The Deposition and Characteristics of Ni Thin Films according to Annealing Conditions for the Application of Thermal Flow Sensors

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In this work, Ni thin films with different thickness from 1,523 Å to 9,827 Å were deposited for the application of micro thermal flow sensors by a magnetron sputtering and oxidized through annealing at 450 ℃ with increasing annealing time. The initial variation of resistivity decreased radically with increasing films thickness, then gradually stabilizes as the thickness increases. The resistivity of Ni thin films with 3,075 Å increased suddenly with increasing annealing time at 450 ℃, then gradually stabilizes as the thickness increases after the annealing time 9 h. In case of 3,075 Å and 9,827 Å films, the average of TCR values, measured for the operating temperature range of 0 ℃ to 180 ℃, were 2,413.1 ppm/℃ and 4,438.5 ppm/℃, respectively. Because of their high resistivity and very linear TCR, Ni oxide thin films are superior to pure Ni and Pt thin films for flow and temperature sensor applications.

Keywords : Flow sensors, Ni thin films, Oxide, Resistivity, TCR

1. INTRODUCTION

Advanced microelectronics technologies such as thin film technology, CMOS technology and micromachining technology[1,2] are currently being used to produce high performance, inexpensive and reliable temperature and flow sensors for many applications, including for example environmental monitoring and control, indoor air conditioning, weather forecasting, and automotive and aerospace systems[3-5]. In general, temperature sensors are used together with flow sensors in order to obtain more accurate flow data. Even though there are some sensors based on mechanical elements[6,7], flow sensors based on a thermal mechanism have been more extensively studied and developed over the years[5]. Various designs have been examined to improve the properties of such sensors.

In sensors using thermal mechanism, resolution and accuracy are mainly dependent on the sensing material's TCR (temperature coefficient of resistance) and linearity of resistance variation, respectively. Additionally, the operation of such sensors within a wide temperature range requires temperature compensation, as the change of offset and sensitivity of the sensor with temperature cannot be ignored. Therefore, resistance and TCR variations with operating temperature are studied in sensors applications[1,3,8-11]. Using resistors with a known resistance R, temperature-dependent characteristics can be characterized conveniently and accurately[11]. Pt thin films resistors have been investigated for flow sensing, in some cases on thin bridge micromechanical structures formed by silicon micromachining[1]. Pt resistors, generally used in temperature sensors, are superior to Ni resistors because of their linearity of response but not resolution. For temperature or flow sensing applications, Ni is better than Cu and Pt due to its higher TCR (6,810 ppm/℃ versus 4,300 ppm/℃ and 3,900 ppm/℃, respectively)[1,9]. The resistivity (6.84 μΩ·cm at 20 ℃) of Ni is much smaller than that (10.6 μΩ·cm at 20 ℃) of Pt. However, Ni can be oxidized easily, increasing its resistivity. (Pt is generally known as a metal that does not oxidize.) In view of these properties, Ni oxide[12] is expected to be superior to Pt[9,13] and Ni as a material for flow sensors application.

Table 1. Deposition conditions of Ni thin films.

Deposition condition	
Target	pure Ni (99.999 %) 4 inch
Power density	7 W/㎠
Base pressure	5×10^{-7} torr
Working pressure	5 mtorr
Substrate	Al_2O_3 (96 %), 0.625 mm(t)
Substrate temperature	23 ℃

In this study, Ni thin films were deposited with different deposition conditions and then oxidized by annealing in atmospheric conditions. The resistivity and TCR of the films were investigated as a function of the oxidation extent. The microstructure of the films was investigated using scanning electron microscopy (SEM) and X-ray diffraction (XRD). Finally, the potential of Ni oxide thin films for flow sensors was examined using resistors made by laser processing[9].

