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研究課題名（和文）Construction of avalanche-like super sensitive photodetectors based on hybrid perovskite photodiode

研究課題名（英文）Construction of avalanche-like super sensitive photodetectors based on hybrid perovskite photodiode

研究代表者

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研究成果の概要（和文）：将来的に優れたアバランシェ型ダイオードを構築することを目的に、スプレー熱分解法によって作製された酸化スズ膜を有するヒステリシスフリーな有機金属ハライドペロブスカイト光電変換素子を開発した。四塩化スズ・5水和物を用い、製膜温度の最適化により、膜抵抗値は200℃にて極小値を示した。膜の良好な電子移動特性がペロブスカイトとの界面の電荷蓄積を緩和したため、電流電圧曲線におけるヒステリシスが解消された。素子のエネルギー変換効率は18.1%、ヒステリシス率は1%以内を示した。異なる光量下の素子の光応答特性を調査したところ、光電流が定常状態に達する時間は酸化チタンより酸化スズが短く、光応答性に優れた。

研究成果の概要（英文）：For future application to Avalanche diode, Hysteresis-less organo metal halide perovskite opto electronic device with tin oxide (SnOx) compact layer prepared by spray pyrolysis are reported. A superior SnO2 compact layer is prepared with tin tetrachloride pentahydrate (SnCl4-5H2O) solution by post thermal annealing at several different temperatures, which revealed the lowest resistance of SnO2 layer was made at 200 °C. Therefore, a good electron transfer property could reduce charge accumulation at the interface to perovskite, which leads to J-V hysteresis-less behavior.
In results, the power conversion efficiency and minimum hysteresis factor were reached to 18.1% and in 1%. As the important property of photodetectors, photo-response of devices under different light intensity with the SnO2 and TiO2 were resulted in faster response on SnO2 until reaching steady state current than TiO2, which indicated that SnO2 based photodetectors shows their superior sensitivity for photocurrent.

研究分野：　opto-electronic device

キーワード：　opto-electronic device　photodetector　solar cells　perovskite　dye sensitized

１．研究開始当初の背景

Perovskite materials have found a number of applications, such as use in field-effect transistors, light emitting diodes, optical sensors, and memories for more than a decade[1]. Ferroelectricity is endured by a spontaneous electric polarization due to a structural transition from high symmetry to low symmetry state, which is caused by external energy like heat and electric field. Polarization property of ferroelectrics can be switched with external electric field[2]. Ferroelectrics are known to act as a rectifier, showing a diode-like current controlled by polarization and this function opens potential applications to high speed switches and high densities random access memories[3]. Perovskite-type oxide material semiconductors are known to serve as ferroelectrics, which are generally highly insulating because of large band gaps[4]. The ferroelectric perovskites of narrow band gaps have been found to exhibit a diode-like current under room temperature. Among narrow band gap oxide perovskites, $BiFeO_3$ (band gap, ~2.2 eV), which has transition metal (Fe) ions with unpaired d electrons generating a large diode-like current. It is known that a ferroelectric exposed to intense light gives rise to the second order optical response and induces asymmetric polarization[6], which is assumed to generate a rectified photocurrent. After the very first pioneering work on the photovoltaic application[6], the organo-metal halide perovskites have been evolved to boost power conversion efficiency (PCE) up to more than 20%, which has a short circuit photocurrent density (J_{SC}) of ~23 mA cm^{-2} without external bias voltage under exposure to sun light intensity (100 mW cm^{-2}).

２．研究の目的

We recently discovered avalanche-like diode current with large current densities (200~300 mA cm^{-2})[7]. Action spectra of external quantum conversion efficiency (EQE) values of giant current (500~700 nm) are as large as 1700%. I found that by using a planar-structured ferroelectric organo-metal halide perovskite enables light detection in a large dynamic range of incident power (10^{-7}~10^{-1} W cm^{-2}) by switching with small voltage (-0.9 to 0.5 V)[7]. For weak light detection, the device works with a high responsivity value up to 620 A W^{-1}. Besides, the photocurrent magnitude is quite stable and reproducible under repeated scans of J-V curves. On our analysis, photo-induce avalanche-like diode current is actually composed of a hybrid of photocurrent (J_{SC}) and photoconductive current. Based on this discovery, important purpose of this research is to investigate the unique performance of photo-induced large avalanche-like diode current in organo-metal halide perovskite opto- electronic devices and clarify its hysteresis effect.

