Electrical Properties of Ultra-thin TiO_2 Compact Layer on FTO for Perovskite Solar cells

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Abstract. A TiO_2 compact layer or blocking layer plays a crucial role in a hybrid organic-inorganic lead halide perovskite solar cell because it can prevent the carrier recombination at the interface of fluorine-doped tin oxide (FTO) and perovskite layers. There are several methods to fabricate this layer such as spray pyrolysis or spin-coating which is solution-based synthesis that is difficult to avoid pinholes in the surface of the blocking layer. In this work, TiO_2 blocking layers are fabricated by radio-frequency (RF) magnetron sputtering using Ti metallic target with O_2 partial pressure in Ar atmosphere on FTO coated glasses. The controlled parameters for the deposition of TiO_2 compact layer are RF power, O_2 partial pressure, and deposition time. The optimization of the TiO_2 compact layers are found from the diode I-V characteristics between the TiO_2/FTO interfaces. The resistance between the TiO_2/FTO interfaces deviates from an ohmic contact towards a diode behavior when the thickness of TiO_2 is increased. The thickness of the films is directly measured by surface profilometer. In addition, the UV-VIS-NIR spectroscopy is used to observe the optical transmission of the films.

1. Introduction

Since 2009, it has been shown that mixed organic-inorganic halide perovskites – a new class of solar cell have an unprecedentedly rapid increase in the energy-conversion efficiency. There are many different materials and several methods to fabricate perovskite-based solar cells that affect the efficiency of this solar cell. For a standard configuration of a planar heterojunction perovskite solar cell, it consists of a transparent conductive oxides coated glass, an electron transport material or compact semiconductor oxides, perovskite materials, a hole transport material and a metal electrode. The compact layer plays an important role to the performance of the device because it can prevent the carrier recombination at the interface of fluorine-doped tin oxide (FTO) and perovskite layers. There are various electron transport materials, but for this solar cell, TiO_2 electron transport material is most frequently used. Although the electron injection rates from perovskite absorber to TiO_2 layer are very fast, the electron recombination rates are also very high due to the low electron mobility and transport properties.[1] Spray pyrolysis and spin-coating methods are two common methods to fabricate this compact layer. However, these two methods have disadvantages because the layer fabricated by these two methods is not high-quality condensed layer, and it is difficult to control the layer thickness.[2] On the other hand, reactive RF magnetron sputtering is an alternative choice of TiO_2 deposition since it can provide easy way to control the structure, composition and properties of the films by their sputtering conditions. Moreover, this technique is an industrial process applicable to large-area deposition and leads to high adherent films even at low substrate temperature.[3-5]

In this work, a very thin TiO_2 blocking layers are fabricated by reactive RF magnetron sputtering using Ti metallic target with O_2 partial pressure in Ar atmosphere on the FTO coated glasses. The controlled parameters for the deposition of TiO_2 compact layer are RF power, O_2 partial pressure, and deposition time.

2. Experiment

In this work, the 3 cm × 3 cm FTO coated glasses with 3 mm thick are used as the substrates for the deposition of TiO_2 compact layers. Prior to the deposition of TiO_2, the substrates are sequentially cleaned in an ultrasonic bath filled with detergent diluted in deionized (DI) water, DI water, acetone, and methanol for 15 minutes each. Finally they are rinsed with DI water and blown dry with N_2 gas. The compact TiO_2 blocking layers are deposited by RF magnetron sputtering onto the FTO coated glasses using a (4-inch diameter) Ti metallic target with a target-to-substrate distance of 60 mm. The base pressure before the deposition is 3.0×10^{-6} mbar. High purity oxygen (99.999% purity) and argon (99.999% purity) gases are used for the sputtering gas. During the deposition, the substrates are loaded in a carousel and rotated above the target at the rate of 5 rpm. The TiO_2 layers are fabricated with different $O_2/(O_2+Ar)$ ratio of 30% and 50%, different RF power from 100 W to 250 W, and different deposition time from 120 to 240 minutes. The total sputtering gas pressure is approximately 1.1×10^{-3} mbar. Due to a very thin layer of TiO_2, the thicknesses of the films are measured by a surface profilometer (Dektak 3ST) and optimization of the TiO_2 compact layers are studied from the diode I-V characteristics between the TiO_2/FTO interfaces measured by a four-point probe technique using a Keithley 238 source-measure unit. The optical transmission is observed by UV-VIS-NIR spectrophotometer (PerkinElmer – Lambda 900).

3. Results and discussion

The thickness of the FTO layer is approximately 800 nm which is directly measured from the step-etched FTO film using the surface profilometer. The resistivity and the carrier concentration at 300 K of the FTO film are approximately $6.5 \times 10^{-4} \Omega \cdot \mathrm{cm}$ and $3.7 \times 10^{20} \mathrm{cm}^{-3}$, respectively, as measured by the van der Pauw technique[6] (using Keithley 237 source-measure unit, Keithley 196 DMM, Agilent 34970A DAQ/Switch unit and 1 Tesla electromagnet). The transmittance of the FTO film is above 80% in the visible – NIR range and rapidly drops when the wavelength is greater than 1,300 nm due to free carrier absorption nature of the heavily-doped semiconductor. Since the carrier concentration in the FTO layer is very high (heavily doped), one may consider it as a good transparent conductor, i.e. the TiO_2/FTO interface could be considered as a semiconductor – metal contact.

