

Fabrication of High Quality $\text{Ni}_{1-x}\text{Pt}_x$ Films for Use as Materials in High-Sensitivity Temperature Sensor

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High-quality thin films of $\text{Ni}_{1-x}\text{Pt}_x$ alloys have been investigated as materials for temperature sensors with a high temperature coefficient of resistance (TCR). Since the high TCR of Ni has been attributed to the spin-disordered scattering occurring just below the Curie temperature (T_C), we considered that a higher TCR can be obtained by decreasing T_C to be slightly greater than room temperature (RT) by alloying Ni with Pt. $\text{Ni}_{1-x}\text{Pt}_x$ alloy films have been prepared on different substrates by RF magnetron sputtering followed by annealing in high vacuum. TCRs as high as 10000 ppm/K at RT were obtained in the case of the $\text{Ni}_{0.75}\text{Pt}_{0.25}$ alloy film prepared on a SrTiO_3 (STO) substrate. This TCR is 2.5 times higher than that of commonly available Pt temperature sensors.

KEYWORDS: $\text{Ni}_{1-x}\text{Pt}_x$, sputtered thin film, temperature coefficient of resistance, high sensitivity, temperature sensor

In recent years, high-precision temperature control has become an important issue for the development of state-of-the-art micro-electro-mechanical systems (MEMSs). The development of temperature sensors with a high temperature coefficient of resistance (TCR) is strongly needed. Although Pt is commonly used owing to its chemical stability and relatively high TCR as high as 3900 ppm/K at room temperature (RT), a higher TCR and a higher resistance are required for high-precision measurements. One of the authors (Ichida) has developed temperature sensors that use Ni foils, which show TCRs as high as 6000 ppm/K at RT¹⁾. The high TCR of Ni is derived from a steep rise in the resistivity-temperature curve just below the Curie temperature (T_C) due to spin-disordered scattering²⁾. We aimed at maximizing TCR by decreasing T_C to a value just above RT by alloying Ni with non magnetic metals. For this purpose, we studied $\text{Ni}_{1-x}\text{Pt}_x$ alloys, in which T_C can be tuned by varying the alloy composition.

According to the equilibrium chemical phase diagram for $\text{Ni}_{1-x}\text{Pt}_x$ alloys³⁾, the face centered cubic (fcc) lattice structure (A1) is stable in the entire composition range. By careful heat treatments, a disordered solid solution is converted into an ordered $L1_2$ structure (Ni_3Pt , NiPt_3) or $L1_0$ structure (NiPt). On the other hand, according to the magnetic phase diagram, the T_C of disordered alloys monotonically decreases from 628 K at $x = 0$ to 0 K at $x = 0.55$. On the other hand, the T_C of ordered alloys sharply decreases at $x = 0.2$. From the above-mentioned diagrams, it is found that the values of x , which decreases T_C to RT in $\text{Ni}_{1-x}\text{Pt}_x$ alloys, are 0.28 for ordered alloys and 0.33 for disordered alloys.

As mentioned above, commercial Ni-temperature sensors use Ni foils. However, it is not easy to obtain $\text{Ni}_{1-x}\text{Pt}_x$ alloy foils of arbitrary composition in the market. Therefore, we prepared $\text{Ni}_{1-x}\text{Pt}_x$ alloy films with different x values by RF magnetron sputtering. The sputtering targets for $\text{Ni}_{1-x}\text{Pt}_x$ alloy films were a circular Ni plate (purity: 99.99 %), 50 mm in diameter and 5 mm in thickness, and square Pt chips (purity: 99.9 %), $5 \times 5 \text{ mm}^2$ in area and 0.3 mm in thickness, placed on the Ni plate. The circular Pt plate was also used for $x = 1$. The composition of $\text{Ni}_{1-x}\text{Pt}_x$ alloy films was varied by placing the appropriate number of Pt tips on the Ni plate.

The background pressure of the sputtering chamber and the pressure during deposition were 1.0×10^{-6} and 2.0×10^{-3} Torr, respectively. Deposition was carried out at a substrate temperature between RT and 550 °C, with a deposition time of 1 h to obtain a film thickness of about 120 nm. Finally, the films were annealed at 1035 °C for 1 h in vacuum (2×10^{-8} Torr), which was necessary for the improvement in crystalline properties.

We employed glass and the (100) face of a SrTiO_3 (STO) single crystal as substrate materials. We also used MgO substrates but found that the crystalline properties of the obtained films were almost the same as those of STO substrates. Therefore, in this paper, only the results obtained with STO substrates will be described. Properties including the

lattice constants and coefficients of thermal expansion of these substrates as well as those of Ni and Pt are listed in Table I.