As the first step of this research, the effect of N-type semiconductor as hole blocking layer for organo-metal halide opto-electronic device was investigated to know the relationship between the photo current hysteresis and photoresponsivity, and its quality as good device performance together with optimized process for fabrication.

３．研究の方法

The opto-electronic device structure is made by Electrode (FTO-glass) / Hole blocking layer (N-type semiconductor layer) / Electron transport layer (meso structured N-type semiconductor layer) / light absorber (organo-metal halide Perovskite layer) / hole transport layer (P-type semiconductor layer) / Electrode (Au). First of all, we test TiO_2 as conventional material and SnO_2 as optimized new materials about Hole blocking layer by changing the process of layer fabrication with using spray pyrolysis and spin coat methods. To understand the property of devices, we utilize the following analysis methods; 1) Photocurrent density-voltage (J-V) measurement: Measuring the devices under various light intensities and forward / backward scanning in the negative and positive voltage ranges to clearly see the current hysteresis. 2) Incident photon to electron conversion efficiency (IPCE): Measuring the devices with or without bias voltage in a full wavelength range, and analyzing the carrier transport problem and amplification of the devices. 3) Electrochemical impedance spectroscopy (EIS): Measuring the devices with bias voltage under illumination and the dark condition, investigating the resistance or photoconductivity difference. 4) Photo-response: Measuring the charging curves under different light intensity, analyzing the photo-response changing of hole blocking layer in devices.

４．研究成果

(1) *Microstructure and properties of SnO_2 compact layer prepared by spray pyrolysis*

Low and high magnification front and cross view SEM images of SnO_2 compact layer prepared by spray and spin coating formed on top of FTO glass substrates are investigated and shown in Fig. 1. The SnO_2 compact layer prepared by spray coating forms a conformal, compact, pinhole-free and uniform layer with thickness of around 15 nm on FTO grains as shown in Fig. 1 (a) and (c). With double amounts of precursors solution will result in almost two times thicker at around 35 nm (Fig. 1 (b) and (d)). As a comparison, the SnO2 compact layer deposited by spin coating on FTO glass possesses lots of pin-holes and partially covering the FTO grains as shown in Fig. 1 (e) and (f). It should be mentioned that with too much amounts of SnO_2 precursors, the SnO_2 compact layer begins to aggregate forming small protrusions on the surface. These bumps were confirmed by SEM images in Fig. 1 (b), which indicates that the SnO_2 compact layer on FTO surface might become rougher when increasing the thickness. The rough surface and the pin-holes are harmful for devices, which will lead to higher recombination rate and leaking currents at the interface between SnO_2 layer and perovskite.

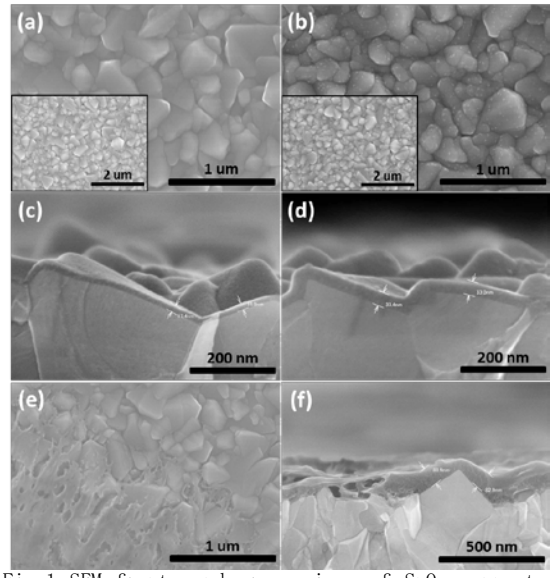

Fig.1 SEM front- and cross-views of SnOx compact layer by spray coating at thickness of (a) (c) ~15 nm, (b) (d) ~35 nm and (e) (f) spin coating.

From cross-views of SEM as shown in Fig. 2, we can observe the thicknesses of the perovskite and the hole-transport layer (Spiro-OMeTAD) are 600 nm and 200 nm, respectively. In addition, there are some gaps at the interface between compact SnO_2 layer and the perovskite layer as shown in Fig. 2 (a), which is probably due to the FTO texture that perovskite layer is hard to fully cover the surface during crystallization. The mesoporous SnO_2 layer which can fill up the FTO texture resulting in much smoother surface to coat the perovskite layer as shown in Fig. 2 (b). Therefore, devices with mesoporous SnO2 layer contain no gaps at the same interface probably due to less FTO texture as shown in Fig. 2 (c) to (f).

