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Electric properties and chemical bonding states of *pn*-junction *p*-CuO/*n*-Si by sol-gel method

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The fabrication of a p-n junction is the most fundamental step in realizing the electronics, therefore it is important to investigate the possible methods of how to integrate artificially designed structures, i.e., growing oxide thin films on semiconductor *n*-Si. For the device applications, the structure of a p-n junction has shown a promise diode, lasers, light emitting diode and solar cells. Cupric oxide is a *p*-type semiconductor with bandgap of about 1.2 to 1.9 eV depending on the current density.

In this study, CuO/*n*-Si thin films were prepared by sol-gel method. I–V characteristics from the CuO/*n*-Si films shown nonlinear I-V curve of *p*-*n* junction. Copper oxide is synthesized in two semiconducting phases (cupric oxide (CuO) and cuprous oxide (Cu₂O)) and hydroxyl species (Cu(OH)₂) in the surface region of CuO/*n*-Si thin films from chemical bonding states. The junction of copper oxide and *n*-Si exhibited nonlinear behavior and rectifying I–V characteristics.

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Introduction

The metal oxides used for a gas sensor application are mostly n-type semiconductors, and the main issues are how to improve their gas sensing performance. [1-7] On the contrary to n-type semiconducting metal oxides, due to an excess of oxygen, cupric oxide (CuO, copper (II) oxide) is a p-type semiconductor and exhibits a number of promising properties as a low-cost material, material abundance, non-toxicity. [8] The cupric oxide has been generally recognized as the prototype material of broad family of strongly correlated oxides. The paramount role of various inhomogeneities in the formation of the unconventional physical properties of these systems is becoming increasingly clear, and the tendency toward electronic phase separation is recognized as their generic feature. [9] In recent years, cupric oxide has received special attention from many technological fields and scientific areas because of their wide potential for industrial applications. Cupric oxide, a p-type semiconductor with a direct bandgap of about 1.2~1.9 eV, has shown a promise for the photovoltaic devices [10, 11], electrochemical, and catalytic properties. [12-15] As for the device applications, the fabrication of a p-njunction is the most fundamental step in realizing electronics, therefore it is important to investigate the possible methods of how to integrate artificially designed structures, i.e., growing oxide thin films on conventional semiconductor n-Si that are compatible with the main stream of semiconducting industry.

In this study, *p*-type semiconductor CuO thin films were prepared by sol-gel method. The phase formation processes and microstructures were examined by X-ray diffraction (XRD), scanning electron microscope (SEM). The chemical bonding states were examined by X-ray photoelectron spectroscope (XPS). The optical properties were examined by UV-Vis spectrophotometer.

Experimental

CuO solution was synthesized by sol-gel method. Firstly, cupric acetate monohydrate (Cu(CH₃COO)₂ \cdot H₂O) was dissolved in a mixture solution of 10 ml of 2methoxyethanol (2-MOE) and 0.1 ml of monoethanolamine. After stirring the mixture solution for 5 hours, 0.1 g of polyvinylpyrrolidone (PVP; $Mw \approx 55,000$) was added and the solution was continually stirred for 10 hours. The PVP were used as chemical additives to modify weak adhesion with substrate for spin-coating. A spincoating technique was used to coat the CuO mixture solution on the FTO and n-Si substrates. The wet films were dried in air at 400 °C on a preheated hot plate for 30 seconds to remove residual solvent. The annealing temperature was set at 500 °C and 700 °C. The crystallinity and crystal orientation of the films were investigated by X-ray diffractometer (XRD; Philips, X'Pert Pro), and all samples were scanned

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from 20 ° to 70 ° (2 θ) in the continuous mode. The morphology and thickness of the films were determined by a field emission scanning electron microscope (FE-SEM; Hitachi, S-4200). The chemical bonding states of the films were determined by X-ray photoelectron spectroscopy (XPS; VG Scientific, ESCALAB250) with a hemispherical electrostatic energy analyzer and an Al K α (1486.6 eV) X-ray source. The transmission and absorbance was examined by UV-Vis spectrophotometer.

Results and Discussion

Fig. 1 shows XRD patterns of (a) CuO/FTO/glass and (b) CuO/*n*-Si thin films prepared by sol-gel method. All the diffraction peaks exhibit CuO phase with a characteristic monoclinic lattice and (100) Si substrate and are indexed only to monoclinic CuO with lattice constants a = 0.4689 nm, b = 0.3428 nm,



Fig. 1. XRD patterns of CuO thin films: (a) CuO/FTO/glass and (b) CuO/*n*-Si films.



Fig. 2. SEM images of CuO thin films: (a) CuO/n-Si films annealed in 700 °C for 1 hour, (b) CuO/FTO/glass films annealed in 500 °C for 1 hour, (c) thickness of CuO/n-Si films and (d) thickness of CuO/FTO/glass films.

Fig. 2 shows SEM images of (a) CuO/*n*-Si films annealed in 700 °C for 1 hour, (b) CuO/FTO/glass films annealed in 500 °C for 1 hour, (c) thickness of CuO/*n*-Si films and (d) thickness of CuO/FTO/glass films. The CuO/*n*-Si films have tightly packed grains and show a relatively rough surface. An average grain size of CuO/*n*-Si films was about 0.25 mm and thickness of films was 0.62 μ m (Fig. 2 (c)). The CuO/ FTO/glass films were annealed in relatively low temperature because of substrate. An average grain size of CuO/*n*-Si films was about 0.079 μ m and thickness of films was 0.22 μ m (Fig. 2 (d)). And, The CuO/*n*-Si films have dense and relatively smooth surface.

