CHAPTER 4

Conclusion

Metal oxide exhibits in wide range of functional properties depending on their physical and chemical properties such as crystal structure, electrical and optical properties. From their fascinating properties, metal oxides have been used a base material for many applications such as light emitting diode, solar cell and many electronic devices. In this thesis, we focused on zinc oxide (ZnO) and cuprous oxide (Cu_2O) because they are earth abundant material, cost effective and non-toxic. ZnO is always an n-type semiconductor with a direct band gap (~ 3.4 eV) while Cu_2O is natural a p-type semiconductor with a direct band gap (~2.1 eV). They have been suitable to innovate an n-ZnO/p-Cu_2O heterojunction.

The main topic of my thesis is properties investigation of Al doped ZnO thin films, and Cu_2O thin films which are synthesized by a sparking process. The fabrication and characterization of AZO/Cu_2O heterojunction are included.

4.1 Al doped ZnO (AZO) thin film

The AZO thin films were deposited on a rotating glass substrate by double tip sparking process. Zn (purity 99.99%, diameter 0.38 mm) and Al (purity 99.99%, diameter 0.5 mm) wires were placed as the main tips and the doping tips, respectively. The gap between tips and the height of the tips above glass substrate were fixed at 1 nm. The sparking process was done for 5 min under flowing Ar atmosphere with a flow rate of 0.5 L/min at room temperature. The doping ratio of Al to Zn was controlled by sparking energy using a different capacitor (C) paralleled Al doping tips. The capacitances paralleled Zn was fixed at 40 nF while those of Al were varied by 0.5, 1.1, 1.5, 3.1, and 4.7 nF. The as-samples were annealed at 400 °C for 60 min. The EDS results showed Al doping ratio in ZnO were 3, 5, 7, 13 and 22 by atomic percent which related to the capacitances of paralleled Al tips were 0.5, 1.1, 1.5, 3.1 and 4.7 nF, respectively. It was seen clearly that the Al doping ratio increased when capacitance paralleled Al tips increased that was explained by increasing sparking energy at the Al doping tips. The SEM cross-section images indicated that the average thickness of prepared films was 1000 nm. The Raman result of AZO films presented the the Raman shift of 333 and 438 cm^{-1}, which associated with a typical ZnO hexagonal structure. The doped films also showed the Raman shift at 275 and 578 cm^{-1}, that was resulted from oxygen vacancy and impurity defect, and higher carrier concentration, respectively. Apart from Raman result, the hexagonal wurtzite ZnO was confirmed by XRD results. The XRD pattern of samples illustrated the lattice planes of (101) and (101) that corresponded to hexagonal structure and lattice parameters of a = b = 3.253 Å and c = 5.213 Å.

For optical investigation, it was found that the AZO films had average transmittance at 60% in visible region. The transmittance of AZO films increased with increasing the doping ratio of Al that probably caused by the energy gap turning that resulting from Al content in ZnO. The calculated energy gap of AZO films were 3.34-3.53 eV. The energy gap of the film increased with increasing Al doping ratio. The energy gap turning can be explained by Burstein-Moss effect that is related to the electron carrier density. Substitution of Al^{3+} to Zn^{2+} in the AZO films, the extra e^- from Al^{3+} makes the electron carrier density increases, that resulted in the increasing of energy gap in the AZO films. Moreover, the AZO film resistivity decreased at a small amount of Al doping as compared to the un-doped sample. As mentioned above that is about substitution of Al in ZnO, Al^{3+} provides extra free electron into the system. That make the resistivity of the film decreased. In contrast, the increase doping levels affected to increase the resistivity of doped films that may be due to an increasing of insulator Al_2O_3 concentration. However, the optimum of Al doping level was found at 5 at. % in AZO film and their resistivity was 4,763.61 Ω-cm.

