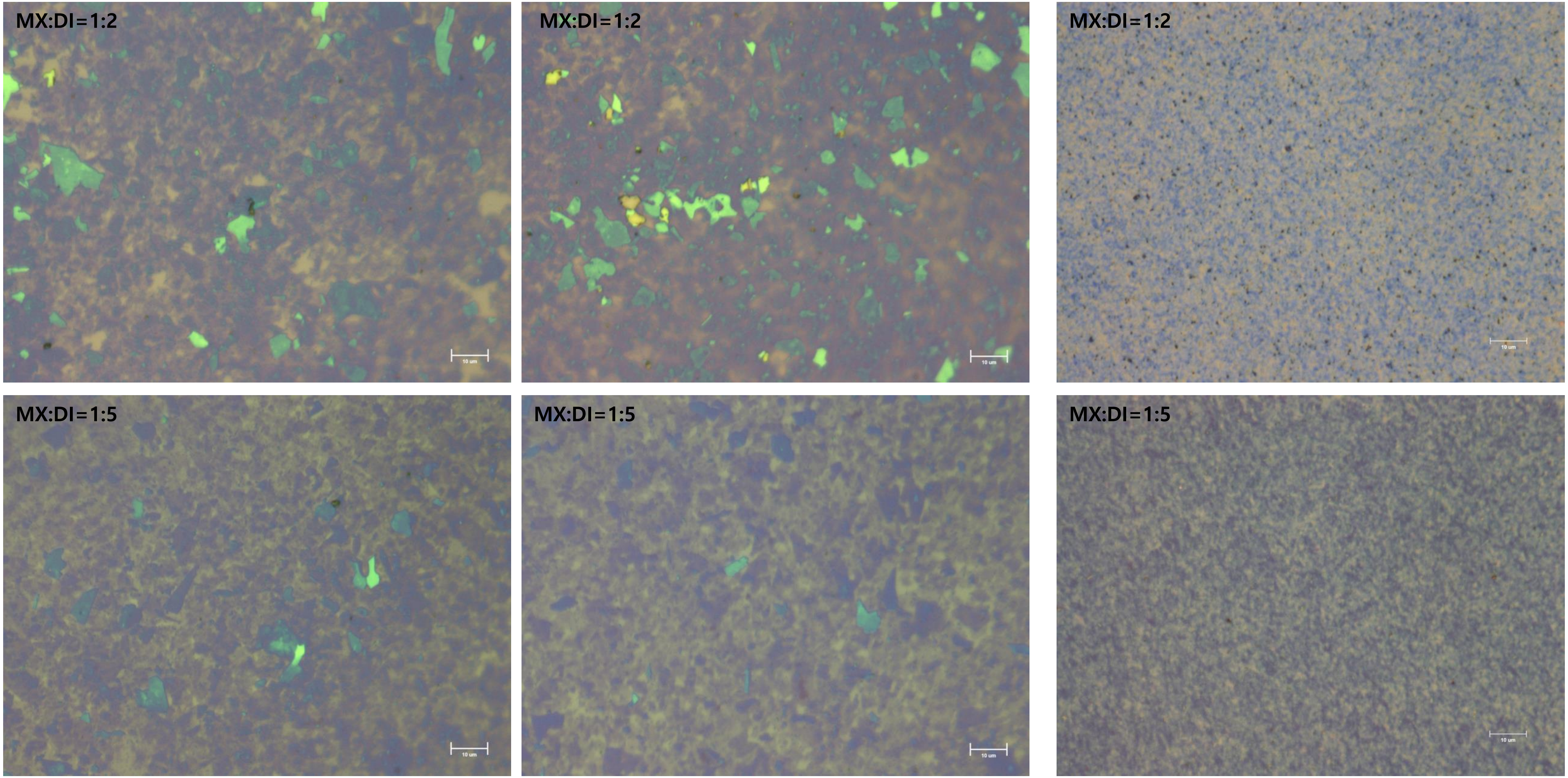


DI 첨가 후
분산시킴

P2

시료 No	**MXene**	**DI**
1	1g	2ml
2	1g	5ml

MXene deposition after sonication



No Sonication

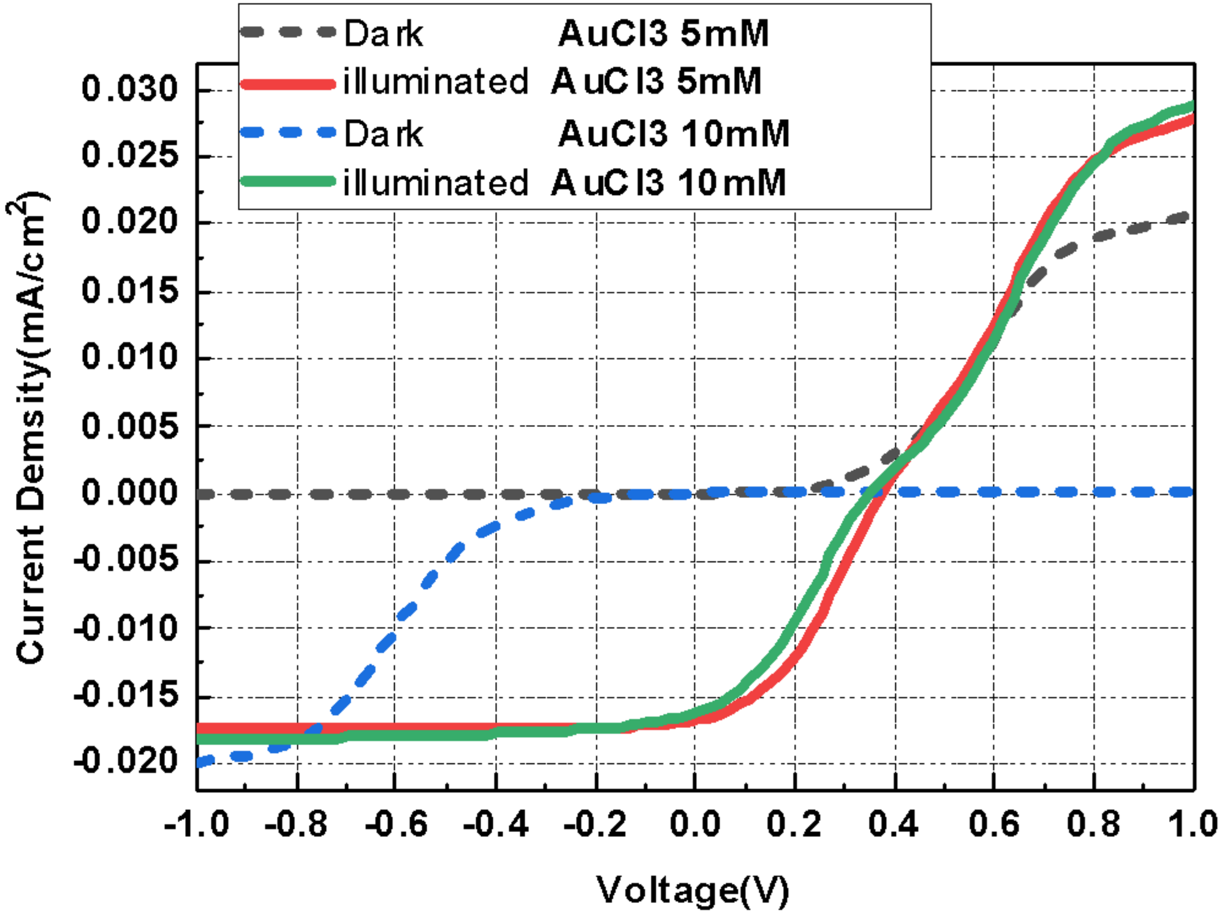
Sonication 30min

Sonication 1hr

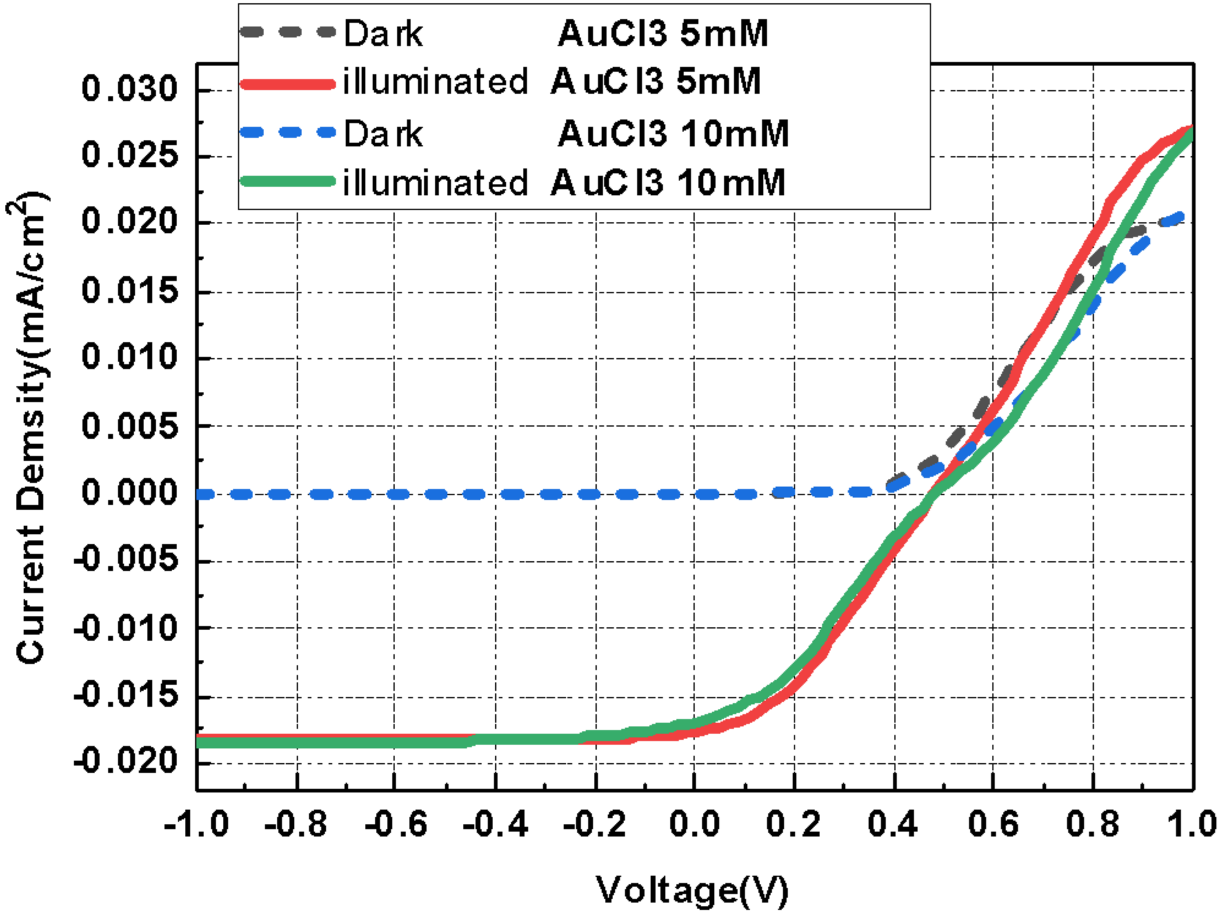
Solar cell measurement – 210708

MX in DI 6ml

Al_2O_3 = 7cycle = 약 9.8Å



Al_2O_3 = 14cycle = 약 19.6Å

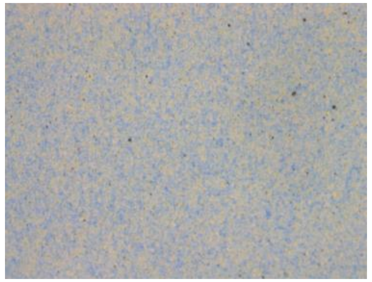


[MX in DI]	Al_2O_3	$AuCl_3$	**Voc [V]**	**Isc [A]**	**Jsc [mA/ cm2]**	**FF**	**Efficiency**
6ml	1nm	5mM	0.3755	0.0168	18.6519	38.4932	2.6964
