Structural and Electronic Properties of Molecular Beam Epitaxially Grown $\text{Ni}_{1+x}\text{TiSn}$ Films

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Abstract

This paper demonstrates the molecular beam epitaxial growth of metallic full-Heusler Ni_2TiSn precipitates within semiconducting NiTiSn host matrix, and discusses the structural and chemical stability of this biphasic epitaxial composite and its influence on the electronic properties. Structural properties of the epitaxial films were characterized by in-situ reflection high-energy electron diffraction and ex-situ by X-ray diffraction and transmission electron microscopy. The results indicate the presence of a secondary phase with full Heusler ordering within half-Heusler host matrix. Both the parent half-Heusler and the secondary full-Heusler phases in the epitaxial films are strained from their bulk lattice parameters. Electronic properties show an increase in resistivity at low Ni excess, ~~consistent with a metallic phase that depletes the semiconductor.~~

Keywords

A3: Molecular beam epitaxy; A3: Multiphase materials; B1: Heusler compounds; B2: Thermoelectric materials;

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1. Introduction

NiTiSn is one emerging material seen as a potential replacement for current thermoelectric materials due to its abundant, non-toxic elements. Crystallizing in the $C1_b$ crystal structure (Fig. 1), it is part of the large family of Heusler compounds, in particular the 18 valence electron per formula unit group of half-Heuslers with predicted semiconducting properties¹. Bulk synthesis of these materials has shown very high power factors, $S^2\sigma$ (the numerator of the figure of merit used to measure device performance, $ZT=S^2\sigma/\kappa*T$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the temperature and κ is the thermal conductivity), the ability to be doped both n and p-type², and also high room temperature thermal conductivities of 6.7-20 W/(m-K)³. For NiTiSn to become a viable thermoelectric material, the lattice thermal conductivity must be reduced significantly.

A number of attempts have been made to engineer the thermal and electrical properties of thermoelectric materials, including isovalent alloying,^{4,5} various means of doping,^{6,7} and combinations of these methods.^{8,9} An additional route is the creation of small inclusions with a different crystal structure but with coherent epitaxial interfaces throughout the material to reduce thermal conductivity by enhancing phonon scattering without significantly compromising the electronic properties. This has been successfully demonstrated for molecular beam epitaxially (MBE) grown heavily rare-earth doped III-V compound semiconductors¹⁰ that resulted in single crystal coherent rare-earth-group-V semi-metallic nanoinclusions with rock salt crystal structure embedded in the III-V zincblende matrix. The Ni-Ti-Sn bulk ternary phase diagram shows a tie line between the Ni_2TiSn ($a=0.610$ nm) and $NiTiSn$ ($a=0.593$ nm)¹¹. This suggests that in $Ni_{1+x}TiSn$ films (with $0<x<1$) precipitates of metallic $L2_1$ full-

Heusler Ni_2TiSn (fH) (Fig. 1) nanostructures could form within a semiconducting NiTiSn half-Heusler (hH) matrix during growth, as has been observed in bulk high temperature annealed samples^{12,13}.

Biphasic $\text{Ni}_{1+x}\text{TiSn}$ has previously been demonstrated in bulk samples^{12,13}, showing improvements in both electrical and thermal performance. However there are no reports of similar attempts in thin film structures, and only a few reports in the NiMSn ($\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$) family in general¹⁴, where less complicated single crystals and tighter control over parameters and material quality are possible. Furthermore, molecular beam epitaxial growth allows the growth of heterostructures, the potential of forming non-equilibrium sample structures and the ability to control strain through the choice of the bulk substrate and use of lattice parameter adjusting epitaxial interlayers.

Recently, molecular beam epitaxy (MBE) has been used to grow single crystal NiTiSn epitaxial layers on $\text{MgO}(001)$ substrates¹⁵. NiTiSn grows rotated 45° relative to the $\text{MgO}(001)$ in-plane crystallographic substrate axes, resulting in a tensile mismatch of 0.65%. By using this same approach and simply controlling the Ni flux, it is expected that $\text{Ni}_2\text{TiSn}/\text{NiTiSn}$ heterostructures and $\text{Ni}_{1+x}\text{TiSn}$ films can be grown. The aim of this paper is to investigate the formation, epitaxial alignment, and electronic properties of metallic fH Ni_2TiSn -semiconducting hH NiTiSn biphasic nanocomposite single crystal epitaxial heterostructures grown by MBE.

