JOURNAL OF SEMICONDUCTOR TECHNOLOGY AND SCIENCE, VOL.17, NO.2, APRIL, 2017
https://doi.org/10.5573/JSTS.2017.17.2.245

ISSN(Print) 1598-1657
ISSN(Online) 2233-4866

Investigation of Nb-Zr-O Thin Film using Sol-gel Coating

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***Abstract*—Niobium doped zirconium oxide (Nb-Zr-O:NZO) thin films were fabricated on Si substrates by a sol-gel technique with an annealing temperatures of 500~1000°C in air (N_2:O_2 = 3:1) for 20 minutes. It was found that the NZO film is based on tetragonal ZrO_2 polycrystalline structure with the Nb 5+ ion state and there is almost no diffusion of Nb or Zr to Si substrate. The relative dielectric constant for the NZO film with the Nb composition of 30 mol% and annealed at 800°C was around 40. The root mean roughness was 1.02 nm. In addition, the leakage current of NZO films was as low as 10^{-6} A/cm^2 at 4.4 V.**

***Index Terms*—Niobium doping, zirconium oxide, tetragonal, high-k**

I. INTRODUCTION

In a generation of gigabit scale memory technology, many kinds of high-permittivity (high-k) dielectrics such as ZrO_2, HfO_2, Ta_2O_5 and so on have been extensively researched [1]. Among various high-k dielectrics, ZrO_2 and Al or Si doped ZrO_2 films are of the greatest industrial interest for current and near future generation technology nodes [2, 3]. The dielectric constant of ZrO_2 thin films depends strongly on their phase and crystallinity, which can be regulated via control of the growth temperature and film thickness. A ZrO_2 has three crystalline structures: monoclinic (m-ZrO_2), tetragonal (t-ZrO_2) and cubic (c-ZrO_2). A ZrO_2 has three crystalline structures at atmospheric pressure and its most stable phase depends on the temperature; cubic over 2300°C, tetragonal over 1170°C and monoclinic under 1170°C [4]. The highest dielectric constant of 46 has been predicted for bulk ZrO_2 crystallized with tetragonal phase. However, to obtain a t-ZrO_2, annealing temperature over 1170°C is needed. To stabilize the tetragonal phase of ZrO_2 at lower temperature, many kinds of dopants such as aliovalent (Y^{3+}, Ca^{2+}) and tetravalent (Si^{4+}, Ce^{4+}, Ge^{4+}) elements have been investigated [5-9]. However, there are only a few reports about the stabilizing effect of pentavalent ions such as Nb^{5+} and Ta^{5+} for ZrO_2, presumably because the size and the charge of pentavalent ions are thought to be unfavorable for stabilization of metastable polymorphs of ZrO_2 according to the traditional concepts [10]. In addition, there are few studies about the electrical properties of Nb doped ZrO_2 thin film on Si substrate.

In this work, we have investigated crystallographic and electrical properties of the Nb doped ZrO_2 (NZO) thin film deposited on Si substrate by the sol-gel method. It was found that sol-gel derived Nb-doped ZrO_2 film showed tetragonal phase even at relatively low annealing temperature, resulting in high dielectric constant.

II. EXPERIMENTS

The NZO film was deposited on the highly doped silicon substrate to make the metal-insulator-semiconductor (MIS) structure. The starting materials for Nb and Zr were niobium 2-ethylhexanoate (NEL: $Nb(O_2C_2H(C_2H_5)C_4H_9)_4$) and zirconium acetylacetonate (Zr(acac) : $C_{20}H_{28}O_8Zr$), respectively. The Zr(acac) was dissolved in the propionic acid in advance. Then, the

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NEL was inserted into the solution to adjust the desired mol ratio. The mol ratio of Nb was varied from 2 mol% to 50 mol%. Then, the Nb-Zr precursor was stirred for two hours at 800 rpm on a hot plate at 130ºC.

Prior to the deposition process, n-type Si(100) substrate was cleaned with acetone, methanol and de-ionized water after dipping into HF solution to remove the native silicon oxide layer. Then, Nb-Zr precursor solution was spin-coated on Si substrate at 3000 rpm for 25 seconds. The coated film was baked at 250ºC for 5 minutes on a hot plate in an atmosphere. Next, baked NZO films were annealed at 500~1000ºC for 20 minutes in air (N_2:O_2 = 3:1) by rapid thermal annealing (RTA) system. Finally, the gold was evaporated to form top and bottom electrodes for electrical measurements.