6ml	1nm	10mM	0.3513	0.0164	18.2374	33.3097	2.1344

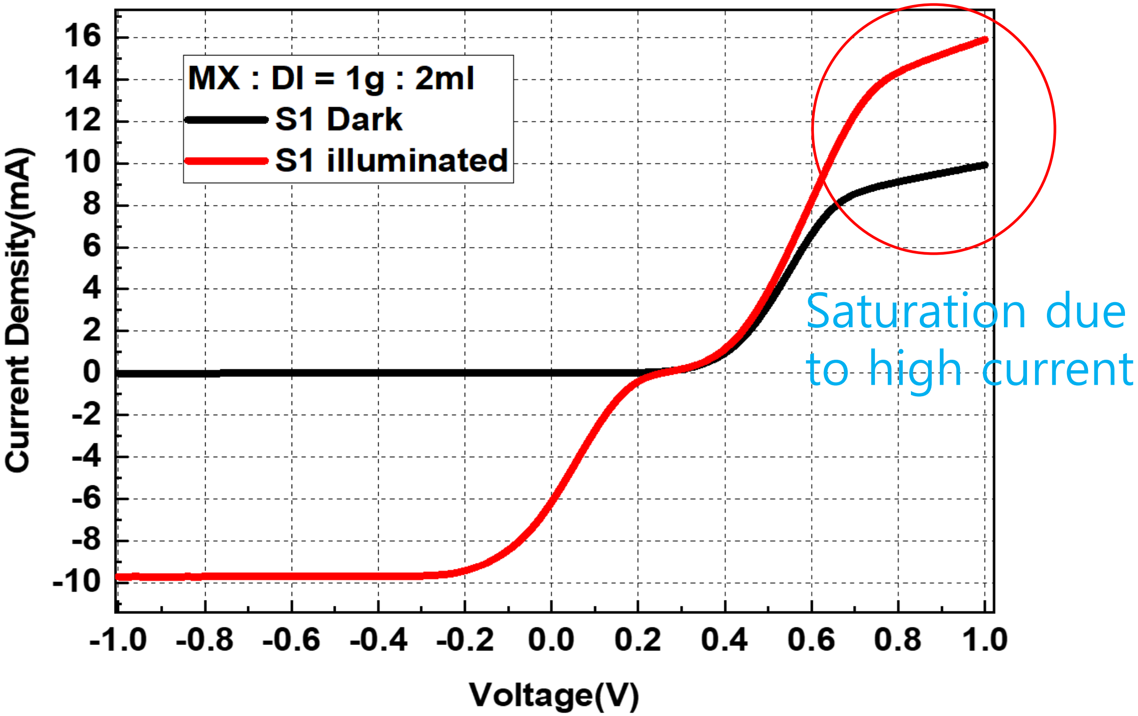
[MX in DI]	Al_2O_3	$AuCl_3$	**Voc [V]**	**Isc [A]**	**Jsc [mA/ cm2]**	**FF**	**Efficiency**
6ml	2nm	5mM	0.4819	0.0176	19.6004	35.6042	3.3628
6ml	2nm	10mM	0.4854	0.0171	19.0241	32.5176	3.0031

Solar simulator measurement

No.	SiO_2 growth	[Mxene : DI]	**Voc [V]**	**Isc [A]**	**Jsc [mA/cm2]**	**FF**	**Efficiency**
S1	2hr	[1 : 2]	0.2546	0.0061	6.8141	17.6482	0.3062
S2	2hr	[1 : 5]	0.2727	0.0121	13.4591	22.6547	0.8315



