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Fabrication and characterization of WO_3 thin films on silicon surface by thermal evaporation

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ABSTRACT

The transition metal-oxide thin films of WO_3 have been prepared by thermal evaporation at a low deposition rate. The material characterization shows that the thin films have stoichiometric composition and the tungsten ions were fully oxidised into W^{6+}. The surface of the WO_3 thin films became smoother when the thickness increased. The results show that the deposition of WO_3 thin film follows island growth. The flatband voltage of WO_3/Si was extracted. The values on n-Si and p-Si were about 0.75 eV and 0 eV, respectively. It was also found that large amounts of negative charges were accumulated at the interface of WO_3/n-Si because of electron transfer.

1. Introduction

The transition metal oxides, such as WO_3 and MoO_3, have attracted interest from many researchers for their excellent optical and electrical properties. Applications on organic light-emitting diodes (OLED), field effect transistors (FET) and organic solar cells are widely researched. One of the outstanding characteristics of these materials is the high work function, which lower the potential barrier of the holes injected from the adjacent materials. Based on this nature, the application on crystalline silicon solar cells as emitters is well researched [1,2]. The WO_3 and MoO_3 thin films induce energy band bending on n-Si surface without doping, which simplifies the fabrication of heterojunction solar cells [3,4]. Besides, these oxide materials have good optical transmittance because of their wide bandgap of over 3 eV, which reduces the intrinsic optical absorption [5,6].

Among these two materials, WO_3 is more stable against humidity and oxidation. Different methods reportedly fabricate WO_3 layers, such as vacuum evaporation [7,8], sputtering [9] and pulsed laser deposition [10]. Although it has been successfully applied on heterojunction solar cells, the deposition process of the evaporated WO_3 are not fully understood. Besides, the interface properties of the hole-selective contacts of WO_3/n-Si were seldom reported. In this work, the surface roughness of WO_3 thin films with different thicknesses was compared. An island model was shown in the growing process. The flatband voltages of WO_3/Si were extracted and large amounts of negative charges were discovered near the interface.

2. Experiment section

The WO_3 thin films were deposited on polished silicon wafers by thermal evaporation. The WO_3 powder (99.99% purity) was placed on tungsten boats for evaporation. The basic pressure of the chamber was 6×10^{-6} Torr in this work. The growth rate was 0.5 Å/s, and the substrates were not intentionally heated. In samples for capacitance–voltage (C–V) measurement, aluminum contacts were fabricated on the as-deposited WO_3 thin film.

The surface of WO_3 thin films was characterised by atomic force microscopy (AFM) measurement (Bruker Nano Inc. Dimension Edge). The X-ray photoelectron spectroscopy (XPS) measurement was performed by Thermo Scientific ESCALab250 to explore the material properties. The C–V was performed by Keithley 4200 SCS.

3. Results and discussion

Fig. 1 shows the XPS spectrum of the evaporated WO_3 thin films. Ion bombardment is not performed before the XPS measure-

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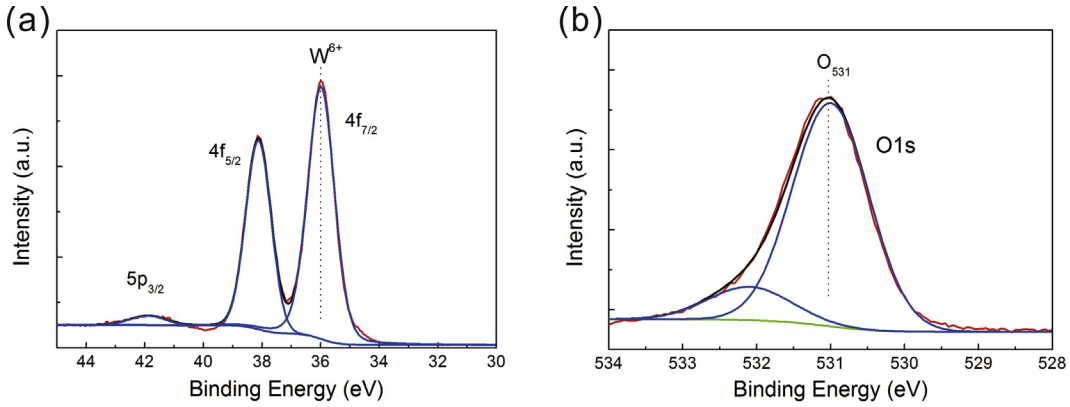

Fig. 1. XPS spectrum of evaporated WO_3 thin film, (a) W peaks; (b) O peaks.

