

Effect of vanadium oxide interfacial layer for electrical contact on p-type silicon



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ABSTRACT

Vanadium oxide interfacial layer between p-type silicon and indium tin oxide was studied as a hole transfer layer in solar cell application. The vanadium oxides deposited by sputtering technique with various conditions were investigated in terms of gap states using spectroscopic ellipsometry. As the Ar gas flow rate increases from 10 sccm to 40 sccm, the gap state of vanadium oxide thin films was reduced, and then it results in decrease of current due to reduction of carriers from p-type semiconductor to electrode for the solar cell applications. In the vanadium oxide films deposited by oxygen gases as reactive gas, a strong confinement of gap state near 1.7 eV as a transition energy appears, and this results in decreasing of total amount of density of states of interfacial layer. In the silicon solar cells with the vanadium oxide thin films deposited at 30 sccm Ar gas flow rate as an interfacial layer between indium tin oxide and p-type Si, it appears that the photoelectric conversion efficiency increases up to about 10% more than that of solar cell without interfacial layer.

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1. Introduction

Vanadium oxide (V_2O_5) as an interfacial layer between transparent conducting oxide (TCO) electrode and p-type contact of solar cells has been extensively studied [1,2]. Because the important part in the characteristic feature of the interfacial layer for solar cells is only for the efficient p-type contact, this could be applied to any semiconductor device applications. To efficiently extract carriers from solar cell structure, a band engineering using proper materials with proper doping is required. Particularly, this engineering is also necessary for contact electrodes of solar cells [3–5]. In general, difference of Fermi level causes potential energy barrier or sometimes there are no quantum states for carrier to go to next cell structure, making a Schottky barrier [6,7]. Therefore, in fabricating efficient cell structure, the band alignment is very important. Vanadium oxide is a high work function (approximately 7) n-type material [8–10]. Thus, this material can achieve smooth contact with TCOs, especially, indium tin oxide (ITO), and p-type semiconductor. The vanadium oxide thin films are usually fabricated by using metalorganic chemical vapour deposition (MOCVD) method [11], sol-gel method [12], or electron beam evaporation technique [13] for organic solar cells or various device applications.

In this study, the electrical properties of sputtered vanadium oxide interfacial layer between p-type silicon substrates and ITO, and its effect as a hole transfer layer in solar cell application was examined. Various experimental conditions such as gas flow rate, base pressure, and amount of oxygen plasma were tested to make efficient electrical properties for p-type silicon substrate. The gap states of vanadium oxide thin films on silicon substrates were investigated by spectroscopic ellipsometry. Also, current-voltage characteristics were measured to find actual behavior of solar cells.

2. Experiments

Vanadium oxide thin films were fabricated by radio frequency (RF) magnetron sputtering system. During sputtering of the vanadium oxide target, substrate holder was rotated at 15 rpm, and the base pressure of sputtering chamber was about 2×10^{-6} Torr. To find optimum condition of deposition, argon gas flow rate was changed with 10, 20, 30, and 40 sccm. Before sputtering process, residual gas in the gas pipe where the argon and oxygen gas flow into sputtering chamber was eliminated to minimize gas contamination by high vacuum. Also, working pressure was controlled with 7×10^{-3} , 1.4×10^{-2} , and 2.1×10^{-2} Torr. To investigate oxygen flow rate dependence, injected oxygen flow rate was 3, 4, and 5 sccm. During reactive RF sputtering with oxygen gas, total gas flow rate was kept at 40 sccm. All the experimental conditions were

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Table 1
Deposition conditions of vanadium oxide thin films by sputtering technique.

#	Ar (sccm)	O ₂ (sccm)	Working pressure (Torr)
1	40	0	7×10^{-3}
2	30	0	7×10^{-3}
3	20	0	7×10^{-3}
4	10	0	7×10^{-3}
5	10	0	1.4×10^{-2}
6	10	0	2.1×10^{-2}
7	37	3	7×10^{-3}
8	36	4	7×10^{-3}
9	35	5	7×10^{-3}

separated with 9 cases, as shown in Table 1. Increasing the reliability of experimental data and making the reproducible results, too low flow rate of oxygen gas (1 or 2 sccm) was not used.