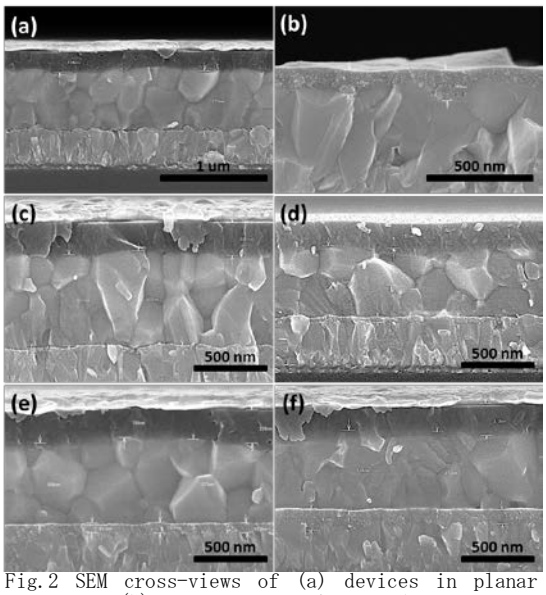

Fig.2 SEM cross-views of (a) devices in planar structure, (b) mesoporous SnO_2 layer and SnOx compact layer devices at FTO substrate and devices with mesoporous SnO_2 structure at thickness of (c) 35 nm, (d) 50 nm, (e) 75 nm and (f) 150 nm.

XRD spectra of SnOx compact layers deposited on FTO and glass after annealing in oven 200 ℃ for 40 min are plotted in Fig. 3 (a). It shows that both SnOx compact layers on glass prepared by spin and spray coating are in amorphous state and does not exhibit any diffraction features commonly attributed to SnO_2; therefore, we just can get the FTO peaks while depositing on FTO glass. It should be mentioned that as-deposited sprayed SnO_2 films processed in the same amorphous state, which means subsequently annealed in oven at 200 ℃ for 40 min will not further form crystallization. We discovered that the direct resistance value of spray coated compact layer is much smaller than the spin coated one through direct measuring by current voltage measurements and estimated by V = IR as shown in Fig. 3 (b). In addition, the high optical transmittance of substrate with compact layer is important to maximize the passage of sunlight into the perovskite absorber in solar cells.

(2) *Thickness effect of compact SnO_2 layer to perovskite solar cells performance*

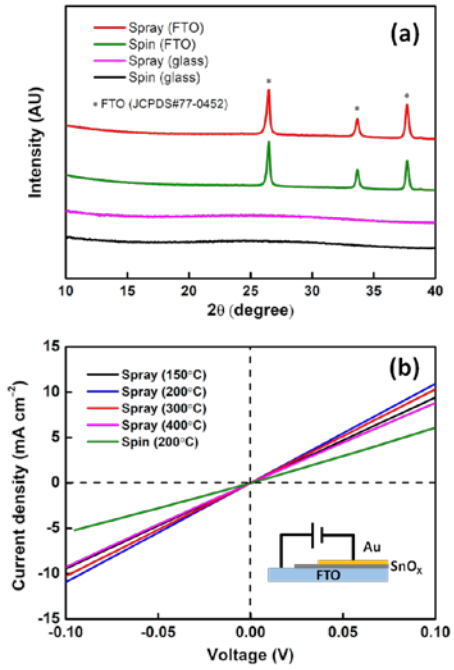

Fig. 3 (a) XRD spectra and (b) current-voltage curves of SnOx compact layer on FTO and glass substrate prepared by spin and spray coating with different post thermal annealing temperature.