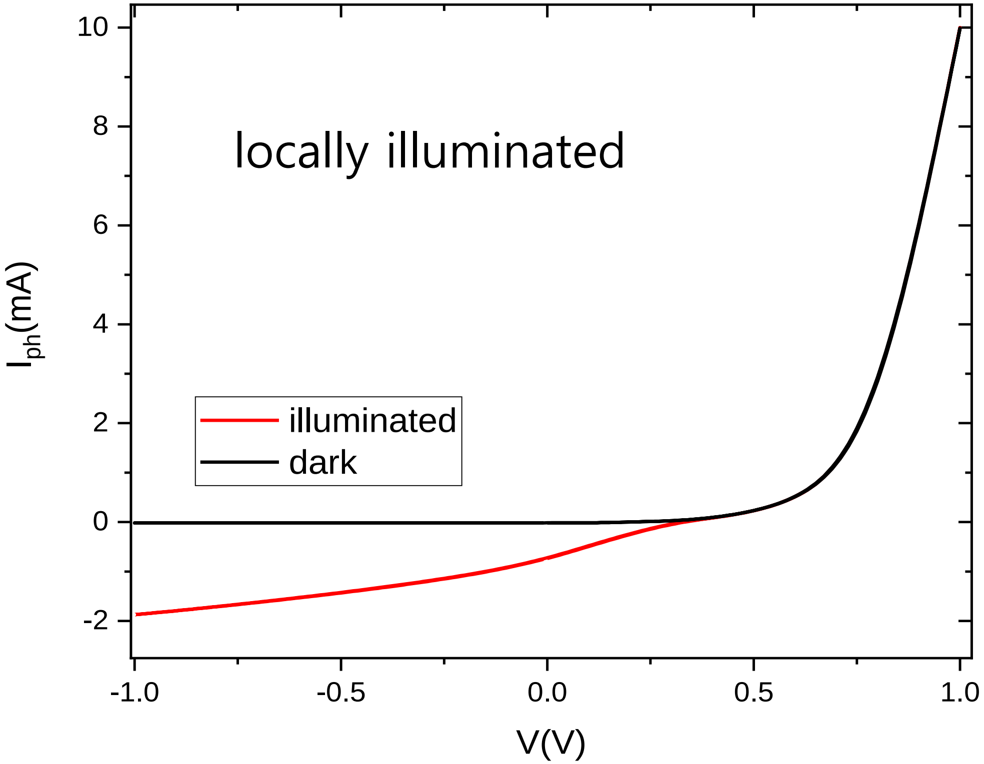
SN210521, MX:DI=1:2/1:5



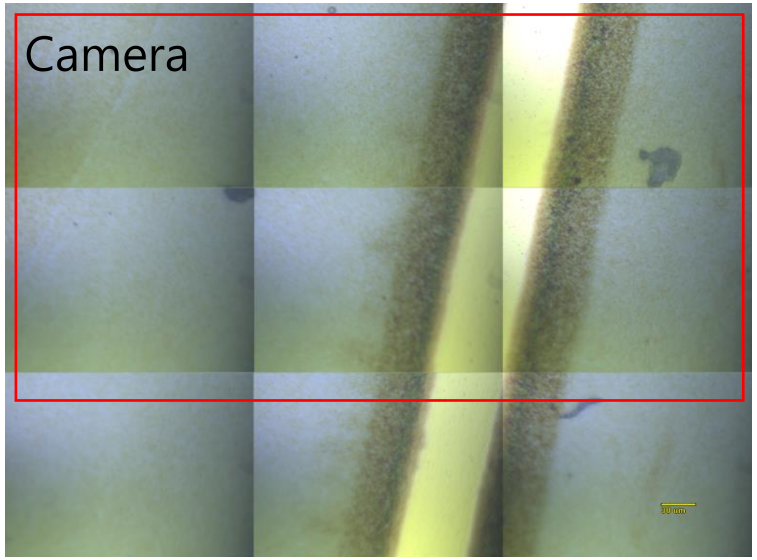
Saturation due to high current

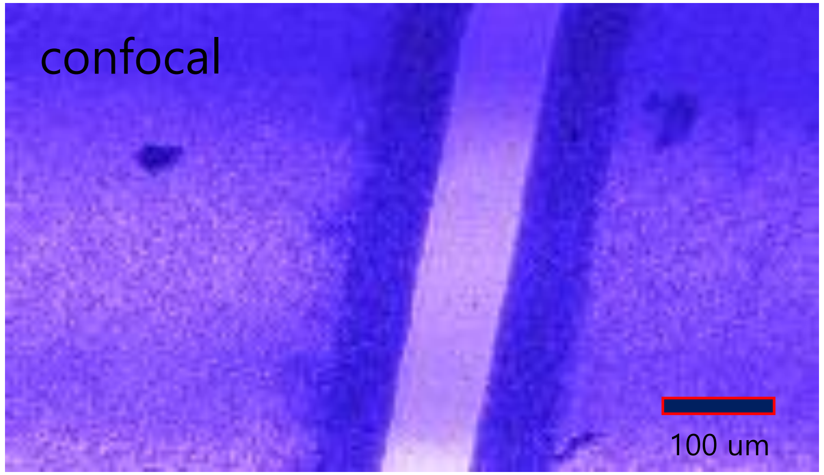
Local illumination measurement

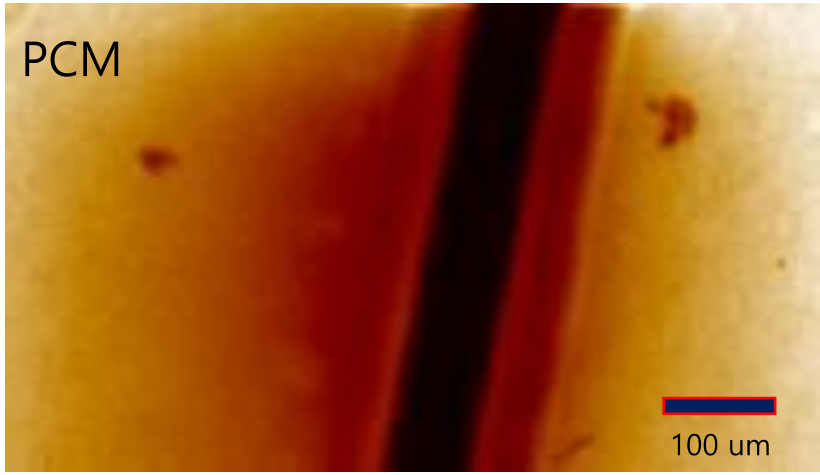
Using PhotoCurrent microscope



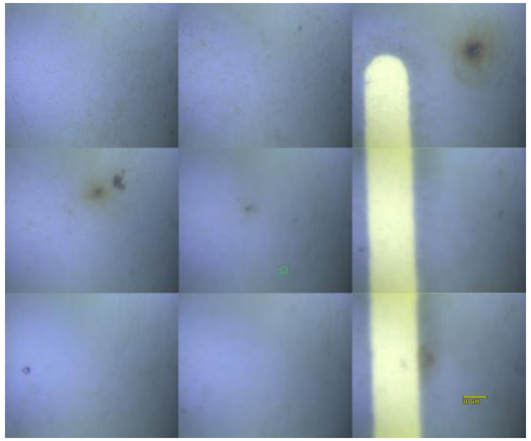
Ultra large area scanning with stability

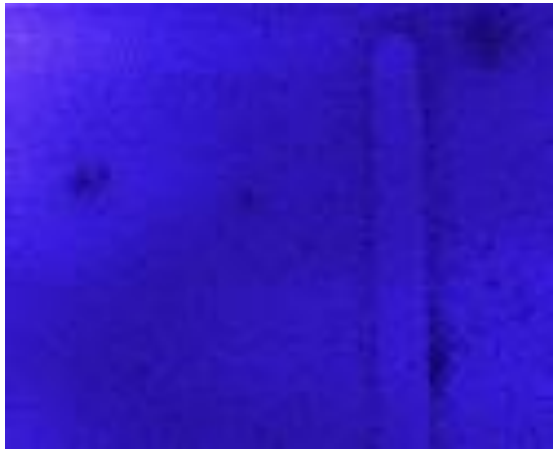


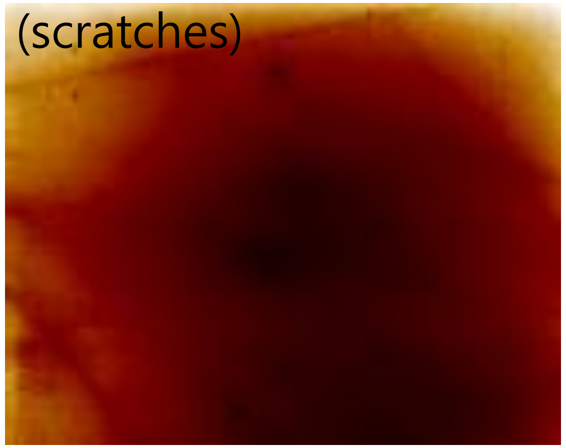




- MXene based solar cell with busbar electrodes
- 9 camera images are patched showing wide area: 600 um x 450 um

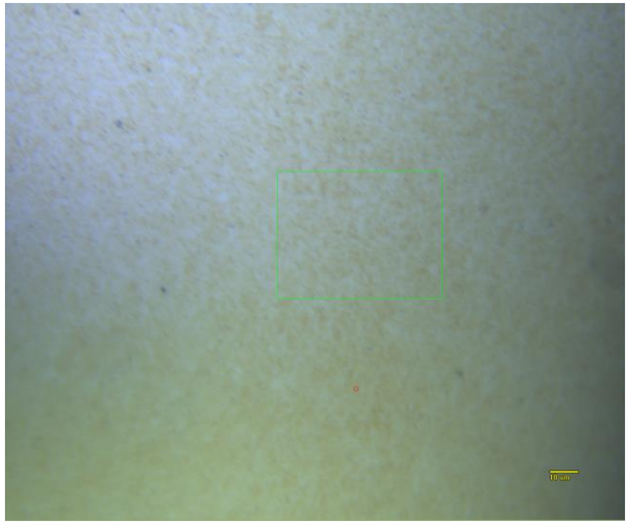






Failure analysis: Degradation by Photon irradiation

- MXene solar cell (thin layer diluted with 4ml DI water)



1st image

56 x 44 um

2nd image

56 x 44 um

3rd image
(30min later)

50 x 38 um

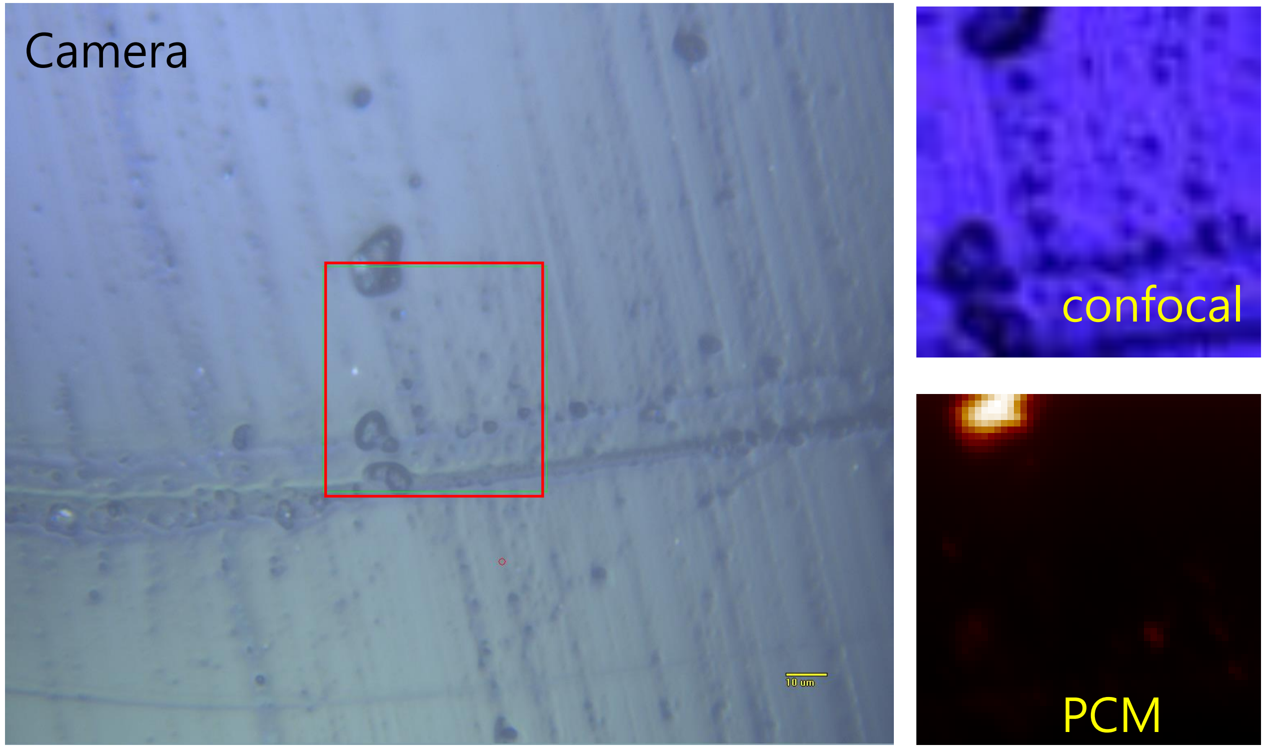
4th image
(30min later)

