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# Dielectric and Magnetic Properties of Cu-doped $Ni_{0.65}Zn_{0.35}Fe_2O_4$ Thin Films Prepared by Using a Sol-gel Method

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**$Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ thin films were prepared by using a sol-gel method. Their crystallographic, dielectric and magnetic properties were investigated as a function of Cu contents by means of an X-ray diffractometer (XRD), X-ray reflectivity, LCZ meter (NF2232), a vibrating sample magnetometer (VSM), and an atomic force microscope (AFM). From typical C-V measurements for $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ thin films on p-type silicon substrate, the surface charge density was calculated as 1.4 $\mu C/m^2$. The dielectric constant evaluated from the capacitance at the accumulation state was 28. The high $H_c$ and low $M_{sat}$ at x=0.0 and 0.1 were due to the growth of the $\alpha$-$Fe_2O_3$ phase having antiferromagnetic properties. The rapidly decreased $H_c$ and increased $M_{sat}$ at x=0.2 and 0.3 can be explained that the $\alpha$-$Fe_2O_3$ phases have completely disappeared at x=0.3 and so, non-magnetic defects are minimized. The $M_{sat}$ was slightly decreased and the $H_c$ was increased above at x=0.3 because the increase of grain boundary due to smaller grain size acts as defects during magnetization process.**

**Key words :** $Ni_{0.65}Zn_{0.35}Fe_2O_4$, Cu contents, NiZn ferrites, sol-gel method

## 1. Introduction

NiZn ferrites with the spinel crystal structure have been extensively used for many years in the electrical and electronic industries because of their high permeability at high frequency, high electrical resistivity, chemical stability, mechanical hardness and reasonable cost [1]. Moreover, there has been a growing interest in NiZn ferrites for the application in producing multilayer-type chips mainly because these ferrites can be sintered at a relatively low temperature with a wide range of composition [2]. The addition of Cu in the composition has been known to play a important role in dropping annealing temperature. For nanometric NiZn ferrites, it is possible to obtain good dielectric properties [3] and high performance [4] at a relatively low sintering temperature. Also the effects of manganese and copper substitution of Fe on the NiZn ferrite ceramics was reported [5, 6]. The objective of the present work is to explain the effect of Cu substituted for Fe on the dielectric and magnetic properties of NiZn ferrite thin film. In this study, $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ thin films were prepared by using a sol-gel method. Their crystallographic, dielectric and magnetic properties were investigated as a function of Cu contents.

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## 2. Experimental

The materials used in the preparation of $Ni_{0.65}Zn_{0.35}$-$Cu_xFe_{2-x}O_4$ were nickel(II) nitrate hexahydrate (99.999%, Aldrich), zinc acetate (99.99%, Aldrich), copper(II) nitrate hydrate (99.999%, Aldrich), and iron(III) nitrate nonahydrate (99.99%, Aldrich). After all the chemicals were weighed and confirmed to be at required stoichiometric proportion, zinc acetate were dissolved in 2 methoxyethanol with an ultrasonic cleaner. Then nickel nitrate and copper nitrate were added to the solution of zinc acetate. After they were dissolved completely, iron nitrate nonahydrator was added. The solution was refluxed at 80 °C for 12 h. Films were deposited onto a p-Si substrate by spin casting a coating sol at 2500 rpm for 30 s. The wet films were dried on a hot plate at 100 °C for 1 min and continuously dried at 300 °C for 2 min. After these coating and heat-treatment processes had been repeated several times, the thickness of films were measured by means of X-ray reflectivity and determined to be 120 nm.

The post-annealing process at 700 °C for 30 min was carried out in air to obtain the ferroelectric properties. In order to measure the capacitance-voltage (C-V) characteristics, Pt-upper electrodes with an area of $7 \times 10^{-4}$ cm$^2$ were deposited on $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ films by means of dc magnetron sputtering using a shadow mask and uniform Al layer was deposited onto the back side of the Si substrate to obtain ohmic contact. Crystallinity as a function of Cu contents(x) was investigated by means of X-Ray diffraction (XRD). An AFM was used for characterizing the surface roughness of the specimens. Dielectric and magnetic properties as a function of Cu contents(x) were measured by a LCZ meter and a VSM.