The crystalline phase of the NZO films on Si substrate was characterized by X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The XPS was conducted using an AXIS ULTRA with a monochromatic Al Kα (1486.7 eV) X-ray source. The TEM was performed using JEM-ARM200F with acceleration energy of 200 keV. The GI-XRD was analyzed using X`PERT PRO with a monochromatic Cu Kα (1.542 Å) X-ray source. The surface morphology was observed by atomic force microscope (AFM). The capacitance-voltage (C-V) and the current density-voltage (J-V) measurements were carried out to characterize the electrical properties.

III. Results and Discussion

From the cross section TEM image shown in Fig. 1(a), the thickness of NZO film fabricated with an annealing temperature of 800ºC was found to be about 10 nm. The 3 nm of SiO_2 interfacial layer was formed between NZO film and Si substrate because of high temperature annealing in air. Although the annealing time was only 20 minutes, it was found that the NZO film was crystallized and there were several large domain regions, which indicated the film had a polycrystalline structure.

The energy dispersive X-ray spectrometry (EDS) mapping for Nb and Zr atom distribution within the thin film are shown in Fig. 1(b) and (c). It was found that Nb was doped in the ZrO_2 film uniformly and no significant diffusion of Zr and Nb into SiO_2/Si substrates was observed.

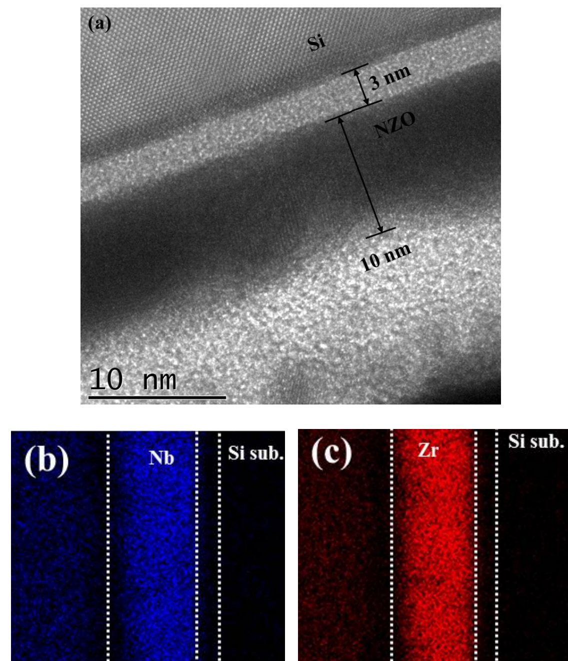

Fig. 1. (a) TEM cross section, EDS image of (b) Nb atom, (c) Zr atom for NZO film fabricated by sol-gel technique on Si substrate with an annealing temperature of 800ºC.

Fig. 2 shows the grazing incidence X-ray diffraction (GI-XRD) patterns for NZO films with various Nb ratios from 0 to 50%. All NZO films were annealed at 800ºC, because pure ZrO_2 showed highest accumulated capacitance when it was annealed at 800ºC as shown in Fig. 7(b). It was reported that a sol-gel derived ZrO_2 film forms a metastable tetragonal phase due to the thermal decomposition of zirconium salts, alkoxides and hydroxide [11]. In our experiments, the spin-coated ZrO_2 film also showed both m-ZrO_2 and t-ZrO_2 as shown in Fig. 2. On the other hand, the XRD peaks due to t-ZrO_2 were observed as shown in Fig. 2 for the sol-gel derived NZO films with Nb compositions of less than 30%. It should be noted that the Nb doped films showed only a tetragonal phase. When the Nb composition is more than 40%, the t-ZrO_2 peak intensities decrease and diffraction peaks from niobium pentoxide (Nb_2O_5) at 53.7º and 55.4º start to appear. Hence, it can be concluded that NZO films fabricated by the sol-gel technique exhibit tetragonal ZrO_2 phase when the Nb composition is less than 30%, and that further doping of Nb does not enhance the growth of the tetragonal phase.

