Correlation between carrier lifetime and photolytic performance of Nb-doped TiO_2 single crystals

Takaya Ozawa[1], Hayao Najima[1],
Masaya Ichimura[1], Masashi Kato[1]

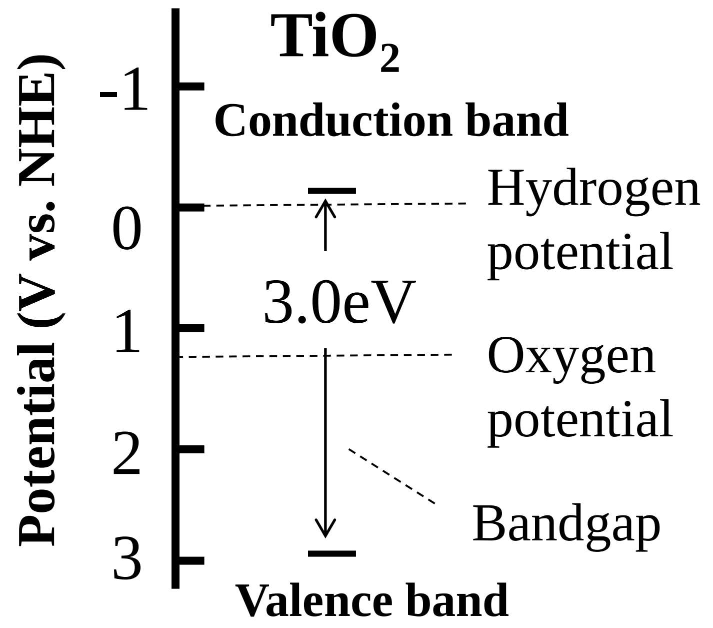
1. Nagoya Institute of Technology

TiO_2 photoelectrode

<u>TiO_2 properties</u>

▪Bandgap sandwiches oxidation-reduction potential (1.23 eV) of water.
- Rutile TiO_2 : 3.0 eV

▪Chemically stable.
- ex) Resistant to corrosion.



TiO_2 can be applied to hydrogen generation by water splitting as photocatalyst.

We used single crystal because we are easy to control doping concentration in single crystal.

Nb-doped TiO_2 single crystal

・Nb doping to TiO_2 enhances electrical conductivity and light absorption, and improves photocatalytic performance.[1]

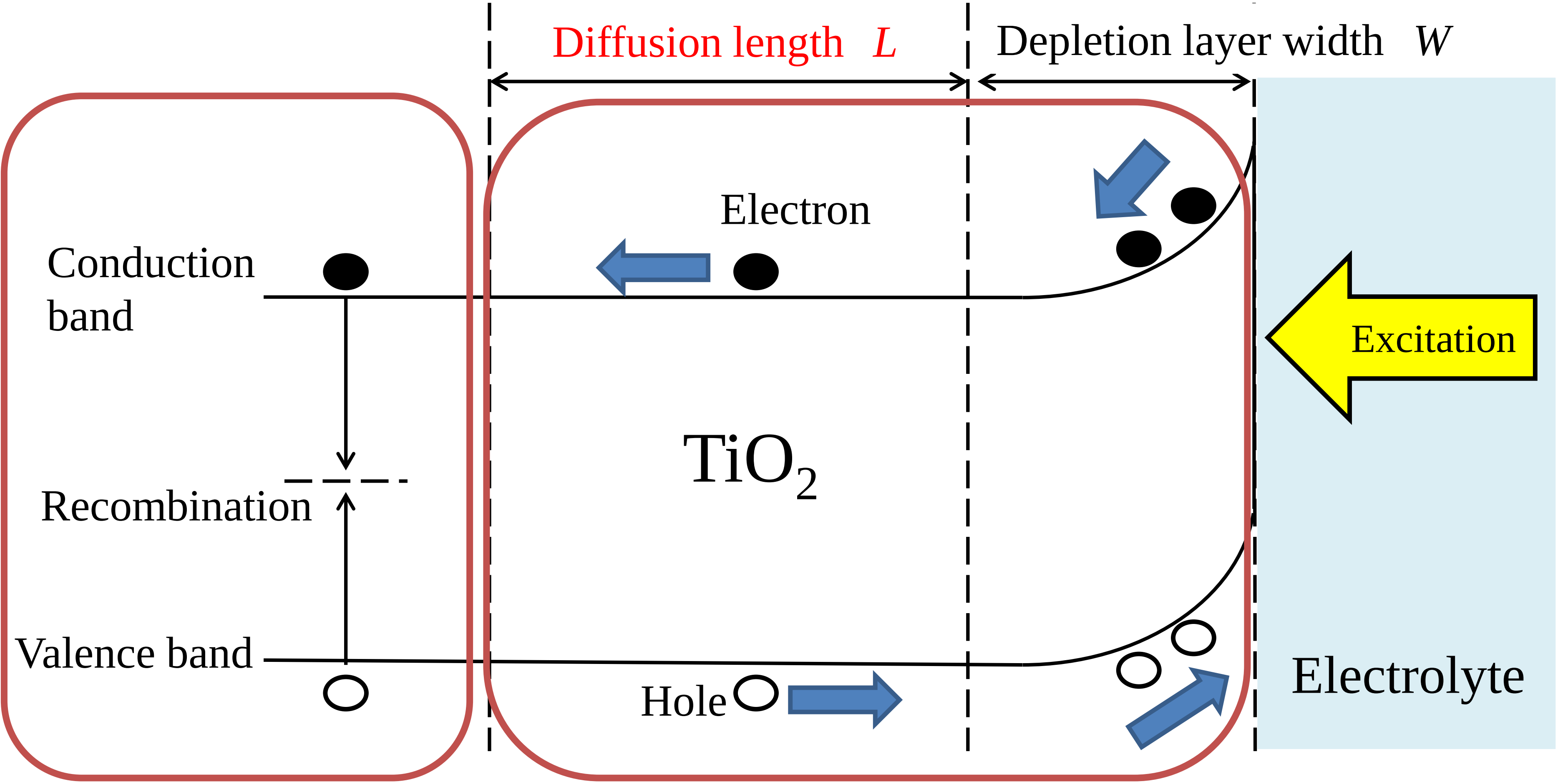
・Carrier lifetime is one of factors limiting photocatalytic performance.[2]

・There is few report on correlation between carrier lifetime and photocatalytic performance.

Evaluate correlation between carrier lifetime and photocurrent for TiO_2 with different doping concentration.

[1] J. F. Baumard, et al., J. Chem. Phys. 67, 857 (1977).
[2] D. Colombo, et al., J. Phys. Chem. 100, 18445 (1996).

Band model on photoelectrode



Only carriers in diffusion length(L) and depletion layer width(W) act as photocurrent.

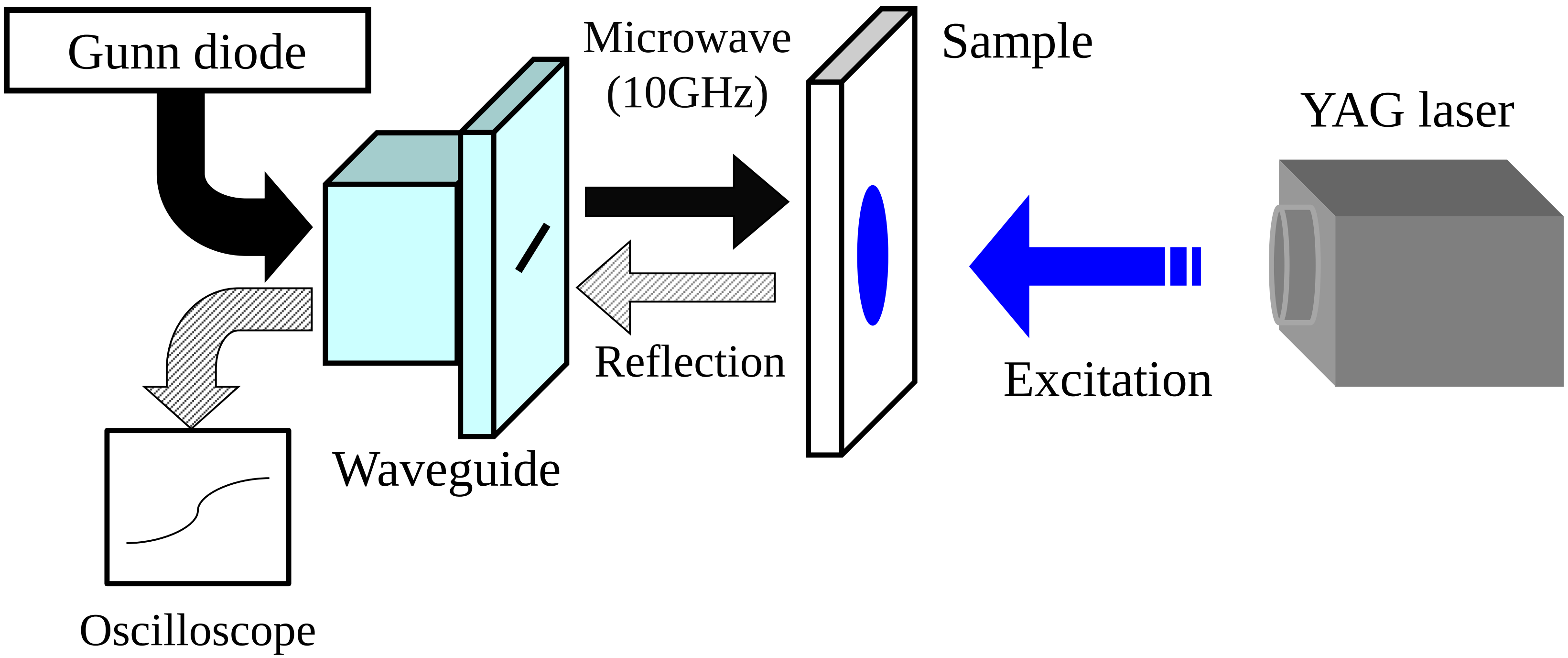
$$L = \sqrt{D\tau}$$

L : Diffusion length, D : Diffusion coefficient, τ : Carrier lifetime

Sample

Name	**undope**	**Nb-0.01**	**Nb-0.05**
Sample	rutile TiO_2 single crystal		
Doping		Nb 0.01 wt%	Nb 0.05 wt%
Growth	Bernoulli method		
Crystal surface	(110)		
Size	5 × 5 × 0.5 mm		

