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Cupric and cuprous oxide by reactive ion beam sputter deposition and the photosensing properties of cupric oxide metal–semiconductor–metal Schottky photodiodes

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ABSTRACT

Cupric (CuO) and cuprous (Cu_2O) oxide thin films have been deposited by reactive ion beam sputter deposition at 400 °C with an Ar:O_2 ratio from 2:1 to 12:1. With an Ar:O_2 ratio of 2:1, single phase polycrystalline CuO thin films were obtained. Decreasing oxygen flow rate results in CuO + Cu_2O and Cu_2O + Cu mixed thin films. As Ar:O_2 ratio reaches 12:1, Cu_2O nanorods with diameter of 250 nm and length longer than 1 μm were found across the sample. Single phase CuO thin film exhibits an indirect band gap of 1.3 eV with a smooth surface morphology. CuO metal–semiconductor–metal (MSM) Schottky photodiodes (PD) were fabricated by depositing Cu interdigitated electrodes on CuO thin films. Photosensing properties of the CuO PD were characterized from 350 to 1300 nm and a maximum responsivity of 43 mA/W was found at λ = 700 nm. The MSM PD is RC limited with a decay time constant less than 1 μs.

1. Introduction

Cupric (CuO) and cuprous oxide (Cu_2O) are *p*-type non-stoichiometric defect semiconductors. Cu_2O is one of the earliest studied semiconductor material [1] due to its natural abundance and potential applications in low-cost solar cells. The band gap of Cu_2O is 2.0–2.5 eV [2] which coincides with the maximum emission of solar spectrum and efforts have been devoted into the research of Cu_2O solar cells [3–6]. However, the efficiency of Cu_2O based solar cells remains low due to lack of *n*-type counterpart, low hole concentration and low Schottky barrier height [7]. On the other hand, CuO exhibits an in-direct band gap of ~1.3 eV [8]. Photovoltaic cells fabricated by *p*-CuP/n-Si heterostructure shows an efficiency of 0.41% [9]. Even though the conversion efficiency is low, CuO might be useful for photosensing applications from the visible (VIS) to near infrared (NIR) regions. CuO and Cu_2O were commonly prepared by thermal oxidation of metallic copper. Single phase CuO, Cu_2O or mixed CuO + Cu_2O can be obtained by adjusting the annealing temperature [3]. CuO and Cu_2O can also be prepared by RF sputtering that both CuO and Cu_2O may be obtained by adjusting Ar:O_2 flow rate ratio [10–12]. In this article, we report the deposition of CuO and Cu_2O thin films by reactive ion beam sputter deposition. CuO metal–semiconductor–metal (MSM) photodiodes (PDs) were fabricated by depositing interdigitated Cu electrodes on CuO. Photosensing properties of the MSM Schottky PD are presented.

2. Experimental

CuO and Cu_2O thin films were deposited on SiO_2/Si substrates at 400 °C by reactive ion beam sputter deposition. Argon and oxygen were controlled by separate mass flow controllers and were passed through the ion source to act as sputter and reactive gases, respectively. A copper target (99.99%) was positioned at 35 mm downstream of the ion source and SiO_2/Si substrates were positioned at 65 mm upstream of the copper target. For transmission measurement, CuO/Cu_2O thin films were deposited on quartz substrates under the same sputtering condition. For all the experiment, the deposition time was 1 h that results in a film thickness of ~300 nm. Surface morphology of thin films was investigated by a field emission scanning electron microscope (FE-SEM, JEOL JSM-6500F, 15 keV). Micro-Raman spectroscopy was characterized in a Renishaw micro-Raman system utilizing an argon laser at 514.5 nm with a power of 10 mW in backscattering configuration. X-ray diffraction (XRD) analysis was carried out utilizing a 12 kW Rigaku D/MAX 8 X-ray diffractometer (Rigaku D/MAX 8 X-ray diffractometer, 12 kW, CuK_α, λ = 0.1541 nm). Copper interdigitated electrodes with thickness of 100 nm and width/spacing = 100 μm/500 μm

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were deposited on CuO thin films utilizing a shadow mask by ion beam sputter deposition at room temperature. The MSM PD is complete by attaching copper wires to the interdigitated electrode using silver paste. Photocurrent was characterized utilizing a xenon lamp dispersed by a 1/8 m monochromator to select the desired wavelength. The full-width-at-half-maximum (FWHM) of the excitation wavelength is less than 20 nm. Transient photoresponse properties were characterized utilizing a nitrogen laser pumped dye laser at 520 nm with a pulse width of 800 ps and a pulse energy of 200 μJ per pulse (PTI Photonics). The repetition rate of the nitrogen laser is 5 Hz. Transient photoresponse is recorded by a Tektronix TDS200 200 MHz digital oscilloscope.