2. Experimental Methods

Epitaxial $\text{Ni}_{1+x}\text{TiSn}$ samples were grown by MBE on $\text{MgO}(001)$ substrates using elemental sources¹⁵. The flux gauge (a vacuum ionization gauge) was used to measure the

effusion cell temperature dependence of the Ni, Ti, and Sn fluxes. The flux gauge was calibrated for each element by using Rutherford Backscattering Spectrometry (RBS) to measure the elemental atomic areal densities of thin calibration films grown on Si substrates. By using RBS to measure samples grown with multiple cell temperatures for each element, the flux gauge and elemental flux versus cell temperature dependence was determined. Following this calibration, the flux gauge was used to determine any cell temperature adjustments required to maintain a Ni:Ti:Sn 1:1:1 flux ratio, as well as to tune the Ni flux for films with different Ni composition. In order to initiate NiTiSn on as clean and well-ordered MgO(001) surface as possible, a 5-10 nm thick buffer layer of MgO was epitaxially grown prior to NiTiSn film growth from an electron beam evaporation source at a substrate temperature of $\sim 350^{\circ}\text{C}$ in the same growth chamber. The NiTiSn films were grown by codeposition to 25 nm thickness using a flux of 3×10^{16} atoms/(cm²-hr) per element and then capped with an additional 5-10 nm thick MgO layer to protect from oxidation after removal from the ultra-high vacuum of the growth system. Only the Ni cell flux was adjusted to change Ni concentration of the films.

Cross-sectional high-resolution high angle annular dark field (HAADF) imaging was performed in scanning transmission electron microscopy (STEM) mode in a transmission electron microscope (Technai G2 Sphera, FEI) operating at 300kV. The cross-sectional TEM lamella was prepared using a focused Ga ion beam sputter etching (Helios, FEI.), resulting in a rectangle of dimensions $10 \times 4 \mu\text{m}^2$ and an electron transparent thickness of approximately 50 nm.

Room-temperature Hall effect measurements were performed using Van der Pauw geometry with annealed indium contacts. Within the range measured ($H = \pm 5000$ Oe), the Hall

voltage was linear with applied magnetic field and hence an effective single Hall carrier density and mobility could be extracted. Seebeck was measured using a thin strip cleaved from the sample and put in thermal contact with Peltier coolers on either side using a silica paste. Annealed indium contacts were used for voltage reading, and thermocouples were attached onto the surface parallel to the contacts using silica paste to measure the temperature on either side. A varying temperature gradient up to 5° C was then applied with a voltage reading at each point. The Seebeck coefficient was then calculated from the slope of the resulting V vs. ΔT line¹⁶.

3. Results and Discussion

3.1 Structural properties via RHEED, X-ray diffraction and STEM

Figure 2 shows in-situ reflection high-energy electron diffraction (RHEED) patterns of $\text{Ni}_{1+x}\text{TiSn}$ (25nm)/MgO(001) with the electron beam incident along the $\text{Ni}_{1+x}\text{TiSn}$ $\langle 110 \rangle$ and $\langle 010 \rangle$ crystallographic directions. The RHEED patterns are streaky for all Ni content, suggesting relatively smooth, epitaxial films throughout the entire composition range. The same diffraction patterns were observed for the electron beam incident along $\langle -110 \rangle$ and $\langle 110 \rangle$, consistent with a 4-fold surface symmetry as would be expected for growth on MgO(001). Further evidence for epitaxial growth comes from the ex-situ 2θ - ω x-ray diffraction scans shown in Fig. 3. Only the (002) and (004) reflections for each film and the MgO (002) substrate peak are evident in the scans. With increasing Ni content the film (002) and (004) diffraction peaks

broaden and shift toward lower angles, corresponding to increasingly larger out of plane lattice constants. The asymmetric broadening of the peaks suggest that they involve more than one component. In Fig. 3 the (002) and (004) reflection peaks have been fitted with two components, peak 1 (a broader peak) and peak 2 (a narrower peak). With increasing Ni content, both peaks shift to lower angles, with peak 1 shifting more. Figure 4 shows out of plane lattice parameters extracted for each peak as a function of excess Ni content x .

A cross-sectional HAADF-STEM image of a $\text{Ni}_{1.25}\text{TiSn}$ film is shown in Fig. 5a. The image has been taken along the $\langle 110 \rangle_{\text{NiTiSn}}$ ($\langle 100 \rangle_{\text{MgO}}$) zone axis. The two high-magnification inserts show representative HAADF-STEM images and corresponding atomic ball and stick models of the two different crystal structures observed within the film. The top image corresponds to Ni_2TiSn in the L2_1 full Heusler structure and the lower to NiTiSn in the half Heusler C1_b structure. Regions throughout the film show both hH ordering and fH ordering, denoted by extra columns of Ni atoms, confirming the results suggested by XRD analysis of 2 phases. Figure 5b shows an image from a $\text{Ni}_{1.05}\text{TiSn}$ film highlighting a fH precipitate, suggesting even at low levels of Ni excess, the films are biphasic. This fH phases appears to be 1-3 nm in size, consistent with previous reports that suggest this occurs by a phase separation process.¹⁷

Optical microscopy was also used and showed no visible changes with Ni content.

