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Formation of nickel oxide thin film and analysis of its electrical properties

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Abstract

Ni oxide thin films with thermal sensitivity superior to Pt and Ni thin films were formed through annealing treatment after Ni thin films were deposited by a r.f. magnetron sputtering method. Resistivity values of Ni oxide thin films were in the range of 10.5 μΩcm to 2.84×10^4 μΩcm according to the degree of Ni oxidation. Also temperature coefficient of resistance(TCR) values of Ni oxide thin films depended on the degree of Ni oxidation from 2,188 ppm/°C to 5,630 ppm/°C in the temperature range of 0~150 °C. Because of the high linear TCR and resistivity characteristics, Ni oxide thin films exhibit much higher sensitivity to flow and temperature changes than pure Ni thin films and Pt thin films.

Key Words : Ni oxode, Thermal sensitivity, Resistivity, TCR, Flow sensors

1. Introduction

Temperature and flow measurement are very important factors in various fields such as environmental monitoring and control systems, indoor air conditioning systems, weather forecasting systems and automotive and aerospace markets which require cheap, reliable and thin films sensors[1-3]. Therefore, a lot of efforts have been made to fabricate advanced and well operating temperature and flow sensors[4,5]. In general temperature sensors are used together with flow sensors in order to obtain more accurate data. Even though there are some sensors based on a mechanical mechanism[5,6], flow sensors that are based on a thermal mechanism have been extensively studied and well developed over many years[5]. Also various structures have been tried and developed to improve the properties of sensors. Compatibility of thin films sensors with Si MEMS technology is key to fulfill these goals. From old time, poly Si had been investigated to fulfill these sensors need, but TCR is very non-linear for suitably doped poly Si, making the required wide temperature range for automotive sensors difficult to attain. However, the fine wire gauge increases the possibility of breakage in flow and level sensing. As an alternative to wire, Pt/Si_3N_4 films(1 μm thick) and Pt films(0.2 μm thick) on Si have been developed for flow sensing, in some cases as active layers on thin bridge sensor structures formed by Si MEMS technology[1]. In flow sensors using the thermal mechanism, the resolution and accuracy are main subject to sensing materials high TCR and high resistivity and linear resistance variation, respectively. Platinum generally used to temperature sensors is superior to nickel in linear properties but not resolution properties. For temperature or flow sensing application, Ni is better than Cu and Pt due to its higher TCR(6,810 ppm/°C vs 4,300 ppm/°C and 3,900 ppm/°C, respectively)[1,6]. And the resistivity (6.84 μΩ·cm at 20 °C) of Ni is much smaller than that (10.6 μΩ·cm at 20 °C) of Pt. Ni is an easily oxidizable metal so its resistivity is increased by oxidation but Pt is generally known as an antioxidant metal. In the view of these properties, Ni is superior to Pt as the material of flow sensors used in the application less than 200 °C[7-10].

In this study, Ni thin films for flow sensors is deposited and then oxidized with annealing treatment in the atmosphere. Resistivity and TCR values of Ni oxide thin films oxide are investigated according to the oxidation degree. Finally, the possibility of Ni oxide thin films for flow sensors is tested using the resistor made by laser processing[8,9].

2. Experimental

Ni films were deposited using the round shape (Φ = 2 inch, t = 1/4 inch) of Ni target by a r.f. magnetron

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sputtering system and a high-purity Al_2O_3(96 %) substrate of roughness, 0.1 μm with a thickness of 0.625 mm is used. After the working chamber is evacuated to below 5×10^{-7} torr, high-purity($\geq = 99.999$ %) Ar gas controlled by mass flow meter (MFC) is introduced into the working chamber. Ni input power density is kept at 7 W/cm^2 and working pressure is kept at 5 mTorr. Ni thin films were oxidized for five hours in the range of 300~500 °C. Thickness of the deposited films is measured with α-step and the sheet resistance is measured by the conventional four-point probe method. The oxidation degree of Ni thin films is analyzed by energy dispersive x-ray spectrometer(EDX). In order to measure TCR, Ni oxide resistors which have resistance of 1 KΩ at 0 °C are patterned with laser processing system and then the other processes for packaging such as wire-bonding, passivation are done sequently[8]. Resistances at freezing and with increasing temperature (~150 °C) are examined using a 4-wires ohm measuring method by applying 1 mA DC current to the Ni oxide resistor and reading the voltage with a highly accurate digital multimeter. And the TCR is calculated following that;

$$TCR = \Delta R/R_0 \cdot \Delta T(ppm/^{\circ}C)$$

where R_0 is the resistance value at 0 °C, ΔR is the resistance change with respect to 0 °C resistance and ?T is the change in temperature.

