

NiO Films Formed at Room Temperature for Microbolometer

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Abstract

Nickel oxide films using RF sputter was formed on the SiO₂/Si substrate at the room temperature controlled with water circulation system. The feasibility of nickel oxide film as a bolometric material was demonstrated. GIXRD spectrum on NiO(111), NiO(200), and NiO(220) orientation expected as the main peaks were appeared in the grown nickel oxide films. The typical resistivity acquired at the RF power of 100W was about 34.25 Ω · cm. And it was reduced to 18.65 Ω · cm according to the increase of the RF power to 400W. The TCR of fabricated micro-bolometer with the resistivity of 34.25 Ω · cm was -2.01 %/°C. The characteristics of fabricated nickel oxide film and micro-bolometer were analyzed with XRD pattern, resistivity, TCR, and SEM images.

Keywords : Nickel oxide, Reactive sputtering, Preferred orientation, Room temperature, TCR, bolometer

1. INTRODUCTION

Uncooled infrared detectors such as micro-bolometer have been studied extensively and commercialized in the fields of medicine, military, environment surveillance, and etc. Developing works on the uncooled infrared detector have been mainly focused on improving sensitivities. Searching a good bolometric material enhancing the performance is one of activities for improving sensitivities. Vanadium oxide (VO_x) [1] and amorphous Silicon (a-Si) [2] are typically widely used infrared sensitive layers in a micro-bolometer applications. VO_x and a-Si have a high temperature coefficient of resistance (TCR) and enough low noise satisfying the acquirements of high resolution thermal images. However, the thermal instability and the weak CMOS compatibility of VO_x are remained disadvantages needs improvement technically. And high 1/f noise appears at a-Si usually occurs in amorphous structure, and thus it causes some restrictions in bolometric

application.

Efforts to find new bolometric materials [3] and to get better performance have been lasted for last decades. Nickel oxide (NiO) is a good candidate replaceable the conventional bolometric materials. Resistivity of NiO can be varied in a wide range according to growth methods and conditions. In addition, the film has advantages in chemical stability, material cost, phase types, and CMOS-compatible process.

Bolometric materials obtainable at low temperature process would be a good merits since sensitive layers are usually should be formed on CMOS Si readout integrated circuits (ROIC). As we previously proposed NiO films as a thermal sensitive layer [4], those films could be deposited on unheated (regarded as room temperature, in other words, without intentional heating) substrate using RF sputtering system. Due to the natural heating of substrate during sputtering process in plasma environment, however, acquiring reliable and reproducible films are restrictive.

In this work, cooling system was introduced to substrate holder to reduce temperature rising that can be occurred during argon and oxygen plasma bombardment. And only the RF power was varied to optimize the power dependence in nickel oxides. Microstructural and electric resistivity kept substrate room temperature during deposition process were investigated. The difference in the electric conductivities of the films deposited with and without water-cooled substrate holder were investigated. The feasibility of the NiO bolometer is demonstrated through the fabrication NiO microbolometer and the

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evaluation of TCR value.

2. EXPERIMENTAL

Ni target using reactive RF sputter in $O_2/(Ar+O_2)$ gas mixture of 50% at room temperature was used for 100 nm-thick NiO films deposition on SiO_2/Si (p-type) substrate. The substrates were loaded on the holder in parallel with the target surface separated by 140 mm. And then, pre-sputtering was performed for 15 min to clean the target surface, and consequently uncertain contaminated materials were removed. Water-cooled substrate holder introduced kept the substrate temperature at room temperature during the sputtering. Thin NiO films were deposited at the RF power of 100, 200, 300, and 400 W. And substrate temperature, O_2 partial pressure, film thickness, and sputtering pressure were kept invariant, simultaneously. FE-SEM (Field Emission Scanning Electron Microscope) was used for film thickness and morphology investigation, and GIXRD (Grazing-Incidence X-Ray Diffraction) adapting monochromatic high-intensity Cu-K α radiation ($\lambda=0.15406$ nm) was used for crystal structure analysis. And sheet resistance acquired with 4-point probe was evaluated as well. Fabricated micro-bolometer with 100 nm thick NiO film estimated as usable TCR value demonstrated the feasibility.

