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Effects of Sintering Holding Time on the Structural, Electrical and Magnetic Properties of $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$

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Abstract. $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ has been synthesized by mixing 5% mol of NiO into ZnO using solid state reaction and high-speed shaker mill method. The samples were sintered at 900 °C with holding time for 2, 4 and 8 hours. Crystal structure, electrical and magnetic properties of $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ were characterized by using XRD, I-V, C-V and VSM. XRD results showed that variation of holding time does not change the structure of ZnO and no other secondary phase observed. The value of lattice parameters (a and c) tends to decrease proportionally to the holding time. The Intensity value changes and the peak shifted to a higher 2θ angle due to holding time variation. In general, the conductance of $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ decreases and the magnetic properties decrease also as the holding time is increased.

Keywords: Sintering, holding time, $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$, structure, electrical and magnetic property

1. Introduction

Magnetic properties transition from paramagnetic to ferromagnetic in the semiconductor material is an interesting topic in solid-state physics. It is because of its advantage in spintronics applications, i.e. data processing speed, non-volatility and higher integration densities [1]. The change of semiconductor material magnetic properties was made by doping the transition-metal elements (TM), i.e. Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu [2]. Control and tuning of magnets properties in dilute magnetic semiconductor (DMS) such as ZnO, TiO_2 , dan SnO_2 have been studied in the last decades. Among other materials, ZnO has advantages, such as non-toxic, low-cost and eco- friendly [3]. Moreover, ZnO as a semiconductor material has the chemical stability and high thermal, with an energy gap of 3.37 eV and exciton binding energy of 60 MeV [4]. It makes the ZnO high potential in many applications, such as solar cells, optoelectronic, magnetic tunnel junctions, photovoltaics, light-emitting diodes, spintronics-based devices, and sensors [5]. Ferromagnetic room-temperature in doped ZnO metal transition, particularly in Ni has been studied intensively in recent years [6]. However, the reported result is still far from the clear explanation on the origin of the magnetism.

Nickel (Ni) is a transition metal with a radius nearly equal to Zinc (Zn). This case is the reason why the Ni^{2+} ions are more easily substituting Zn^{2+} ions in the ZnO crystal [7]. Ni-doped ZnO has been studied through various synthesis methods, such as solid state reaction [5], sol-gel [4], co-precipitation [2,8,13], sputtering [9,10] and hydrothermal [11]. Solid state reaction method using a milling tool is an inexpensive and simple laboratory scale. Until today, only a few work reported on Ni-doped ZnO synthesized by using solid-state reaction method. In this study, we synthesized Ni-doped ZnO with a



solid-state reaction method by using high-speed shaker mill. Then we discussed the effect of the Sintering holding time on the structure, electrical and magnetics properties of $Zn_{0.95}Ni_{0.05}O$.

2. Experimental Method

$Zn_{0.95}Ni_{0.05}O$ synthesis was done by using solidstate reaction method with ZnO and NiO powder as starting material. ZnO and NiO were mixed and milled in a vial cylindrical stainless steels by using a high-speed shaker mill with frequency oscillation of 700 / min. Steel ball diameter (ϕ) of 4 mm was used with the powder weight ratio to the ball was 1:10. The process carried out for 3 hours in wet conditions by adding toluene as a solvent. The powder was then dried in an oven at a temperature of 100 °C for 3 hours; then powder was turned into the pellet shaped by using the automatic axial hydraulic pressure of 1500 kgf/cm². The resulted pellet samples have a diameter of 15 mm and thickness of 2 mm. In the final process, the samples were sintered at temperature of 900 °C with holding time of 2, 4 and 8 hours in the air atmosphere. The crystal structure of the $Zn_{0.95}Ni_{0.05}O$ of pellets was investigated by using X-ray diffraction (XRD)-Smartlab-Rigaku. Meanwhile, electrical and magnetics properties of the samples were analyzed by using the I-V meter (Fluke 8842A multimeter high impedance), C-V meters (Keithley 590 CV analyzer) and a vibrating sample magnetometer (VSM 250, Dexing Magnet.ltd).

