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# RF sputtered CdS films as independent or buffered electron transport layer for efficient planar perovskite solar cell

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ABSTRACT

Metal sulfide has the potential to take the place of high temperature sintered $TiO_2$ as electron transportation layer for perovskite solar cell (PSC) with improved light stability and suppressed hysteresis. In this work, CdS films were used as independent or buffered electron transport layer for planar perovskite solar cell by a low-temperature RF sputtering method for the first time. The effects of surface roughness and optical absorption of CdS films on the photovoltaic performance of PSCs were discussed. The PSC with sputtered CdS film shows a higher open-circuit voltage ($V_{oc}$) and efficiency of 13.17% than high temperature sintered $TiO_2$ ETL (12.71%). Moreover, a RF sputtered CdS buffer layer between $TiO_2$ and perovskite could tune the conduction band edge of $TiO_2$ and perovskite and passivating the surface defects. Time resolved photoluminescence results indicate the RF sputtered CdS film buffer layer could accelerate charge transportation and a higher conversion efficiency over 16% has thus been achieved, with enhanced air stability and minimized hysteresis. These findings offer new research directions for low-temperature sputtered metal sulfide film as a promising electron transport material for stable and high efficient planar perovskite solar cell.

## 1. Introduction

With the increase of world's energy needs, great efforts have been made in searching for cheap and efficient photovoltaic materials. Photovoltaic cell using organic–inorganic hybrid perovskite as the absorber material has achieved a highest record efficiency up to 22.1% [1]. Compared with mesoscopic structure perovskite solar cell, planar perovskite solar cell simplifies the structure of solar cell and fabrication process. The electron transportation layer (ETL) is necessary in planar perovskite solar cell and their quality directly plays an important role in device performance. Crystallized $TiO_2$ is a wide band gap semiconductor with considerable electron mobility and has been considered as ideal ETL material for PSC [2]. However, high temperature annealing (above 450 °C) condition was required for crystallized $TiO_2$ film [3] which increases the cost of time and energy and impedes the perovskite solar cell commercialization on a large scale. Recently, $SnO_2$ [4], $In_2O_3$ [5] and $CeO_x$ [6] have been used as ETL in PSCs by low temperature solution-method with a high efficiency over 10%. However, additional annealing processes were still needed in those ETLs which increase the cost of preparation.

Owing to the good electron mobility, appropriate optical band gap and low temperature preparation condition, several metal sulfides, such as ZnS [7], CdS [8] and $In_2S_3$ [9], have been viable alternative to crystallized $TiO_2$. However, the conduction band offset of ZnS was proved to be unmatched with Pb-based perovskite material and rare material In in $In_2S_3$ would improve the cost of solar cell module. On the contrary, CdS, as one of the most common n-type material, has drawn much interest of the researchers due to its low cost and widely application in CdTe [10], $Cu_2ZnSnS_4$ (CZTS) [11] and Cu(In,Ga)$Se_2$(CIGS) [12] solar cell. CdS thin films could be easily synthesized by wet chemical method, such as sol-gel spinning method [13,14], chemical bath deposition [15], hydrothermal process [16] et al. The perovskite solar cell based on chemical bath deposited CdS ETL has achieved a high efficiency over 15% [17]. However, CdS deposited by wet chemical method could cause serious environmental problems due to the large amount of cadmium-containing waste during the preparation process. A ultra-high vacuum thermal evaporation method has also been used to prepared CdS film and a champion efficiency of 12.2% has been achieved for a photostable planar perovskite solar cell [8]. However, the efficiency is still lower than that of PSC based on solution method

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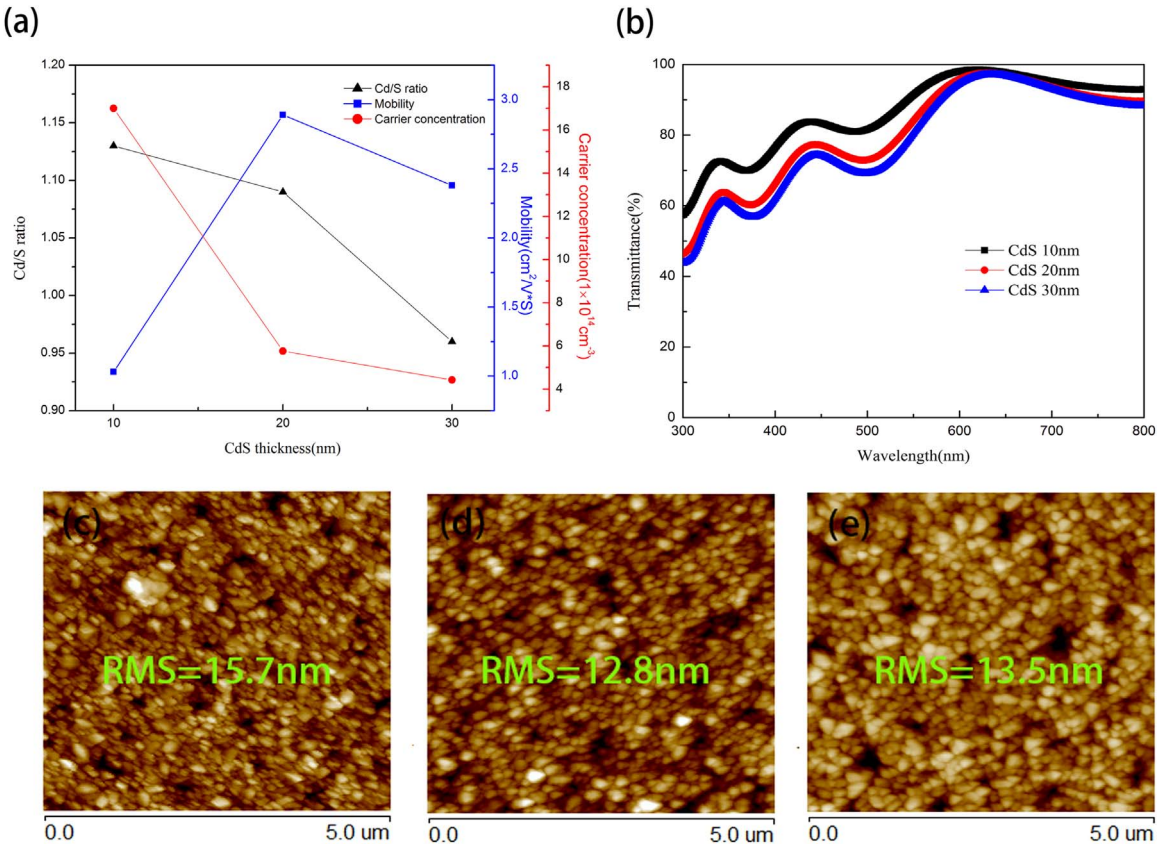