3. RESULTS AND DISCUSSIONS

Deposition rates of nickel oxides dependent on RF sputtering power are shown in Fig. 1. Linearly increasing deposition rate rising from 0.6 to 5.2 nm/min as sputtering power up can be observed. Enhanced bombardment resulted from elevated RF power by argon and oxygen ions sputtered at nickel oxide target surface increase deposition rate [5]. No remarkable deposition rate variation is not shown whether water-cooled substrate holder is used or not.

Figure 2 shows the XRD spectra of nickel oxides formed at a room temperature in 50% of $O_2/(Ar+O_2)$ mixture with changing in RF sputtering power. Major diffraction peaks are being observed at 36.54° , 42.78° , and 64.02° correspond to the (111), (200), and (220) planes of nickel oxides [6]. Nickel oxide crystals acquired here are polycrystalline existing in the form of single NiO phase.

Main peaks appeared in NiO phase are representing (200) orientation with (111) and (220) minor orientations. The intensities of (111) and (200) orientation increase and being sharper as the sputtering power increases. This can be caused by the larger contribution of ejected higher energy particles to the growth of crystallized phase [7]. No recognizable orientation preferred changes are found either of with or without water-cooled substrate holder. Thus, XRD patterns obtained from uncooled substrate are not drawn in Fig. 2.

Sheet resistance can be measured using four-point probe, and then resistivity is calculated from multiplying sheet resistance by the film thickness. Calculated resistivity of samples acquired in cooled and uncooled condition are shown in Fig. 3. Electric conductivities in Fig. 3 are negatively relying on sputtering power. The conductivities

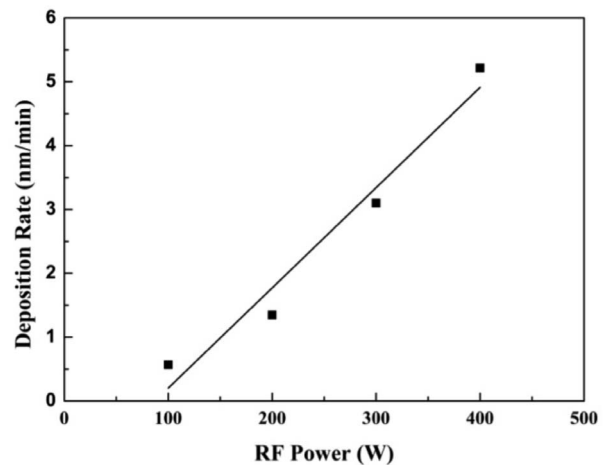


Fig. 1. The effect of RF power on the growth rate of NiO films.

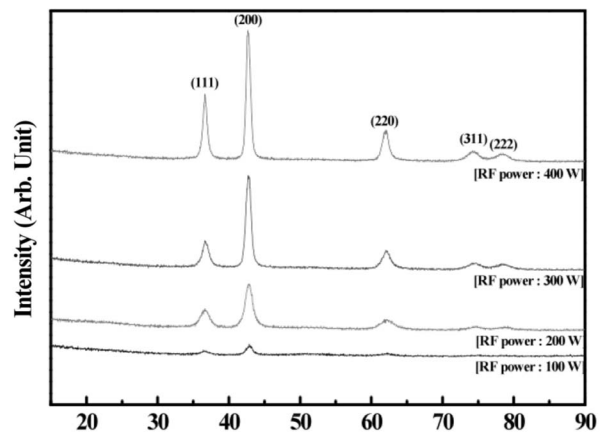


Fig. 2. Change of XRD profiles depending upon sputtering power.

in nickel oxides are strongly dependent on microstructure defects of nickel oxides crystallites such as nickel vacancies and interstitial oxygen atoms. Furthermore, deposition conditions and environments generating microstructure distortion and non-stoichiometry are the main factors affecting the electrical conductivities in nickel oxides [8].