The capacitance-voltage (C-V) characteristics of the MIS structure with pure ZrO_2 and 30% Nb-doped ZrO_2

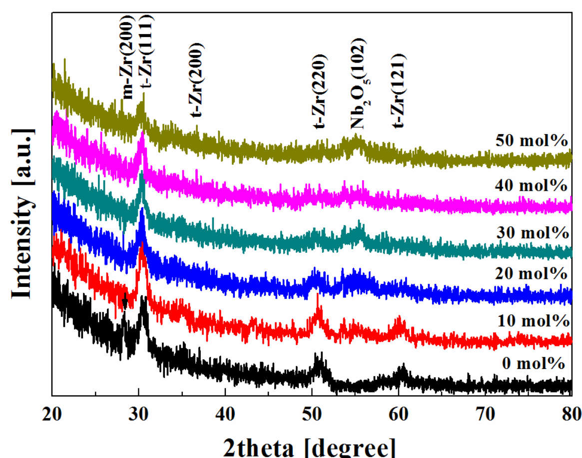

Fig. 2. GI-XRD spectra of Nb 0 ~ 50 mol% doped ZrO_2, annealed at 800ºC.

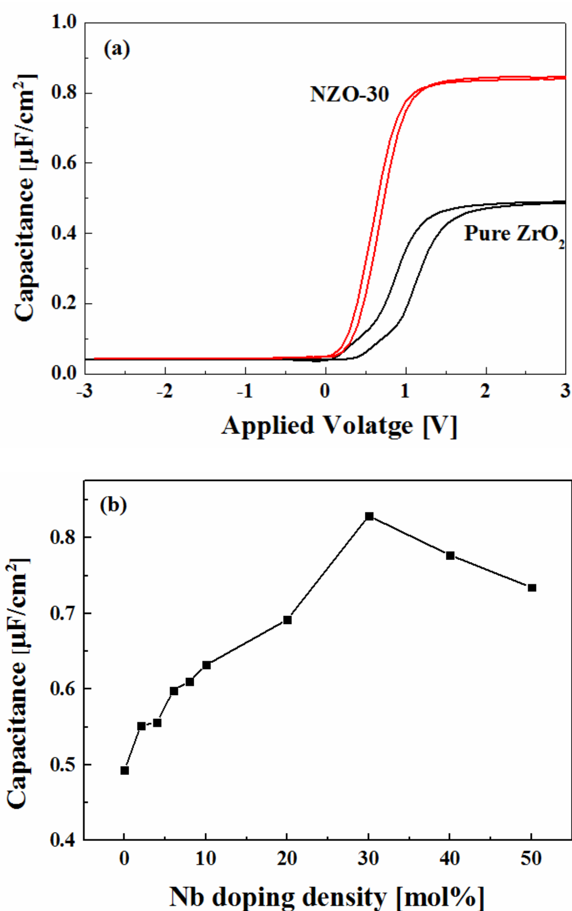

Fig. 3. (a) Capacitance-voltage (C-V) curves of MIS structures with pure ZrO_2 and Nb (30%) doped ZrO_2 annealed at 800 °C, (b) accumulation capacitance of the NZO MIS structures as a function of Nb doping density.

(NZO-30) are shown in Fig. 3(a). The accumulation capacitance of the MIS structure with NZO film is much larger than that of the MIS structure with pure ZrO_2 film.

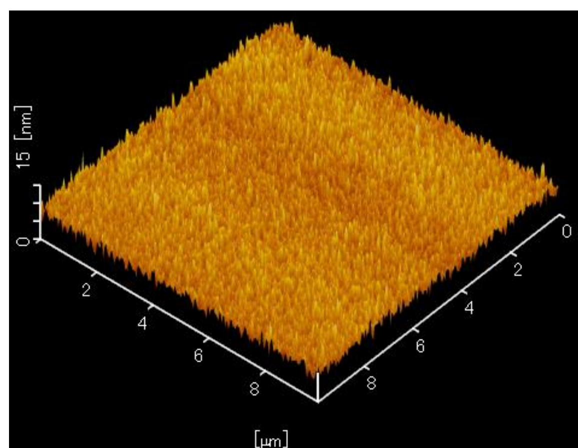

Fig. 4. AFM image of Nb 30 mol% ZrO_2 film.

This suggests the dielectric constant of the NZO is larger than that of pure ZrO_2. In addition, the threshold voltage shift and hysteresis of C-V curve of the MIS structure with NZO film are smaller than those of the MIS structure with pure ZrO_2 film.