The deposition of vanadium oxide thin films by various sputtering conditions on silicon substrate was carried out to measure optical constant with spectroscopic ellipsometry in the region from 1.2 eV to 3.2 eV. Also, the vanadium oxide thin films as interfacial layer between indium tin oxide electrode and p-type silicon substrate were studied by measuring the current-voltage relation. That is, each device for the measurement of current-voltage characteristics has the structure of ITO/V₂O₅/p-Si/V₂O₅/ITO to see ohmic contact properties of junction between semiconductor and electrode. The size of electrode (V₂O₅/ITO) to make the electrical contact with p-type silicon was 1 mm in diameter. After formation of electrode, silver metal was thermally evaporated upto 200 nm thickness to contact with ITO thin films. Finally, the interfacial layer was applied to Si-based solar cells, which have the structure of ITO(90 nm)/V₂O₅(10 nm) hole transfer layer deposited on p-type side of silicon solar cells in several deposition conditions. The solar cell which was used in this experiment was heterojunction with intrinsic thin layer (HIT) solar cell. The HIT cell is thin film solar cell consisting of p-i-n junction made of silicon. To measure electrical properties of the solar cells, solar simulator (ORIEL Sol1A) was used, and the applied power was one sun (1000 W/m²) based on reference solar cell (ORIEL SRC-1000-TC-K-KG5-N). The measured area of active region of the cells was approximately 40 mm², which was used to calculate the photoelectric conversion efficiency.

3. Results and discussion

Table 1 presents the sputtering conditions for deposition of vanadium oxide thin films. In this table, experimental conditions can be separated with three groups. From the samples deposited with the conditions 1, 2, 3, and 4, a dependence of argon flow rate can be obtained. And comparing the condition 4, 5, and 6, working pressure dependence can be analysed. Until now, there is no oxygen gas flowed into chamber. Comparing the 1, 7, 8, and 9 with each other, oxygen gas dependence can be measured.

Fig. 1 shows the results of spectroscopic ellipsometry for the each experimental group. With spectroscopic ellipsometry, complex dielectric constant reactive in various optical frequencies can be measured. In the measured results, the imaginary part of dielectric constant in the range from 1.2 eV to 3.2 eV was shown in Fig. 1. In particular, this imaginary part presents the information of transition in solid material, which is proportional to transition probability calculated from density of pair of possible transition energy, commonly called the joint density of state [14,15]. Because of that reason above, optical measurement with spectroscopic ellipsometry can find out the electrical transition properties of solids [16]. From the raw data, every dielectric constant was analysed by dispersion relation called Lorentz oscillation model without consideration of film roughness [17].

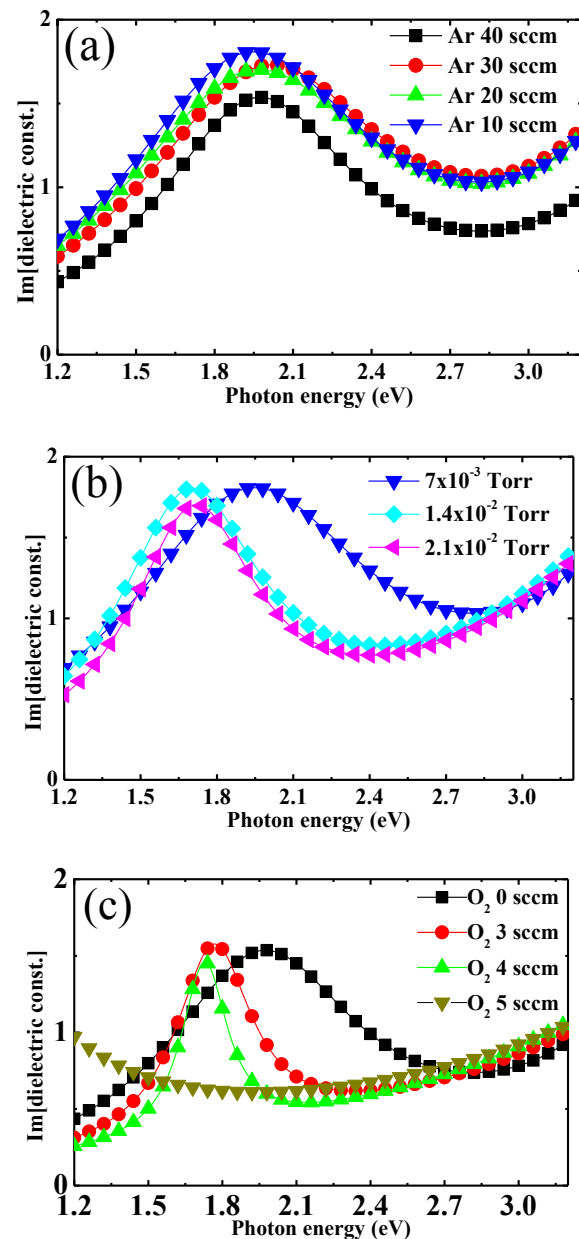


Fig. 1. Imaginary part of dielectric constant measured by spectroscopic ellipsometry for (a) argon flow rate dependence, (b) working pressure dependence, and (c) oxygen flow rate dependence.