## 3. Results and Discussion

Fig. 1 shows the X-ray diffraction patterns for the $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ thin films annealed at 700 °C for 30 min. Two features are apparent in this figure. First, the crystal structure can be indexed as a single-phase of a cubic spinel according to its diffraction lines except for $\alpha$-$Fe_2O_3$ phase at $2\theta = 33°$. Second, the intensity of $\alpha$-phase peaks is decreased as Cu contents are increased, and disappears at x=0.3. For stoichiometric spinel phase $AB_2O_4$, the cubic unit cell comprises eight formula units and contains 64 tetrahedral and 32 octahedral sites, generally designed as A and B sites, respectively. This indicates that Cu is well substituted for Fe in B sites at above x=0.3.

Fig. 2(a)-(f) show the surface morphology of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ thin film annealed at 700 °C for 30 min. The film surfaces are uniform without any cracks. With the increase of Cu contents (x), long-ellipse shaped grains are changed to spherical shaped grains. The films with x=0.0 have a relatively larger grain size of about 200 nm. The grain size decreases with the increase of the Cu contents and is about 20 nm at x=0.5.

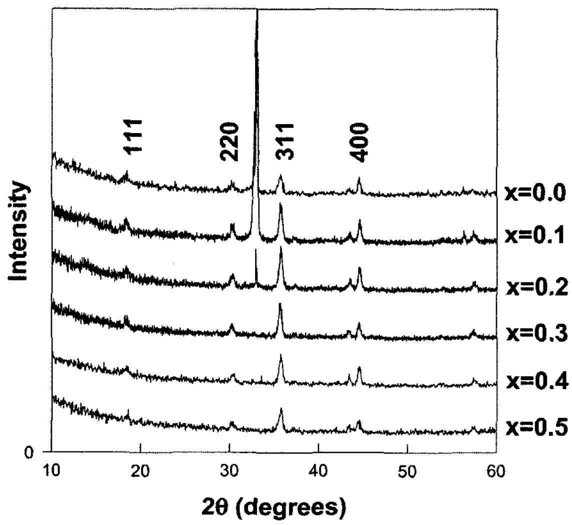


**Fig. 1.** X-ray diffraction patterns of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ thin films annealed at 700 °C for 30 min. as function of Cu contents (x).