The accumulation capacitances deduced from the C-V curves of the NZO MIS structures with various Nb mol ratios were plotted in Fig. 3(b) as a function of Nb doping density. It was found that the accumulation capacitance increased with Nb doping density until the largest capacitance of 0.83 $\mu F/cm^2$ for the NZO film with Nb composition of 30 mol%. However, the accumulation capacitance decreased when the doping density was more than 30 mol%. The relative dielectric constant of NZO film with Nb ratio of 30 mol% (NZO-30) was estimated to be approximately 40 by taking the capacitance of SiO_2 interfacial layer into account. On the other hand, the relative dielectric constant of pure ZrO_2 fabricated in this work was 20, which reasonably agrees with a reported values for monoclinic ZrO_2 [12]. It is worth noting that the dielectric constant is increased by Nb doping and reaches the maximum value at Nb mol ratio of 30%. This may correlate with the XRD data, which suggests that the formation of the tetragonal phase is limited when the Nb content is more than 40%.

Surface flatness is one of the important factors that alter the operation of microelectronic devices [13]. The surface morphology of NZO-30 annealed at 800°C for 20 min, as shown in Fig. 4. The root mean square roughness was 1.02 nm. This value is comparable with pure and yttrium doped ZrO_2 [14] even though the NZO film is crystallized. However, it was observed that if the film

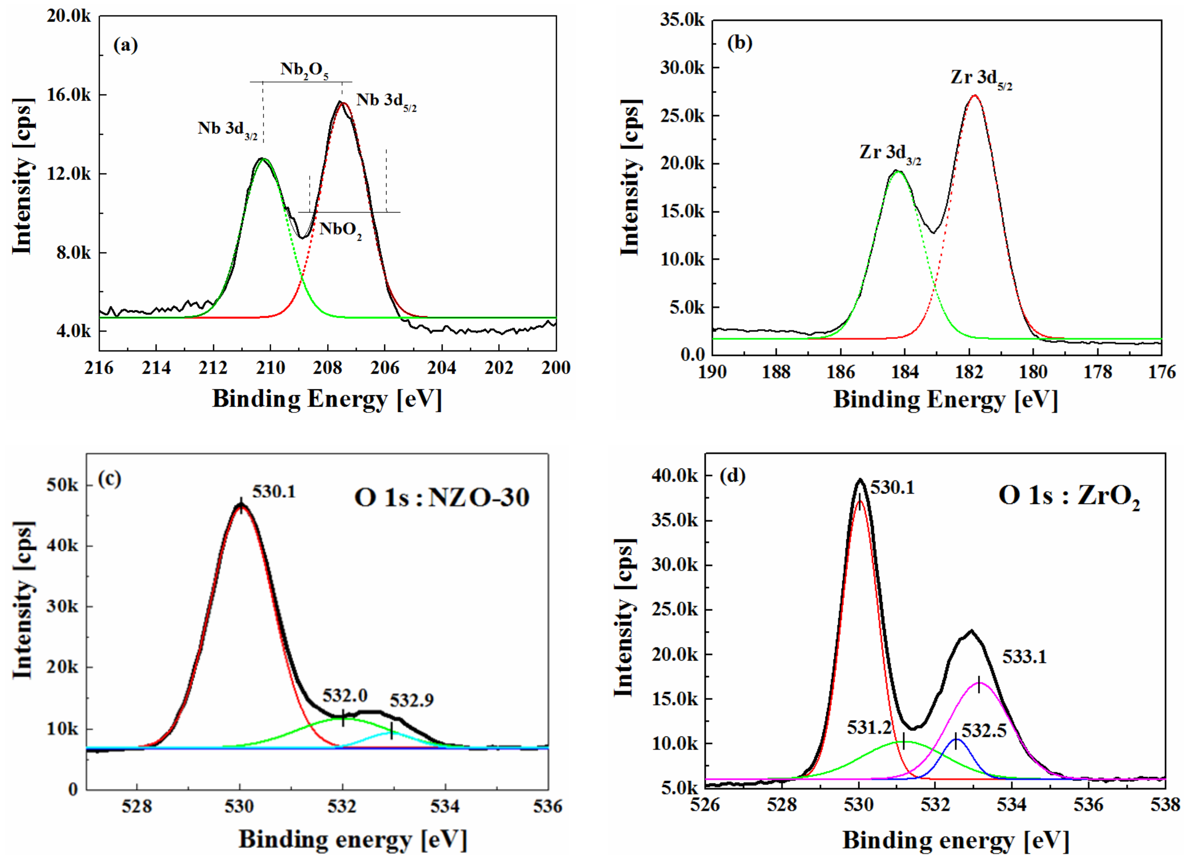

Fig. 5. XPS spectra for (a) Nb 3d, (b) Zr 3d, (c) O 1s of NZO-30, (d) O 1s of ZrO_2.

was annealed for a longer time (~1.5 h) or higher temperature (1000°C), the mean square roughness increased to 7~8 nm. Hence, the optimization of annealing conditions is important for practical device applications.