Microwave photoconductivity decay (μ-PCD)



Third harmonic YAG laser

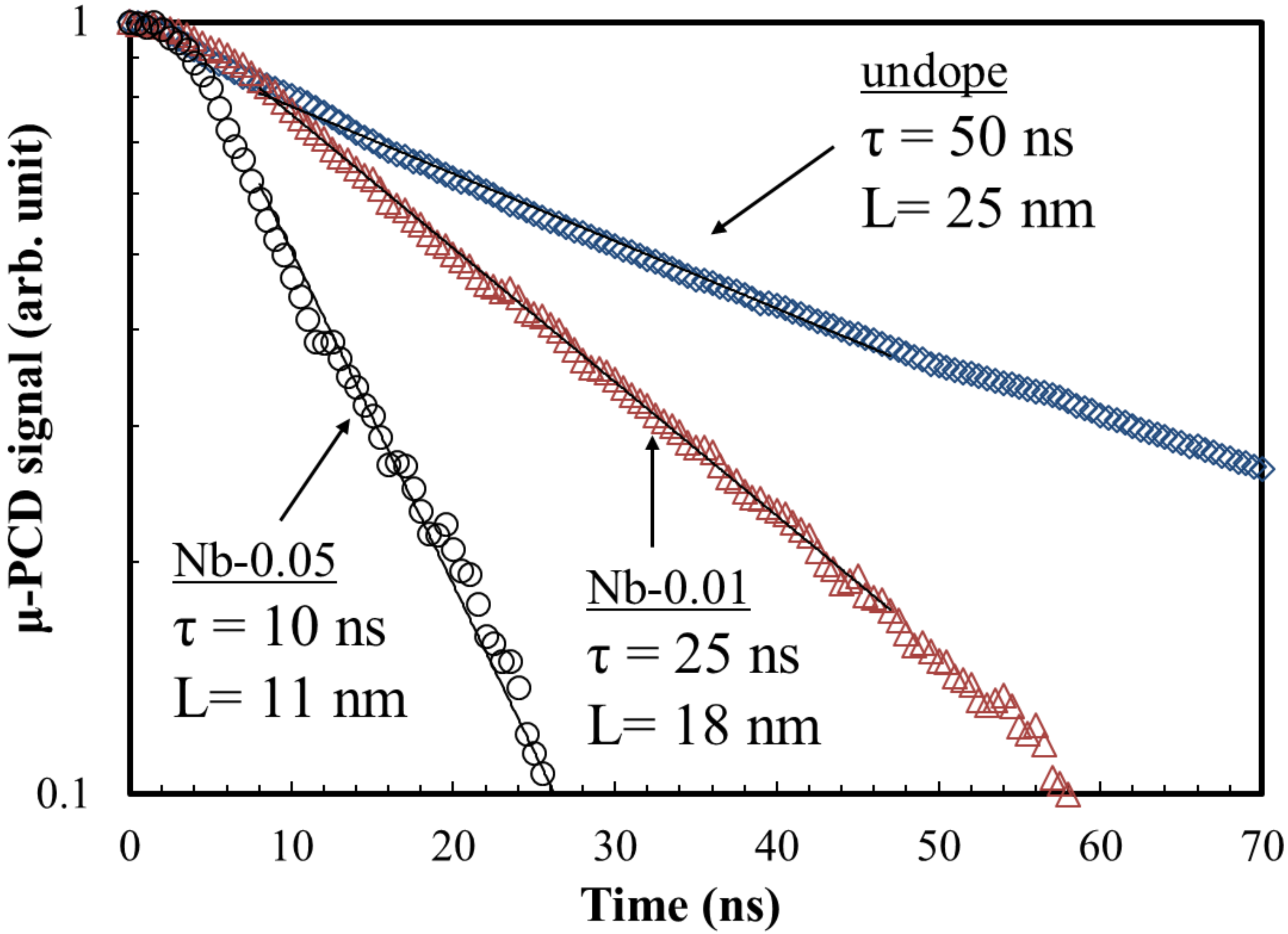
Wavelength : 355nm
Pulse width : 1 ns
Injected photon : 8.5×10^{13} cm^{-2}

Penetration depth

About 75 nm[3]

[3] Y. R. Park and K. J. Kim, Thin Solid Films. 484, 34-38 (2005).

μ-PCD decay curve



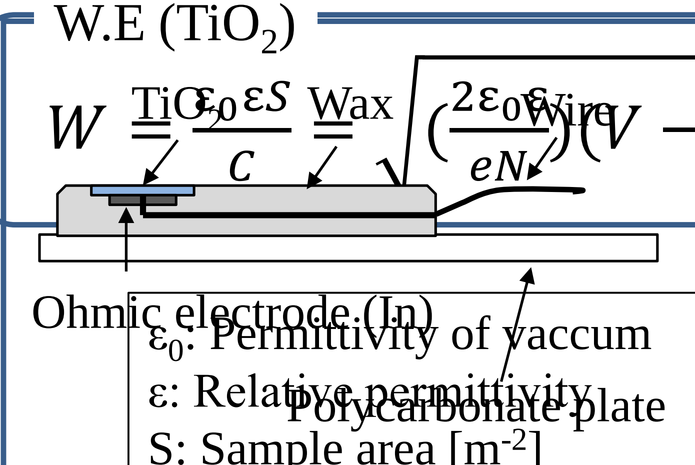
- τ became longer with less Nb doping sample.
- Calculated L from D of literature value (D [4]= 1.29×10^{-4} cm^2/s).

[4] N. A. Deskins and M. Dupuis, J. Phys. Chem. 113, 346-358 (2009).

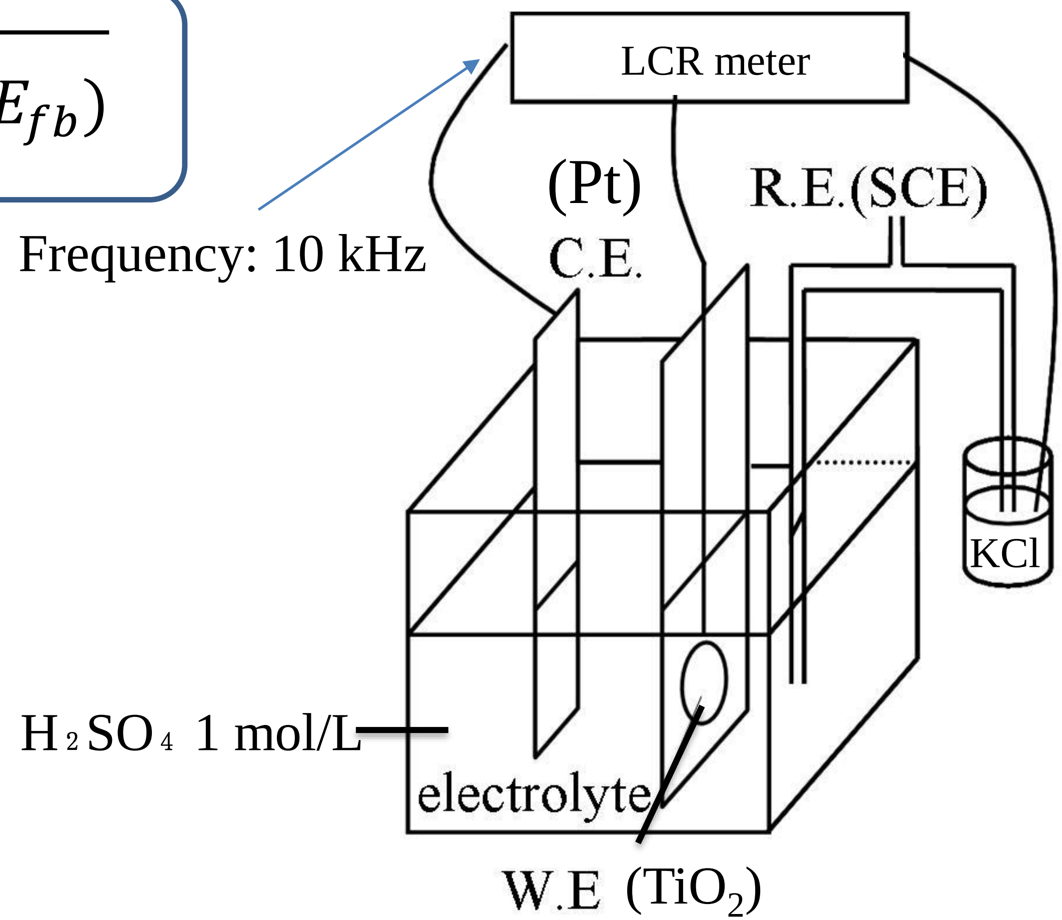
Capacitance-Voltage (C-V) measurement

- We couldn't make ohmic contact in undope sample.
- Calculated depletion layer width (*W*) from Mott-Schottky plot.

