Role of materials chemistry on the electrical/electronic properties of CuO thin films

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Abstract—CuO thin films with different levels of compositional deviation from 50:50 stoichiometry have been fabricated using radiofrequency sputtering deposition wherein the sputtering gases consisted of oxygen and argon in various proportions. The microstructures of the thin films were characterized by combining a series of advanced methods including X-ray diffraction, energy dispersive X-ray analysis, scanning and high-resolution transmission electron microscopy, electron energy loss spectroscopy, and high-resolution X-ray photoelectron spectroscopy. The results showed that the chemical states of Cu and O in the thin films depended upon CuO composition and sputtering conditions, so that different levels of Cu vacancies dictated the electrical/electronic properties of the thin films. The ability to control the compound composition and associated alloying chemistry enables tuning of the concentration and mobility of holes in CuO, hence creating a low-cost and environmentally friendly semiconductor from abundant materials. This offers an essential technical basis in engineering photonic devices such as pn or Schottky diodes, thus opening new avenues for economic harvest of solar energy using diodes solely based on sustainable oxides.
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1. Introduction

Interest in the Cu–O system started from the early years of semiconductor physics, with many experimental phenomena and applications having been originally discovered or demonstrated in Cu_2O, the cuprous oxide. This cubic compound exhibits mostly p-type semiconducting characteristics, with a band gap of 2.1–2.6 eV [1–3]. There has been continued interest in studying this cuprous oxide material for various applications such as photonic devices [2], superconductivity [4,5] and photovoltaic (PV) harvest of solar energy [6–8]. Another copper oxide in the Cu–O system is the cupric oxide CuO, a monoclinic p-type semiconductor with a reported narrow band gap of 1.10–1.71 eV [9–11].

In recent years, CuO has attracted increasing attention due to its interesting electrical and optical properties [12–14], together with its low cost and environmental friendliness. Such experimental work has demonstrated great potential in using CuO for a wide range of applications such as gas sensing [15], catalysis [16], field emission [17,18] and PV cells [6,19]. While previous work [15,16,20–22] on CuO mostly focused on its catalytic and gas-sensing properties, PV cells based on CuO have received more attention recently because of the suitable band gap [9,19] of CuO and its easy fabrication into thin films or nanowires [23,24]. The band gap of CuO is close to that of Si [25] and GaAs [26], and in theory the achievable solar conversion efficiency could be up to 33% for a single-junction PV cell with a CuO band gap of ~1.4 eV [27–30]. Recent theoretical modeling has shown that PV cells with even higher efficiency can be achieved by utilizing Cu_2O, CuO and wide-gap oxides in a WAV (window/absorber/voltage-enhancer) architecture [28,29]. It is envisaged that such oxide PV cells can offer a desirable technological means to reduce the cost of PV cells remarkably, while using non-toxic materials with sustainable resources [28,29,31].

However, experimental realization of CuO-based PV cells has proved very difficult, and to date only 0.41% efficiency has been achieved for heterojunction PV cells based on CuO/Si thin films [19]. We have shown from numerical analysis that one needs to be able to tune the optical and electrical properties of copper oxides to maximize their potential for PV energy harvest [28–30]. It is essential to be able to control the charge carrier concentrations in copper oxides, so that a suitable potential profile around the p–n junction(s) can be realized to confine the depletion region

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in the CuO layer for optimized production of electron–hole pairs [28–30]. Fundamentally, these properties of oxide semiconductors depend strongly on the materials chemistry associated with native defect concentration, which in turn depends strongly on the fabrication conditions and particularly the achievable oxygen contents [32–36].

A systematic study of the control of hole concentration and the associated electrical properties is still lacking, despite efforts having been made to synthesize cupric materials using various methods such as reactive sputtering deposition [37,38], wet chemical synthesis [39], thermal evaporation [9], sol–gel processing [40], etc. It is widely recognized that for large area applications such as thin-film PV cells, the reactive sputtering deposition technique stands out for process control and overall material and interfacial qualities.

In this work, we attempt for the first time to investigate the effect of materials chemistry associated with oxygen content in sputtering deposited CuO thin films, aiming at controlling the optoelectrical properties essential for the fabrication of high-efficiency PV cells. The results show that CuO films with compositions close to the ideal cupric stoichiometry have lower hole concentrations than those of lower or higher oxygen contents, and deviation of compositions from the ideal stoichiometry leads to enhanced p-type conductivity through self-doping via increased density of native defects. In spite of the different oxygen contents, the optical band gaps of CuO thin films in this work are all ~1.4 eV, which is within the 1.2–1.6 range for maximum efficiency for solar cells. This ability to control hole concentration through tailored oxygen content offers a fundamental materials basis for engineering high-efficiency solar cells based on copper oxides.