ment because the W peaks will be affected by the Ar^+ [11]. The binding energies of $W4f_{7/2}$ and $W4f_{5/2}$ peaks were 36.0 eV and 38.1 eV, respectively. According to the literature, these W4f peaks are attributed to the fully oxidised tungsten ions (W^{6+}) [10]. The spectrum was well fitted by these two peaks, which demonstrates that the W ions were well oxidised. The $W5p_{3/2}$ peak, which was 41.9 eV in this spectrum, invariably accompanied with W4f peak and their relative peak position and intensity were nearly unchangeable [11]. The O1s peak contained O_{532} and O_{531}, as shown in Fig. 1(b). The O_{532} is attributed to the surface contamination, while the O_{531} peak is attributed to the O^{2-} combined with W ions. The atom ratio of $O1s_{532}$/W4f is calculated to be 2.999, which is very close to the stoichiometric ratio of 3. The XPS results show that under low deposition rate, the thermal evaporated WO_3 thin film is quite stoichiometric and the WO_3 molecules are not significantly changed during the evaporation.

Table 1
Thicknesses of WO_3 thin films measured by quartz crystal oscillation and spectroscopy ellipsometry.

Sample	QCO thickness (nm)	SE thickness (nm)	MSE
A	12	11.32	0.41
B	20	18.91	0.42

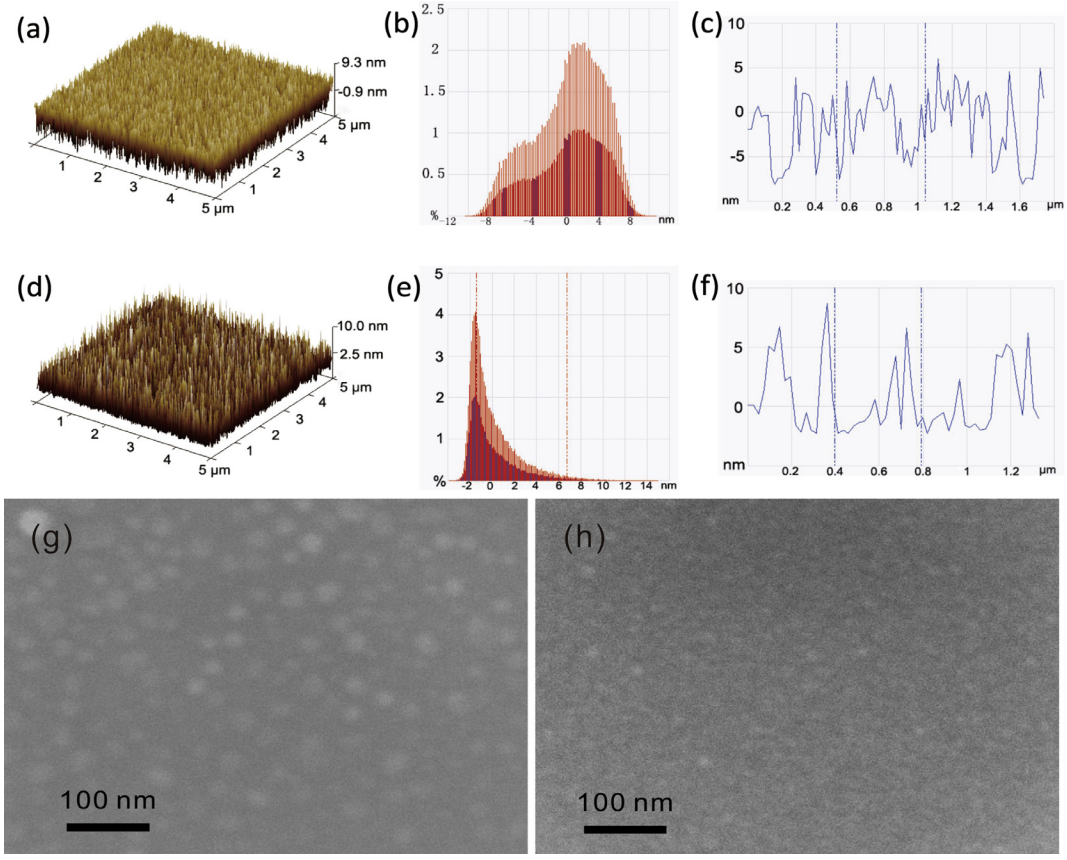

Fig. 2. Surface characterizations of WO_3 thin films with different thickness. AFM 3D micrographs, depth profiles and 1D scanning micrographs of (a–c)12 nm layer and (d–f) 20 nm layer. SEM micrographs are shown in (g) 12 nm layer and (h) 20 nm layer.