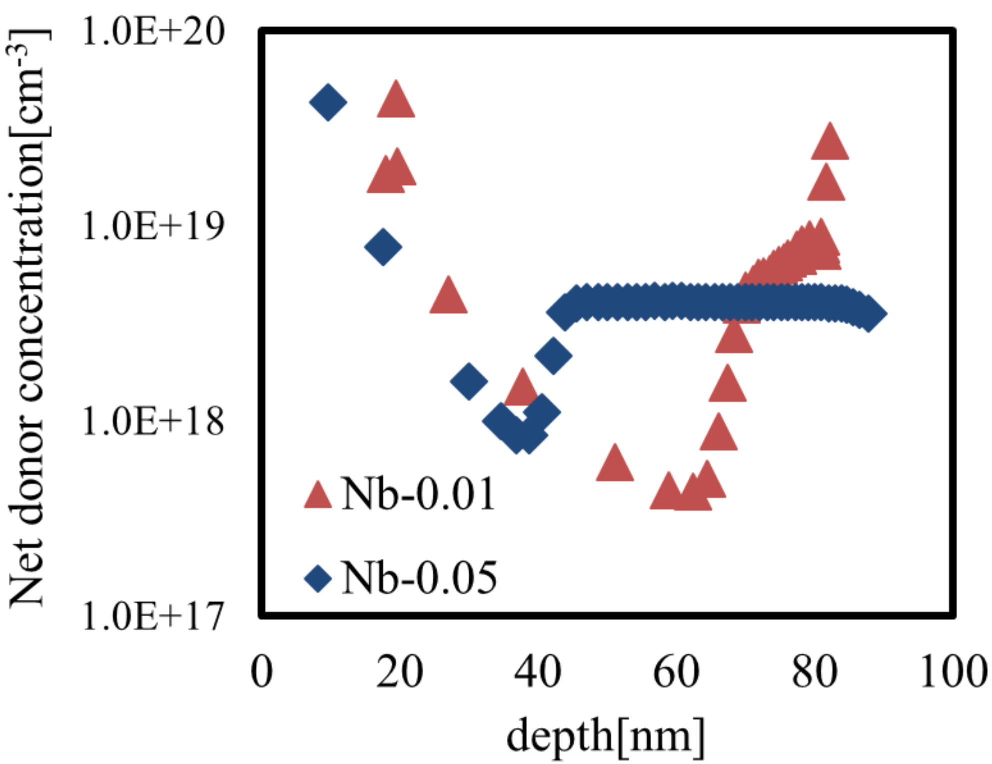
$$W = \frac{\varepsilon_0 \varepsilon S}{C} = \sqrt{\left(\frac{2\varepsilon_0 \varepsilon}{eN}\right)(V - E_{fb})}$$

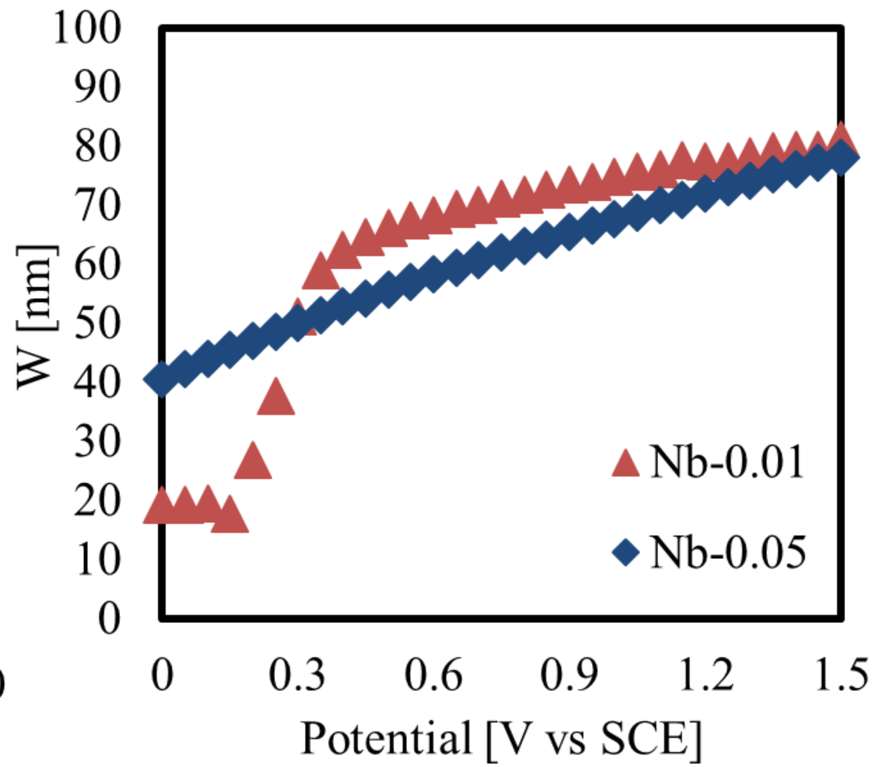


- ε_0: Permittivity of vaccum
- ε: Relative permittivity
- S: Sample area [m^{-2}]
- C: Capacitance [F]
- e: Elemental charge [C]
- N: Carrier density [cm^{-3}]
- V: Potential [V]
- E_{fb}: Flat band potential [V]



Net donor concentration and *W*



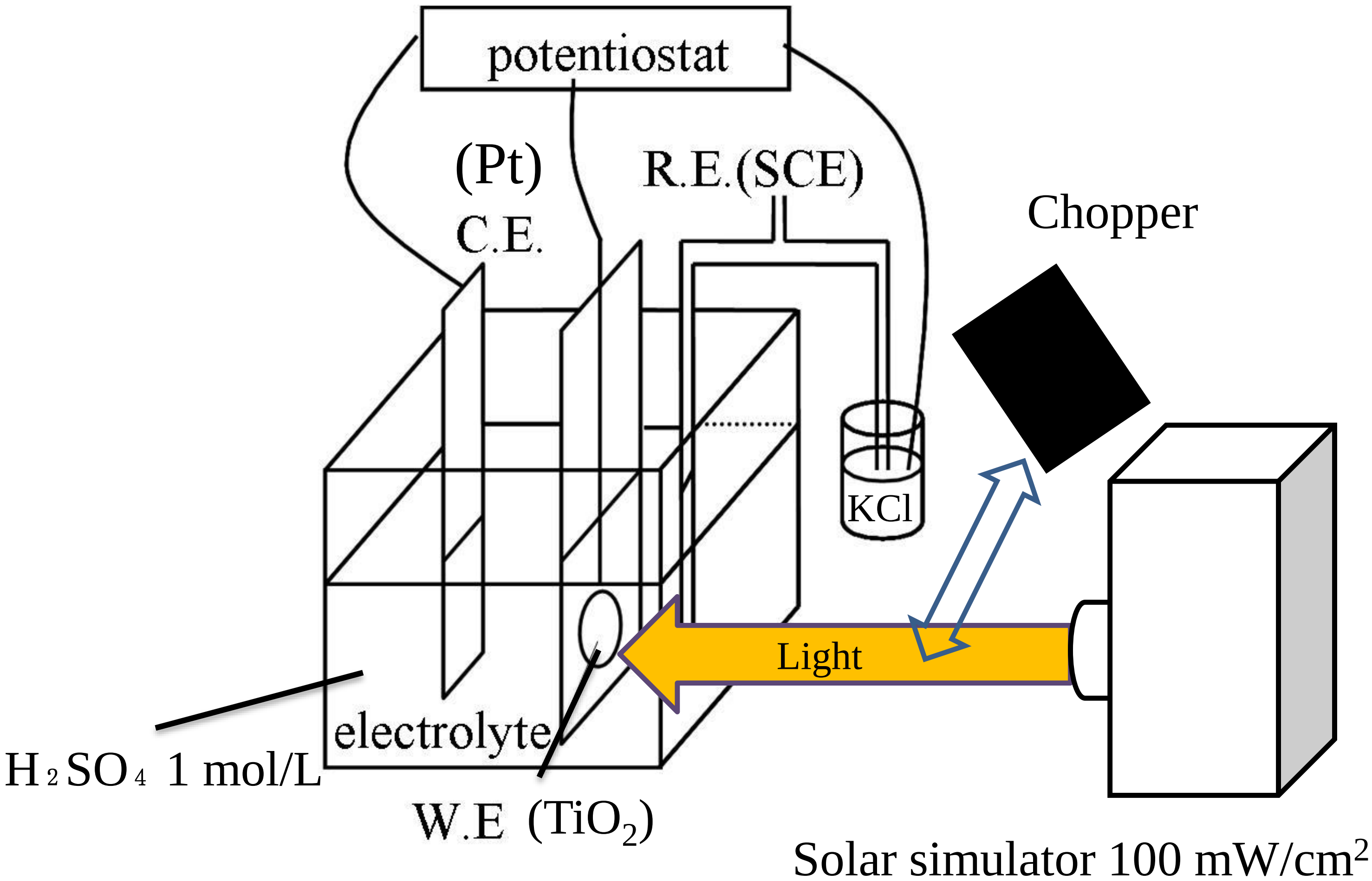


For both samples, net donor concentration was of the order of 10^{18}.