To obtain the best performance, the SnO_2 compact layer should fully cover the FTO substrate, but it must not be so thick as to introduce a high series resistance. Therefore, a decent thickness of SnO_2 compact layer should be considered in case of spray pyrolysis. Perovskite solar cells with planar structure of glass / FTO / SnO_2 compact layer / $FA_{0.83}MA_{0.17}Pb(I_{0.83}Br_{0.17})_3$ (with 5 mol% CsI) / spiro-OMeTAD / gold are fabricated to test the performances of spray pyrolysis and spin coated SnOx compact layers at different thickness. The J-V curves and EQE spectra for the devices with SnO_2 compact layer prepared by spray and spin coating are plotted in Fig. 4. The J-V hysteresis behavior as shown in Fig. 5 (a), and the devices with spin coated SnO_2 compact layer shows the highest hysteresis factor (absolute value of (forward scan efficiency - backward scan efficiency) / higher efficiency), which could be attributed to lots of pin-holes and less uniform layer compare to spray coated SnO_2 compact layer. In addition, the EQE shows that in short wavelength region from 300 to 500 nm, the devices with spray coated SnO_2 compact layer show higher EQE value and integrated current density in whole wavelength than the spin coated one. It can be attributed to the higher transmittance of spray coated SnO_2 compact layer in the UV-visible ranges. Furthermore, FF is notably improved compared to Voc and Jsc as shown in Fig. 5, so the optimized thickness of spray coated SnO_2 compact layer in our case is around 25 nm.

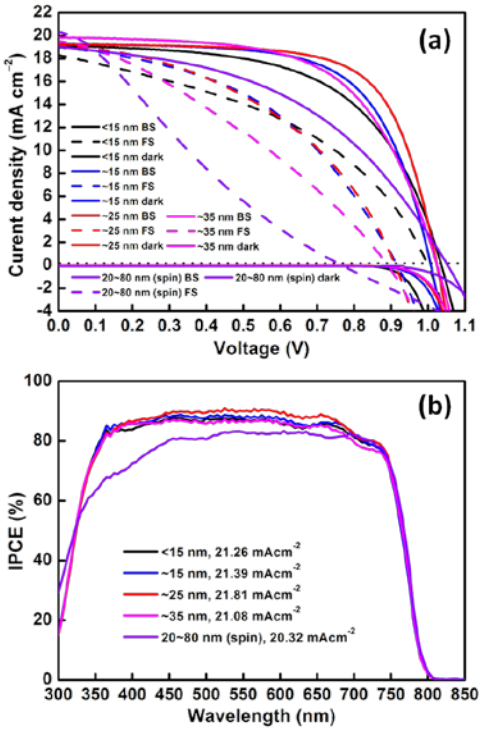

Fig. 4 (a) The current density-voltage (J-V) curves and (b) external quantum efficiency (EQE) spectrum for thicknesses dependence of device performance with compact SnO_2 layer prepared by spray coating.

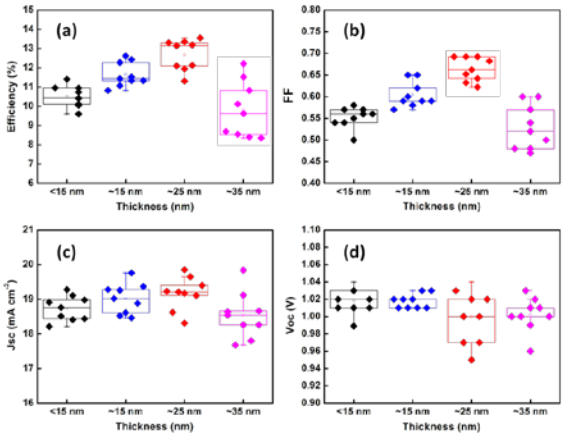

Fig. 5 Statistical parameters of (a) power conversion efficiency, (b) fill factor (FF), (c) short-circuit current density (Jsc) and (d) open-circuit voltage (Voc) for thicknesses dependence of with compact SnO_2 layer prepared by spray coating.

(3) *Effect of post annealing for the SnO_2 layer, J-V hysteresis behavior, impedance spectroscopy and photoresponsivity*

Although the smooth and pin holes free coating are beneficial for hole blocking, the low temperature deposition may leave residual organic species (from the precursors) on the surface and/or in the deposited SnO_2 compact layer, which may affect electrical conductivity. Besides, the properties of SnO_2 / perovskite interface are crucial for electron

transfer and J-V hysteresis behavior. Therefore, we conduct post thermal annealing treatments on spray coated SnO_2 compact layer at several different temperatures, 150, 200, 300 and 400 ℃ in oven with natural convection for 40 min, before applying mesoporous SnO_2 layer. As discussed by Ke et al., one of the main reasons to adopt a low temperature process, normally below 200 ℃, in perovskite solar cells is to obtain a good surface coverage because the films sintered at high temperature (500 ℃) undergo huge volume shrinkage. We find that post thermal annealing treatment on the as-deposited SnOx compact layers with mesoporous SnO_2 layer (~75 nm) has a profound effect on the device performance due to the resistance difference, which shows the lowest resistance while annealing at 200 ℃ as shown in Fig. 5 (b). Therefore, the post annealing treatment can significantly reduce J-V hysteresis as shown in Fig 6(a).