2. EXPERIMENTALS

Ni thin films with the different thickness from 1,523 Å to 9,827 Å were deposited using a circular (4 inch-diameter and 0.25 inch-thick) Ni target in a r.f. magnetron sputtering system. The deposition conditions for Ni thin films are summarized in Table 1. A high-purity Al_2O_3 (96 %) substrate with 0.1 ㎛ surface roughness and a thickness of 0.625 ㎜ was used. After the working chamber was evacuated to below 5×10^{-7} Torr, high-purity (≥99.999 %) Ar gas was introduced into the chamber. Ni input power density was kept at 7 W/㎠ and working pressure was kept at 5 mTorr. The Ni thin films with different thickness were oxidized at 450 ℃ with increasing the annealing time. Thickness of the deposited films was measured with α-step and sheet resistivity measurement was obtained by use of a Tencor RS35C 4-Point Probe. The film crystal orientation was studied by means of an x-ray diffraction system (XRD), using a Scintag X-1 diffractometer with a Cu K_α X-ray tube (λ=1.542 Å), configured in symmetrical θ - 2 θ mode. The oxidation extent of Ni thin films was analyzed by energy dispersive x-ray spectrometer (EDX). In order to measure TCR, Ni oxide resistors with a resistance of 1 KΩ at 0 ℃ were patterned by a laser processing system, with remaining processes for packaging such as wire-bonding and passivation done subsequently[9]. Resistances were measured in the temperature range of 0 ℃ to 180 ℃ using a 4-wire resistance measuring method by applying a 1 mA DC current to the Ni oxide resistors and measuring the voltage with a highly accurate digital multimeter. The TCR was then calculated following:

$$TCR = \Delta R / R_0 \cdot \Delta T \ (ppm/℃)$$

where R_0 is the resistance value at 0 ℃, ΔR is the resistance change with respect to 0 ℃ resistance, and ΔT is the change in temperature.

3. RESULTS AND DISCUSSION

The resistivity of the Ni thin films and their properties depended on the thickness of Ni thin films strongly as seen in Fig. 1. The initial variation of resistivity drops suddenly with increasing films thickness, then gradually stabilizes as the thickness increases further. In case of metal thin films, electrons scatter because of the property of thin films giving a lot influences on the scattering effect as well as many internal structural-defects so that the properties of thin films are different from the bulk properties. In general, these effects decrease as the thickness of metal thin films increases. The resistivity of Ni thin films with the thickness of 1,523 Å and 9,827 Å were 26.45 μΩ-cm and 14.75 μΩ-cm, respectively .

Figure 2 shows the resistivity variations of Ni thin films with increasing the annealing time at 450 ℃ in the thickness range of 1,523 Å to 9,827 Å. The resistivity

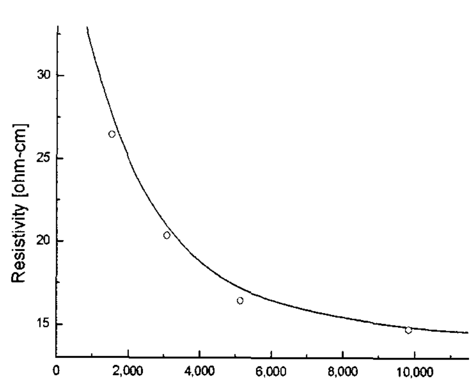

Fig. 1. Resistivity variations according to the thickness of Ni thin films.

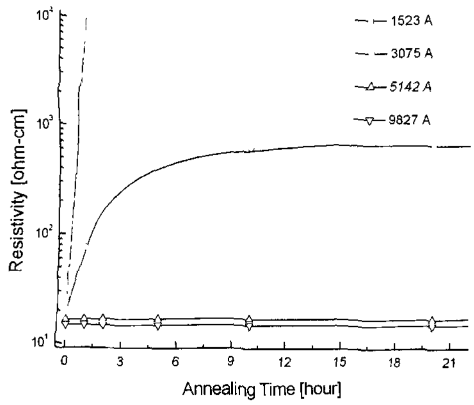

Fig. 2. Resistivity variations of Ni thin films with increasing annealing time at 450 ℃.