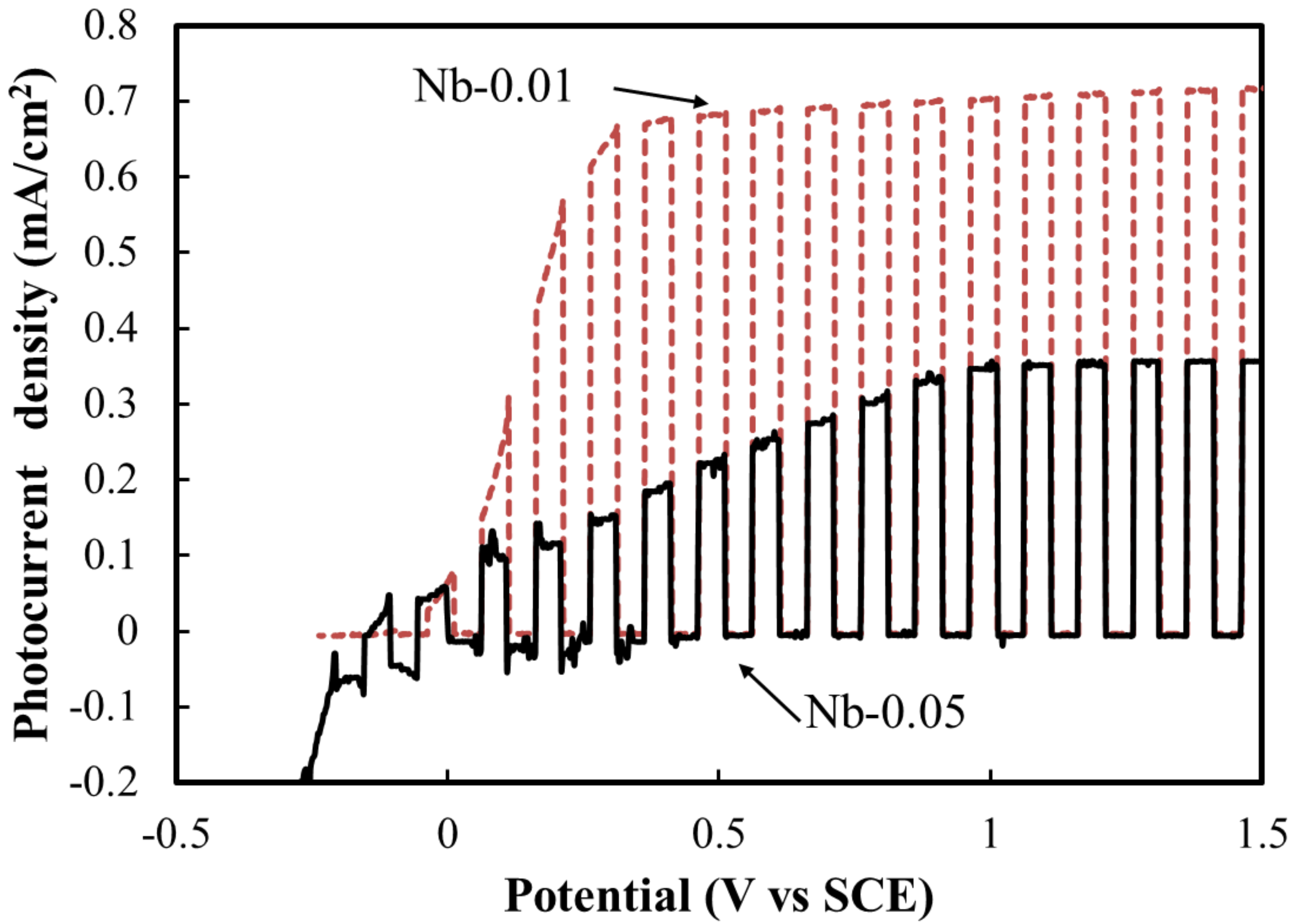
- *W* increased as potential increases.

Chopped light I-V measurement

Photocurrent was observed with three-electrode system.



Chopped light I-V measurement

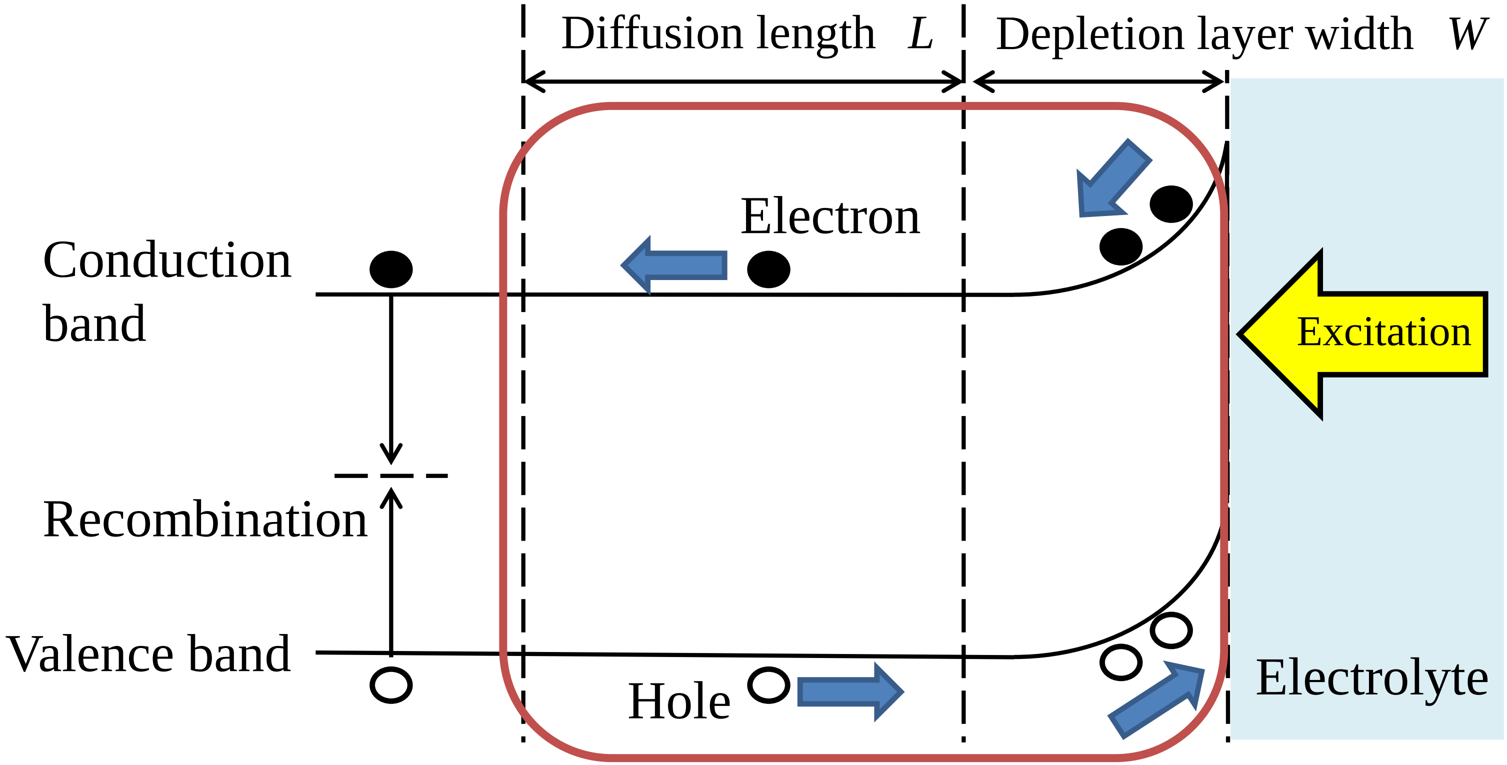


Photocurrent density (1.5 V vs SCE)

Nb-0.01: 0.72 mA/cm^2

Nb-0.05: 0.36 mA/cm^2

Theoretical estimation of photocurrent density



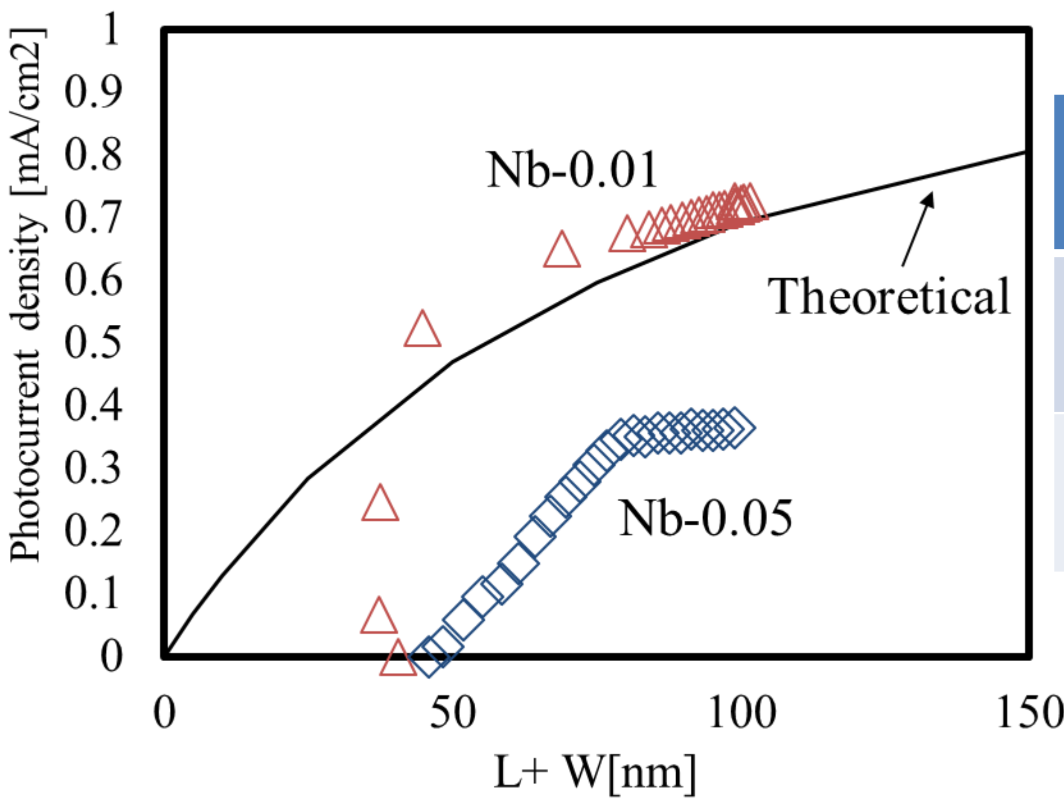
Theoretical

Calculate photons can be absorbed within *L*+*W* from reported absorption coefficient[3],[5].

