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Titanium doped cupric oxide for photovoltaic application

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ABSTRACT

The potential of titanium (Ti) incorporation into cupric oxide (CuO) is demonstrated. The optical, electrical, microstructural, material quality, chemical composition, surface morphology, and photovoltaic properties of Ti doped CuO, CuO(Ti) have been systematically investigated. It is shown that Ti doped CuO reduces sheet resistance and improved the charge transport properties. Furthermore, by tuning the Ti concentration, the conductivity of CuO(Ti) can be improved, while retaining the optical properties and crystallinity of the samples. Heterojunction solar cells of *p*-type Ti doped CuO on *n*-type silicon (Si) substrate, *p*-CuO(Ti)/*n*-Si, prepared by using conventional sputter deposition at room temperature followed by rapid thermal annealing at 300 °C to investigate the impact of Ti doped CuO on the performance of photovoltaic properties. The short circuit current and efficiency of *p*-CuO(Ti)/*n*-Si heterojunction have been significantly improved compared to the cells without Ti doped CuO.

1. Introduction

Cupric oxide (CuO) is one of the promising candidates for low cost and large scale photovoltaic deployment due to its abundant availability and low cost production [1,2]. It exhibits high optical absorption and ideal band gap of ~1.4 eV for the solar light absorption in the whole visible spectral region [3,4]. However, despite the predicated theoretical conversion efficiency of 31%, the highest reported conversion efficiency is only around 1% [5,6].

Low carrier concentration and high series resistance of absorber layer are the possible reasons for poor conversion efficiency of copper oxide based solar cells [7,8]. Therefore, to improve the efficiency of CuO based solar cells, a systematic investigation is needed to develop CuO material with lower resistivity. Doping of CuO can increase the carrier concentration and hence the conductivity, which will reduce the resistive power loss and also improve the efficiency of CuO based solar cells. Therefore, finding a suitable dopant to reduce the resistivity of CuO, while retaining the optical properties and crystal quality of CuO, is of considerable interest. It was theoretically shown that at Fermi energy level around or less than 0.8 eV, the Ti dopant has maximum solubility in CuO and lower formation energy than copper vacancies [9]. However, maximum solubility of Ti into CuO happens when the samples are grown under O-poor condition. In this paper, systematic investigation is conducted to study the impact of incorporating Ti into CuO.

N-type CuO has proven to be challenging, thus heterojunction solar cells based on copper oxides were implemented [3]. Crystalline-silicon (c-Si) is the most stable material and also the most dominant technology for PV applications. The electron affinity of CuO is similar to that of Si, which makes Si a suitable candidate for preparing the *p*-CuO/*n*-Si-based heterojunction solar cell to study the Ti-doped CuO as photovoltaic (PV) material. Toward this, in this paper, the potential of Ti doping for improving the conductivity and photovoltaic properties of CuO devices has been investigated. The effects of Ti concentration on the crystal quality and electrical properties as well as optical properties and surface morphology have also been studied in detail. It was found that the conductivity of Ti doped samples can be enhanced by Ti concentration, while retaining optical properties and crystal quality of samples. Heterojunction solar cell of Ti doped *p*-type CuO on *n*-type Si substrate was also demonstrated to study the impact of Ti-doped CuO on the solar cells performance.

2. Experiment

Si and glass substrates were used for the thin film deposition of CuO(Ti). The substrates were ultrasonicated in IPA for 10 min. For Si substrates, the native oxide was removed by dipping into 2% HF solution for 5 min before loading into the sputter chamber.

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Titanium doped CuO was deposited under O-poor condition. Argon gas was purged during sputtering of stoichiometric CuO and pure Ti through co-sputter. The sputtering power was held constant at 50 W for CuO deposition and it was varied from 1 to 10 W for Ti cosputtering to obtain CuO films with different Ti concentrations. For the control CuO sample without doping, Ar gas flow rate was set to the 25 sccm. A rapid thermal annealing (RTA) system was used for thermal treatment of samples in the nitrogen ambient at 300 °C and 600 °C for 1 min. Ti followed by Al was deposited after the thermal treatment on the front side of copper oxide film and back side of Si substrate to make the contact for solar cells.

X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HR-TEM), Raman spectroscopy and atomic force microscopy (AFM) were used to investigate the effects of Ti concentration on the characteristics of CuO(Ti) thin films.

