Magnetron sputtering of (TiZr)NiSn thin films on different substrates for thermoelectric applications

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Abstract. Half-Heusler alloys are considered to be high-efficiency thermoelectric materials. Such thin film devices are expected to have a wide range of applications. In the present study, a dense 1\( \mu \)m thin films of (TiZr)NiSn were deposited by magnetron sputtering on different substrates including Ni-, Cu-, Ti-metals, or Si wafers. SEM-EDX observations confirmed a homogenous element distribution. X-ray diffraction measurements indicated a hexagonal \( P\text{-}6_2/m \) space group (#189). All thin films showed reasonable Seebeck coefficients with the highest values obtained for (TiZr)NiSn thin films deposited on Cu or Ti, as explained by the values of the work function. As the Seebeck coefficient is significantly different from the values measured for bulk specimens, this research opens a new dimension for the development of thermoelectric materials.

1. Introduction

Intermetallic phases composed of \((Ti_{\text{x}}Zr_{1-x})Ni_{1+y}Sn_{1-y}\) crystallize with a half-Heusler (HH) structure and are considered to be effective thermoelectric (TE) materials [1-3] with a maximum Seebeck coefficient for \(x = 0.4, y = 0\) [2], where Ti and Zr commonly share one of the three available crystallographic sites in the MgAgAs structure. In contrast to bulk material, thin film composites integrated into Si technology are expected to be of large interest for practical applications in small devices. This paper describes magnetron sputtering of (TiZr)NiSn on different substrates, including Si wafers, for the first time. Deposition of such films on MgO led to a slightly smaller Seebeck coefficient than bulk specimens [4], but our intention is to measure the difference when deposited on metallic substrates.

The conventional design of thermoelectric devices has a \( \Pi \)-shape in which one leg is an n-type, and the other is a p-type semiconductor [5]. Modifications have been reported such as an arch-shape for utilizing the heat of water pipes [6], or a Y-shape when composites are used [5]. In the latter geometry the interface between different materials lies parallel to the heat gradient and is designed to reduce their mutual thermal expansion stresses. This idea has even been brought to an extreme by placing a layered structure with an interface on the hot and cold ends of a thermoelectric device [7, 8]. This design provides an easy and cheap way to utilize interface effects in thermoelectric materials and, hence, it is used in the experiments presented in this paper. After explaining the experimental details.
and microstructure observations, this paper describes the thermoelectric performance of such layered structures under a large temperature gradient [2, 9, 10] and compares their properties to bulk samples.

2. Experimental

After preparing bulk specimens, typically 2 mm in thickness and 15 mm in diameter, by arc melting from powder pellets [2], a sputtering target was manufactured by attaching about ten such sliced specimens on top of a brass disc, 60 mm in diameter, which was covered by a 1-mm-thick Ti sheet and glued with silver paste. The substrate consists of 10x8x1 mm pieces of Si wafer (5” n-type, Sumco, Finebrand, Japan) with polished (111) or (100) surfaces and pieces of Ni, Cu and Ti pure metals (High Purity Chemicals Ltd, Japan). The pieces were mounted on the substrate holder by conducting tape.

The sputtering conditions were 50 W plasma power, target-to-substrate distance of 60 mm, temperature 200 °C, and sputtering time of 30 min. As shown in table 1, two sputtering experiments were performed using sputtering targets of different compositions. Specimen characterization was performed using a Hitachi SEM system operated at 30kV, equipped with a Noran EDX instrument, and a Rigaku Miniflex XRD system with a Cu Kα beam. The Seebeck voltage was measured by attached Ni wires, as shown in the insets of Figure s. 4 and 5. One Ni wire was attached to the cold side and the other to the hot side of the specimen, which was heated by a ceramic heater (Sawaguchi

![Figure 1. XRD of (TiZr)NiSn bulk specimens with the different compositions shown.](image)

![Figure 2. XRD of (TiZr)NiSn thin film on Si (111) wafers with peaks marked with “S”. The results match best to the MoPZr (189) phase, whose peaks are marked with “R”.

![Figure 3. SEM-EDX chemical mapping of the thin film deposited on Si (111) wafer.](image)

| Composition [at%] | Bulk 1.Exp. | Bulk 2.Exp. | Thin Film 1.Exp. | Thin Film 2.Exp. |
|------------------|------------|------------|-----------------|-----------------|
| Ti               | 16         | 16         | 18              | 12              |
| Zr               | 16         | 13         | 23              | 7               |
| Ni               | 33         | 22         | 35              | 18              |
| Sn               | 33         | 49         | 20              | 63              |
| $S$ [mV/K]       | 0.075      | 0.01       | -0.05           | -0.02           |
MS1000, Japan); details have been described previously [2, 9, 10]. The measurements were performed under a high temperature gradient up to \( \Delta T = 650 \) K, which results in slightly larger Seebeck coefficients than that usually measured under small temperature gradients [2]. By closing the circuit between the hot and cold end with different resistors (1 \( \Omega \), 100 \( \Omega \), 1 k\( \Omega \), 100 k\( \Omega \), 1 M\( \Omega \)), the electric current versus voltage \((I-U)\) characteristics can be measured [2].