We converted photons to theoretical photocurrent density.

[5] N. G. Park, J. van de Lagemaat and A. J. Frank, J. Phys. Chem. B 104, 8989-8994, (2000).

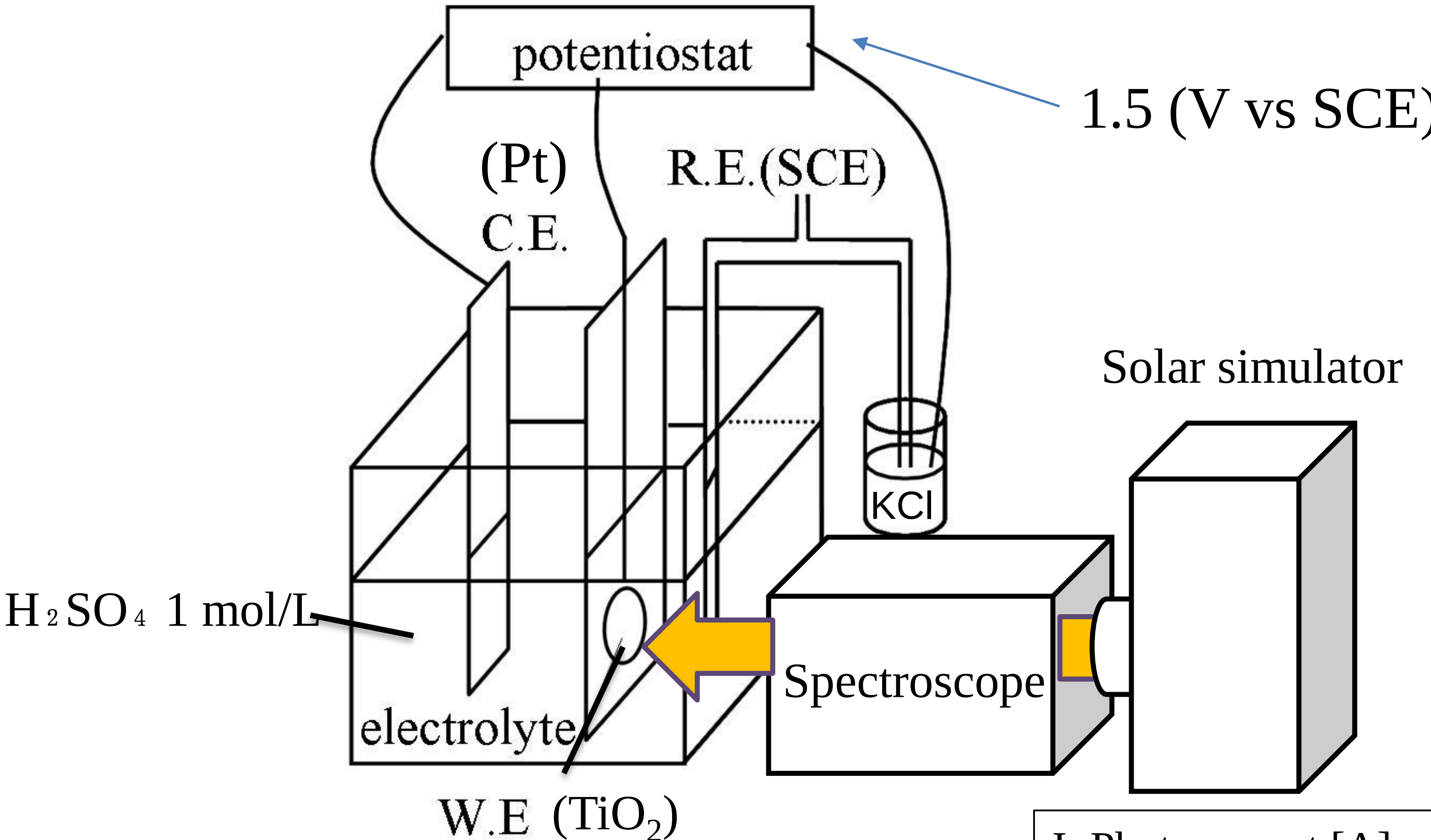
Photocurrent density for *L* + *W*



	L	*W* (1.5 V vs SCE)
Nb-0.01	18 nm	79 nm
Nb-0.05	11 nm	78 nm

- As *L*+*W* increased, photocurrent density increased.
- For Nb-0.01, experimental value exceeded theoretical value.
- For both samples, contribution of *W* was larger than *L*.

Spectral response

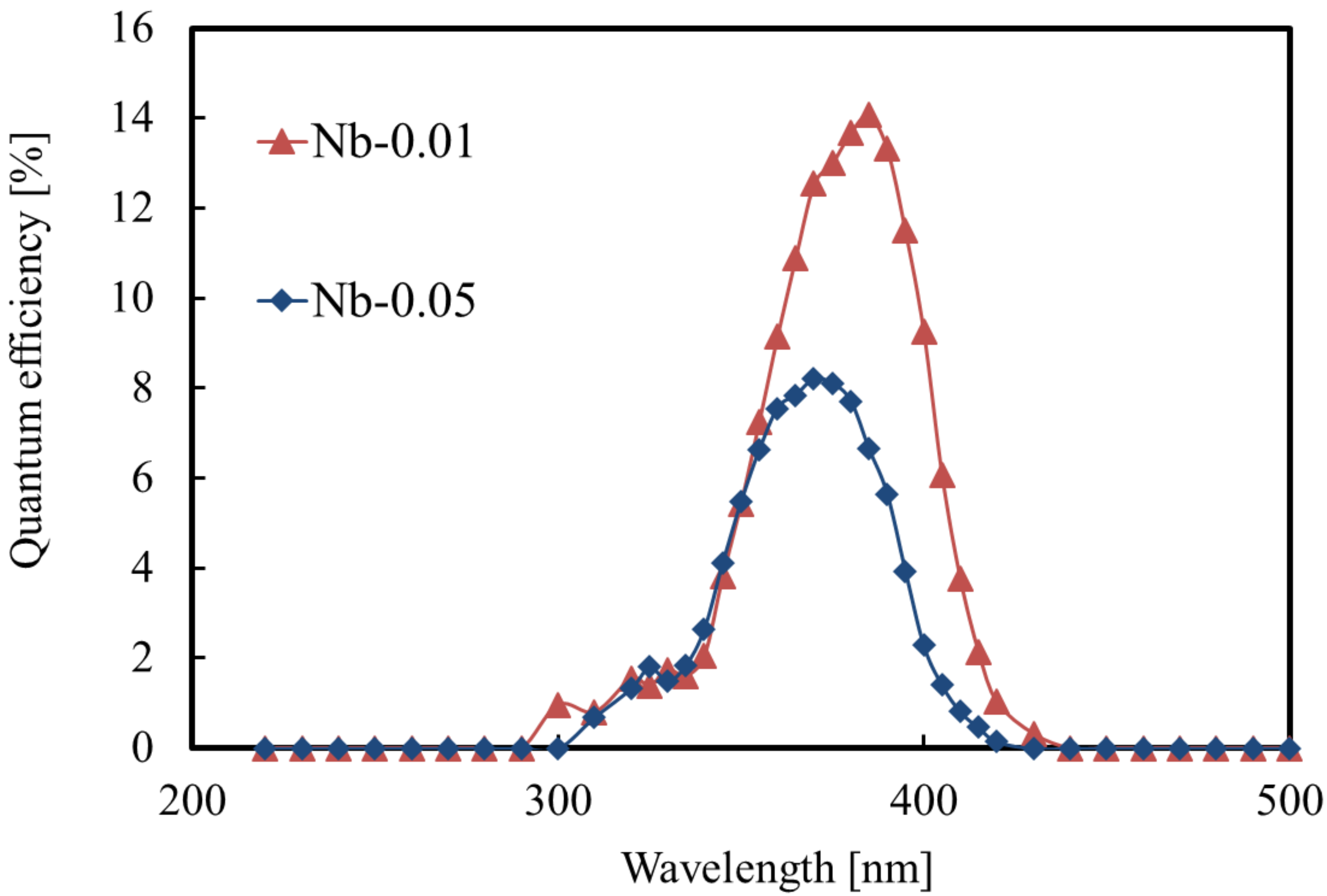


Quantum efficiency

$$= \frac{\text{Output electron } [I(\lambda)/e]}{\text{Incident photon } [W(\lambda)/h\nu]} \times 100 \quad \%$$

I: Photocurrent [A]
λ: Wavelength [m]
W: Irradiation power [W]
e: Elemental charge [C]
h: Plank's constant [J・s]
ν: Frequency [s^{-1}]

Quantum efficiency



- For Nb-0.01, photocurrent was observed in long-wavelength region.

→ Nb-0.01 used deeply penetrated photons more than Nb-0.05.

- We underestimated *L* of Nb-0.01 in calculation.