50 x 38 um

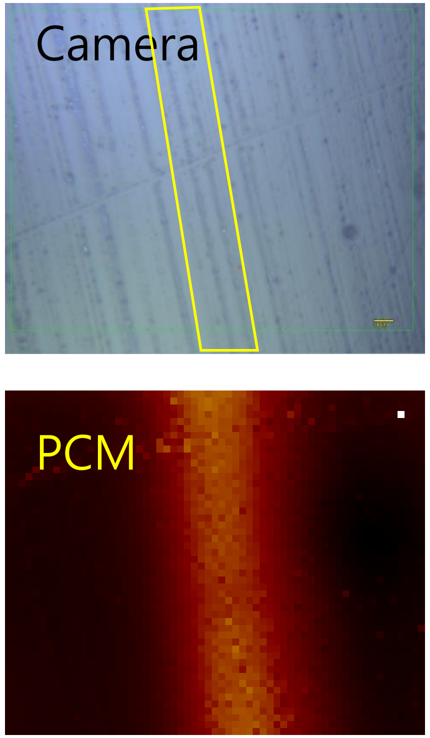
5th image
(30min later)

50 x 38 um

Failure analysis: defect on Si solar cell



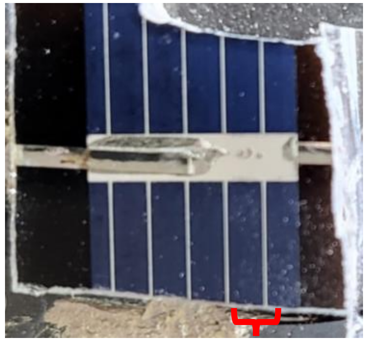
defect causes low photocurrent

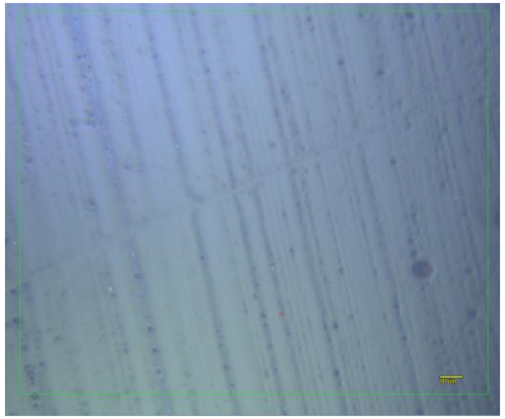


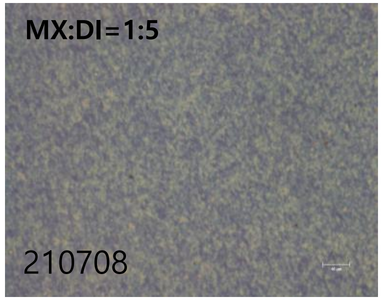
Hidden Electrode
located below

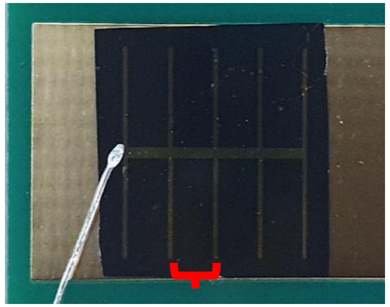
Degradation by Photon irradiation (Si vs MXene)