3. Results and Discussion

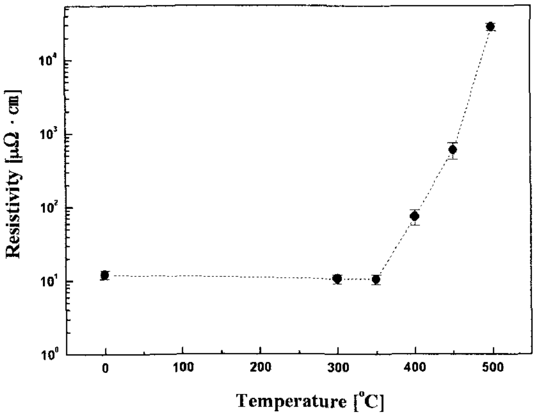

Fig. 1. Resistivity variations of Ni thin films with increasing annealing temperature.

The resistivity of the Ni oxide films was found to be a function of the oxidation temperature in Fig. 1 and increased from 12.1 μΩ·cm after oxidation at 300 °C to 2.84×10^4 μΩ·cm after oxidation at 500 °C for five hours. The resistivity of Ni thin films decreased after annealing treatment at 300 °C and 350 °C during three hours because of the effects such as stabilization of thin films due to the disappearance of defects and unstable energy states and crystallization improvement due to the increase of grain size[10]. Ni thin films were dramatically changed into Ni oxide thin films over 450 °C so that the resistivity of Ni thin films at 450 °C was as 6.004×10^2 μΩ·cm, higher than 74.3 μΩ·cm at 400 °C. The resistivity of Ni thin films annealed at 500 °C was too high to be applied to the sensing material.

Fig. 2 shows the oxidation degree of Ni thin films

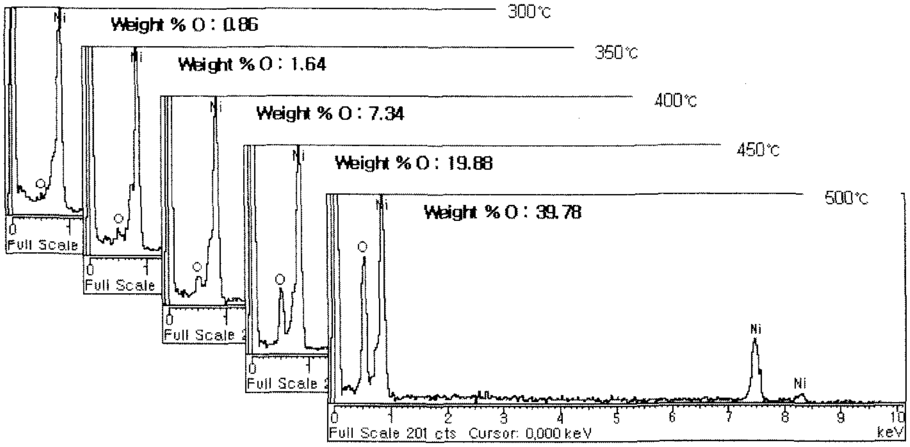

Fig. 2. Variations of Weight % O in Ni thin films with increasing annealing temperature.

according to annealing temperature in the range of 300 °C~500 °C for five hours. The weight % O in Ni thin films is less than 0.55 before annealing treatment but the values are 19.88 and 39.78 after annealing treatment at 450 °C and 500 °C for five hours, respectively. This fact is explained by that the oxidation energy become more active with increasing oxidation temperature. The oxidation energy may also increase if annealing time is increased more than five hours over 450 °C.