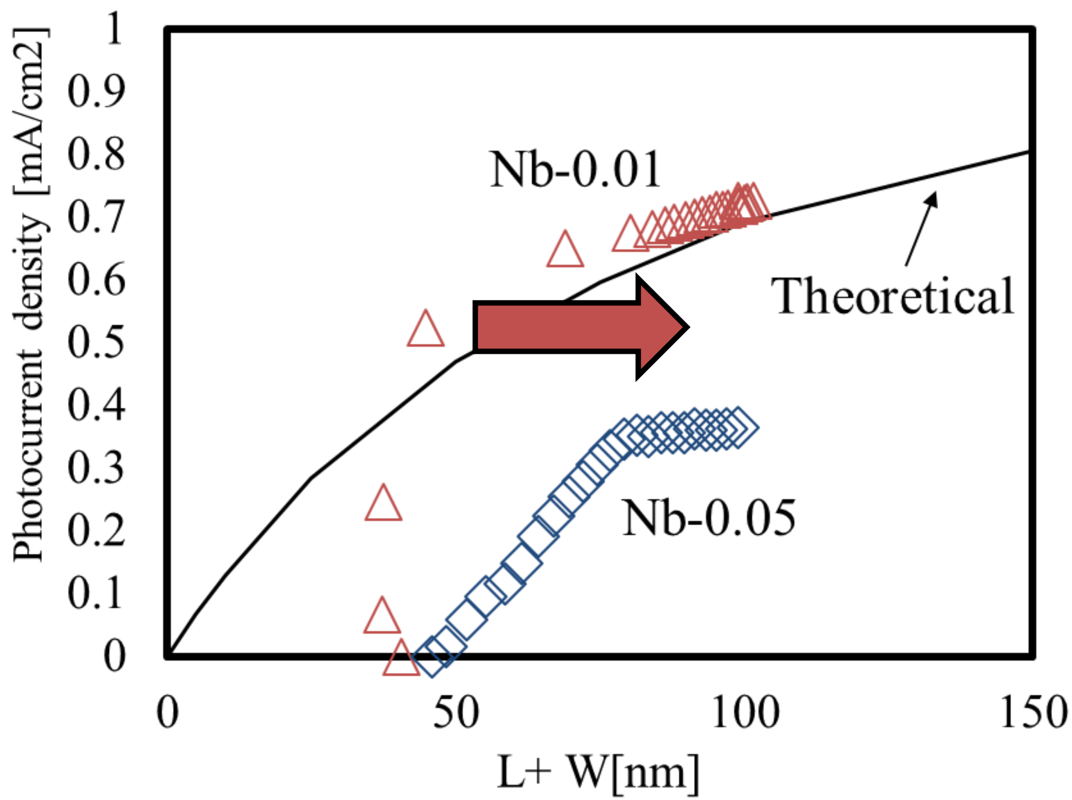
Consideration of L

Measurement

$$\boxed{\frac{1}{\tau_{eff}}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_S}$$

$\Rightarrow \tau_{eff} < \tau_{bulk}$

τ_{eff}: Effective carrier lifetime
τ_{bulk}: Bulk carrier lifetime
τ_S : Carrier lifetime by surface recombination



- L must be calculated by using τ_{bulk}.
- In this study, L was calculated by using τ_{eff}

→We underestimated L.

We can't ignore τ_S.

Summary

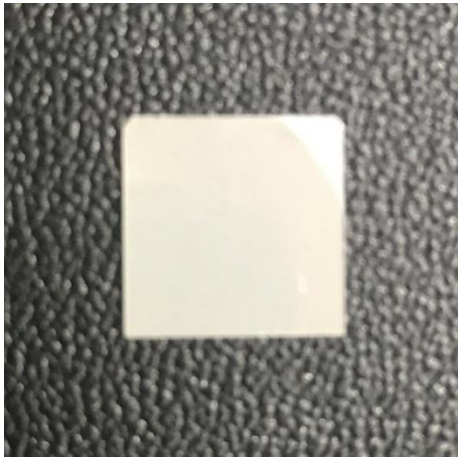
- τ became longer as Nb doping concentration decreases.
- Photocurrent and quantum efficiency were high in sample with large τ.
- In photolytic performance, we can’t ignore surface recombination.

Photolytic performance is improved by reducing Nb doping concentration.

On the other hand, it is necessary to suppress surface recombination.