Si solar cell

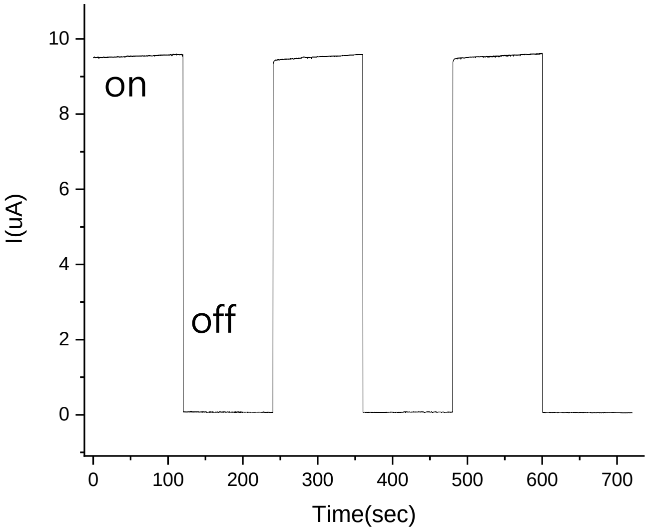


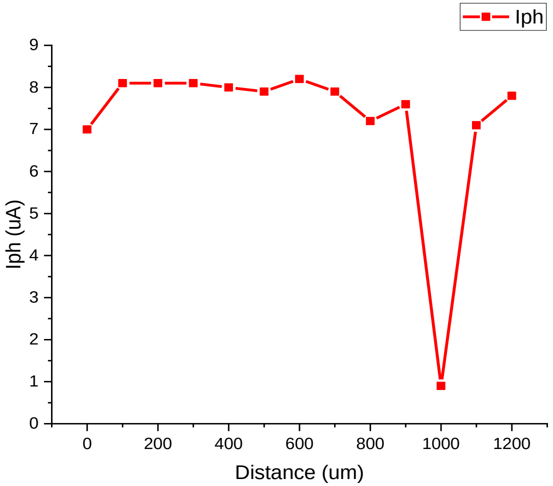




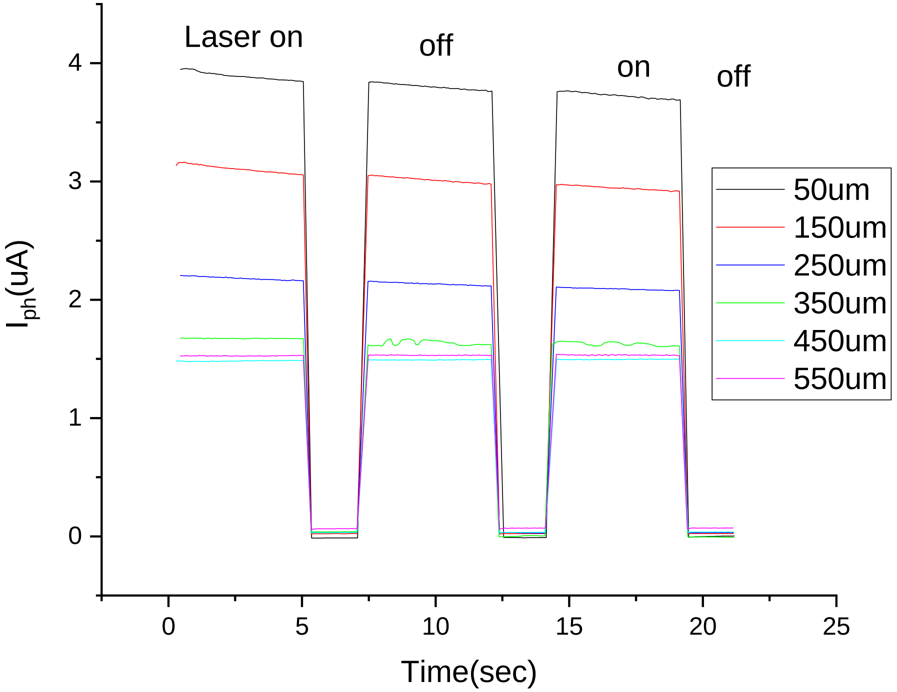


Laser





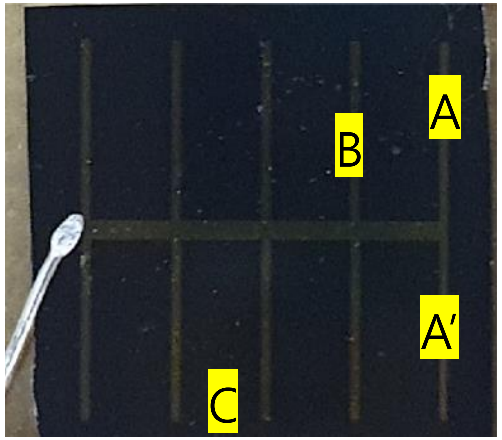
MXene solar cell

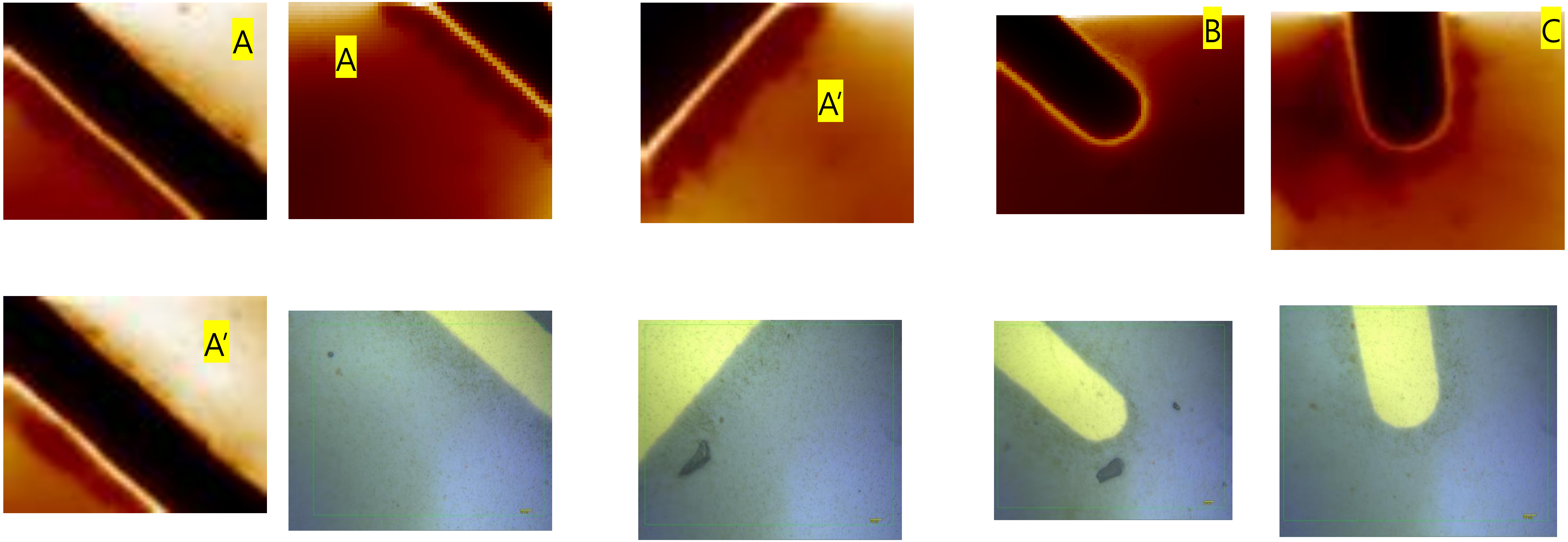


210708

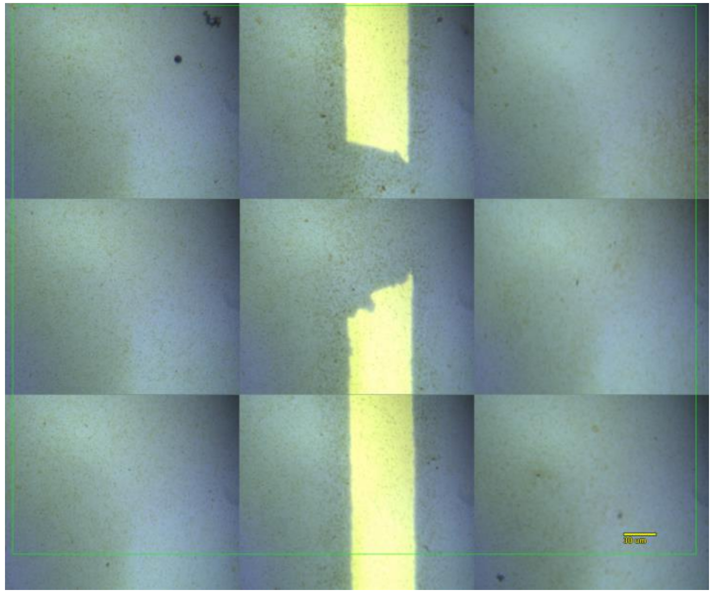
Photocurrent near electrodes

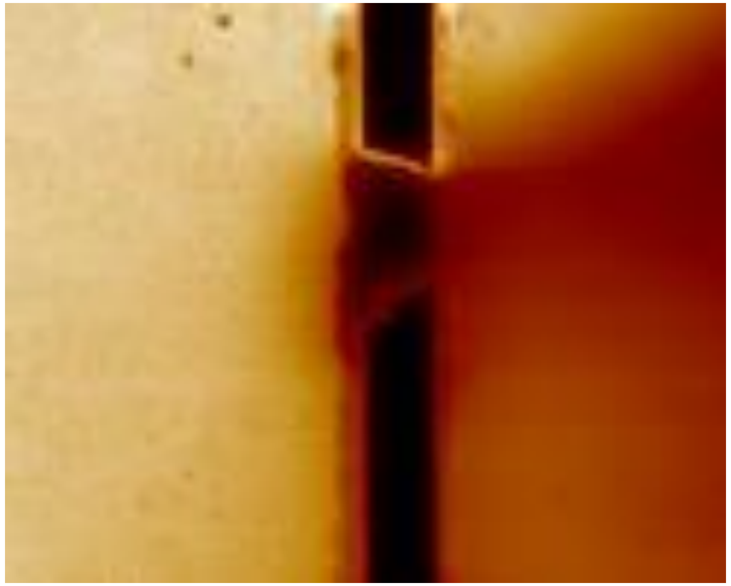
- For thin MXene layer high photocurrent density degrades MXene
- Serious degradation at narrow current path

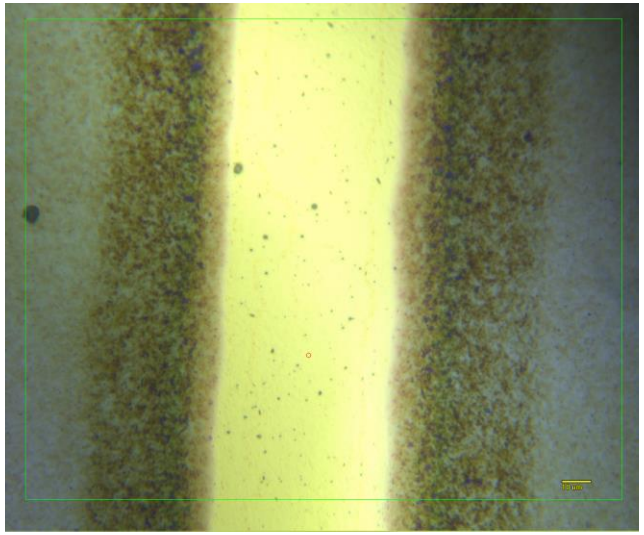


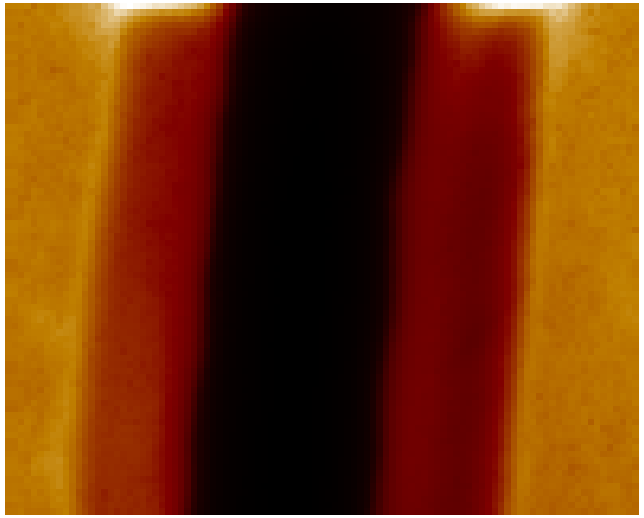


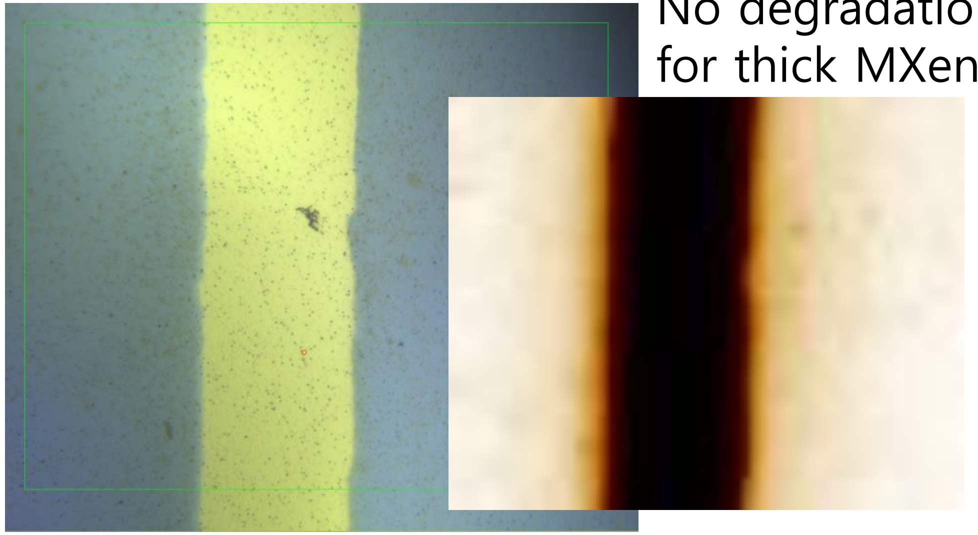
Current Profiling from asymmetric electrodes