The resistivity of the $\text{Ni}_{1-x}\text{Pt}_x$ alloy films was measured between 30 and 300 K using a four-point-probe method, from which the normalized resistivity $\rho(T)/\rho(\text{RT})$ was evaluated with the current kept at $150 \mu\text{A}$. Magnetic properties were measured using a vibrating sample magnetometer (VSM). The composition of the $\text{Ni}_{1-x}\text{Pt}_x$ alloy films was estimated using an energy dispersive X-ray spectroscopy (EDX) system attached to a Hitachi type S4500 scanning electron microscopy (SEM) system. Structural properties were analyzed using a Rigaku type RINT2000 X-ray diffraction (XRD) system. An SII type SPI3800N atomic force microscopy (AFM) system was used to observe the microstructures of the film surface.

From their XRD patterns, the Pt films deposited on glass substrates at RT showed only weak diffraction lines; on the other hand, $\text{Ni}_{1-x}\text{Pt}_x$ alloy films deposited under the same conditions showed no conspicuous diffraction lines suggesting that the films were amorphous or microcrystalline. AFM demonstrated that the films are microcrystalline with a grain size less than 20 nm. The TCRs of Pt and $\text{Ni}_{0.71}\text{Pt}_{0.29}$ films were about 1000 and 410 ppm/K at RT, respectively. Such a low TCR may be ascribed to the high residual resistance of these films, which may be caused by the poor crystalline quality. The Pt-composition dependence of the saturation magnetization (M_S) of as-grown $\text{Ni}_{1-x}\text{Pt}_x$ films prepared on glass substrates at RT is shown in Fig. 1. The M_S of $\text{Ni}_{1-x}\text{Pt}_x$ alloy films shows a monotonic decrease with an increase in Pt composition, and disappears at approximately $x = 0.4$. x , which decreases T_C to RT in $\text{Ni}_{1-x}\text{Pt}_x$ disordered alloys, was determined to be $x = 0.4$.

In the second step, $\text{Ni}_{1-x}\text{Pt}_x$ alloy films were deposited on STO (100) substrates at a deposition temperature of 300 °C. In this case, the films were polycrystalline with an fcc structure. Figure 2 shows XRD pattern of $\text{Ni}_{0.57}\text{Pt}_{0.43}$ alloy films as a typical example of the $\text{Ni}_{1-x}\text{Pt}_x$ disordered alloy films prepared at 300 °C, as well as those of Pt and Ni films on STO substrates as references. The 200 diffraction line of $\text{Ni}_{1-x}\text{Pt}_x$ shifted toward the lower-angle side with an increase in Pt composition. The temperature dependences of the resistivity normalized to the resistivity at RT for Ni, Pt, and $\text{Ni}_{0.57}\text{Pt}_{0.43}$ films are plotted in Fig. 3. The TCRs of Pt and $\text{Ni}_{0.57}\text{Pt}_{0.43}$ films became 2000 and 1000 ppm/K at RT, respectively. Improvement by a factor of 2 was achieved using single-crystalline substrates and a substrate temperature of 300 °C.

In the third step, deposition temperature was increased to 550 °C. As shown in the lower curve in Fig. 4, the XRD pattern of as-deposited $\text{Ni}_{0.75}\text{Pt}_{0.25}$ alloy films exhibited a relatively strong diffraction compared with that of the substrate, suggesting a substantial increase in crystalline quality. AFM revealed that the size of the crystal grain increases to a value as large as 200 nm in diameter. The resistance-temperature curve of the $\text{Ni}_{0.55}\text{Pt}_{0.45}$ alloy film shown in Fig. 5 exhibits a clear hump at approximately 200 K due to spin-disordered scattering

around the estimated T_C , whereas the curve of the $\text{Ni}_{0.78}\text{Pt}_{0.22}$ alloy film is linear, giving higher TCRs at RT. However, these films still showed a high residual resistivity, resulting in no increase in TCR compared with the films prepared at 300 °C. The high residual resistivity may be ascribed to the poor crystalline quality, which results in the scattering of electrons.