Samples

undope

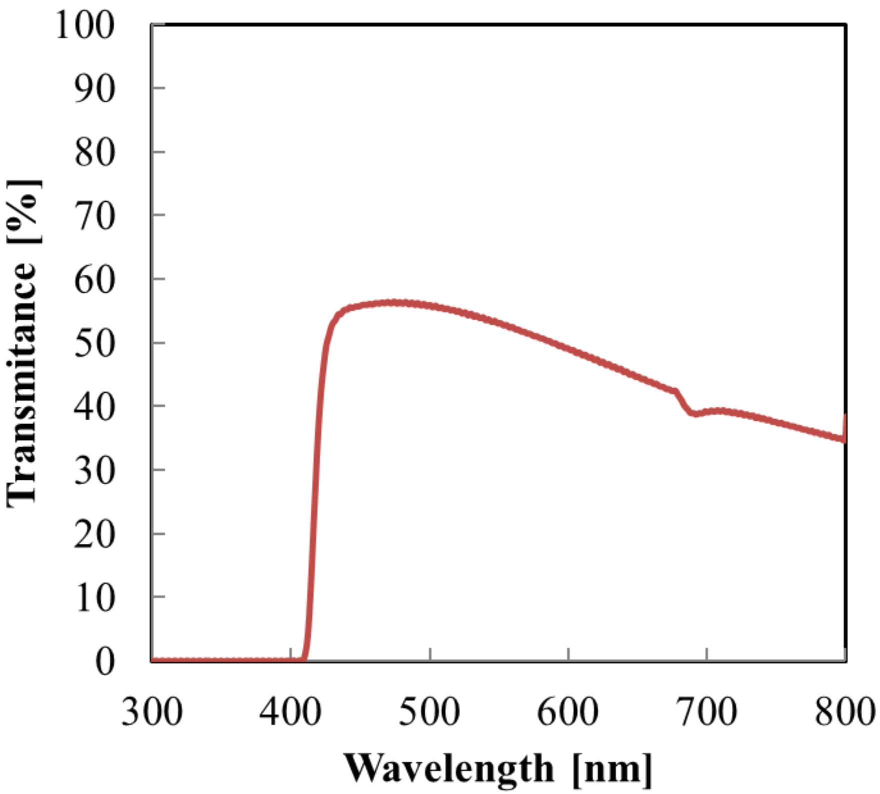


Nb-0.01

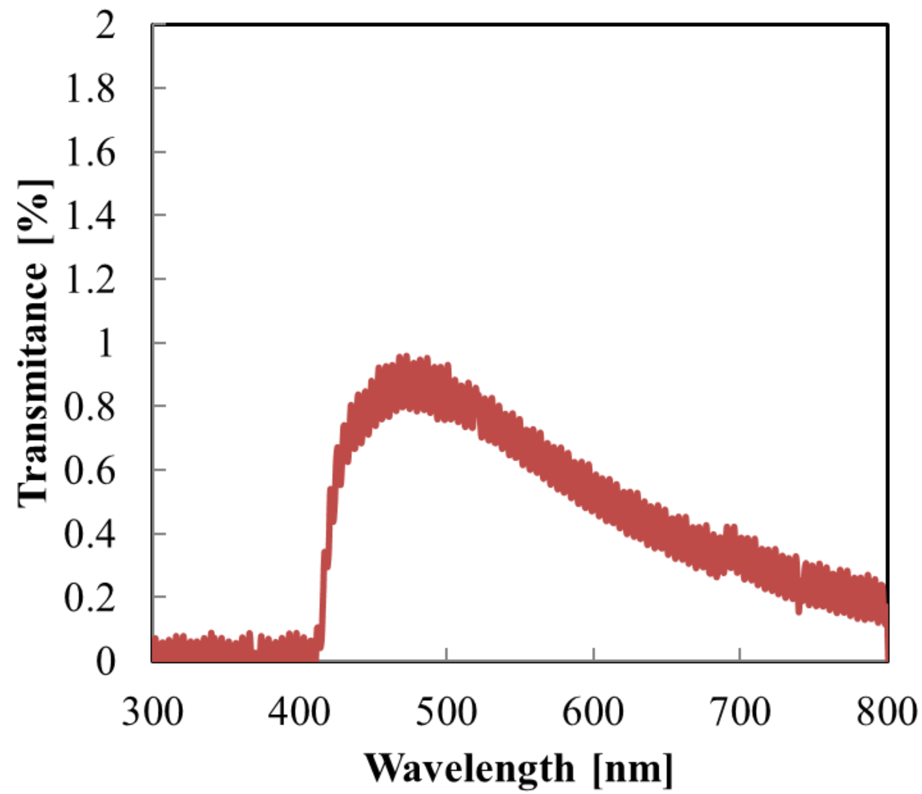
Nb-0.05

Transmittance

Nb-0.01



Nb-0.05

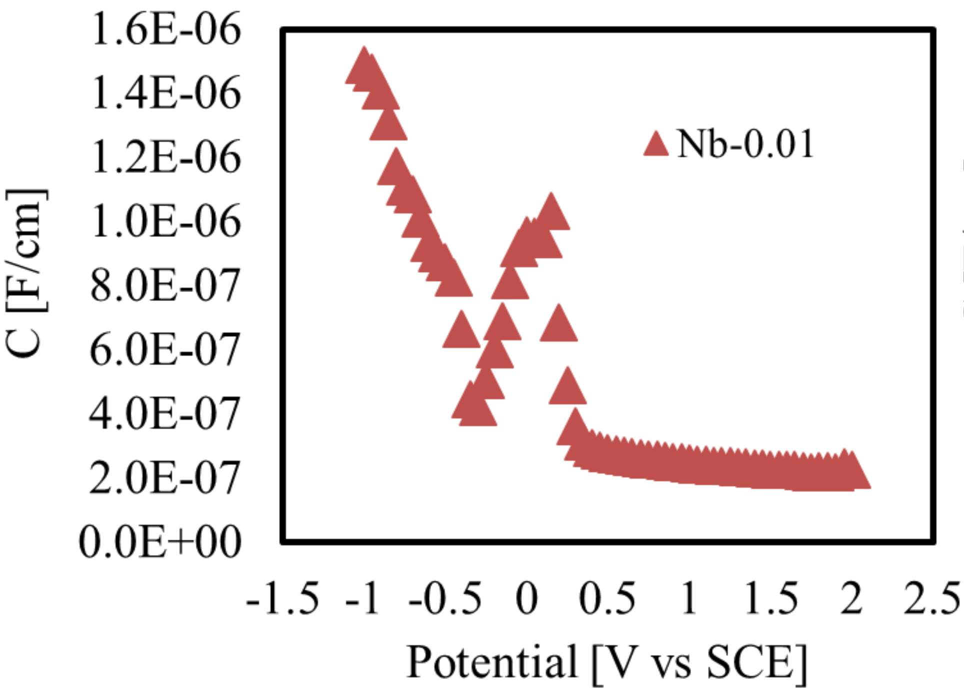


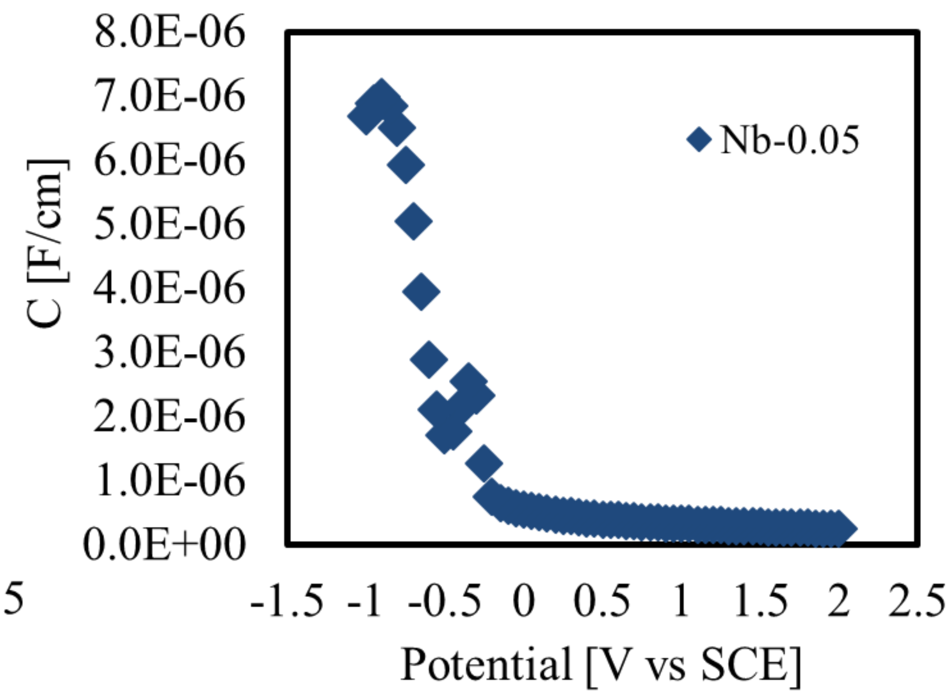
<u>Absorption edge</u>

Nb-0.01 : about 420 nm

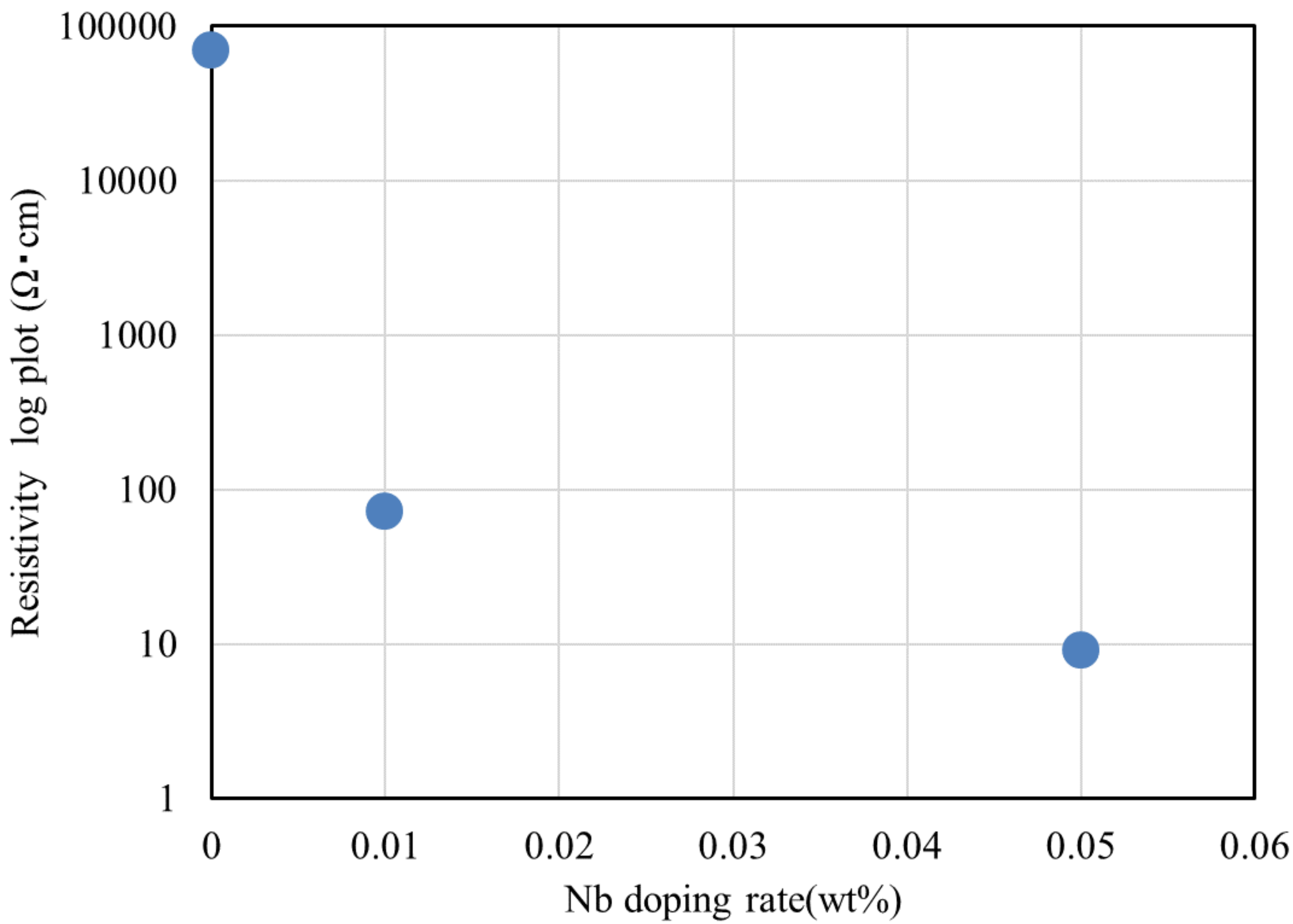
Nb-0.05 : about 420 nm

C-V measurement





Resistivity

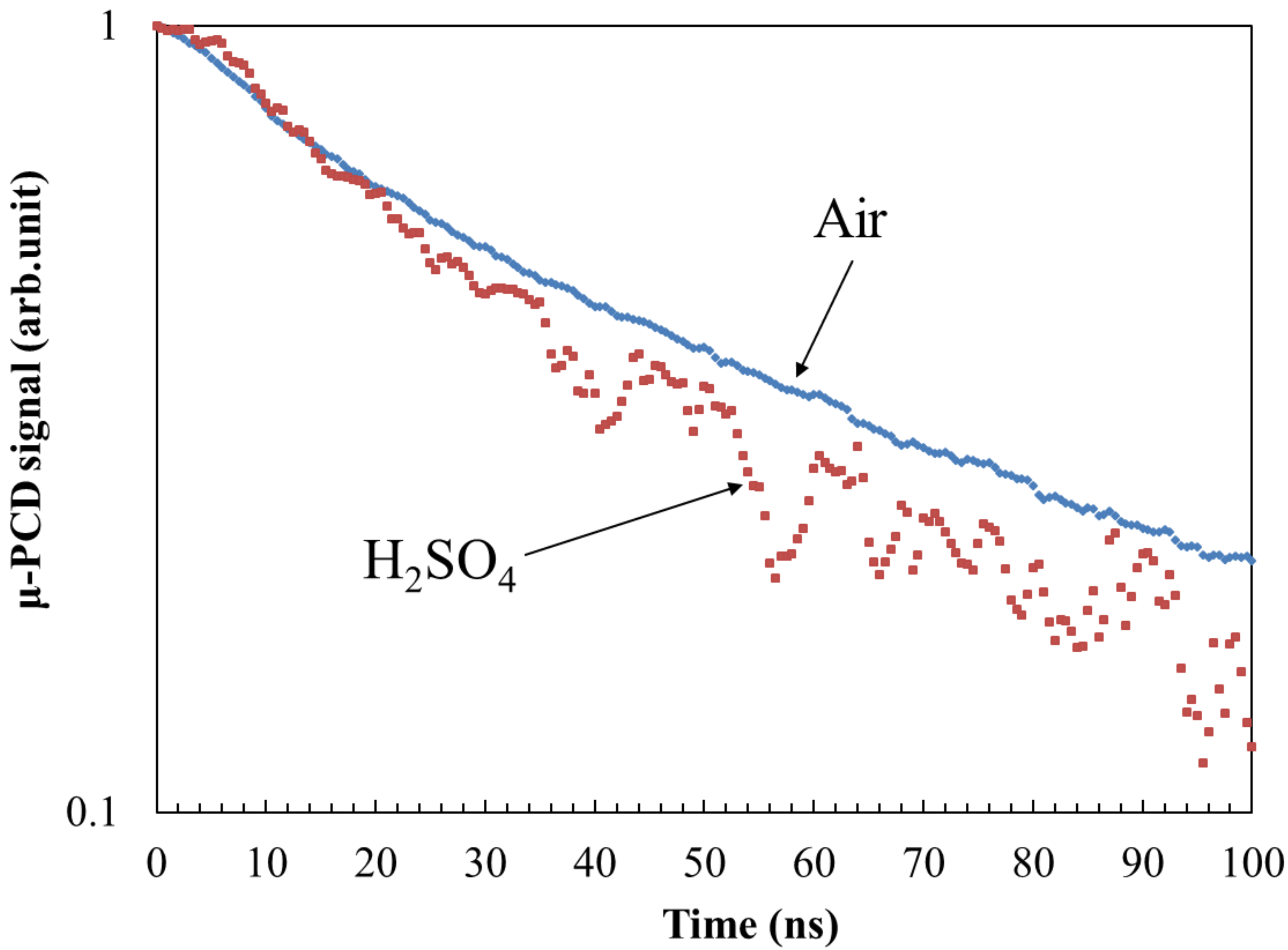


<u>Resistivity</u>