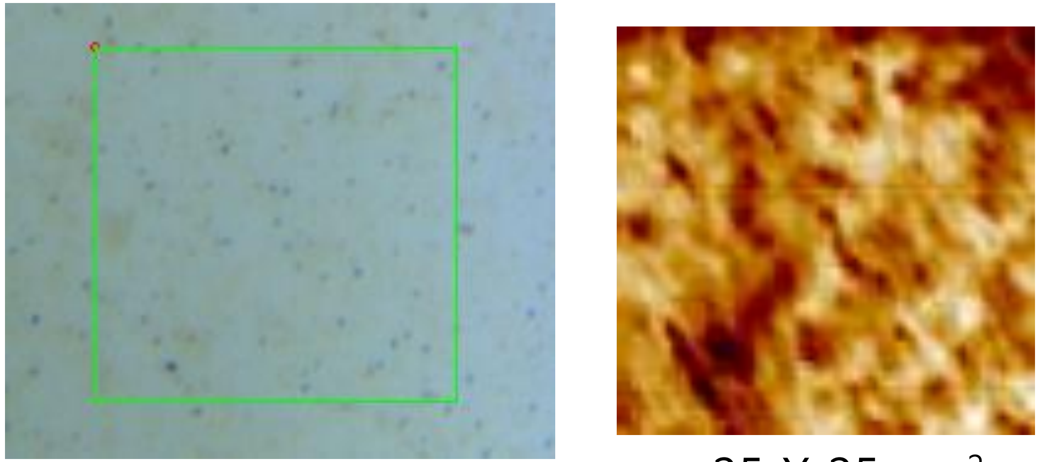




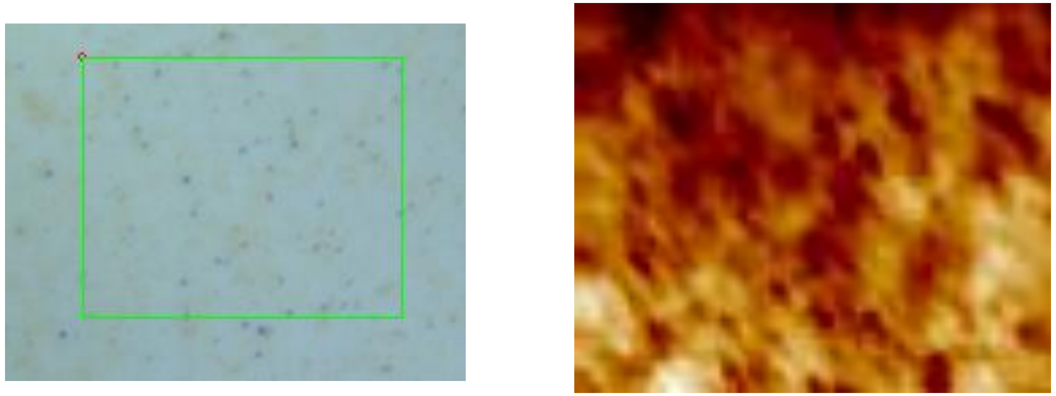


No degradation
for thick MXene

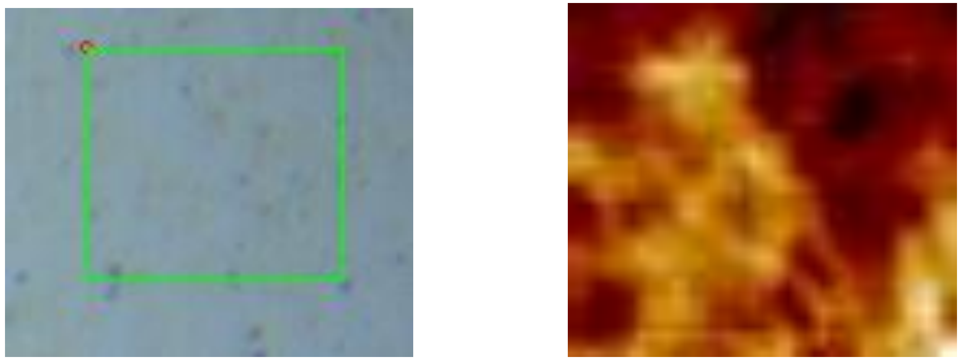
High resolution photocurrent map images (MXene solar cells)



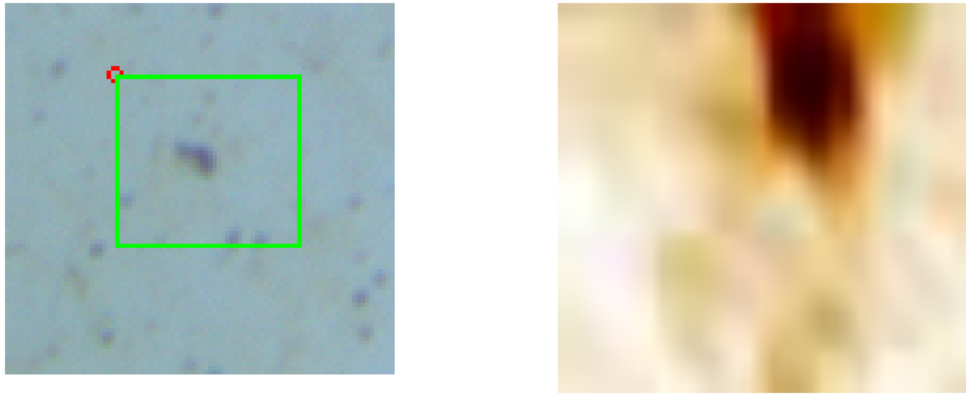
25 X 25 μm²



26 x 21 μm²



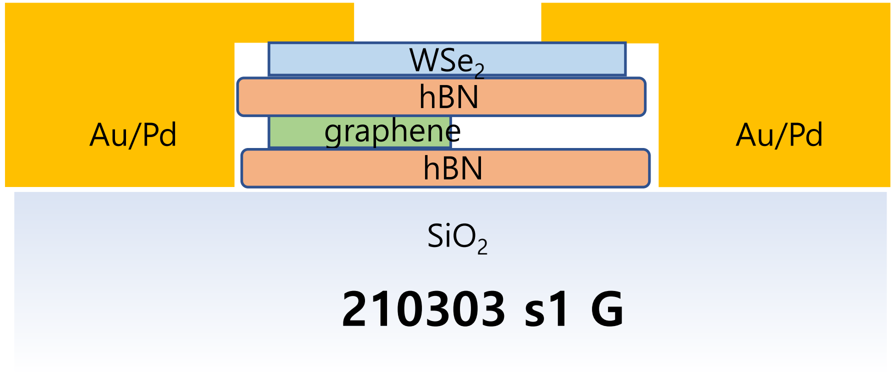
13 x 12 μm²

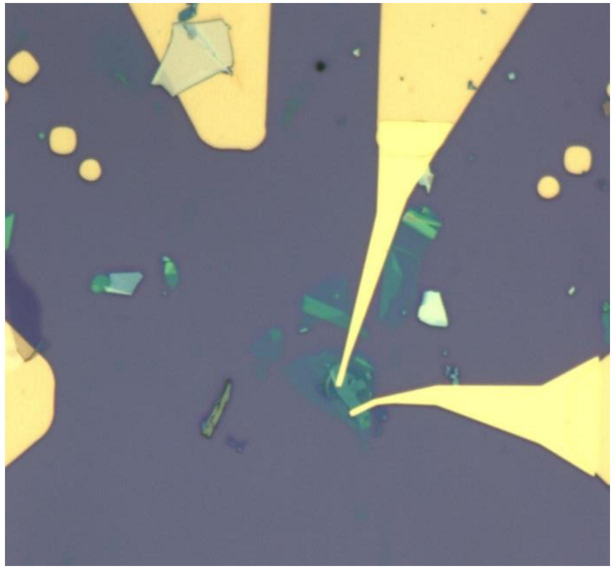


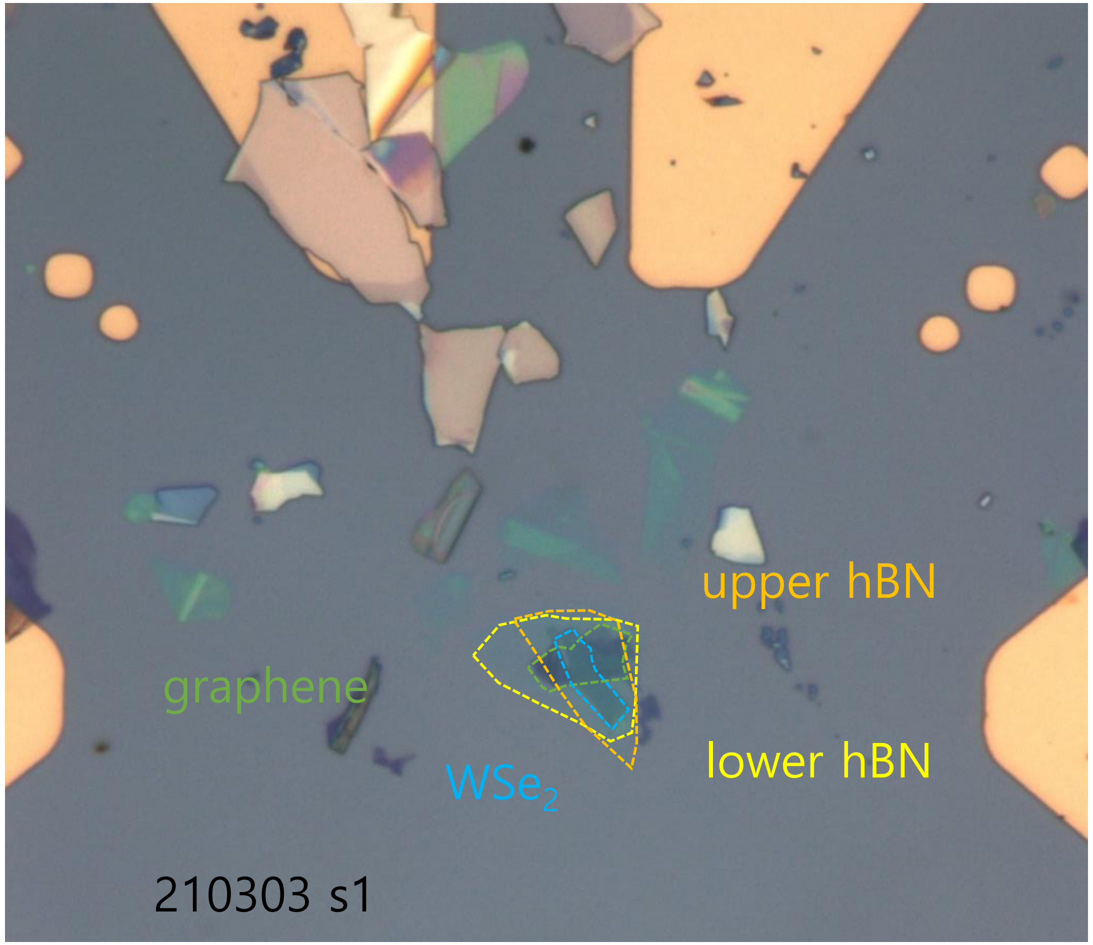
10 x 10 μm²

2D materials based nano device

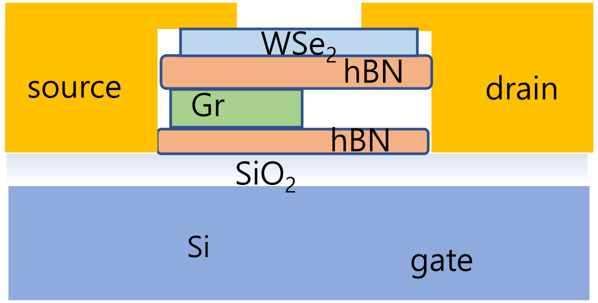
- Homo P-N junction with semi-floating gate device