Fig. 1(a) shows dependence of vanadium oxide thin films on silicon substrate by the argon gas flow rate. As shown in Fig. 1(a), the peak position near 2 eV, was changed from 2.014 to 2.075. There is not obvious trend in peak position, but more outstanding features of Fig. 1(a) are the increase of imaginary part of dielectric constant in entire measurement region with decrease of argon gas flow rate. This means that films not only become optically opaque films when the argon gas flow rate increases, but also has more transition state inside of films. Considering the band gap of vanadium oxide materials (2.8), this should be transition associated with gap state, the electronic state inside forbidden gap. Because this is from imperfection of crystal, this is also called defect state. The argon gas was carefully controlled to keep the purity. However, because all chambers have inherently small leak, the only possible reason of difference in dielectric constant are from difference in purity of argon gas by the injected amount of argon gas. Therefore, the more

argon gases are flowed into chamber, the purer sputtering conditions are formed. As shown in Fig. 1(a), the imaginary part of dielectric constant shows that actual transparency was improved when there were more injected argon gas. The vanadium oxide thin films were most transparent at 10 sccm with the least defect state in Fig. 1(a) due to its purity of sputtering gas.

Fig. 1(b) presents dependence of vanadium oxide thin films on silicon substrate by the working pressure. In the high working pressure, pumping ability of vacuum chamber becomes lowered. This gives rise to accumulation of impurity gas such as oxygen flowed gradually from outside of chamber into vacuum chamber. Fig. 1(c) shows characteristic shift of peak around 1.7 eV when there is reactive oxygen gas in the sputtering system. From this result, the fact that the characteristic shift of high working pressure was stemming from accumulation of unwanted oxygen impurity gas as the chamber has less pumping ability, can be deduced. Comparing Fig. 1(b) with (c), entirely lowered imaginary part of dielectric constant and sharper peak intensity were observed at Fig. 1(c), as discussed in Fig. 1(a).

After characterization of the vanadium oxide thin films on silicon substrate, to see the carrier transport characteristics, ITO/ V_2O_5 /p-Si/ V_2O_5 /ITO structure was formed on p-type silicon substrates. To avoid asymmetric barrier effect stemming from different metal electrode and different Schottky barrier and built-in potential, measured device structure was symmetrically designed (ITO/ V_2O_5 /p-Si/ V_2O_5 /ITO) to see the only vanadium oxide interfacial layer effect for ohmic contact.

Fig. 2(a) presents the result of current-voltage (IV) measurement when there is argon flow rate dependence. The current was sampled at 0.3 V from the current-voltage characteristics of the insets of Fig. 2, and this shows more obvious trend than full IV curve. As shown in the graph, current (closed square) shows decreasing trend with increasing argon flow rate. The integrated area (open square) means integrated area of imaginary part of dielectric constant shown in Fig. 1 below the vanadium oxide band gap (2.8 eV) from 1.2 eV to 2.8 eV. (1.2 eV is measurement limit). This integrated area is total amount of possible optical transition between 1.2 eV and 2.8 eV. As seen in Fig. 2(a), the integrated area also shows decreasing trend with increasing the argon flow rate like trend of current. Also, this can be observed in Fig. 2(b) and (c).

The reason why the vanadium oxide thin films which contains more defect states showed better current transport properties can be explained by their high work function and formation of movable quantum states which are defect states inside band gap of vanadium oxide thin films. Fig. 3(a) shows band diagram of ITO, V_2O_5 , and p-Si in terms of vacuum level before electrical contact. All the parameters were obtained from references. To show simplistic qualitative results, Fig. 3 assumed that when electrical contact occurs, Fermi level pinning effect in the interface are negligible [18]. After electrical contact, due to high work function of vanadium oxide, carrier transport path is open by band offset. In contrast, if ITO and p-Si make direct contact as shown in Fig. 3(c), Schottky barrier and built-in potential are formed by band bending. Here, we can now discuss the result of Fig. 2. The result can be explained as increase of current by increase of defect state helping to make more quantum state possible to be occupied by carriers. Therefore, as seen in Fig. 2, every current transport shows increasing trend with increase of defect density of vanadium oxide interfacial layer.