The hH crystal structure can be thought of as a NiSb zincblende compound with Ti occupying the octahedral sites and, like any zincblende structure, is intrinsically two-fold symmetric. The RHEED pattern for the films with $x \leq 0.2$ shows a $\frac{1}{2}$ order streak for the RHEED beam aligned in the $\langle 110 \rangle$ and $\langle 1-10 \rangle$ directions, which is indicative of a doubling of the surface unit cell in the $\langle 110 \rangle$ and $\langle 1-10 \rangle$ directions. However, the lack of a $\frac{1}{2}$ order streak in

the $\langle 010 \rangle$ and $\langle 100 \rangle$ directions suggest a mixed $(2 \times 1)/(1 \times 2)$ reconstruction rather than a (2×2) surface reconstruction when referenced to the surface unit cell depicted in Fig. 1 for the hH Ti-Sn terminated surface. The mixed $(2 \times 1)/(1 \times 2)$ surface reconstruction is a result of 90 degree rotated domains of a two-fold symmetric material grown on a 4-fold symmetric surface. A $2 \times$ reconstruction is often observed for zincblende semiconductors and is attributed to the formation of surface dimer formation. Similarly, Sb dimer formation has been attributed to the $2 \times$ reconstruction on the hH compound PtLuSb¹⁸. It is therefore speculated that the (2×1) surface reconstruction in NiTiSn is a result of Sn dimer formation as shown in Fig. 2.

The large change in the RHEED diffraction patterns for $x \geq 0.3$ for the electron beam incident along $\langle 110 \rangle$ suggests a significant change and decrease in size of the surface unit cell. The surface unit cell depicted for the Ni terminated fH shown in Figs. 1 and 2 corresponds to a 45° rotation and $1/\sqrt{2}$ reduction of size compared to the hH surface unit cell. This surface unit cell would also be expected if Ti and Sn atoms were randomly mixed as in a B2 rather than ordered in the $L2_1$ crystal structure or the surface were Ni terminated. Hence, the change in the RHEED patterns for $x \geq 0.3$ suggests the formation of a Ni terminated or Ti-Sn disordered fH-like surface. The formation of a fH-like phase within the hH phase with increasing Ni concentration, x , is consistent with the x-ray diffraction data in Fig. 3 and the HAADF-STEM images in Fig. 5. For $x > 0$, peak 1 would be associated with an fH-like phase and peak 2 with an hH-like phase. The formation of two distinct peaks confirms the lack of complete solubility between fH and hH phases, which is consistent with the ternary phase diagram¹¹. Calculations have shown the hH phase is expected to be stiffer than the fH,¹⁹ which could explain why the hH lattice parameter does not change significantly at low Ni concentrations. However, the increase in out of plane

lattice parameters for both peaks with increasing x could suggest a significant variation in composition for both the fH (Ni deficiency) and hH phases (Ni excess) (Fig. 4). Recent studies of bulk samples made through a melt process have shown that the hH phase is capable of accepting some excess Ni²⁰. These thin films are grown at much lower temperatures in a kinetically limited regime and therefore could be able to accept even higher metastable Ni concentrations, and even with phase separation, some level of anti-site defects are to be expected²¹. Fig. 5 however, suggests the formation of a fH-hH nanocomposite with the formation of epitaxial fH nanoprecipitates embedded in a hH matrix. No systematic changes were observed in the morphology of the films, with phase separation appearing to have the same length scales throughout, and no visible changes on the surface roughness using optical microscopy or RHEED. Attempts to quantitatively study the stoichiometry of these regions have been unsuccessful using electron dispersive spectroscopy (EDS). This can be explained by the small length scales of the observed phase separation relative to the TEM foil thickness of approximately 50 nm, resulting in an overlap of both phases. Given phase separation is observed even at 5% Ni excess, it is likely these phases have little solubility as predicted²².

3.2 Electronic Properties

Having demonstrated the MBE growth of a fH-hH nanocomposite, the influence of the fH precipitates on the electronic properties and, in particular, the thermoelectric properties are important to determine. Figure 6 shows results from room-temperature Hall measurements assuming a single charge carrier, Seebeck coefficient measurements and resulting power factor for samples with varying excess Ni concentration, $0 \leq x \leq 0.5$. Single phase NiTiSn ($x=0$) gave a

room-temperature n-type carrier concentration of $3 \times 10^{20} \text{ cm}^{-3}$ and a mobility of $15 \text{ cm}^2/(\text{V}\cdot\text{s})$, consistent with previous MBE film results¹⁵. Increasing the Ni concentration slightly ($x = 0.05$) resulted in increased resistivity, decreased carrier concentration and increased mobility. Further increases in Ni concentration resulted in decreased resistivity, increased carrier concentration and decreased mobility. The Seebeck coefficients mirrored the resistivity trends, with a net result of increased magnitude of the power factor for the $x=0.05$ sample.