3. Results and Discussion

The detail results of XRD analysis of $Zn_{0.95}Ni_{0.05}O$ with holding time variation are shown in Figure 1. The XRD pattern of pure ZnO was used as a reference. The analysis result revealed that overall $Zn_{0.95}Ni_{0.05}O$ samples have the main hexagonal wurtzite structure (Figure 1-a). The presence of peaks can also be seen at an angle of 2θ , approximately at 31,7°; 34,4°; 36,3°; 47,6°; 56,6°; 62,9°; 66,4°; 67,9°; 69,1°; 72,6°; and 76,9°, that are related to planes of wurtzite structure (100) (002) (101) (102) (110) (103) (200) (112) (201) (004) and (202). Furthermore, a peak that indicates NiO phase appears at an angle of 2θ at 37.1° and 43.2° (Figure 1-b). Further analysis indicates that some of the Ni^{2+} ions diffuse into the ZnO lattice, and some are still in the form of NiO compound. This phenomenon is confirmed by detailed analysis on ZnO plane (002) given in Figure 1-c. The peak intensity is decreased and shifted when ZnO doped with NiO. The change of intensity and peak position confirmed that the Ni^{2+} ion is already penetrated into the ZnO lattice and substituting the Zn^{2+} ion [8]. Then the increase of holding time causes the peak shifted to a higher 2θ angle. Figure 1-c also reveals that the full width at half maximum (FWHM) decreases by increasing the holding time. The peak shift and FWHM changes, in this case, may be affected by the changes in other crystal parameters.

Crystal parameters such as lattice parameters (a and c) and crystal size were estimated based on the XRD data. Hexagonal lattice parameters of the phase weredetermined by using the equation:

$$a = \frac{\lambda}{\sqrt{3} \sin \theta} \sqrt{h^2 + hk + k^2} \quad (1)$$

and

$$c = \frac{\lambda}{2 \sin \theta} l \quad (2)$$

where λ is the wavelength of X-rays, θ is the Bragg diffraction angle, and hkl is miller index, whereas the crystal size was determined according to ZnO plane (002):

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (3)$$

where β is the FWHM of (002) diffraction peak. The calculation result of crystal parameters is shown in Table 1. The results of a and c of $Zn_{0.95}Ni_{0.05}O$ remain the same as the holding time was increased. As a result the c/a value is also constant to a change of holding time. This case is due to Ni^{2+} ion has partially substituted Zn^{2+} ions in ZnO lattice. However, the lattice parameter values obtained from this

research is smaller than that of the theory value (ICDD No. 00-005-0664, $a = 3.249\text{\AA}$ and $c = 5.205\text{\AA}$). The Ionic radius of Ni^{2+} (0.55\AA) is smaller than the radius of Zn^{2+} (0.60\AA) which is the main factor of the change of the lattice parameter values [12]. The lattice parameter changes were also reported by previous studies [4,5,8]. The $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ crystal size increases with increasing holding time. This phenomenon can be explained that the longer the holding time causes the diffusion longer derived by the heat effect so that the small grains have enough time to grow into larger grains [13].