3. Results and discussion

Fig. 1 shows XRD patterns of copper oxide thin films deposited at 400 °C with Ar:O_2 flow rates from 2:1 to 12:1. From Fig. 1, with an Ar:O_2 ratio of 2:1, single phase CuO is achieved. As oxygen flow rate decreases, mixed CuO + Cu_2O thin films were obtained. As Ar:O_2 ratio reaches 6:1, single phase Cu_2O is achieved instead. Further reducing oxygen flow rate results in the presence of Cu phase, indicating incomplete oxidation of Cu. Fig. 2 shows SEM micrographs of thin films deposited at 400 °C at various Ar:O_2 ratios. From Fig. 2a, single phase CuO thin films exhibit a smooth surface morphology. Increasing Ar:O_2 flow rate ratio to 4:1 (Fig. 2b) results in increased surface roughness. The increased surface roughness is due to the co-existence of both CuO and Cu_2O which has different crystalline structures. From Fig. 2c, single phase Cu_2O deposited with Ar:O_2 ratio of 6:1 also shows a smooth surface morphology.

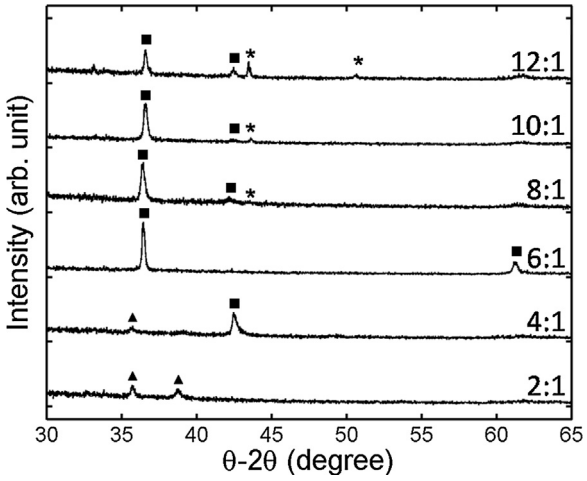

Fig. 1. XRD patterns of samples deposited at various Ar:O_2 ratios. ▲: diffraction peaks of CuO (JCPDS#410254), ■: diffraction peaks of Cu_2O (JCPDS#050667), * diffraction peaks of Cu (JCPDS#851326).

However, mixed Cu_2O + Cu deposited with Ar:O_2 ratio of 8:1 shows an increased surface roughness (Fig. 2d) again. With an Ar:O_2 ratio of 10:1 (Fig. 2e), nanorod with diameter of ~250 nm becomes discernable. The nanorod length increases further to more than 1 μm as Ar:O_2 ratio reaches 12:1 (Fig. 2f). Cross-sectioning EDS analysis of the nanorod shows a Cu:O atomic percentage ratio of 2:1, indicating that they are actually Cu_2O nanorods. From XRD and SEM

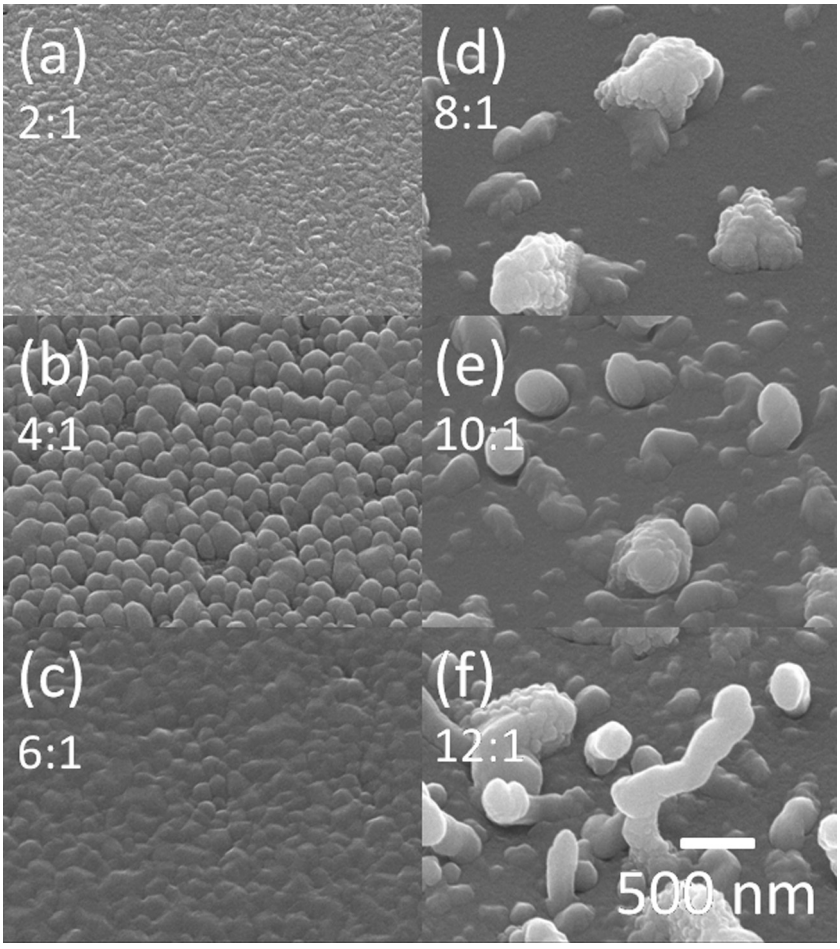

Fig. 2. SEM micrographs of samples deposited at Ar:O_2 ratios of (a) 2:1, (b) 4:1, (c) 6:1, (d) 8:1, (e) 10:1 and (f) 12:1.