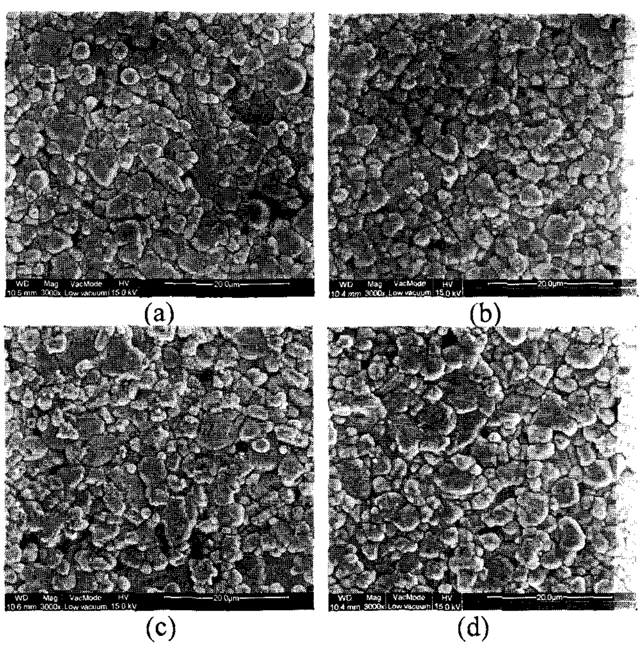

Fig. 3. Surface SEM micrographs of Ni thin films with the thickness of (a) 9,827 Å without annealing treatment and (b) 1,523 Å, (c) 5,142 Å and 9,827 Å with annealing treatment at 450 ℃ for 5 h.

of Ni thin films with 1,523 Å increased extremely due to Ni oxidation after the annealing treatment at 450 ℃ for 1h so it could not be measured. And the resistivity of Ni thin films with 3,075 Å increased suddenly with increasing annealing time at 450 ℃, then gradually stabilizes as the thickness increases after the annealing time 9 h. But there is no noticeable difference of resistivity variation in the case of Ni thin films over 5,142 Å. This results can be derived from that the oxidation of Ni thin films under the annealing treatment with increasing annealing time at 450 ℃ progresses from the surface of thin films and the oxidation just progresses shallowly from the surface. Accordingly, the influence

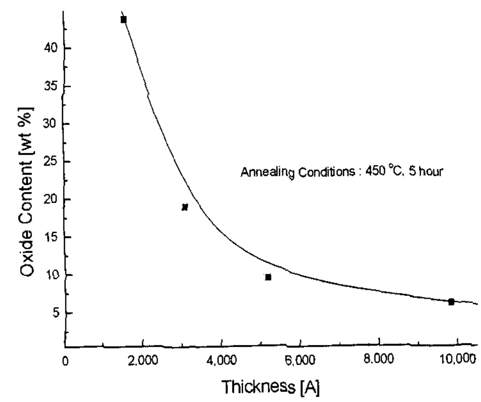

Fig. 4. Variations of weight %O in Ni thin films annealed at 450 ℃ for 5 h according to different thickness.

of oxidation on resistivity gets bigger relatively as the thickness of Ni thin films decrease.

Figure 3 show SEM micrographs of Ni thin films with different thickness before and after the annealing treatment at 450 ℃ for 5 h. SEM photos of Ni thin films with 9,827 Å before the annealing treatment(a), and with 1,423 Å(b), 5,124 Å(c), 9,827 Å(d), after the annealing are shown in Fig. 3. It's not easy to tell the difference of surface morphology according to the thickness of Ni thin films both before and after the annealing treatment in Fig. 3. Comparing Fig. 3(a) with others in Fig. 3, there is no any difference, excepting just the fact that the outline of grains faded a little after the annealing treatment.

Figure 4 shows the oxidation extent of Ni thin films with different thickness. It's considered that the oxidation extent according to the thickness of Ni thin films is the same in all conditions but the oxidation effect gets bigger relatively as the thickness of Ni thin films decreases in the resistivity and EDX analysis.