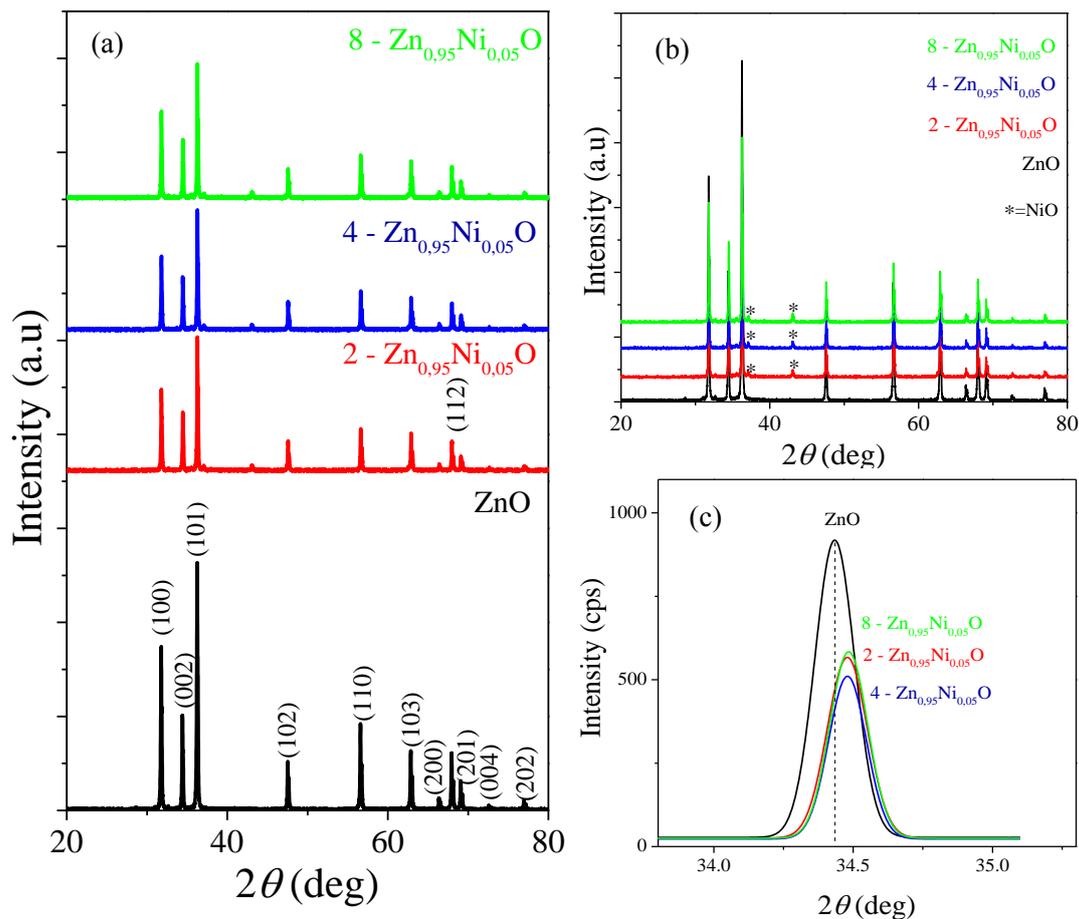


Figure 1. XRD Pattern of (a) $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ with holding time of 2, 4 and 8 hours; (b) $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ and (c) detailed observation at (002) plane.

Table 1. Calculation of lattice parameters (a and c) and average crystal size of $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ at (002) plane as the effect of holding time.

Sintering holding time (hour)	a (Å)	c (Å)	c/a	FWHM (deg.)	D (nm)
0	3.249	5.205	1.602	0.154	50.6
2	3.245	5.198	1.601	0.112	74.6
4	3.246	5.199	1.601	0.106	75.0
8	3.246	5.198	1.601	0.102	77.9

The electrical properties of $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ were observed in different holding time at room temperature. Conductivity value (σ), capacitance (C) and dielectric constant (ϵ_r) are listed in Table 2. It can be seen that the increase of the holding time leads to changes in conductivity and dielectric constant value of $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$. The capacitance value of $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ increases as holding time is

increased. The changes in the electrical conductivity on this study may be due to the Ni doping, which can also create crystal defects [14]. The difference value between the radius of Zn^{2+} and Ni^{2+} ions also causes the internal stress on the ZnO lattice [15] that also causes the defects on the grain boundaries. Then the charge movement will be blocked by the grain boundaries defect. Moreover, the absence of oxygen is also believed to contribute to the electrical conductivity values [9]. Meanwhile, the high obtained dielectric value of the $Zn_{0.95}Ni_{0.05}O$, since Ni^{2+} ions occupy the center position in Zn^{2+} , which leads to the permanent electric dipole. The absence of oxygen is also another aspect that affects the dielectric properties of $Zn_{0.95}Ni_{0.05}O$ [11,15]. The sintering holding time influences very much on reducing defects at the grain boundaries. Thus, the holding time has an important role in improving the structure and electrical properties of $Zn_{0.95}Ni_{0.05}O$.