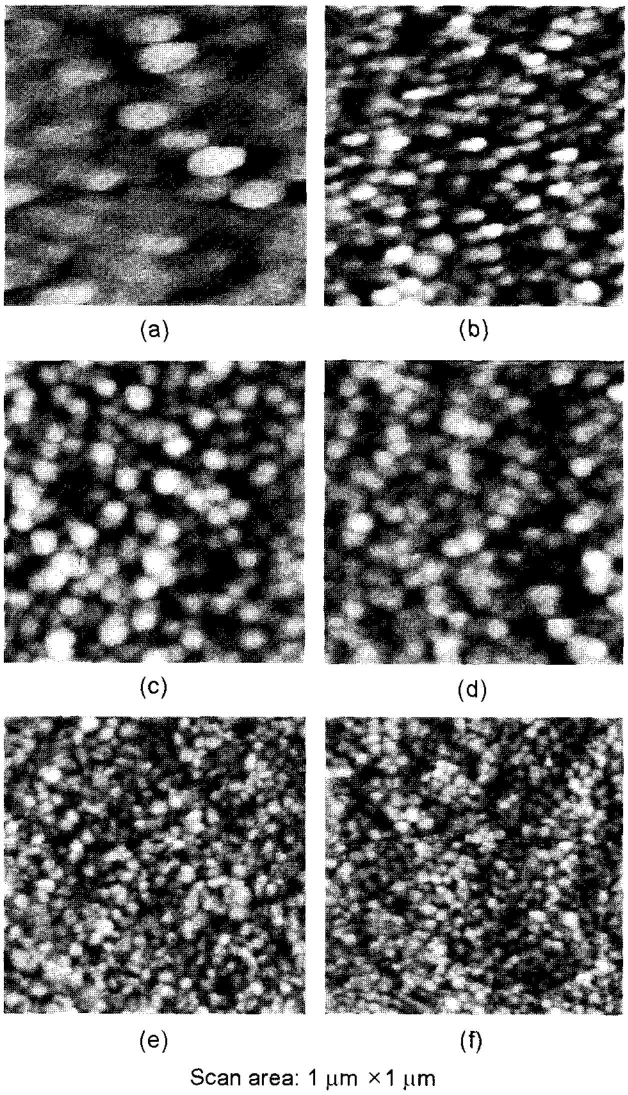


**Fig. 2.** 2-dim images of AFM for the $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ thin films with various Cu contents (x) after annealing at 700 °C for 30 min. (a) x=0.0, (b) x=0.1, (c) x=0.2, (d) x=0.3, (e) x=0.4, (f) x=0.5.

Fig. 3 shows typical high frequency (100 kHz) C-V characteristics for $Ni_{0.65}Zn_{0.35}Cu_{0.1}Fe_{1.9}O_4$ thin film, which was measured at room temperature without illumination. The sweep rate was 200 mV/s. The saturated C-V curve shows that the capacitance value varies from the accumulation to the inversion state. The dielectric constant evaluated from the capacitance at the accumulation state was 28. The film on p-type silicon substrate showed a carrier injection type hysteresis (as indicated by arrows on

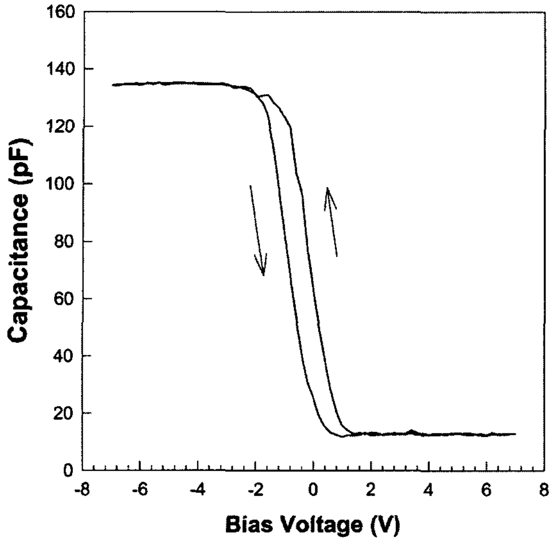


Fig. 3. Typical C-V characteristics for $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ thin film measured at room temperature, a frequency of 100 kHz and sweep rate of 200 mV/s.

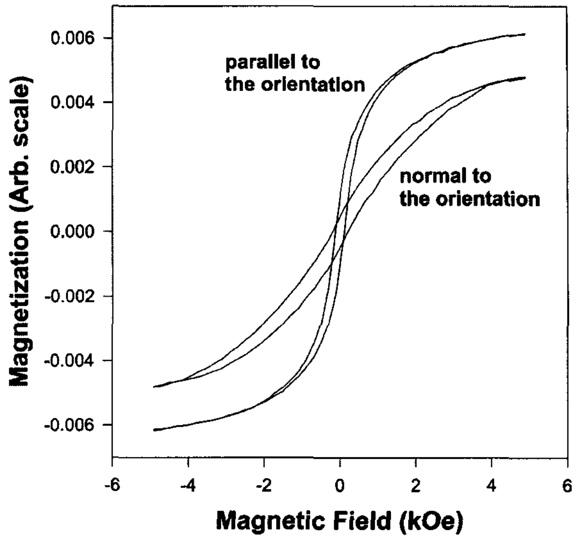


Fig. 4. Typical M-H hysteresis loops of the $Ni_{0.65}Zn_{0.35}Cu_{0.4}$-$Fe_{1.6}O_4$ thin film measured normal and parallel to the film plane with an external field up to 5 kOe.