It is expected that an increase in crystalline quality will bring about a decrease in the residual resistivity, thus increasing TCR. Therefore, we annealed as-deposited films at 1000 °C in high vacuum. As shown in the XRD chart (upper curve) of Fig. 4, the full width at half maximum (FWHM) of the 200 diffraction in the annealed sample decreased to half that in the as-deposited films, suggesting that a substantial improvement in the crystalline quality of the $\text{Ni}_{0.75}\text{Pt}_{0.25}$ alloy film is achieved. As shown in the solid curves in Fig. 5, residual resistivity is markedly reduced in the annealed specimen of the $\text{Ni}_{0.75}\text{Pt}_{0.25}$ alloy film, resulting in TCRs as high as 10000 ppm/K at RT.

Since no superlattice diffraction line was observed in the $\text{Ni}_{0.75}\text{Pt}_{0.25}$ film (Figs. 2 and 4), it is concluded that $\text{Ni}_{1-x}\text{Pt}_x$ alloys do not crystallize in the ordered $L1_2$ phase but rather in the disordered $A1$ structure. The T_C of $\text{Ni}_{1-x}\text{Pt}_x$ alloy films estimated from the deflection point of the resistivity-temperature curve agreed with that of a disordered $\text{Ni}_{1-x}\text{Pt}_x$ alloy described in ref. 3. From VSM measurement, it was found that annealed $\text{Ni}_{1-x}\text{Pt}_x$ alloy films are very soft without appreciable remanent magnetization, suggesting that the temperature sensor using the film is free from an irreversible magnetic field effect. Interestingly the TCR of the annealed $\text{Ni}_{0.75}\text{Pt}_{0.25}$ alloy film reached 10000 ppm/K at RT, despite the fact that T_C was not very close to RT. Therefore, a higher TCR could be obtained if $\text{Ni}_{1-x}\text{Pt}_x$ alloy films with a lower T_C are prepared with optimum Pt composition.

The observed improvement in TCR may be a consequence of a decrease in the number of grain boundaries and an improvement in crystalline quality. In one study, it was reported that annealing at temperatures higher than 1200 °C decreases TCR in Pt sensors⁴). Since vacuum annealing at temperatures as high as 1000 °C is not recommended from the viewpoint of fabrication ease, the lowering of annealing temperature is also a subject for future studies.

In summary, we have developed high-quality $\text{Ni}_{0.75}\text{Pt}_{0.25}$ disordered alloy films on STO (100) substrates with a TCR as high as 10000 ppm/K at RT. This large TCR is derived from the spin-disordered scattering just below the T_C of a $\text{Ni}_{1-x}\text{Pt}_x$ alloy. We can optimize TCR for any temperature region by varying $\text{Ni}_{1-x}\text{Pt}_x$ alloy composition.

References

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Table I. Material information.

| | Ni | Pt | STO | Glass |
|---|--------|--------|---------|-----------|
| Crystal structure | Cubic | Cubic | Cubic | Amorphous |
| Lattice constant [\AA] | 3.5238 | 3.9231 | 3.90500 | - |
| Melting point [$^{\circ}\text{C}$] | 1450 | 1770 | 2080 | 593* |
| Coefficient of thermal expansion [$10^{-6}/\text{K}$] | 13.4 | 8.8 | 11.1 | 4.6 |

* Strain point

Figure Captions

Fig. 1. Composition dependence of saturation magnetization measured at RT for as-grown $\text{Ni}_{1-x}\text{Pt}_x$ alloy films prepared at substrate temperature of RT.

Fig. 2. XRD patterns of as-grown Ni, $\text{Ni}_{0.57}\text{Pt}_{0.43}$, and Pt films deposited on STO (100) substrates at 300 °C.

Fig. 3. Temperature dependence of normalized resistivity of as-grown Ni, $\text{Ni}_{0.57}\text{Pt}_{0.43}$, and Pt films deposited on STO (100) substrates at 300 °C.

Fig. 4. XRD patterns of as-grown and annealed $\text{Ni}_{0.75}\text{Pt}_{0.25}$ alloy films deposited on STO (100) substrates at 550 °C.

Fig. 5. Temperature dependence of normalized resistivity of as-grown (dashed lines) and annealed (solid line) $\text{Ni}_{1-x}\text{Pt}_x$ alloy films deposited on STO (100) substrates at 550 °C.

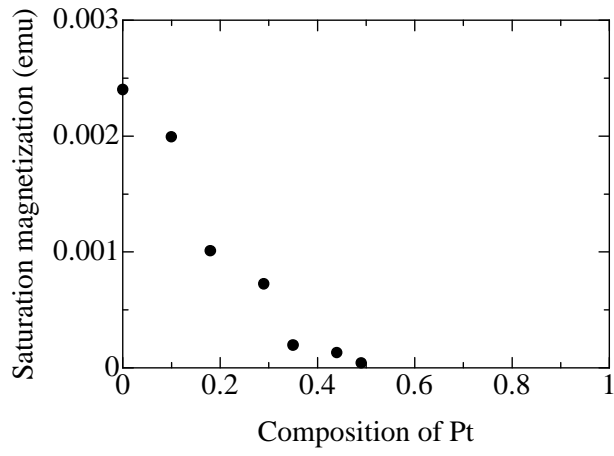


Fig. 1.