2. Experimental

CuO thin films were deposited on silicon and glass substrates at room temperature by reactive radio frequency (RF) magnetron sputtering using an AJA multi-target system. Before sputtering deposition, silicon and glass substrates were cleaned by a sequence of acetone, isopropyl alcohol and deionized water in an ultrasonic bath. The Si substrate was B doped p-type wafer with a hole density of 10^{14} cm^{-3} (University wafer Ltd, Part No. S4P01SP, ID 452). The thin surface layer of amorphous SiO$_2$ (~2 nm thick) on the Si wafer was kept in order to avoid a seeding effect in the initial stage of coating.

For sputtering, the distance between the Cu target (purity 99.995 wt.%) and substrates was 6.5 cm. The base pressure of the deposition chamber was evacuated down to 1.07×10^{-3} Pa and the substrates were precleaned by plasma irradiation for 10 min with a 30 W substrate bias power, in order to ensure the substrate surface was clean. The oxygen level in the reactive sputtering gas was varied by controlling the gas flow rates at different Ar/O$_2$ ratios. A lower range of oxygen percentage (O$_2$/(O$_2$ + Ar)) from 13% to 47% was administered by using Ar/O$_2$ ratios of 20 sccm/3 sccm, 20 sccm/8 sccm, 20 sccm/10 sccm, 20 sccm/14 sccm and 20 sccm/18 sccm. A higher oxygen percentage range from 57% to 77% was achieved by keeping the oxygen flow rate at 20 sccm and reducing the argon flow rate from15 to 6 sccm. The deposition duration was either 3 h for sputtering at lower oxygen percentage range with

a 120 W RF power, or 20 h for sputtering at the higher oxygen percentage range with a 90 WRF power. The substrates were rotated at 20 rpm during deposition to improve film uniformity.

X-ray diffraction (XRD) was carried out with a PANalytical PERTPRO system using Cu K_α radiation. Scanning electron microscopy (SEM) was carried out using a JSM6510 system equipped with an Oxford Instruments system for energy dispersive X-ray analysis (EDX). For improved accuracy in quantitative EDX measurement, the Cliff–Lorimer factors were calibrated using standard oxide samples of known compositions (stoichiometric CuO, SiO$_2$). Cross-section samples for transmission electron microscopy (TEM) was prepared using focused ion beam milling; details are presented elsewhere [41]. The TEM study was carried out using a Philips CM200 microscope with a field-emission source operating at 200 kV.

X-ray photoelectron spectroscopy (XPS) spectra were recorded by a Thermo VG Multilab 2000 spectrometer under a vacuum of 3×10^{-7}Pa. The radiation source was AlK_α with a power of 300 W. Survey scans were performed at a pass energy of 100 eV and a step size of 1 eV, while a pass energy of 25 eV and a step size of 0.05 eV were adopted for the high-resolution scans of Cu2$p_{3/2}$, O1s and Cu L$_3$VV. The C 1s photoelectron peak of the adventitious carbon at 284.6 eV was used as a reference for charge shift calibration. The Auger parameter of Cu was calculated by adding the binding energy of photoelectrons for Cu2$p_{3/2}$ and the kinetic energy of Auger electrons for CuL$_3$VV. The overlapped XPS peaks were deconvoluted, and fittings were performed using the OriginLab (version 8.0) peak-fitting module with the Gaussian peak type. The values of the full width at half maximum (FWHM) were restricted to be close for same core-level photoelectron peaks for curve fitting.

Optical absorption properties were measured by a Shimadzu UV3600 system, covering a spectral range from ultraviolet (UV) to infrared light. Carrier mobility and concentration were determined by Hall measurement (Sel-Tek HMS-3000 system with a magnetic field of 0.5T). The current–voltage (I–V) characteristics of the samples were recorded between laterally arranged Cu contacts over the top surface of oxide films. The Cu contacts were deposited by electron beam evaporation at room temperature, with insulating glass substrates being used for such oxide films to avoid errors due to substrate conductance.

3. Results and discussion

3.1. Microstructural characteristics

Typical XRD patterns for copper oxide films deposited with different Ar/O$_2$ flow fractions are shown in Fig. 1, wherein the standard XRD powder patterns for both CuO (PDF No. 80–0076) and Cu$_2$O (PDF No. 77–0199) are shown in the lower panels. The thicknesses of the oxide films were in the range of 0.86–1.93 m (measured by cross-sectional SEM). For all samples deposited with the sputtering gas containing >45% oxygen, only one peak corresponding to the CuO (002) peak is present in the XRD patterns. Referring to the standard powder CuO pattern, one can see that such dramatic enhancement in one diffraction peak is apparently attributed to the formation of