Fig. 4 shows current and voltage characteristics of silicon solar cells with vanadium oxide interfacial layer under the solar illumination. As shown in Table 2, the solar cell with vanadium oxide interfacial layer deposited at the condition of 30 sccm Ar gas flow rate, showed better photoelectric conversion efficiency (11.3%) than that of solar cells without interfacial layer (10.3%), showing 10% of improvement in the photoelectric conversion efficiency. As

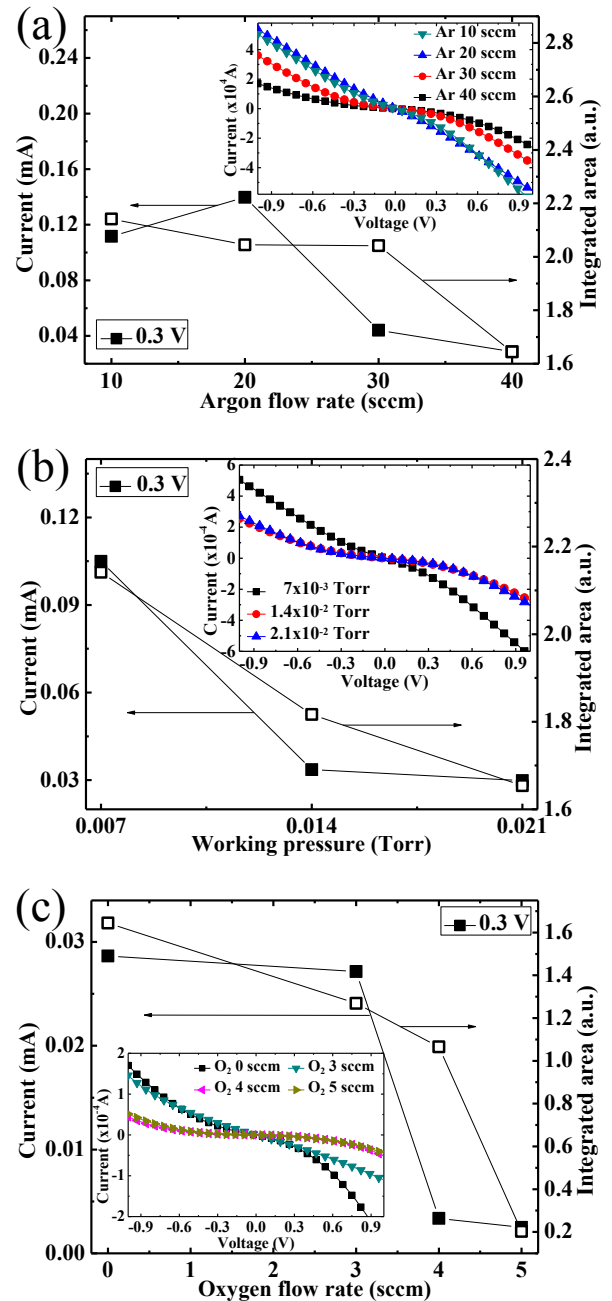


Fig. 2. Comparison of integrated area of imaginary part of dielectric constant from 1.2 eV to 2.8 eV, with current level at 0.3 V for the structure of ITO/ V_2O_5 /p-Si/ V_2O_5 /ITO with controlled sputtering condition of vanadium oxide interfacial layer in terms of (a) argon flow rate dependence, (b) working pressure dependence, and (c) oxygen flow rate dependence. The insets of figures shows the current-voltage relation of ITO/ V_2O_5 /p-Si/ V_2O_5 /ITO of each deposition condition.

working pressure increases, due to decrease of total amount of gap state in the vanadium oxide band gap, the solar cell efficiency was decreased (7.3%). In this case, it is thought that the carriers passing through the vanadium oxide interfacial layer are possibly captured by deep level state existing near the 1.7 eV in terms of transition energy. Comparing the reference cell and the cells grown at 10 sccm of Ar gas flow rate, the series resistance of the cell with vanadium oxide interfacial layer (10 sccm) showed much higher value of 23.2Ω than that of the cell without interfacial layer of 11.7Ω due to contact resistance, which severely degrades series resistance of solar