Fig. 5 shows the XPS data of NZO-30 for (a) Nb 3d, (b) Zr 3d and (c) O 1s states with carbon (C) 1s peak at 284.8 eV. XPS spectrum for O 1s of pure ZrO_2 is also shown in Fig. 5(d) for comparison. It is known that Nb oxides has 3 phases; Nb_2O_5, NbO_2 and NbO [15]. From Fig. 5(a), there are only Nb_2O_5 related peaks at 210.2 eV and 207.5 eV, which indicate that only Nb^{5+} is observed. This agrees with previous researches [16, 17] that the stable ion state of Nb in ZrO_2 is 5+. The well-known ZrO_2 peaks were observed at 186.0 eV and 183.5 eV for NZO-30 film as shown in Fig. 5(b). The O 1s peaks of NZO-30 and pure ZrO_2 are divided by Gaussian function as shown in Fig. 5(c) and (d). The O 1s peak of pure ZrO_2 can be divided into four peaks, which suggests the solution processed ZrO_2 has the several absorbed species such as water to form the hydroxide (Zr-O-H at 531.2 eV) and carbon to form the metal carbonate (Zr-C-O at 532 ~ 533 eV) as shown in Fig. 5(d). These bonds are induced to the oxygen vacancy and surface defects [18]. On the other hand, the XPS peak of NZO-30 can be divided into three peaks. It shows no hydroxide bond and it has relatively small peaks for metal carbonate as shown in Fig. 5(c).

These results suggest the absorption of undesired species could be suppressed by Nb doping. This may be one of the reasons why the C-V curve of the MIS structure with NZO-30 film shows small hysteresis and threshold voltage shift as shown in Fig. 3(a).

We next examined annealing temperature dependence on crystallinity and electrical properties of NZO film with a fixed Nb content of 30%. The XRD analysis (Fig. 6) showed that when the annealing temperature was more than 700ºC, clear diffraction peaks from the tetragonal phase were observed. As the annealing temperature was increased, the peak intensity of the tetragonal phase increased.

Fig. 7 shows the C-V characteristics of the MIS

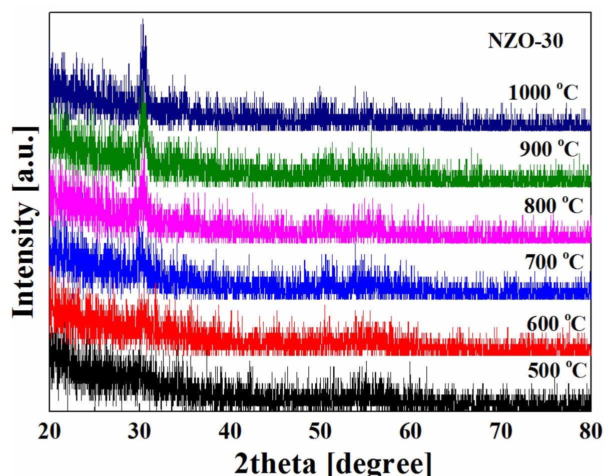

Fig. 6. GI-XRD for NZO with variation temperature from 500~1000°C.