3. Results and discussion

Figure 1 shows the XRD results for bulk specimens with different compositions. The bulk specimens were confirmed to possess the half-Heusler crystal structure phase with a systematic decrease in diffraction angle, and hence increase of the lattice parameter, when the Ni content is increased (\( y = -0.1, 0, +0.1 \)). The only exception is the \((\text{Ti}_{0.4}Zr_{0.6})\text{Ni}_{1.1}\text{Sn}_{0.9}\) specimen, which consists of several phases obviously beyond the half-Heusler stability limit. Concerning the XRD data for the sputtered thin film on the Si\((111)\) wafer (Figure 2), the simulated XRD patterns for several crystal structures are drawn in the upper part of Figure 2, including the Si substrate marked with “S”. The best fit is achieved to a phase, in literature referred to as ZrNiAl, MoPZr or CrNiAs prototypes, and also called the ordered \( \text{Fe}_2\text{P} \) phase, with space group of \( \text{P}\ -6_2\ m \) number 189 and lattice constants of 0.629 and 0.376 nm. The simulated XRD peaks are marked with the letter “R”. This phase occurs in Pettifor maps [2] in regions neighbouring the full- and half-Heusler phases. The XRD results for the thin films in both sputtering experiments agree with each other, and the same XRD patterns are observed for thin films on the Cu, Ni and Ti- substrates, indicating that the thin film growth is not limited by epitaxial strain originating from the substrate, but is mainly driven by the thermodynamic stability of its crystallographic phase. The SEM-EDX chemical maps confirmed the film homogeneity (Figure 3).

Thermoelectric measurements of the bulk specimens show a linear increase of the Seebeck voltage with increasing temperature difference, as indicated by an orange line and arrows in Figure 4, while the blue line indicates cooling in each figure in this paper. This behaviour indicates a p-type semiconductor with a maximum Seebeck voltage of 53 mV yielding a Seebeck coefficient \( S = 0.07 \) mV/K (dotted line in Figure 4). The Seebeck voltage of the thin film was measured in the geometry shown in the inset of Figure 5. Two main differences can be recognized. The Seebeck voltage reverses its sign yielding n-type behaviour and the maximum appears at around \( \Delta T = 500K \).

![Figure 4. Seebeck voltage as a function of temperature difference for the \((\text{Ti}_{0.3}Zr_{0.7})\text{Ni}_{1.0}\text{Sn}_{1.0}\) bulk specimen.](image1)

![Figure 5. Seebeck voltage as a function of temperature difference for (TiZr)NiSn deposited on Si(100) wafer in the geometry shown in the inset.](image2)
The Seebeck coefficient is reduced to less than $S = -0.06 \text{ mV/K}$. When the specimen is put upside down, and the Ni wires are attached on the side of the substrate, quite similar values are obtained.

Measurements on the bulk specimens were extended compared to a previous study [2] over a large range of composition and are shown in Figure 6. When the Ni content increased to $y = 0.1$, or decreased to $y < -0.1$, the Seebeck voltage drops drastically. The corresponding closed circuit current shows a behavior similar to that reported previously; here we show the current-voltage characterization for $(\text{Ti},\text{Zr})_{1-x}\text{Ni}_1\text{Sn}_1$ specimens for the first time (Figure 8). The current is very high with a maximum of 410 $\mu$A for the specimen with $x = 0.2$ (filled squares in Figure 8), and the Seebeck voltage remains almost constant at 45mV, when loaded with different resistors or even short-circuited.

For the sputtered $(\text{TiZr})\text{NiSn}$ thin films (Table 1, conditions of experiment #2) on different metallic substrates negative Seebeck voltages were also measured, as shown in Figure 7. The Seebeck coefficient for films on Ni substrates is about the same as that on Si (Figure 5), $S = -0.06 \text{ mV/K}$ shown as the dotted line in Figures 5 and 7. On the Cu substrate, however, it is much higher, $S = -0.25 \text{ mV/K}$ with saturation occurring for $\Delta T > 400 \text{ K}$. In the case of Ti substrates a Seebeck voltage of more than $-250 \text{ mV}$ is measured between $\Delta T = 200 \text{ K}$ and 300 K with a decrease at higher temperature differences.