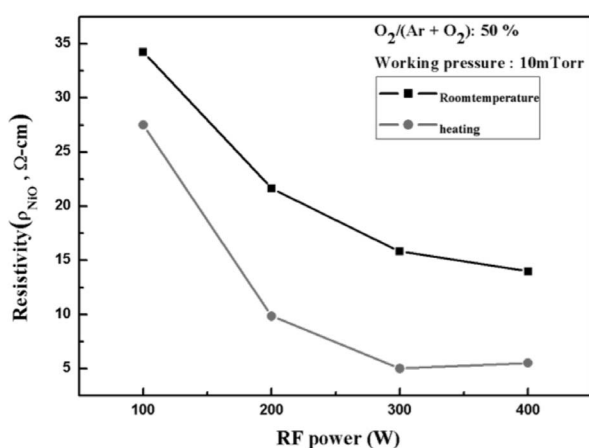


Fig. 3. The resistivity of NiO thin films that were prepared under the different RF powers.

Resistivity of pure stoichiometric nickel oxide is known as high as $10^{13} \Omega \cdot \text{cm}$ at room temperature [9]. However, as-deposited films are usually non-stoichiometric NiO structure. And the electric resistivity of deposited nickel oxides reduced drastically are less than tens of $\Omega \cdot \text{cm}$ including non-stoichiometric nickel oxides which have three orders smaller magnitude than that of bulk NiO ($\geq 10^4 \Omega \cdot \text{cm}$) [10]. Increased RF power seems to drive stronger forces to migrate each atom into more suitable lattice sites resulting in more stable and perfect crystals. The thin film holding better crystalline would have lower resistivity. This RF power dependence is may originated from the higher energy of the sputtered particles which lead to improved nucleation, crystallinity, and degree of ionization. At each RF power, nickel oxide films deposited with cooling system show larger resistivity in Fig. 3. The difference of resistivity can be explained by Chen et al report describing that resistivity could be decreased with increasing substrate temperature [11]. Thus the heated substrate due to the uncooled process probably lowers the electric resistivity in nickel oxide films.

Compare to the cooled film, there is great variation in resistivity of uncooled films as shown in Fig. 3. This is

mainly due to heating up caused by RF sputtering process. Thus, for the better resistivity control of nickel oxide film, adapting the cooling system is necessary. Nickel oxide selected for micro-bolometer is also uncooled one.

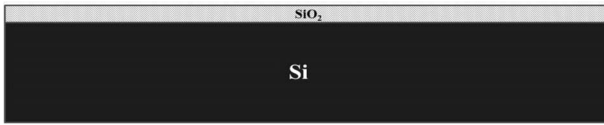
$200 \times 200 \mu\text{m}^2$ micro-bolometer was fabricated with surface micromachining technology to fabricate a floating structure for thermal isolation structure efficiently reducible the thermal loss.

The fabrication process of NiO microbolometer is shown in Fig. 4. First of all, the SiO_2 with the thickness of 100 nm deposited by the plasma enhanced chemical vapor deposition (PECVD) was prepared on the (100) p-type silicon substrate (1). And then, 200 nm-thick aluminum layer which can reflect infrared was deposited on the SiO_2 insulated layer by electron beam evaporator (E-beam) and patterned by lift-off method (2). For the floating structure of membrane, 2 μm -thick polyimide (PI) as the sacrificial layer is coated and patterned (3). After curing process, Si_3N_4 (300 nm) supporting layer and legs were deposited by PECVD at 150°C on the PI film (4). Au (200 nm)/Cr (100 nm) electrodes for ohmic contact were evaporated on the Si_3N_4 layer and patterned by lift-off method (5). Then, the 100 nm thickness of nickel oxide was deposited as a sensitive layer by reactive RF sputter at room temperature and then it was patterned by lift-off method (6). For the forming self-supporting structure of the micro-bridge, Si_3N_4 and PI was removed by RIE and oxygen plasma asher, respectively (7, 8). The fabricated micro-bolometer structure was inspected by using field emission scanning electron microscopy (FE-SEM). Figure 5 is SEM images of fabricated nickel oxide microbolometer.