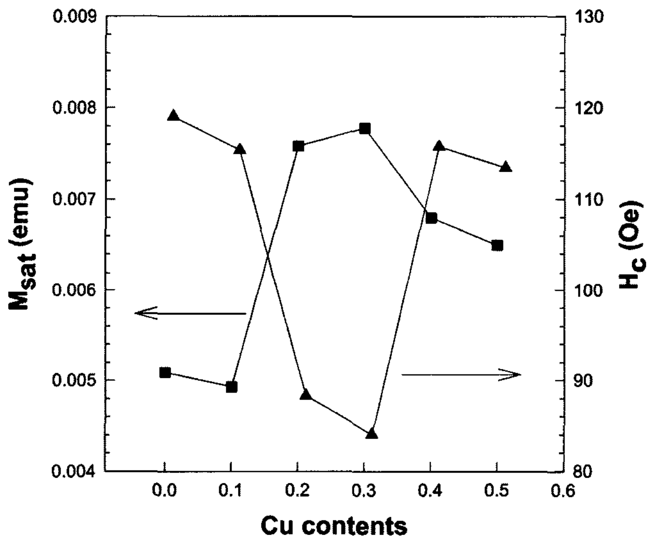


Fig. 5. Saturation magnetization ( ■ ) and coercivity ( ▲ ) at room temperature vs Cu contents (x) of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ thin films, which are measured parallel to the plane.

the curve). The hysteresis voltage width was not changed by the varying sweep rate, indicating that during the bias scan period, the charges were injected into the film, trapped, and then emitted with the same emission time [7]. The amount of hysteresis $V_H$ was estimated to be about 0.75 V. In a MIS (metal-insulator-semiconductor) diode, it is known that movable or trapped charges in the oxide film or at the oxide/semiconductor interface make the parallel shift in the C-V curve from an ideal state along the abscissa [8]. Therefore, the voltage shift in the C-V curve can be considered as the surface charge induced by the dipole moment of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ thin film. The surface charge density, defined by $Q_c = \varepsilon_0\varepsilon_r E$ was calculated as 1.4 $\mu C/m^2$, based on the information from C-V measurements, where E is the applied electrical field.

Figure 4 shows the typical hysteresis loops of the film measured normal and parallel to the film plane with an external field up to 5 kOe. Figure 5 shows the saturation magnetization ($M_{sat}$) and coercivity ($H_c$) against the Cu contents for the samples annealed at 700 °C for 30 min. which are measured parallel to the plane. The coercivity is high and the saturation magnetization is low at x=0.0 and 0.1. This phenomena is due to the growth of the $\alpha$-$Fe_2O_3$ phase having antiferromagnetic properties. Therefore increasing non-magnetic defects by the $\alpha$-$Fe_2O_3$ phase make the magnetization process difficult to reverse. This is also confirmed in x-ray diffraction patterns, as shown in Fig. 1. The $H_c$ at x=0.2 and 0.3 decreases rapidly down to the minimum value because $\alpha$-$Fe_2O_3$ phases have completely disappeared at x=0.3. This means that non-magnetic defects are minimized at x=0.2 and 0.3. Therefore the saturation magnetization, $M_{sat}$, was increased up to a near maximum value at x=0.3. On the other hand, the $M_{sat}$ is slightly decreased and the $H_c$ is increased at x=0.4 and 0.5. According to the X-ray patterns, the $\alpha$-$Fe_2O_3$ phases do not exist at this region and therefore the existence of non-magnetic defects can be negligible. But the grain sizes are getting smaller (see Fig. 2) and so the numbers of grain boundary are increased. The increase of $H_c$ can be thought to be due to the increasing grain boundary existed as defects during magnetization process.

## 4. Conclusions

Structural, dielectric and magnetic characteristics of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ thin films prepared by using a sol-gel method were investigated. We found that spinel structure was successfully produced on bare silicon substrates. With the increase of Cu contents (x), long-ellipse shaped grains were changed to spherical shaped ones and the grain size decreased by about 200 nm at x=0.0 to 20 nm at x=0.5. Typical C-V characteristics for $Ni_{0.65}Zn_{0.35}Cu_x$-$Fe_{2-x}O_4$ thin film on a p-type silicon substrate showed a carrier injection type hysteresis and the surface charge density was calculated as 1.4 $\mu C/m^2$. The typical hysteresis loops of the film were measured as normal and parallel to the plane with an external field up to 5 kOe. The $M_{sat}$ and $H_c$ were also measured parallel to the plane. Their phenomena were explained with the growth of the $\alpha$-$Fe_2O_3$ phase having antiferromagnetic properties, grain sizes and the increase of grain boundary, depending on Cu contents (x).

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