3. Results and discussion

Ti concentration in CuO was determined using secondary ion mass spectrometry (SIMS) after thermal treatment at 300 °C and the values are tabulated in Table 1. As shown in the table, the Ti concentration varied approximately in a linear manner from 0.049 to 0.598% by increasing the cosputtering power of Ti target from 1 to 10 W. The effect of Ti concentration on the electrical conductivity of CuO(Ti) thin films was investigated using a four point probe system. As included in Table 1, the undoped CuO exhibits a higher resistivity than the Ti doped thin films. Higher incorporation of Ti decreased the resistivity of CuO(Ti) thin films continuously, and the value was found to decrease by three orders of magnitude when the Ti concentration was 0.598%. The significant reduction of resistivity of CuO(Ti) can be explained based on charge compensation effects. Recently, Minami et al. also reported Na-doped Cu_2O with improved electrical conductivity through charge compensation effects [10]. The radius of Ti^+ (0.095 nm) is very close to Cu^+ (0.096 nm). Therefore, it is very difficult for Ti atom to incorporate at substitution sites of CuO lattice to act as an acceptor. It is also well known that oxygen vacancy self-compensates copper vacancy in undoped CuO. The mechanism of the resistivity reduction for titanium doped CuO is possibly due to the charge compensation effects which occur because of the incorporation of Ti atom at an interstitial site of CuO lattice and acts as a donor. This hypothesis is also supported by the fact that the peak positions of (002) and (111) in XRD spectra were changed by the incorporation of Ti, as shown in Fig. 1.

Table 1
Ti concentration and sheet resistance of 60 nm thick CuO (Ti) samples after annealed at 300 °C.

	Undoped CuO	B1	B2	B3	B4
Ti Sputtering power (W)	0	1	2	4	10
Ti concentration (%)	0	0.049	0.099	0.19	0.598
Sheet resistance (Ω/square)	$\sim 6\times10^8$	$\sim 8\times10^6$	$\sim 5\times10^6$	$\sim 2\times10^6$	$\sim 5\times10^5$

The crystalline quality of CuO samples was investigated using Bruker D8 general area detector XRD system (GADDS) in θ–2θ scan using a CuKα ($\lambda = 0.15418$ nm) radiation. Fig. 2 shows the XRD spectra of as-deposited CuO(Ti) samples with various Ti concentrations denoted as (AsD) together with the results of annealed samples at different temperatures. XRD spectra of sputter deposited control CuO thin films are also presented in this figure. FWHM (full width at half maximum) of XRD peaks are listed in Table 2. The XRD spectra clearly show presence of CuO (002) at 35.482 and CuO (111) at 38.764 for all the undoped and Ti doped CuO. As shown in Fig. 2(a) and (b), for the as-deposited CuO(Ti) and annealed CuO(Ti) at 300 °C exhibited no significant change in the peak intensity and FWHM value as the Ti concentration was increased from 0% to 0.099% (sample B2), maintaining good crystalline quality. However, further increase of Ti concentration resulted in the reduction of the peak intensity as well as widening of FWHM value, highlighting the dependence of crystal quality on Ti concentration. Indeed, in the lightly doped CuO, due to proper substitution of Ti in CuO lattice, no secondary defect phases are observed. However, in the highly Ti-doped CuO samples, the presence of more Ti-induced crystalline disordering resulted in lattice imperfection degrading the crystal quality of thin films. According to Fig. 2(c), formation of additional CuO(110) peak at 32.548 can be clearly observed in the samples annealed at 600 °C temperature. However, the crystal structure of copper oxide was retained in all the samples and no other phases such as Cu_2O and/or CuTi appeared.

The sputter deposited CuO and CuO(Ti) thin films on glass substrates were analyzed by Raman spectroscopy using Witec Alpha 300R confocal Raman microscope equipped with a 532-nm Nd:YAG laser. The samples were always measured from the air side to understand and evaluate the effects of Ti concentration on the structural disorder, defects in the host lattice and crystallinity of the samples. Fig. 3 presents Raman spectra of CuO and CuO(Ti) thin films with various Ti concentrations after annealed at 300 °C for 1 min. The distinct peaks, observed at ~125, 288 and 599 cm^{-1} indicate the formation of CuO [5,6]. The intensity of all the Raman peaks does not significantly change with increasing Ti concentration from 0% to 0.099%, further confirming that good crystallinity is retained in the case of lightly doped samples. However, the Raman peaks become broad and the intensity shows a gradual decrease as the Ti

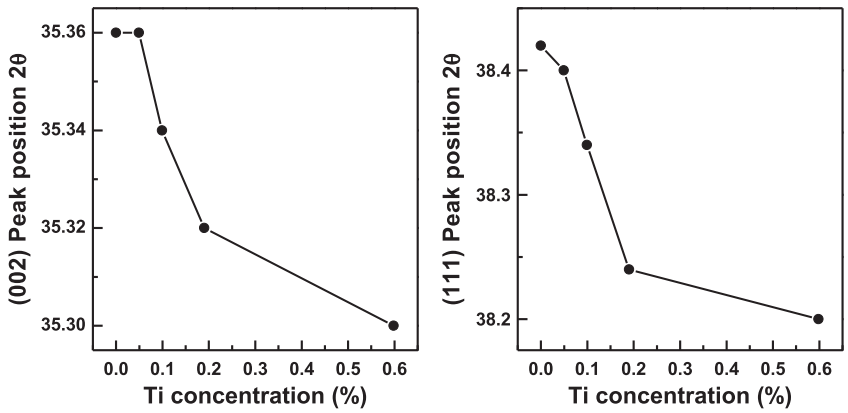

Fig. 1. Peak position of (002) and (111) XRD spectra as functions of Ti concentration for CuO(Ti) samples annealed at 300 °C.