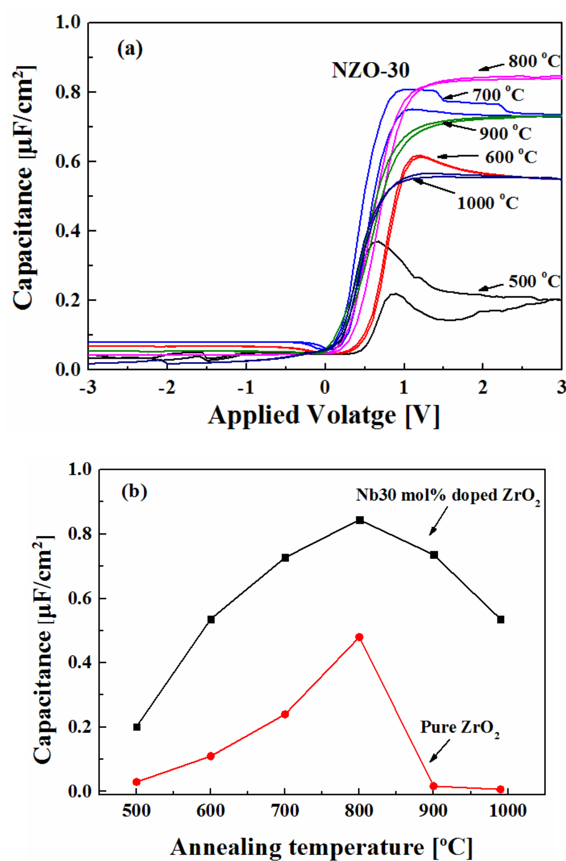

Fig. 7. (a) Annealing temperature dependence of C-V curves for Nb 30 mol% ZrO_2 film, (b) accumulation capacitance of the MIS structures with pure ZrO_2 and Nb 30 mol% ZrO_2 films.

structure where NZO film with Nb30% was used. The annealing temperature was varied from 500 to 800ºC. When the annealing temperature was below 500ºC, the C-V curve for MIS structure with NZO film showed

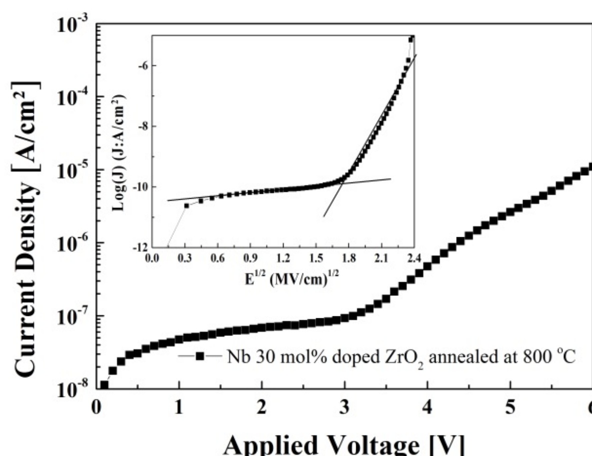

Fig. 8. The leakage current density of NZO-30 annealed at 800ºC.

hysteresis with a low accumulation capacitance because the crystallization of the NZO film was not enough. When the annealing temperature is over 800ºC, the accumulation capacitance starts to decrease because the thickness of the SiO_2 interfacial layer between NZO and Si substrate was increased due to the high temperature annealing which enhances unintentional oxidation of Si substrate. From the film thickness of NZO and SiO_2 as shown in Fig. 1, the calculated dielectric constant of NZO film with 30 mol% Nb was about 40. This value is comparable with the value for a tetragonal ZrO_2.

Fig. 8 shows the leak current density of NZO film with a Nb composition of 30 mol%, annealed at 800ºC. There are linear and non-linear regions because of mixing the current mechanism such as Schottky, Poole- Frenkel, and Fowler Nordheim tunneling [19]. Chang and Lin have reported that the dominated conduction mechanism of ZrO_2 films prepared by the chemical vapor deposition method is due to Pool Frenkel conduction [20].

The NZO film with the Nb composition of 30 mol% fabricated in this work has 10^{-6} A/cm^2 under 4.4 V. The current graph is redrawn with log (J)-E$^{1/2}$ scale as shown in the inset of Fig. 8. It was found under electric field of 1.7 MV/cm, the current mechanism is Pool Frenkel conduction as Chang and Lin reported. In addition, Fowler Nordheim tunneling was observed over 1.8 MV/cm.

IV. CONCLUSIONS

In this work, the crystalline structure and electrical

properties of NZO films spin-coated on Si substrate were studied. The sol-gel derived NZO thin film exhibited polycrystalline structure, when the film was annealed at more than 700ºC. It is found that the Nb doping is helpful to stabilize the tetragonal ZrO_2 but it is also found that high Nb doping density (over 40 mol%) interferes with the formation of tetragonal ZrO_2 phase. In our experiments, a large relative dielectric constant of 40 was obtained for the NZO film with a Nb doping density of 30 mol% when the annealing temperature was 800ºC. The MIS structure with NZO film shows a reasonably low leakage current of 10^{-6} A/cm^2 at 4.4 V. From these results, it can be concluded that Nb could be a promising dopant for stabilized t-ZrO_2 which has good electrical properties for capacitor applications.

ACKNOWLEDGMENTS

The authors would like to thank Mr. K. Higashimine of the Center for Nano Materials and Technology in Japan Advanced Institute of Science and Technology for the TEM observation.

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