4.2 Cu_2O film

Cu_2O thin films were deposited on a rotating glass substrate by a tip sparking process. Cu (purity 99.99%, diameter 0.5 mm) wires were placed as the main tips. The capacitances paralleled Cu tips was fixed at 40 nF. The gap between tips and the height of the tips above glass substrate were fixed at 1 nm. The sparking process was done under flowing Ar atmosphere with a flow rate of 0.5 L/min at room temperature. The samples were annealed at 200 °C. The surface morphologies was pretty porous. The Raman results of Cu_2O films for different annealing time showed the Raman sifts at 150, 220, 628, and 645 cm^{-1}, that corresponded to database of Cu_2O. It also showed Raman shift of 150 and 628 cm^{-1} (IR active modes) that related to a perfect Cu_2O crystal. Moreover, synthesized Cu_2O films for different annealing time were confirmed by XRD. The XRD pattern presented crystalline plane (111) at 36.5°, which corresponded to cubic Cu_2O structure and lattice parameter of a = b = c = 4.260 Å. For optical investigation, the Cu_2O films for different annealing time illustrated that all samples had absorption in visible region, but the annealed Cu_2O at 2 hours presented higher absorbance than others. The energy gap of Cu_2O were 2.00, 2.20, 2.18, 2.10 and 2.29 eV for annealing time at 10 min, 30 min, 60 min, 2 hrs., and 3 hrs., respectively.

According to Raman, XRD and absorbance results, Cu_2O annealed for 2 hours demonstrates outstanding properties compared to another annealing time as well as its energy gap corresponded to typical properties of Cu_2O. Therefore, optimize condition of Cu_2O prepared by sparking process was annealing treatment at 200 °C for 2 hours.

On the other hand, a study of relation of sparking time to Cu_2O film thickness was found that Cu_2O prepared by sparking process have the deposition rate at 18.4976 nm/min. the resistivity of Cu_2O film was 810.7873 Ω.cm.

4.3 AZO/Cu_2O heterojunction

AZO/Cu_2O Heterojunction was fabricated by the sparking process. The first layer of AZO thin film was deposited on a Fluorine doped Tin Oxide (FTO) substrate and was annealed at 400 °C for 60 min. The Cu_2O layer was deposited on AZO as a second layer and was annealed at 200 °C for 2 hrs. The two step sparking process were done under flowing Ar atmosphere with a flow rate of 0.5 L/min at room temperature. The cross-section image demonstrated the film as two layer, AZO was first layer and Cu_2O was second layer. The carrier transportation mechanisms at the heterojunction was examined by I-V characteristic under dark. The calculated ideality factor (n) was 2.644. This reveals that the tunneling process is the dominant carrier transportation mechanism at interface of AZO/Cu_2O heterojunction.

4.4 Suggestions

4.4.1 According to the sparking method, it is very useful to synthesize metal oxide nanoparticle and nanoparticle thin film in single step. Besides, many tips sparking process is better for synthesis compound metal oxide, for example, Al doped ZnO was synthesized by double tips sparking process, as mention in this thesis.

4.4.2 According to the doping ratio of two materials prepared by double pairs sparking process. The doping ratio was controlled by sparking energy using a different capacitance of paralleled the doping tips, while the capacitance of paralleled the main tips was fixed as constant.

4.4.3 According to current-voltage measurement for investigation the I-V characteristic of heterojunction. Further work, the data should be collected by precise step (0.01) of measurement in voltage bias of 0-1 volt.

4.4.4 According to XRD pattern of thin film prepared by sparking process. To investigate the crystalline structure by XRD, it should be use X-ray scanning in very precise step (20 dpm, step 0.01) in order to get the high quality data with low background noise. That can identify clearly dominant peak of those material.

4.4.5 According to SEM surface morphology of AZO films, it was seen that the different peak to valley surface characteristic decreased with AZO film which have capacitance paralleled Al tips increased. To confirm surface morphologies of AZO films, it should be use Atomic Force Microscope (AFM) to investigate the roughness of the surface.

4.4.6 To investigate the atomic substitution of Al in Zn of crystalline structure, X-ray photoelectron spectroscopy (XPS) is a powerful method to determine chemical bonding of atoms in the film structure. And X-ray absorption near-edge spectroscopy (XANES) has been a powerful technique for structural determination of materials.

4.4.7 According to the cross-section image of AZO/Cu_2O heterojunction, for investigation the element composition in each layer, it should be use SEM-EDS mapping scan which is a function operated in SEM system.