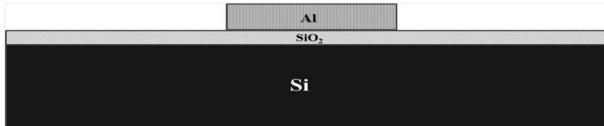
The temperature coefficient of resistance (TCR) is one of the figures of merit can guarantee the performance of uncooled micro-bolometer. Precisely controllable TEC (thermo-electric cooler) including probe station and semiconductor parameter analyzer was used for the measurements of resistance change in accordance to the temperature variation of nickel oxide film. We calculated average value at the temperature range from of 5°C to of 60°C in increment of 5°C , allowing enough time for the samples being stabilized at each measurement temperature points.

Conduction in polycrystalline materials is a thermally activated process [12] and hence, the resistivity $R(T)$ can be indicated as equation (1), where Ea is the activation energy [13].

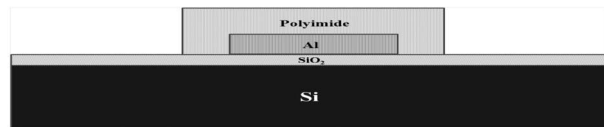
1. SiO₂ deposition : PECVD (SiO₂ : 100 nm)



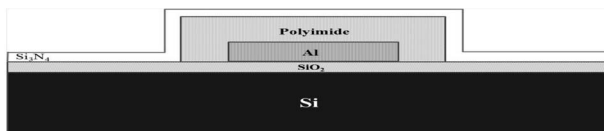
2. Reflecting layer : E-beam evaporator (Al : 200 nm)



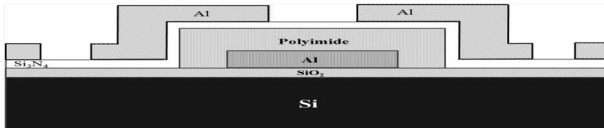
3. Sacrificial layer : Photolithography (Polyimide : 2 um)



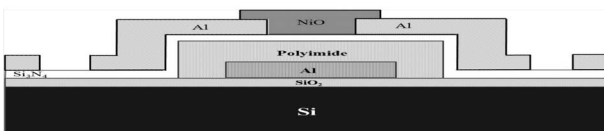
4. Supporting layer : PECVD (Si₃N₄ : 300 nm)



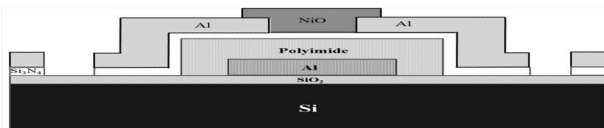
5. Metal contact pad : E-beam evaporator (Al : 500 nm)



6. Sensitive layer : Reactive RF sputter (NiO : 100 nm)



7. Si₃N₄ etching : RIE (Reactive ion etching)



8. Polyimide elimination : Plasma Asher

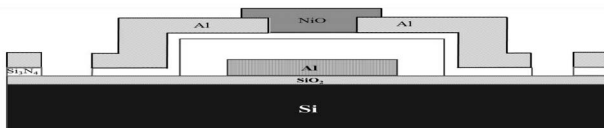
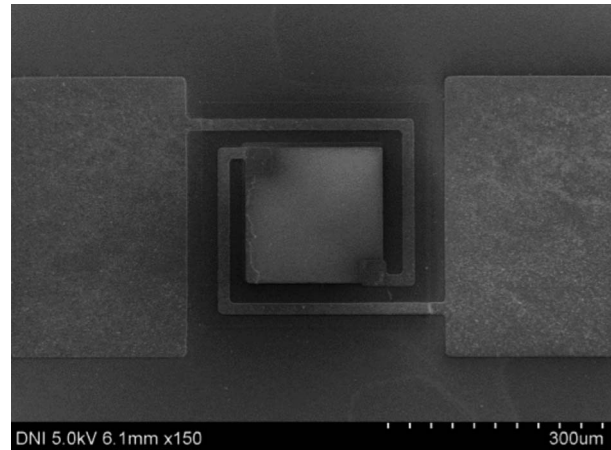