The XPS measurements were carried out in order to investigate the valence states of Cu and O in the *p*-CuO/*n*-Si films. Before carrying out the XPS measurements, the film surface was etched at a rate of 0.05 nm/s for 30s. The measurement area had $200 \times 200 \text{ }\mu\text{m}^2$. All the peaks were calibrated with respect to the C 1s peak at 284.6 eV. Fig. 3(a) shows XPS patterns of Cu 2p core level and satellite peak of CuO/*n*-Si films. The XPS patterns of Cu 2p core level are accompanied with a satellite peak at about 9 eV higher binding energies. [16], which is not appeared



Fig. 3. XPS patterns of CuO/*n*-Si films: (a) Cu 2p core level and (b) fitting results of $Cu2p_{3/2}$ core level.



Fig. 4. XPS patterns of O1s core level and fitting results of CuO/*n*-Si films.



Fig. 5. The absorbance and transmission spectrum of p-CuO films.

in the case of Cu₂O. It was reported the satellite feature observed for the CuO is related to d⁹ configuration in the ground state of Cu. The d shell of Cu₂O is full hence the screening via a charge transfer into the d states is not possible and this is the cause of the absent of a satellite peak in Cu₂O spectra [16]. Fig. 3(b) shows the XPS patterns of Cu $2p_{3/2}$ core level and fitting results the Gaussian functions of CuO/*n*-Si films. It is seen that the characteristic peaks of Cu $2p_{3/2}$ core level located at 933.4, 934.6 and 935.1, Cu₂O, CuO and Cu(OH)₂, respectively [17].

Fig. 4 shows the XPS patterns of O 1s core level and fitting results with the Gaussian functions of CuO/*n*-Si films. The O 1s peak in Fig. 4 was comprised of three peaks which are located at 529.8 eV, 530.3 eV and 531.9 eV. The former (two peaks) is resulted from the cupric oxide (CuO) and cuprous oxide (Cu₂O) [18], while the latter peak is resulted from hydroxyl species (Cu(OH)₂). Therefore, copper oxide can exist in two semiconducting phases, namely, cupric oxide



Fig. 6. I-V curve of CuO/n-Si film annealed in 700 °C for 1 hour.

(CuO) and cuprous oxide (Cu₂O) [18]. The binding energy peaks of CuO and Cu₂O are relatively sharp with the FWHM of about 1.3 eV at 529.8 eV and 530.3 eV, respectively. On the other hand, the binding energy peak of Cu(OH)₂ is relatively broad with the FWHM of 2.0 eV at 531.9 eV. The FWHM of copper oxide semiconductor peak (1.3 eV) is smaller than the reported value of 3.4 eV for the bulk CuO [19] but close to corresponding reported value for bulk Cu₂O (1.9 eV) [18].

The absorbance and transmission spectrum of p-CuO films deposited by sol-gel is shown in Fig. 5. In absorbance measurement, CuO/n-Si film was annealed in 700 °C for 1 hour. A broad absorption peak centered at 260 nm is seen. Compared with the value of 360 nm of CuO microspheres reported by Hong et al. [20], an obvious blue-shift is seen. In transmission measurement, CuO/FTO/glass film was annealed in 500 °C for 1 hour.

Fig. 6 shows a typical current-voltage (I-V) characteristic of the CuO/n-Si film annealed in 700 °C for 1 hour. The inset in Fig. 6 shows the CuO/n-Si thin films device structure for electrical characterization. The circular Au electrodes with an area of 2.2×10^{-3} cm² were deposited by dc sputtering. Liao et. al. [8] reported the ohmic characteristic in the Au and CuO The junction exhibited nonlinear contact. and rectifying I-V characteristics. A small leakage current was observed in the reverse bias region, but the ratio of forward current to the reverse current was larger than 80 in the applied voltage range of -4.0 to +4.0 V and the turn-on voltage was 0.8 V. Therefore, any rectification in I-V characteristics from the CuO/n-Si films should come from the *p-n* homojunction in CuO and n-Si. The nonlinear I-V curve is typical of p-njunctions. The p-n heterojunctions are formed at the interfaces of *p*-type CuO and *n*-type Si substrate because CuO grown without any intentional doping generally show *p*-type semiconducting properties.

Conclusions

The *p*-type semiconductor CuO thin films were prepared by sol-gel method. The synthesized copper oxide was deposited in the surface region of *p*-CuO/*n*-Si thin films; *p*-cupric oxide (CuO) semiconductor, *p*cuprous oxide (Cu₂O)) and hydroxyl species (Cu(OH)₂). The CuO/*n*-Si films have tightly packed grains and a relatively rough surface. An average grain size of CuO/*n*-Si films was about 0.25 mm and thickness of films was 0.62 mm. I-V characteristics of CuO/*n*-Si films exhibited the nonlinear curve, which is typical of *p*-*n* junctions. It is found that the *p*-*n* heterojunctions are formed at the interfaces of *p*-type CuO and *n*-type Si substrate.

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