![Figure 6. Seebeck voltage as a function of the Ti/Zr ratio x for several bulk specimens with the Ni and Sn compositions shown.](image)

![Figure 7. Seebeck voltage as a function of temperature difference for (TiZr)NiSn thin films deposited on Ni, Cu and Ti.](image)

![Figure 8. Current-voltage characteristic of $(\text{Ti},\text{Zr})_{1-x}\text{Ni}_1\text{Sn}_1$ bulk specimens as a function of Ti/Zr ratios x, as indicated on the right side.](image)

![Figure 9. Absolute values of the electric current as a function of Seebeck voltage for (TiZr)NiSn thin films deposited on Ni, Cu, and Ti.](image)
This large Seebeck voltage was confirmed for two specimens and also for the reversed orientation, when the substrate is lying on the wires opposite to the case shown in the inset of Figure 5. When the electric circuit is closed, bulk specimens show currents up to 400 µA (Figure 8), while for thin films deposited on Ti the electric current is only -2 µA, much lower than the case for (TiZr)NiSn on Cu or Ni (Figure 9) with a maximum value of -16 µA for Cu. The difference from bulk specimens can be explained by the far lower thickness of 1 µm compared to 2 mm for bulk specimens.

The results showed that depositing (TiZr)NiSn thin films on different substrates led to different Seebeck voltages and I-U-characteristics. The large Seebeck voltage on Ti seems to be contrary to the large current on Cu -substrates or bulk specimens. The change from the p-type behaviour of bulk specimens to the n-type behaviour of the thin films can be explained by the large amount of negative charge carriers provided by the metal. For the same reason, the thin film on n-doped Si has a reversed sign of the Seebeck voltage. The sequence Ti, Cu, Si, Ni, for the value of the Seebeck coefficient can be explained by the sequence of values of the work functions Ti 4.33 eV, Cu 4.65 eV, Si 4.85 eV, and Ni 5.15 eV. Assuming that the largest Seebeck coefficient is expected for a composite with a large difference in work function, it can be deduced that the work function of a (TiZr)NiSn thin film has a value around 5.2 eV.

The results of thermoelectric measurements presented in this paper suggest that a layered structure composed of metallic substrate and (TiZr)NiSn thin film allows the tuning of both, the Seebeck voltage and the current and opens a new dimension for development of thermoelectrics.

4. Conclusions
The following results have been obtained.
(1) The (TiZr)NiSn bulk specimens consisted of half-Heusler crystals, with decreasing lattice parameter when the Ni content is increased.
(2) (TiZr)NiSn thin films deposited on Si(111) consists of a crystalline ZrNiAl structure with hexagonal P-6 2 m space group number 189, a phase which appears in other ternary intermetallic compounds as well.
(3) The thin film showed a deficit of Sn compared to the bulk, which can be explained by its large vapor pressure.
(4) The Seebeck coefficient shows a remarkable high value, but becomes negative, when the (TiZr)NiSn thin film is deposited on a Cu substrate. Thin films deposited on Ti show a very low electric current, and those on Ni or Si show a very low Seebeck voltage.
(5) The obtained Seebeck coefficients for thin films on four different substrates follow the order of the difference in work functions between the thin film and substrate.

References
[1] Culp S R, Poon S J, Hickman N, Tritt T M and Blumm J 2006 Appl. Phys. Lett. 88 042106
[2] Wunderlich W, Motoyama Y, Sugisawa S and Matsumura Y 2011 J. Electr. Mat. 40 583
[3] Wunderlich W and Motoyama Y 2009 MRS Symp. Proc. 1128-U01-10 1
[4] Jaeger T, Mix C, Schwall M, Kozina X, Barth J, Balke F, Finsterbusch M, Idzerda Y U, Felser C and Jakob G 2011 Thin Solid Films 520 1010
[5] Crane D T and Bell L E 2006 IEEE Proc. ICT2006 p 11, doi: 10.1109/ICT.2006.331259
[6] Funahashi R, Mihara T, Urata S, Hisazumi Y and Kegasa A 2006 IEEE Proc. ICT2006 58, doi: 10.1109/ICT.2006.331269
[7] Span G, Wagner M, Holzer S and Grasser T 2006 IEEE Proc. ICT2006 23, doi: 10.1109/ICT.2006.331261
[8] Span G, Wagner M, Grasser T and Holmgren L 2007 Phys. stat. sol. (RRL) 1 241 doi: 10.1002/pssr.200701171
[9] Wunderlich W and Soga S 2010 J.Cer.Proc. Res. 11 233 http://jcrpr.kbs-lab.co.kr/english/journal/JCPR/vol11num2/233.pdf
[10] Wunderlich W 2009 J. Nucl. Mat. 389 57