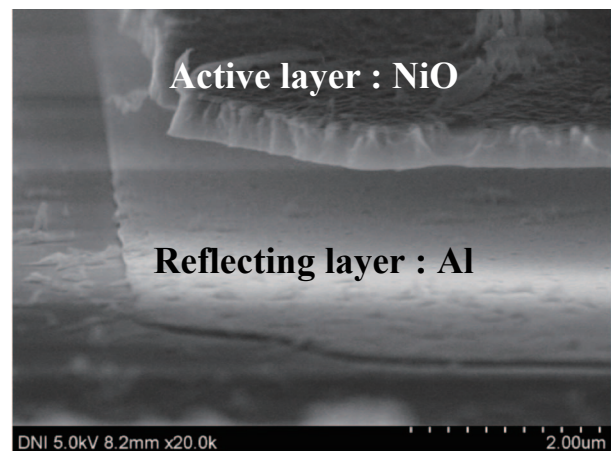
Fig. 4. Schematic flow chart of micro-bolometer fabrication.

$$R(T) = R_o \exp\left(\frac{-E_a}{kT}\right) \tag{1}$$

$$TCR(\%/^{\circ}C) = \alpha = \frac{1}{R} \frac{dR}{dT} \times 100 \tag{2}$$



(a)



(b)

Fig. 5. SEM images (a) and cross-sectional structure (b) of micro-bolometer using NiO formed at room temperature.

Calculated TCR value by equation (1) and (2) is drawn in Fig. 6. At equation (2), the constant α is known as the temperature coefficient of resistance, and symbolizes the resistance change factor per degree of temperature change. If materials have a certain specific resistance that is changed by temperature: a positive property in pure metals, a negative property in the elements carbon, silicon, and germanium.

The resistivity used in this microbolometer is $34.25 \Omega \cdot \text{cm}$. And the estimated TCR at room temperature is about $-2.01 \%/^{\circ}C$ which are usable for bolometric materials.

Since TCR can be variable if deposition temperature increased or ohmic contact resistance changed, deeper

research is required for resistivity and TCR control. TCR of nickel can be varied between 1% and 3.3% at the resistivity from 1 to 40 $\Omega \cdot \text{cm}$. It is reported that a surface treatment combined O_2 plasma and Ar^+ bombardment to contact can suppress the $1/f$ noise in NiO film [14]. This surface treatment can reduce contact resistance which yields drastic reduction of $1/f$ noise. Thus it is supposed that experimentally acquired results on nickel oxide microbolometer will be much better improved.

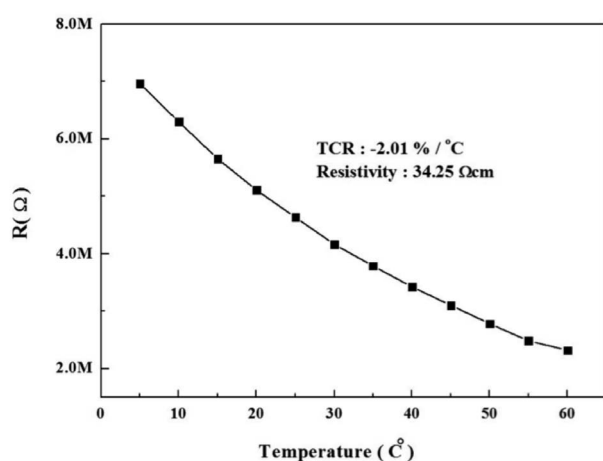


Fig. 6. TCR of nickel oxide microbolometer.

4. CONCLUSIONS

The NiO polycrystalline films were successfully deposited by reactive RF sputtering at different RF power. The growth rate of NiO film increases with increasing RF power. All the NiO(111), NiO(200) and NiO(220) peaks appear and the intensity of the NiO(200) peak is higher than that of both NiO(111) and NiO(220). The resistivity was decreased with the increase of RF power. The electric resistivity of the NiO film is in the range 1 to 40 $\Omega \cdot \text{cm}$ and is three orders of magnitude smaller than that of bulk NiO. The micro-bolometer is fabricated with the 100 nm thick the NiO films, and the estimated TCR value of it is -2.01 %/°C at room temperature. The feasibility of NiO microbolometer fabricated with a reactive RF sputter using a water-cooled substrate is demonstrated.