**Fig. 1.** (a) Cd/S ratio and electrical properties of CdS films with different thickness; (b) The optical transmittance of CdS films with various thicknesses; AFM images for CdS films with different thicknesses for (c) 10 nm; (d) 20 nm; (e) 30 nm.

prepared CdS films. In addition, the compactness and uniformity of CdS film cannot be well-controlled by a vacuum thermal evaporation method. Radio-frequency (RF) sputtering to process a compact CdS layer as electron transport layer or buffer layer has been reported in CdTe [18], $Cu_2ZnSnS_4$ [19] solar cell, which is suitable to reduce the environmental impact and thin film solar cells can be manufactured by an in-line process for massive production.

Based on above consideration, planar perovskite solar cell with CdS and $TiO_2$/CdS films as the ETL are fabricated. The CdS layer is prepared by radio-frequency sputtering process. The structural, morphological, optical and photoelectric properties of prepared films were investigated in detail. The power conversion efficiency of $TiO_2$/CdS based device can be as high as 16%, as compared to 12.71% for $TiO_2$ based device and 13.17% for CdS based device.

## 2. Material and methods

### 2.1. Preparation detail

#### 2.1.1. Preparation of $TiO_2$ layer

Prior to deposition process, chemically FTO glass was cleaned with detergent solution, acetone, ethanol and then dried by nitrogen gas. To prepare $TiO_2$ ETL, 350 μl Titanium isopropoxide was diluted in 5 mL isopropanol with 0.013 M HCl. The FTO substrates were coated by spin coating the precursor solution for 60 s with different revolutions, and annealed at 500 °C in a rapid thermal process device (RTP-500 , Beijing East Star Research Office of Applied Physics).

#### 2.1.2. Preparation of CdS layer

The CdS films were sputtered from 3-in. CdS ceramic target. The base pressure was kept at $5 \times 10^{-4}$ Pa and the work gas was pure Ar. RF magnetron sputtering was used for depositing CdS film with the 100 W RF power and 0.2 Pa work pressure. The substrate temperature was kept at 423 K and CdS layer thicknesses were obtained by controlling sputtering time.

#### 2.1.3. Perovskite solar cell device preparation

Given the demand of convenience and repeatability in further massive production, a highly reproducible one-step method [20] without antisolvent process has been taken to prepare perovskite films. 37 wt% precursor solutions of 3:1 MAI:$Pb(Ac)_2$ were spin on substrate at 2000 rpm for 30 s. The layers were further annealed on the hot plate at 90 °C for 5 min and then coated with a hole-transporting material solution (68 mM spiro-OMeTAD, 26 mM Li-TFSI and 55 mM TBP in chlorobenzene) at 2000 rpm for 30 s. The substrate was transferred to a evaporation equipment where ~ 80 nm Au back electrodes were deposited under high vacuum ($6 \times 10^{-4}$ Pa).

### 2.2. Characterization

The structure of films were obtained by X-ray diffraction (XRD, Bruker D8 Advance). Surface morphology were collected by Scanning electron microscopy (SEM,JEOL) and atomic force microscopy (AFM, Bruke). The optical parameters of the films were measured by UV–VIS–NIR spectrophotometer (Cary5000). The thickness of the films were measured by stylus profilometry (Veeco, dektak 150). The chemical component of the films were estimated by X-ray fluorescence (XRF) spectrometer (XRF, SHIMADZU EDX-7000). The ultraviolet photoelectron spectra (UPS) was obtained by a Thermo Scientific ESCALab 250Xi. Time resolved photoluminescence (TRPL) measurements were investigated with an excitation wavelength of 420 nm. The incident photo-to-current conversion efficiency (IPCE) was obtained by Qtest Station 1000AD with a calibrated Si-cell as reference. Current density–voltage (J–V) characteristics were measured with a Keithley