In order to analyze the crystalline structure of Ni thin films, XRD spectra was used. Figure 5 shows that the

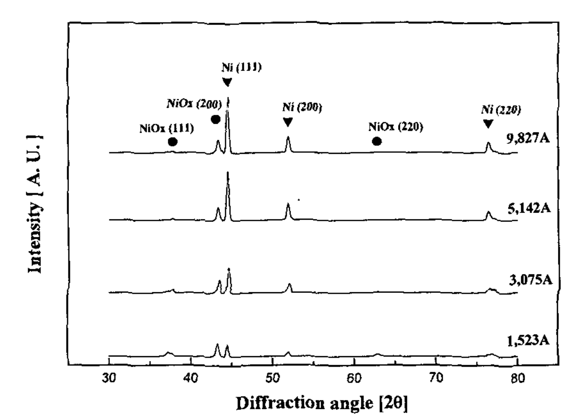

Fig. 5. XRD patterns of Ni thin films annealed at 450 ℃ for 5 h according to different thickness.

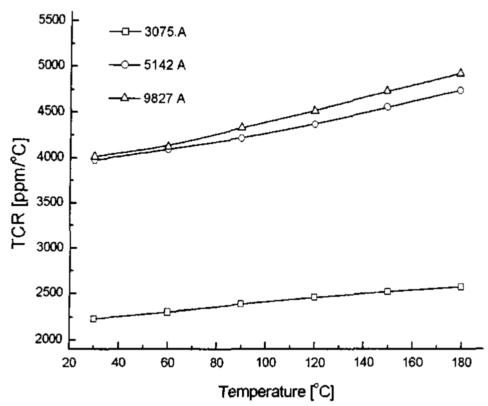

Fig. 6. TCR variations in Ni thin films annealed at 450 ℃ for 5 h.

XRD spectra of Ni thin films with different thickness after the annealing treatment at 450 ℃ for 5 h. The peaks of Ni oxide such as NiOx(111), NiOx(200) and NiOx(220) don't change according to the thickness of Ni thin films, while the peaks of Ni(200) and Ni(220) increase as the thickness increases because Ni components, detected by X-ray, increase relatively. This result also can be explained in Fig. 2 and Fig. 4.

Resistors were made from Ni oxide films with different thickness after the annealing treatment at 450 ℃ for 5 h. TCR values from 0 ℃ to 180 ℃ were measured and were shown in Fig. 6. With decreasing thickness, TCR decreased but the linearity of resistance variation improved because the oxidation extent increases relatively. In case of 3,075 Å and 9,827 Å films, the average of TCR values, measured for the operating temperature range of 0 ℃ to 180 ℃, were 2,413.1 ppm/℃ and 4,438.5 ppm/℃, respectively. However, the resistance variation was far more linear in the former case.

4. CONCLUSION

Ni thin films with different thickness from 1,523 Å to 9,827 Å were deposited for the application of micro flow sensors by a magnetron sputtering and oxidized through annealing at 450 ℃ with increasing annealing time. The characteristics of the resulting Ni oxide thin films were investigated. Resistivity of Ni thin films drops with increasing films thickness, then gradually stabilizes as the thickness increases around 10,000 Å. The resistivity of Ni thin films with 3,075 Å increased suddenly with increasing annealing time at 450 ℃ and it stabilized gradually as annealing time increased over 9 h. From the analysis of resistivity, EDX and XRD, it was known that the oxidation of Ni thin films, annealed at 450 ℃ for 5 h, has more influence on the properties of Ni thin films as the thickness decreases. In case of 3,075 Å and 9,827 Å films, the average of TCR values, measured for the operating temperature range of 0 ℃ to 180 ℃, were 2,413.1 ppm/℃ and 4,438.5 ppm/℃, respectively. Therefore, in design of sensors based on resistance variation of Ni thin films, formed by the annealing treatment, as a function of temperature, there is a significant trade off between sensitivity and linearity.

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