Table 2 Conductivity, capacitance and dielectric constant of $Zn_{0.95}Ni_{0.05}O$ as the effect of holding time

Sintering holding Time (Hour)	ρ (Ω cm)	σ (S/cm)	C (pF)	ϵ_r
0	3.25×10^7	3.06×10^{-8}	3.28	10.75
2	4.80×10^7	2.08×10^{-8}	25.29	47.55
4	5.99×10^7	1.67×10^{-8}	27.48	36.28
8	4.79×10^7	2.09×10^{-8}	35.35	58.33

Figure 2 shows the magnetic field versus the magnetization of $Zn_{0.95}Ni_{0.05}O$ sample with different Holding Time at room temperature below 20 kOe. As shown in Figure 2-a, the initial magnetic behavior of ZnO before Ni doped is diamagnetic. Doping with Ni causes the change in the magnetic properties of ZnO into ferromagnetic. This result is consistent with previous studies reported somewhere [4,5,7,8,9]. The ferromagnetic properties are formed due to part of Ni^{2+} ions substituting Zn^{2+} in ZnO lattice.

The exchange interaction between local spin-polarized electrons of Ni^{2+} and conduction electrons or free carriers caused the ferromagnetic interaction [2]. Figure 2-a reveals that the increase of holding time leads to the change in the magnetic properties. Figure 2-b till 2-c with different scale on the x-axis (H value) are also shown to make the effect on the magnetics properties due to the holding time become clearer. The details of $Zn_{0.95}Ni_{0.05}O$ magnetic properties as the effect of holding time is shown in Table 3. It can be seen that, coercivity value (Hc) decreases with increasing of holding time. The coercivity value decreases from 147.78 to 117.99 (Oe), where the saturation magnetization (M_s) values are vary from 0.220 (emu/g) to 0.339 (emu/g). Holding time is close related to the grain growth during the sintering process as shown in the XRD results. The increase of holding time will increase the density value of $Zn_{0.95}Ni_{0.05}O$, and it will contribute to its magnetics behavior. Atoms have a spin in the same direction, which will increase its magnetics behavior. However, the presence of the crystal defects in the sample will also strongly affects the atomics spin rotation, so that the M_s value does not change linearly with the density value.

Table 3. Magnetic properties of the sintered $Zn_{0.95}Ni_{0.05}O$ at 900°C for different holding time

Holding Time (hours)	Magnetic Properties		
	Mr (emu/g)	Hc (Oe)	M_s (emu/g)
2	0.038	147.78	0.288
4	0.038	117.99	0.339
8	0.041	115.96	0.220