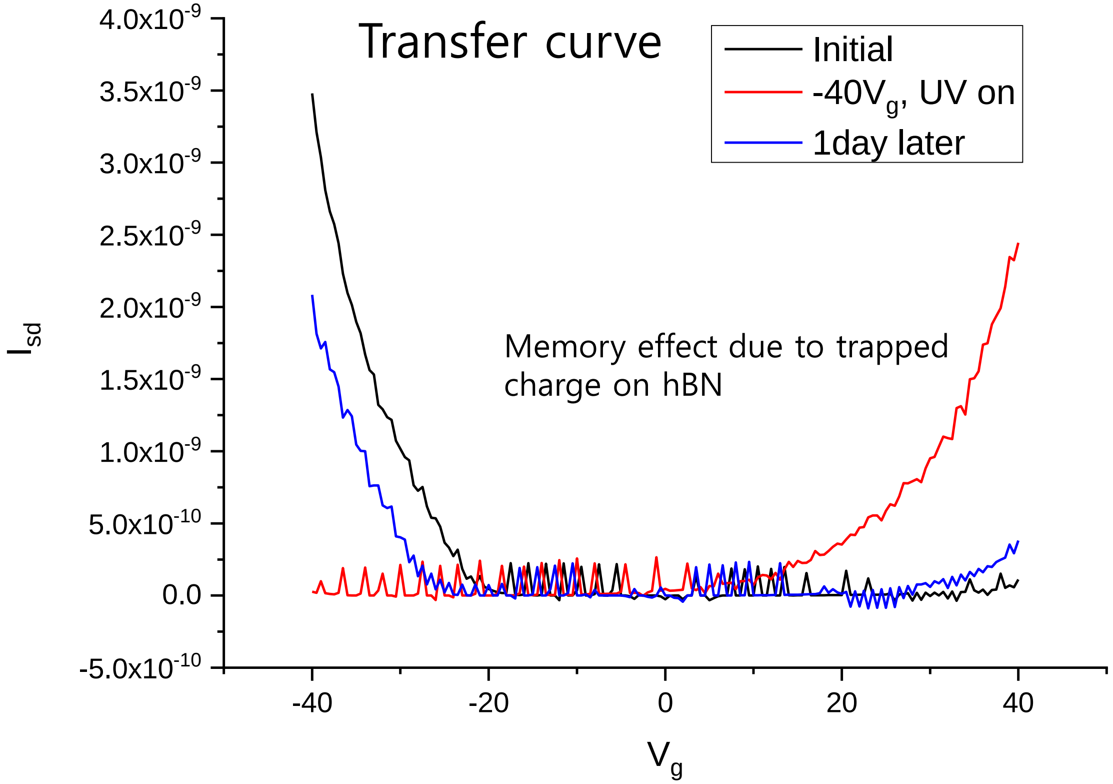




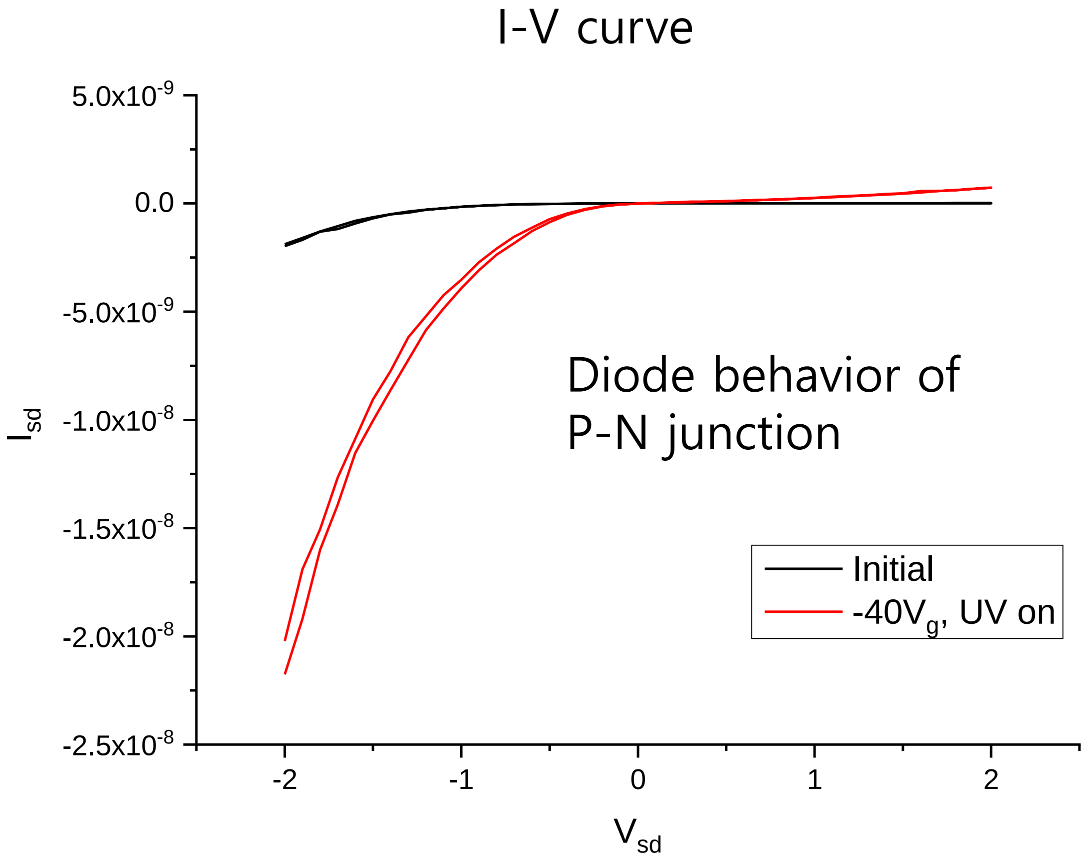
Transport measurement of P-N homojunction device



210303 s1



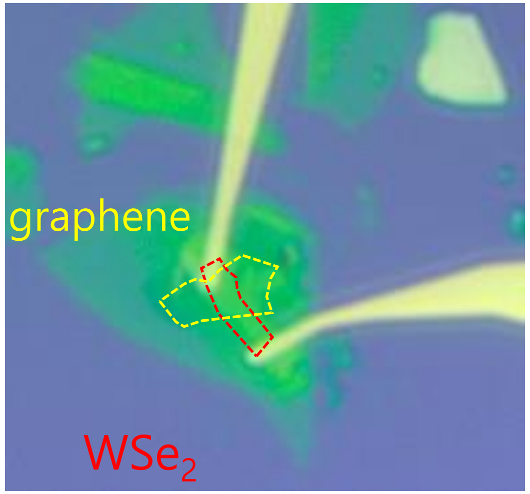
Memory effect due to trapped charge on hBN



Diode behavior of P-N junction

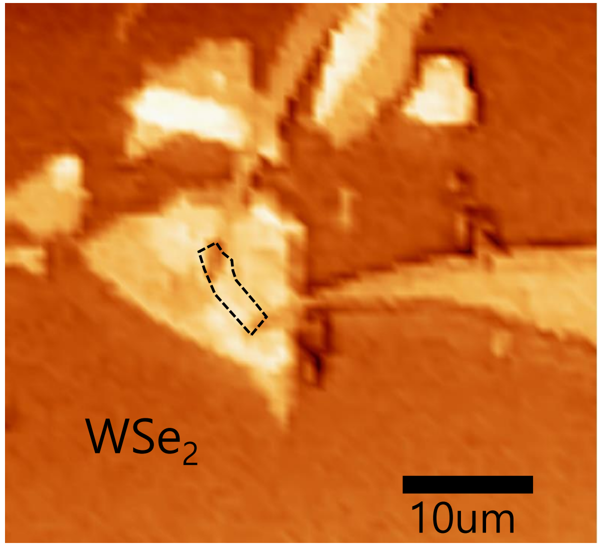
Photocurrent images of Nano device

210303 s1 semi-floating(G)