To find the suitable sputtering condition for the TiO_2 film as an electron transport layer, first the RF sputtering power is varied from 100 W to 250 W by maintaining the $O_2/(O_2+Ar)$ ratio at 30% and the sputtering time of 120 minutes. The results from the I-V characteristics of TiO_2/FTO interface (figure 1(a)) show that the resistance between the TiO_2/FTO interface deviates from an ohmic contact towards a diode behavior and thus the current is blocked in the reverse bias when the sputtering power is increased. A good film coverage is obtained when the sputtering power is increased and results in a better semiconductor – metal interface. For the 200 W and 250 W sputtering power, the I-V curves show no current leakage for the reverse bias. This confirms that the TiO_2 layers act as hole blocking layers.

When considering the effect of 30% and 50% $O_2/(O_2+Ar)$ ratio on the I-V characteristics of TiO_2/FTO interface with 200 W sputtering power and 120 minutes sputtering time (shortest deposition time), the results in figure 1(b) show that series resistance from 50% of $O_2/(O_2+Ar)$ ratio is less than that from 30% of $O_2/(O_2+Ar)$ ratio. It can be inferred that 50% of $O_2/(O_2+Ar)$ ratio sputtering condition was better than 30% of $O_2/(O_2+Ar)$ ratio. Different $O_2/(O_2+Ar)$ ratios can cause different structures due to transport process of the sputtering particles between the substrate and the Ti metallic target.[7]

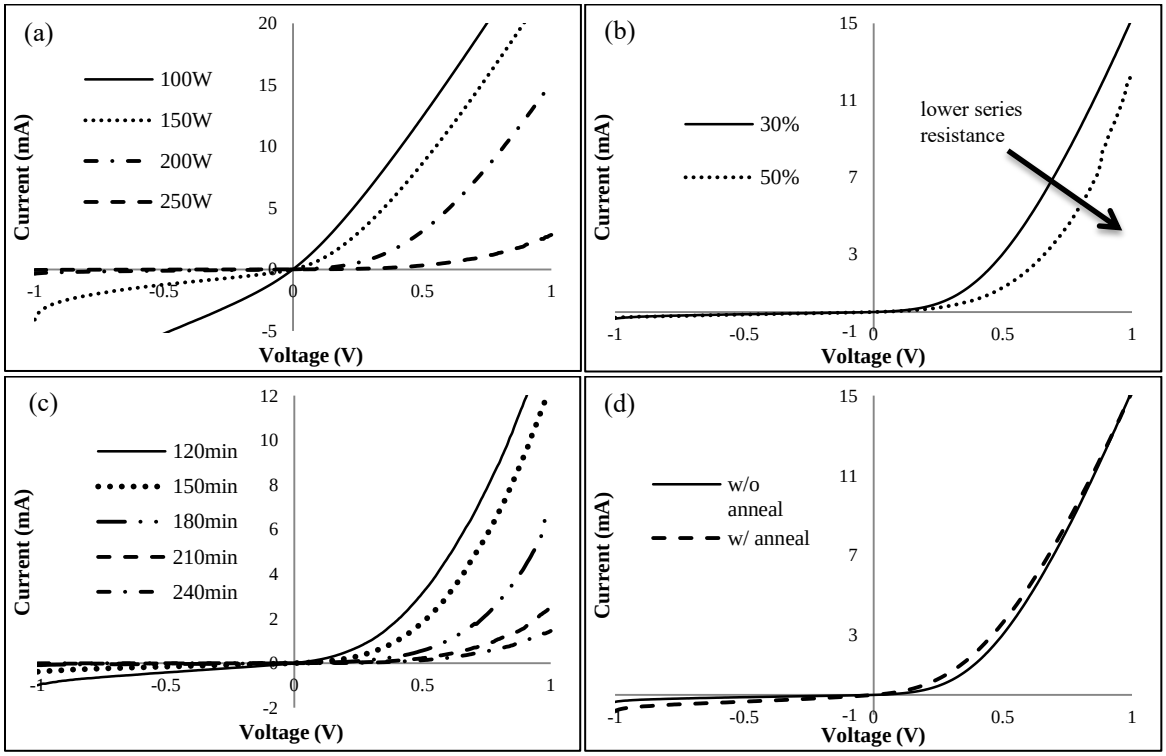

Figure 1. I-V characteristics of TiO_2/FTO interface (a) with different RF power (b) with different $O_2/(O_2+Ar)$ ratios (c) with different deposition time and (d) with and without annealing.

Figure 1(c) shows the I-V characteristics of TiO_2/FTO interface with different deposition time from 120 to 240 minutes. For the sputtering time from 210 to 240 minutes, there is no current leakage for the reverse bias. Some small current leakage for reverse bias is observed with the sputtering time from 120 to 180 minutes. However, the samples with the sputtering time from 120 to 180 minutes have a trend of higher series resistance than those of the sputtering time from 210 to 240 minutes.