Nb-0.01 : about 9.1 Ω/cm

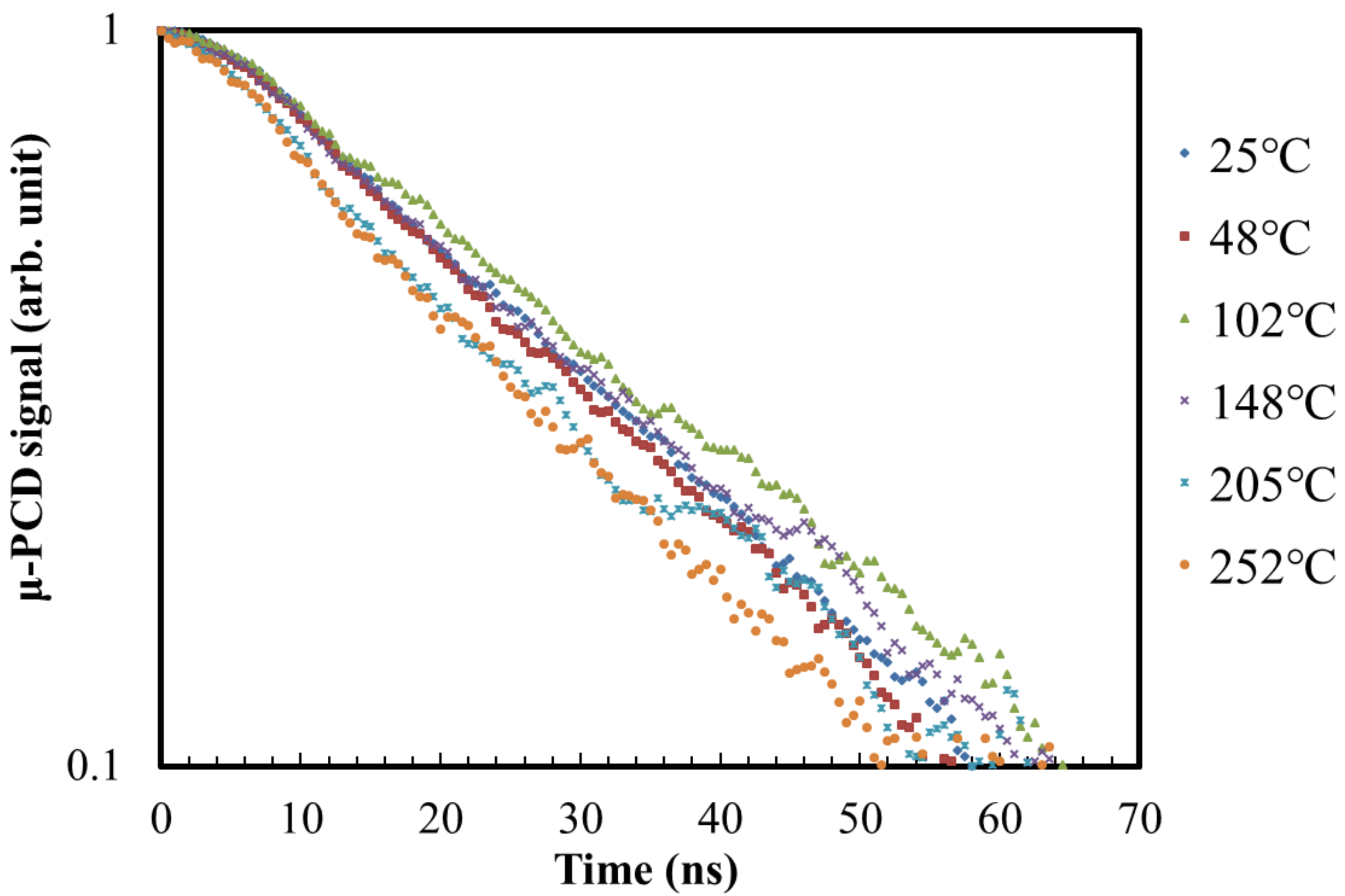
Nb-0.05 : about 71.3 Ω/cm

Solution dependence in undope



There is no difference in carrier lifetime in solution.

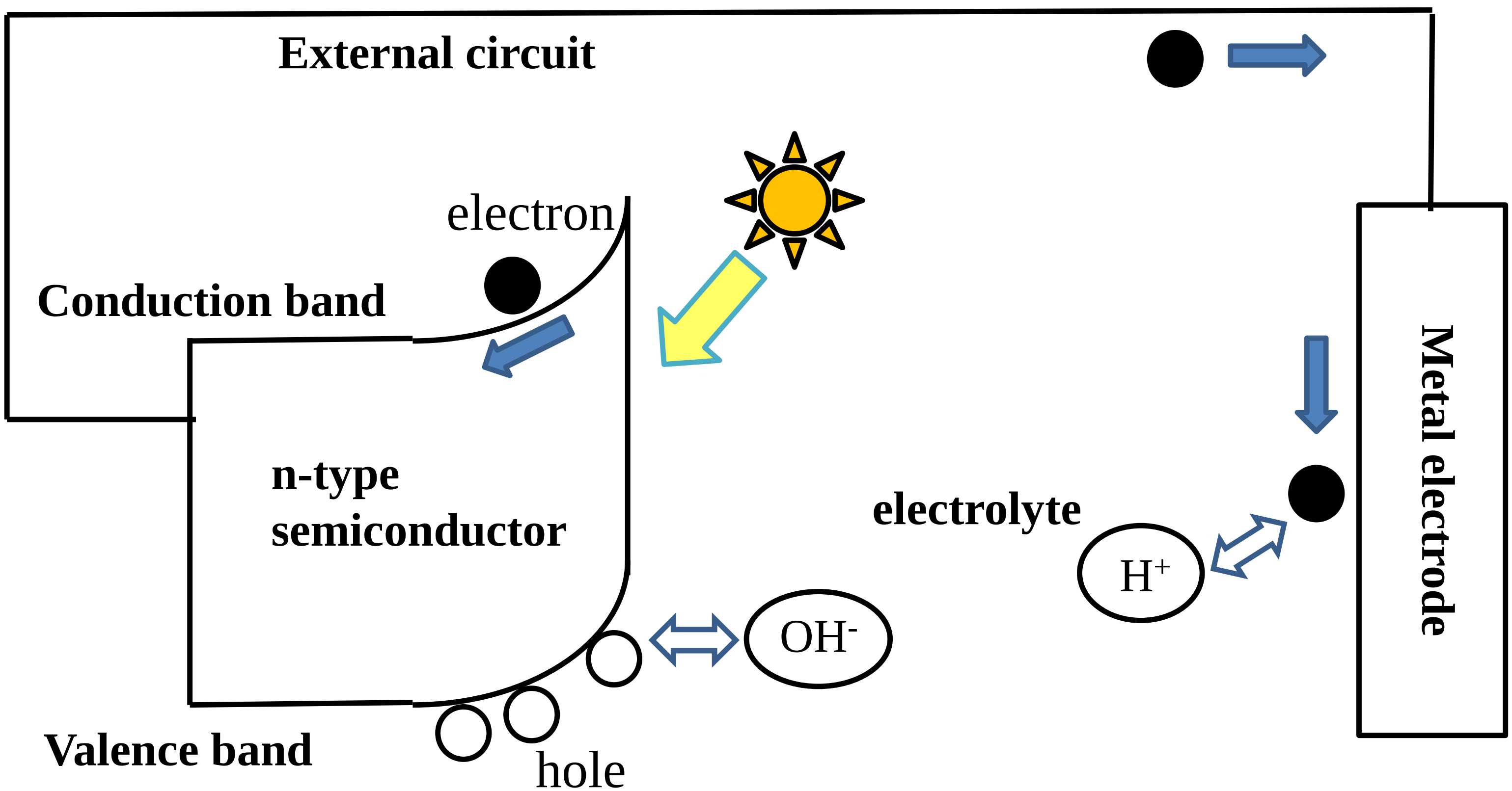
Temperature dependence in Nb-0.01



No temperature dependence at 250 ℃ or lower

For undope and Nb-0.05, they were similar tend.

Water splitting by photocatalyst



n型半導体の場合
Semiconductor side :
金属側 : 電子が水を還元し水素を発生