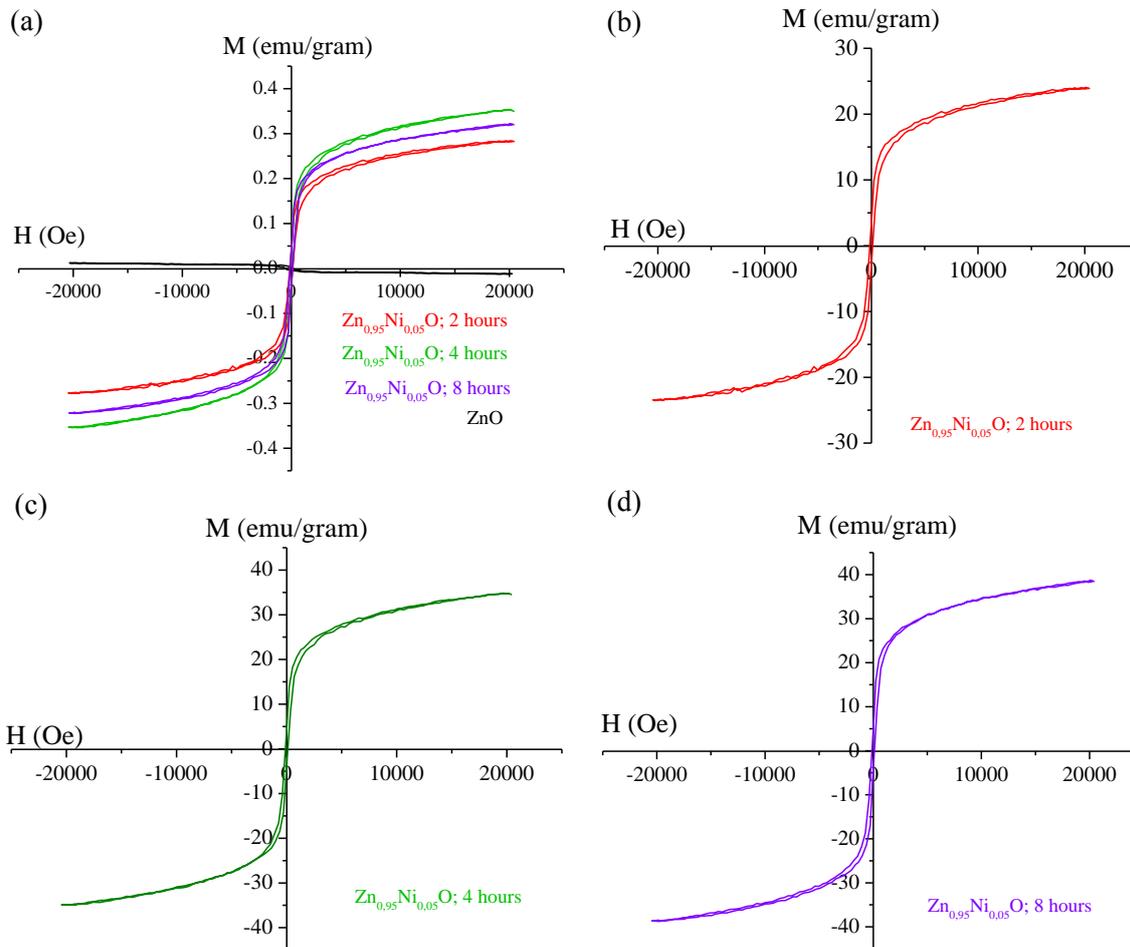


Figure 2. (a) The magnetic hysteresis loop of $Zn_{0.95}Ni_{0.05}O$ for Holding Time of 2, 4 and 8 hour at room temperature below 20 kOe, (b) The magnetic hysteresis loop of $Zn_{0.95}Ni_{0.05}O$ with Holding Time of 2 hour (c) The magnetic hysteresis loop $Zn_{0.95}Ni_{0.05}O$ with Holding Time of 4 hour and (d) The magnetic hysteresis loop of $Zn_{0.95}Ni_{0.05}O$ with Holding Time of 8 hour

4. Conclusion

$Zn_{0.95}Ni_{0.05}O$ was successfully synthesized by using solid-state reaction method with a holding time variation of 2, 4 and 8 hours. It is found that structural, electrical and magnetic properties change to the change of holding time. The XRD results shown that overall $Zn_{0.95}Ni_{0.05}O$ samples have wurtzite hexagonal major structural. The $Zn_{0.95}Ni_{0.05}O$ sample resistivity and capacitance values increase with the increasing of the holding time. From VSM measurements shown that overall samples are ferromagnetic. The remanence value slightly increases with the increasing of the holding time, while the coercivity decreases significantly.

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