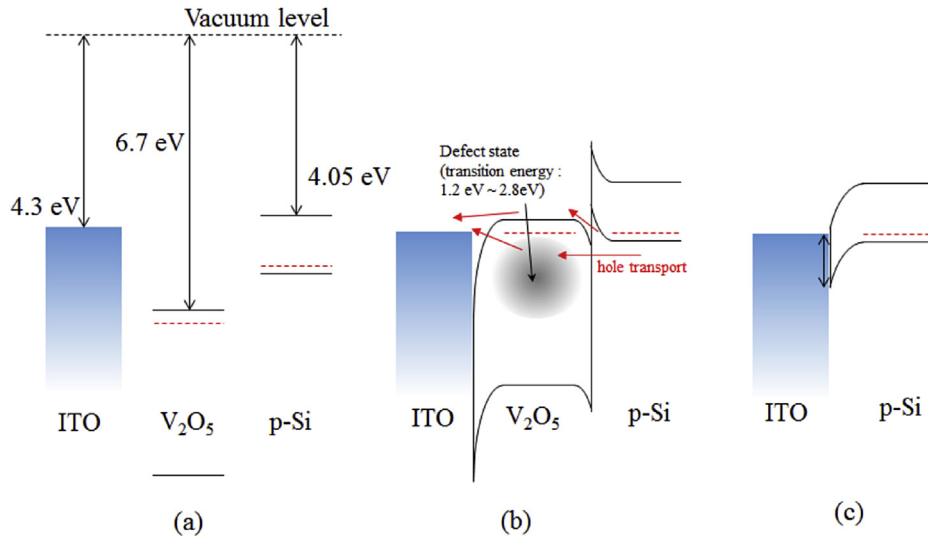


Fig. 3. Band structure of indium tin oxide, vanadium oxide, and p-type silicon (a) before contact, (b) after contact with vanadium oxide interfacial layer, and (c) after contact without interfacial layer.

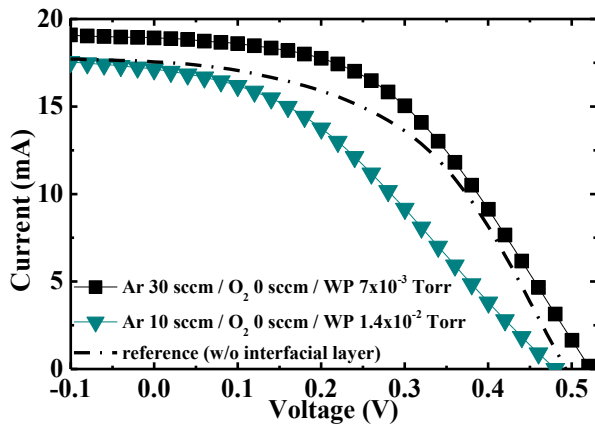


Fig. 4. Current-voltage characteristics of solar cell structures with and without interfacial layer under solar radiation (one sun condition). Here, WP means working pressure.

Table 2

Characterization of solar cell with and without the V_2O_5 interfacial layer. R_s is series resistance, R_{sh} is shunt resistance, FF is fill factor, V_{oc} is open circuit voltage, I_{sc} is short circuit current, and η is photoelectric conversion efficiency.

Ar (sccm)	O ₂ (sccm)	WP (Torr)	R_s (Ω)	R_{sh} (Ω)	FF	V_{oc} (V)	I_{sc} (mA)	η (%)
30	0	7×10^{-3}	13.2	699	0.46	0.52	18.9	11.3
10	0	1.4×10^{-2}	23.2	187	0.35	0.48	17.1	7.3
Reference			11.7	469	0.48	0.49	17.6	10.3

cells. The solar cell with vanadium oxide thin film grown at 30 sccm of Ar gas flow rate showed slightly higher series resistance of (13.2 Ω) compared to the reference cell. However, the reference cell showed lower short circuit current than that of the solar cell with vanadium oxide thin film grown at 30 sccm. It is considered that the reference cell was also affected by series resistance with limited shunt resistance induced by solar cell structure, which lowered the short circuit current compared to the cell with vanadium oxide interfacial layer grown at Ar gas flow rate of 30 sccm. Another reason of higher short circuit current of the cell with the interfacial layer can be explained with formation of back surface field stemming from band bending as seen in Fig. 3.

4. Conclusion

To make smooth hole transfer from p-type silicon to indium tin oxide electrode, vanadium oxide thin films deposited by sputtering technique were investigated in terms of gap states using spectroscopic ellipsometry. As the Ar flow rate increases from 10 sccm to 40 sccm, the gap state of vanadium oxide thin films were reduced. However, the reduction of gap states caused decrease of carrier path from p-type silicon to indium tin oxide electrode, resulting in decrease of series resistance for the solar cell applications. When the oxygen gases were used as reactive gas in sputtering deposition, this brought reduction of total amount of density of states, showing strong confinement of density of states near 1.7 eV in terms of transition energy. When the vanadium oxide thin films were applied to silicon solar cells as an interfacial layer, the photoelectric conversion efficiency of solar cell with interfacial layer at 30 sccm Ar gas flow rate increased up to 10% more than that of solar cell without vanadium oxide interfacial layer.

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