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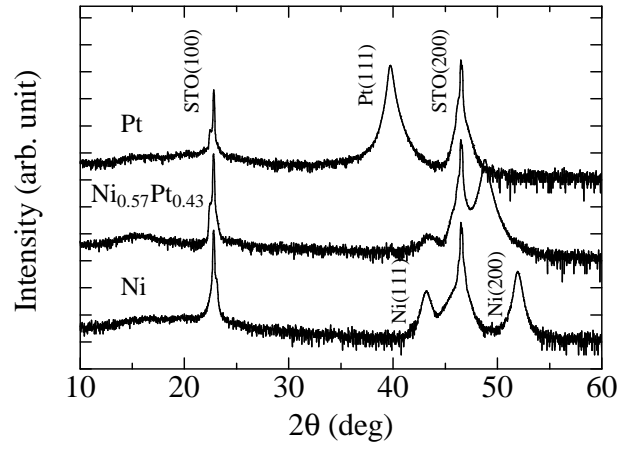


Fig. 2.

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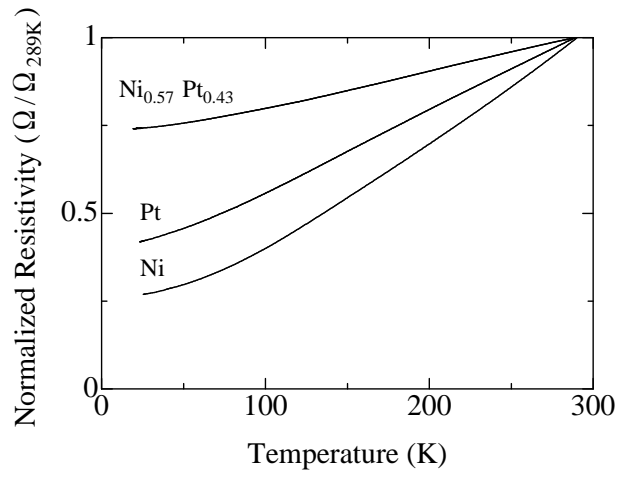


Fig. 3.

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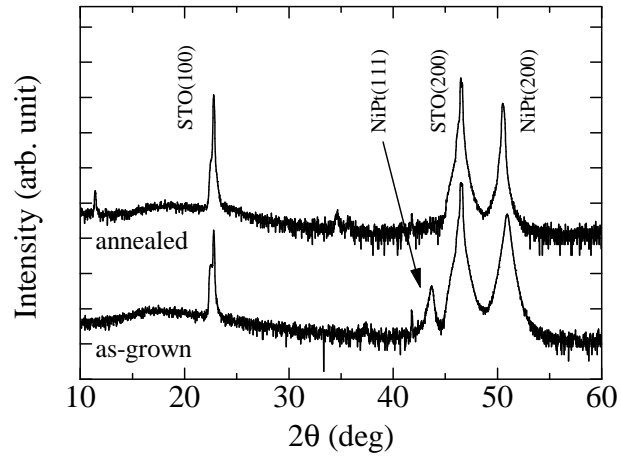


Fig. 4.

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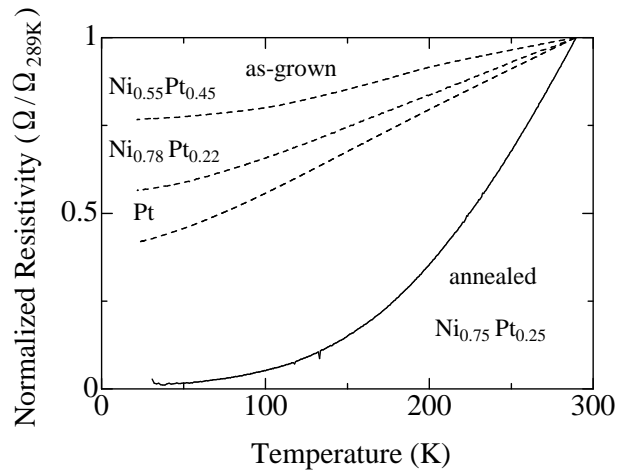


Fig. 5.

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