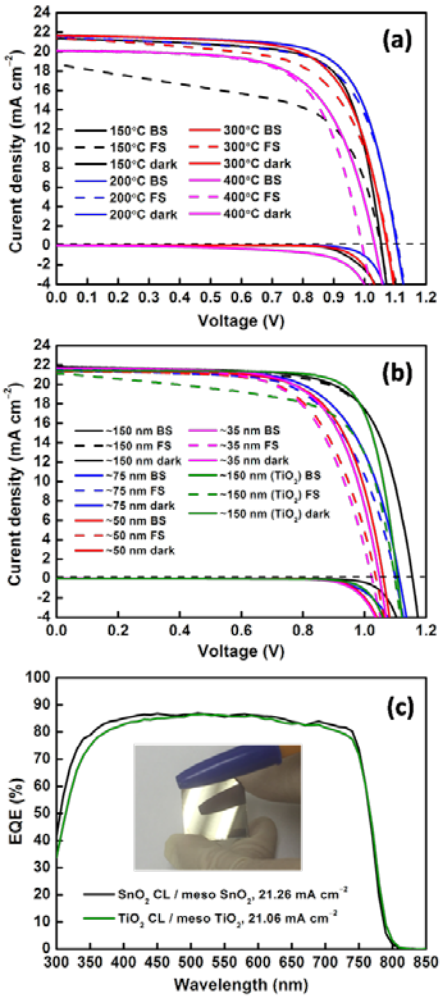

Fig. 6 The J-V curves of device performance for (a) post thermal annealing treatment on SnOx compact layers at different temperatures and (b) thicknesses dependence with mesoporous SnO_2 layers. (c) External quantum efficiency (EQE) spectrum of the optimal performance with SnO_2 and TiO_2 based devices and the inset is the electrode with perovskite layer.

According to the literature, the post thermal annealing over 100 ℃ in ambient air and mesoporous SnO_2 layer can reduce the imbalance of charge transportation at the SnO_2 / perovskite interfaces. Therefore, a good electron transport layer with fast charge extraction could reduce charge accumulation, which leads to signify-cantly reduced J-V hysteresis behavior. To further illustrate the role of the SnO_2 layer in reducing the hysteresis, we also made the same mesoporous structure devices using TiO_2 as electron transport layer. The devices with TiO_2 electron transport layer showed serious J-V hysteresis behavior as shown in Fig. 6 (b). From Fig. 6 (b) and Fig. 7, the FF and Voc are notably improved by using thicker mesoporous SnO_2 layer, which is ascribed to more SnO_2 / perovskite interfaces resulting in better charge collections. It is worth mentioning that the best performance of mesoporous SnO_2 layer with thickness of 150 nm leads to the highest Voc of 1.16 V and almost free of J-V hysteresis behavior, and the electrode is mirror like without cracks as shown in the inset of Fig. 6 (c). In addition, compared to our TiO_2 based reference with the same perovskite and mesoporous layer thickness, a slight improvement in Jsc is observed, which can be attributed to the higher transmittance and EQE of SnO_2 in the UV-visible ranges as shown in Fig. 6 (c).

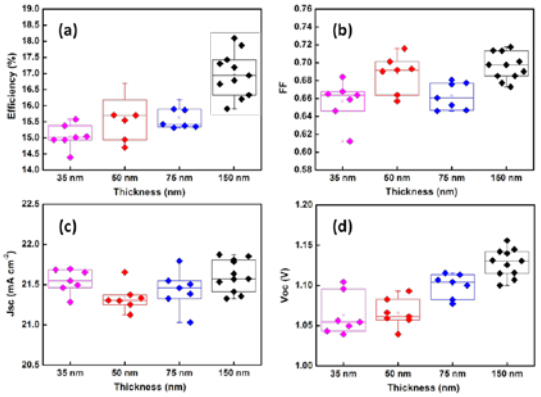

Fig. 7 Statistical parameters of (a) power conversion efficiency, (b) fill factor (FF), (c) short-circuit current density (Jsc) and (d) open-circuit voltage (Voc) for thicknesses dependence of device performance with mesoporous SnO_2 layers.