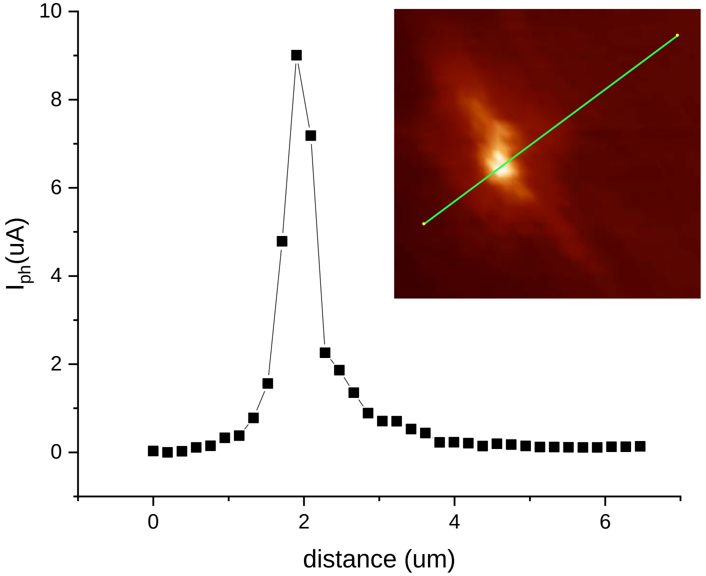
MoS2/WSe2/hBN Heterostructure

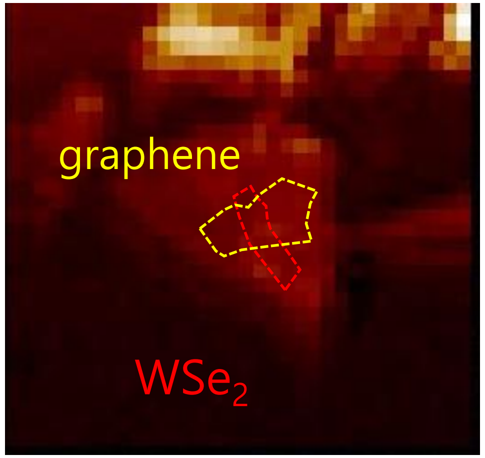
width:47um height:42um



Reflective image

Photo Current





Reflective

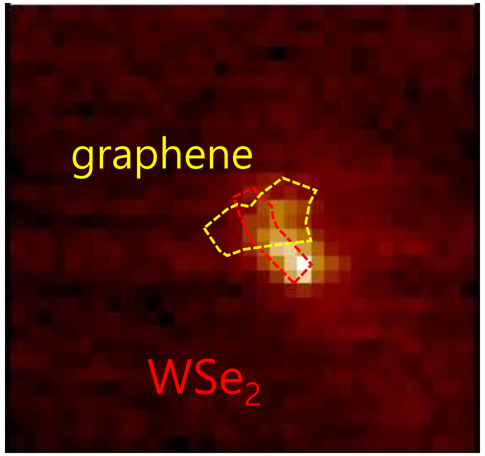
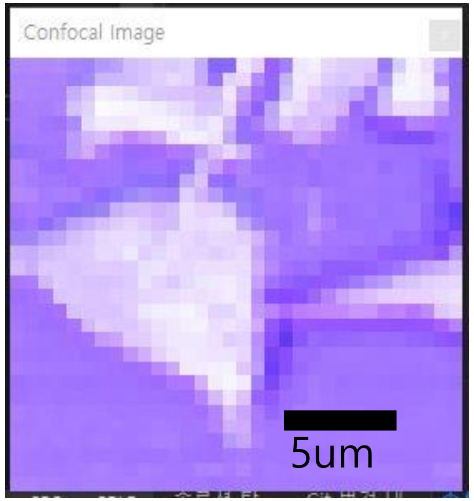


Photo Current
bias 0.5v



Confocal image

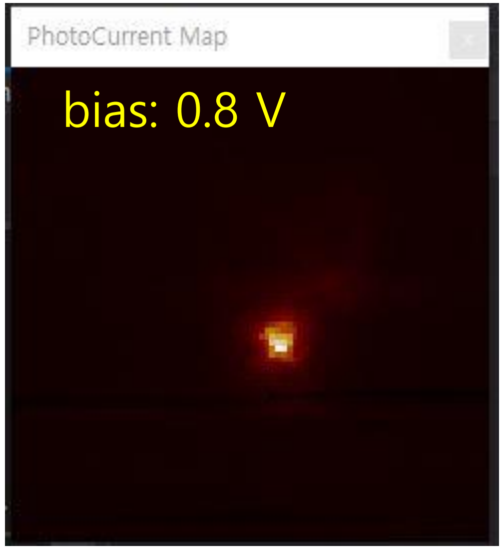
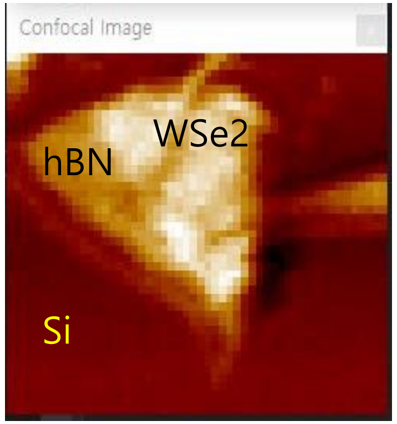


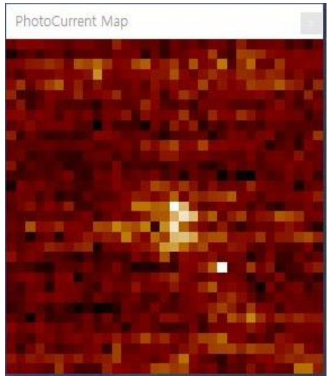
Photo Current

Images depending on bias voltages (V_b)

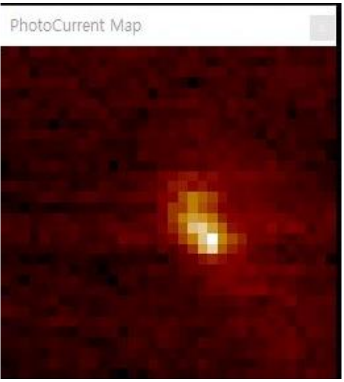


Confocal image

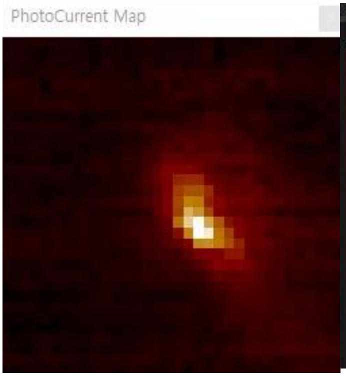
V_b=0.2 V



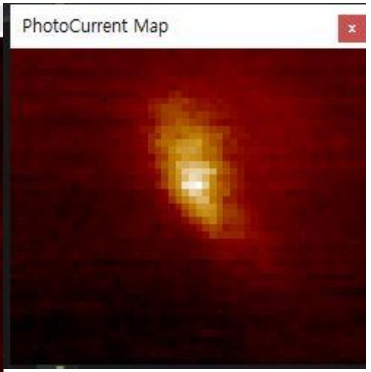
V_b= 0.5 V



V_b= 0.8 V

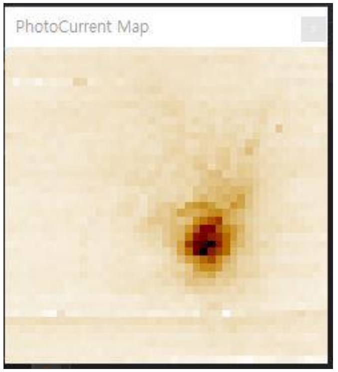


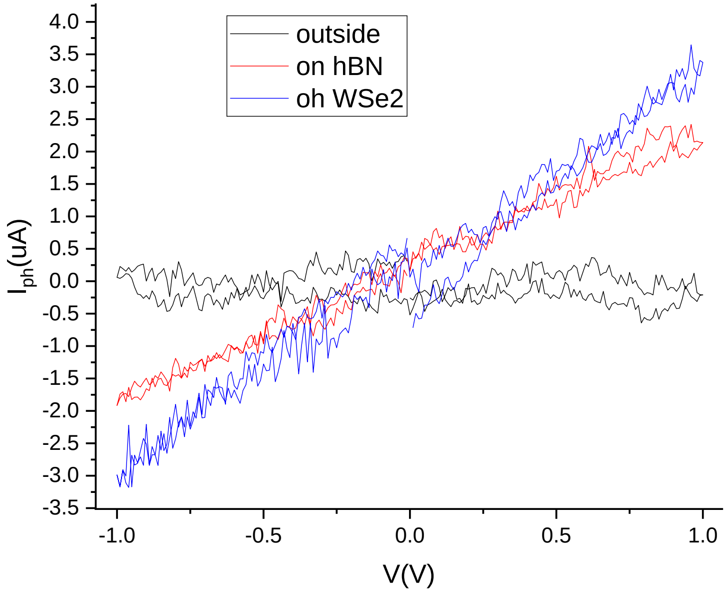
V_b= 0.9 V



V_b= -0.5 V

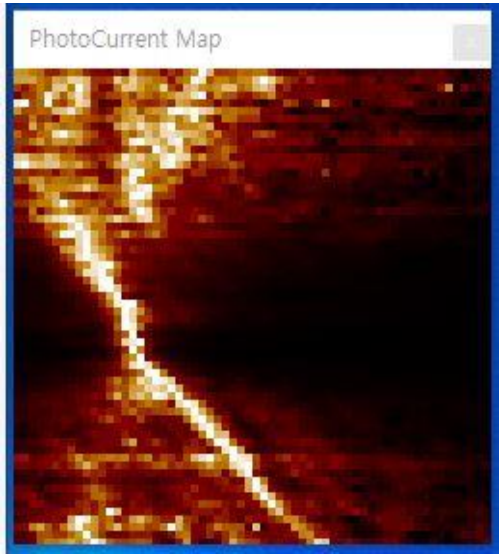
V_b= -0.8 V

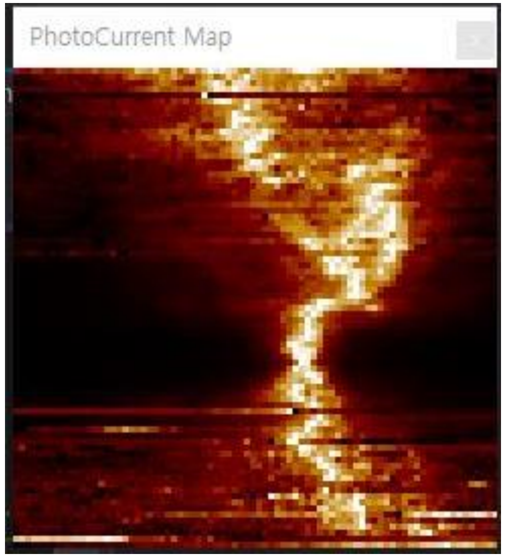




Line by line plotting

V_b = 0.8 V





Current path shifted after repeated measurements

Conclusion

- Scanning Photocurrent microscope can be utilized for analyzing photoelectric devices like solar cell, P-N diode, nano device, etc.
- Large scale uniformity test was demonstrated for MXene base solar cell device.
- Nano scale P-N homo junction device was analyzed with SPCM