Resistors were made of Ni oxide thin films after annealing treatment at 300 °C to 500 °C. TCR values from 0 °C to 150 °C were measured and showed in Fig. 3. With increasing the weight % O in Ni oxide films, TCR was decreased but the resistance variation was improved more linearly. In case of annealing treatment at 300 °C and 450 °C, the average of TCR from 0 °C to 150 °C is 5,630 ppm/°C and 2,188 ppm/°C, respectively. But the resistance variation is fare more linear in the latter case. Considering the previous factors such as resistivity, TCR value and linearity, the Ni thin films resistor with annealing treatment at 400 °C showed the best properties for the application to thermal micro flow sensors.

Using the Ni oxide thin films, resistor with 1 KΩ at 0 °C was made with laser process technology and then its long terms stability was tested at 150 °C in air for a continuous 60-day test. Corrosion and long term performance are concerns for application of the Ni oxide based sensor films. The resistance somewhat increased for first 20 days because Ni thin films is exposed to oxidation condition for long time even if 150 °C is low temperature for Ni oxidation. Particularly, the part trimmed by the laser beam among Ni thin films is supposed to be mainly affected by this oxidation. Because this effect was finished, the resistance remained almost unchanged over 20 days. The films also had the properties of no variation resistance at room temperature in air for 4 months.

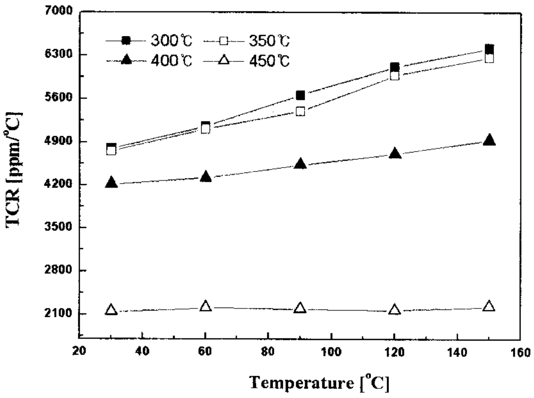

Fig. 3. TCR variations with increasing annealing temperature.

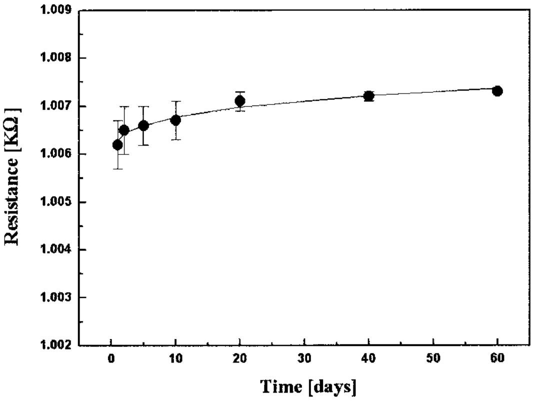

Fig. 4. Long term stability test at 150 °C for 60 days.

4. Conclusions

Ni thin films are deposited for application of micro flow sensors by a magnetron sputtering method and oxidized through the annealing treatment from 300 °C to 500 °C. The characteristics of Ni oxide thin films are investigated. Ni oxide thin films made through the annealing treatment at 400 °C for three hours had 7.34 weight % O. Resistivity and TCR of the films are 74.30 μΩ·cm and 4,542 ppm/°C, respectively. Because of the high TCR and resistivity characteristics, Ni oxide thin films are more advantageous for micro flow sensors than pure Ni and Pt thin films less than 200 °C. In the future the experiments and analysis about the annealing treatment from 400 °C to 450 °C will be followed in detail according to annealing temperature and time to obtain more excellent thin films for micro flow sensors.

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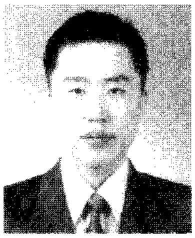

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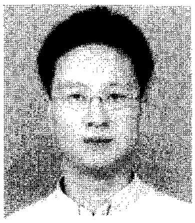

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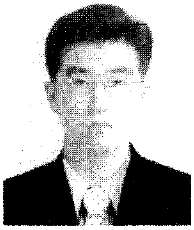

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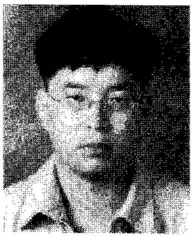

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