Electrochemical impedance spectroscopy (EIS) was used to research the interfacial charge transfer at the FTO / metal oxide / perovskite / spiro-OMeTAD interfaces. We measured the EIS spectra at an applied bias of Voc and a frequency range of 1 MHz to 0.1 Hz with an AC amplitude of 10 mV under 1 sun illumination and in the dark. Fig. 8 shows the Nyquist plots derived from the results of EIS spectra of devices with SnO_2

compact layer, mesoporous SnO_2 / compact layer and mesoporous TiO_2 / compact layer (a) under 1 sun and (b) in the dark. A simplified circuit model reported previously was used to fit these Nyquist curves (see the inset of Fig. 8). Here, two semicircles were observed, one in the high frequency region and the other in the low frequency region. The first arc at high frequencies corresponds to the charge transfer behavior of the whole device. Since all of the devices used the same perovskite, spiro-OMeTAD and substrate, so the main difference is at the interfaces of metal oxide / perovskite. We can clearly observe the decrease of the charge transfer resistance (RCT) of the devices at Voc under illumination while applying meso SnO_2 layer onto the compact SnO_2 layer as shown in Fig. 8 (a). That means the mesoporous SnO_2 layer can enhance the charge transfer at the interface with perovskite compares to the devices with only SnO_2 compact layer. In addition, EIS measured in the dark at forward bias voltage 0.6 V (Fig. 8 (b)), which shows the recombination resistance of planar structure is the smallest. It is meaning that devices in planar structure showed stronger recombination reaction than the structure with mesoporous layer. Fig. 9 shows photoresponsivity under different light intensity of the TiO_2 and SnO_2 based perovskite photodetector, which shows that faster response until reaching steady

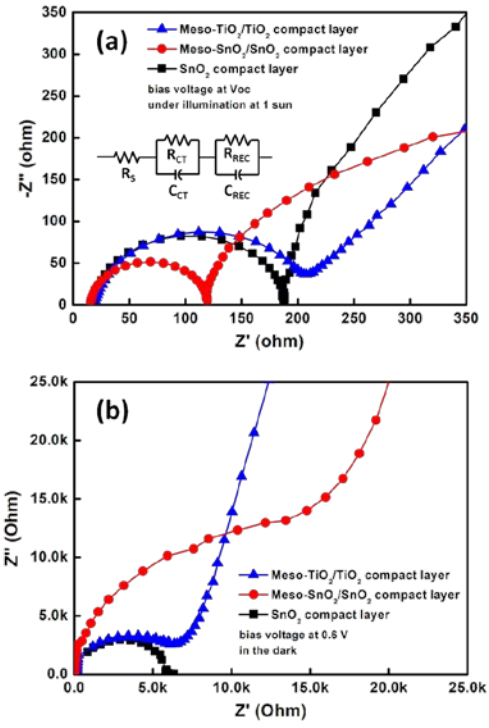

Fig. 8 The impedance spectroscopy measured (a) under illumination and (b) in the dark.

state current density in SnO_2 based device compared to TiO_2. Therefore, SnO_2 based photodetectors show their potential in determining the intensity of incident light simply by measuring the photocurrent in practical applications.

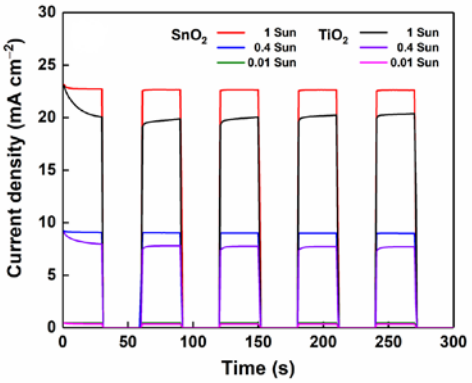

Fig. 9 photoresponsivity under different light intensity of the TiO_2 and SnO_2 based perovskite photodetector.

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５．主な発表論文等

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６．研究組織

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