For the effect of anneal process, the I-V characteristics of TiO_2/FTO interface with and without annealing at 500°C for 30 minutes from the sample of 50% of $O_2/(O_2+Ar)$ ratio and 200 W sputtering power and sputtering time of 210 minutes are shown in figure 1(d). There is a slightly increase in both current leakage in the reverse bias and the series resistance in forward bias for the annealed sample.

The optical transmission of the TiO_2 layers is measured by the UV-VIS-NIR spectrophotometer. Figure 2(a) shows the transmittance of compact TiO_2 layers on the FTO coated glasses sputtered at 50% of $O_2/(O_2+Ar)$ ratio and 200 W with different deposition time from 120 to 240 minutes. It is noted here that the transmittance measurement of the TiO_2 compact layer was normalized with the

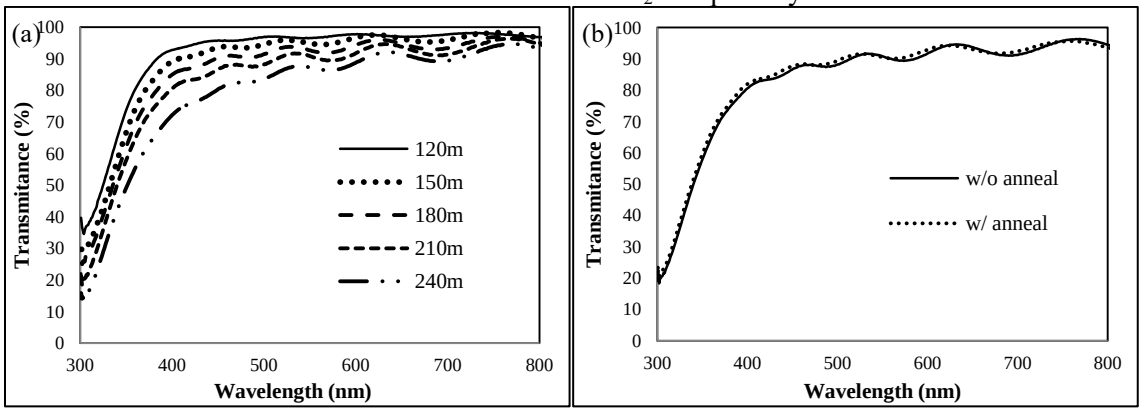

Figure 2. Transmittance of compact TiO_2 layers on FTO coated glasses; (a) with different deposition time and (b) with and without annealing.

Table 1. The thicknesses of TiO_2 with different deposition time.

Sputtering time (min)	Average thickness (nm)
240	33
210	29
180	25
150	21
120	17

FTO/glass substrates. When deposition time increases, the transmission decreases due to thicker TiO_2 film as expected. The average transmittance of the TiO_2 layers is above 80% in the visible regions. In addition, annealing the film does not affect optical transmission of TiO_2 layers as shown in figure 2(b).

Due to a very low yield of sputtered Ti atoms, the TiO_2 films obtained by this technique are very thin. The thickness could not be easily measured by FE-SEM due to the nonconductive substrate. The thickness of the thickest TiO_2 layer obtained from longest deposition time of 240 minutes, RF power of 200 W and 50% of $O_2/(O_2+Ar)$ ratio is measured by the surface profilometer. The thicknesses of TiO_2 with less deposition time are deduced from the deposition rate of the thickest one (1.375 Å/ min) and summarized in Table 1.

In addition, the energy gap (E_g) of the TiO_2 can be calculated from the relationship $\alpha hv = A(hv - E_g)^{1/2}$, where A is a constant, h is the Planck's constant, v is the frequency of radiation and α is an optical absorption coefficient.[8] The wavelength dependent optical absorption coefficient is determined from the optical transmission spectrum; $\alpha(\lambda) = \frac{1}{d}\ln\frac{100}{T(\lambda)}$, where $T(\lambda)$ is a percentage of optical transmission of the film at the wavelength λ, and d is a thickness of the film. The energy gap is obtained from the extrapolation from the linear section of the plot between $(\alpha hv)^2$ and hv, where hv is the photon energy.[8] From the calculation, the TiO_2 films deposited using 50% of $O_2/(O_2+Ar)$ ratio and 200 W has the energy gap about 3.66 eV.

4. Conclusion

The reactive RF magnetron sputtering is used to fabricate transparent TiO_2 ultra-thin film from a Ti metallic target. The suitable sputtering conditions are 200 W RF power, sputtering pressure of 1.1×10^{-3} mbar with 50% of $O_2/(O_2+Ar)$ ratio for the sputtering time of 180 minutes or more. This gives the thickness of TiO_2 compact layer of approximately 25 nm. It can selectively block the transport of holes from TiO_2 to the FTO layer as indicated by the diode behavior in the I-V characteristics between the TiO_2/FTO interface. These properties are suitable to be used as the electron transport component of the perovskite solar cells.

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