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REFERENCES

- [1] Y. H. Han, K. T. Kim, N. C. Ahn, H. J. Shin, I. H. Choi, and S. Moon, "Fabrication and characterization of bolometric oxide thin films based on vanadium tungsten alloy", *Sens. Actuator A-Phys.*, Vol. 123-124, pp. 660-664, 2005.
- [2] T. Ichihara, T. Watabe, Y. Handa, and K. Aizawa, "A high performance amorphous $\text{Si}_{1-x}\text{C}_x$: H thermistor bolometer based on micro-machined structure", *International Conference on Solid State Sensors and Actuators Papers*, Vol. 2, pp. 1253-1256, 1997.
- [3] N. C. Anh and S. Moon, "Excess noise in vanadium tungsten oxide bolometric material", *Infrared Phys. Technol.*, Vol. 50, pp. 38-41, 2007.
- [4] J. H. Kim, G. H. Kyo, C. J. Lee, S. H. Hahm, Y. C. Jung, and Y. S. Lee, "The surface morphology and electrical properties of NiO with various RF power and $\text{O}_2/(\text{Ar}+\text{O}_2)$ gas mixture", *Asia-Pacific Workshop on Fundamentals and Applications of Advanced Semiconductor Devices*, Japan, 2012.
- [5] Y. M. Lu, W. S. Hwang, W. Y. Liu, and J. S. Yang, "Effect of RF power on optical and electrical properties of ZnO thin film by magnetron sputtering", *Mater. Chem. Phys.*, Vol. 72, pp. 269-272, 2001.
- [6] K. J. Patel, M. S. Desai, C. J. Panchal, and B. Rehani, "p-type transparent NiO thin films by e-beam evaporation techniques", *J. Nano-Electron. Phys.*, Vol. 3, pp. 376-382, 2011.
- [7] D. Hwang, K. Bang, M. Jeong, and J. Myoung, "Effects of RF power variation on properties of ZnO thin films and electrical properties of p-n homojunction", *J. Cryst. Growth*, Vol. 254, pp. 449-455, 2003.
- [8] H. L. Chen, Y. M. Lu, and W. S. Hwang, "Effect of film thickness on structural and electrical properties of sputter-deposited nickel oxide films", *Mater. Trans.*, Vol. 46, No. 4, pp. 872-879, 2005.
- [9] H. L. Chen and Y. S. Yang, "Effect of crystallographic orientations on electrical properties of sputter-deposited nickel oxide thin films", *Thin Solid Films*, Vol. 516, pp. 5590-5596, 2008.

- [10] O. Kohmoto, H. Makagawa, F. Ono, and A. Chayahara, "Effect of heat treatment on the oxygen content and resistivity in sputtered NiO films", *J. Magn. Magn. Mater.*, Vol. 226-230, pp. 1627-1630, 2001.
- [11] H. L. Chen, Y. M. Lu, and W. S. Hwang, "Characterization of sputtered NiO thin films", *Surf. Coat. Technol.*, Vol. 198, pp. 138-142, 2005.
- [12] T. Kamins, *Polycrystalline Silicon for Integrated Circuit Applications*, Kluwer Academy Publishers, Boston, 1998.
- [13] S. Sedky, P. Fiorini, M. Caymax, A. Verbist, and C. Baert, "IR bolometers made of polycrystalline silicon germanium", *Sens. Actuator A-Phys.*, Vol. 66, pp. 193-199, 1998.
- [14] D. S. Kim, S. M. Park, and H. C. Lee, "Surface treatment method for 1/f noise suppression in reactively sputtered nickel oxide film", *J. Appl. Phys.*, Vol. 112, pp. 24501-24504, 2012.