Since the hH is predicted to be semiconducting and the fH metallic, any fH clusters within the semiconducting matrix would act as isolated Schottky barriers that would result in a carrier depletion region in the semiconductor around them. This could explain the decrease in carrier density for $x = 0.05$. An alternate explanation could be energy filtering effects by the second phase interface²³. As x increases, the density of metallic fH particles increases, increasing the possibility of percolation between clusters and thus forming a parallel metallic conduction path. This would result in a significant decrease in resistivity and increase in carrier density as observed in Fig. 6. Similar results were observed in bulk samples²⁴. However, changes in the electronic properties of the hH matrix may also be contributing the change in the overall electronic properties of the composite as its out of plane lattice parameter increases with x .

If the Seebeck coefficient is determined as a function of conductivity, it is straightforward to make a prediction for the highest possible power factor for a particular material system. Figure 7 shows the dependence of Seebeck coefficient versus conductivity. The slope of $-52.5 \text{ } \mu\text{V}/\text{K}$ per decade is smaller than the predicted value of k_B/e ($86.2 \text{ } \mu\text{V}/\text{K}$) by the Price model²⁵. This can potentially be explained by 2 carrier conduction (electron and hole), where the minority carrier would add to conductivity and subtract from the Seebeck voltage, or

increasing number of conduction paths involving the metallic phase (percolation). Calculations show that impurity states from Ni interstitials may reduce the effective band gap to as small as 0.12 eV, suggesting that bipolar conduction is very plausible.¹⁷ By fitting the Seebeck versus conductivity plot, the predicted power factor versus conductivity was determined and plotted as the dotted blue line in Fig. 7. The peak in the power factor is predicted to be for a conductivity of ~ 1000 S/cm.

The RHEED, x-ray diffraction and TEM studies clearly show the presence of fH inclusions in a hH matrix. These have a strong influence on the electronic and thermoelectric power factor. The optimum conductivity for the highest power factor was found to be ~ 1000 S/cm, which could be achieved with an excess Ni of $x \leq 0.1$. For $x > 0.1$ the high conductivity and decreased Seebeck coefficient results in a decreased power factor. The presence of fH nanoclusters is expected to have a strong influence on the thermal conductivity due to increased phonon scattering, further enhancing the thermoelectric figure of merit (ZT). In order to determine the influence of impurity states, bipolar conduction, and precipitates, a detailed temperature dependent magneto transport study would be required and is beyond the scope of this paper.

4. Conclusions

In conclusion, $\text{Ni}_{1+x}\text{TiSn}$ films were shown to grow epitaxially on $\text{MgO}(001)$. For films with $x > 0.05$ there was clear evidence of 2 phases, one phase being hH-like (NiTiSn) and the second fH-like (Ni_2TiSn). Their out of plane lattice parameters increase with x , suggesting substantial composition ranges but yet not miscible. The lattice mismatch between the phases result in observed strain in both the $\text{Ni}_{1-x}\text{TiSn}$ and the $\text{Ni}_2\text{TiSn}/\text{NiTiSn}$ samples, moving them

away from their bulk values, yet not coherently strained to each other. Electronic properties appear superior for samples with small amounts of Ni excess. However, thermal conductivity measurements will be needed to gain a complete understanding of thermoelectric performance.

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Figure 1. 2 unit cells of the half-Heusler structure and 2 half-unit cells of a full-Heusler unit cell with an added Ni terminated surface. The surface unit cells are highlighted with dashed lines.

Figure 2. a) RHEED measured during growth of $\text{Ni}_{1+x}\text{TiSn/MgO}(001)$ in both $\langle 110 \rangle_{\text{hH}}$ and $\langle 010 \rangle_{\text{hH}}$ directions for different values of x . b) Schematic model of a half-Heusler with a (2×1) surface reconstruction due Sn-dimer formation. C) Schematic of an unreconstructed full Heusler with a Ni terminated surface. A mixture of 90° hH domains for low Ni excess would result in a $(2 \times 1)/(1 \times 2)$ surface reconstruction, while for higher x values a smaller and rotated surface unit cell as shown in c) for a fH Ni terminated surface.

Figure 3. X-ray diffraction scans of $\text{Ni}_{1+x}\text{TiSn}/\text{MgO}(001)$ epitaxial films. (a) Wide range 2θ - ω scans showing $\text{Ni}_{1+x}\text{TiSn}$ (002) and (004) film reflections. (b-e) XRD 2θ - ω scans of the $\text{Ni}_{1+x}\text{TiSn}$ (004) film reflections as a function of excess nickel content x in $\text{Ni}_{1+x}\text{TiSn}(001)$. Films show an increase in both lattice parameter and peak width with Ni content, with no sign of a distinct second film peak at either reflection. A 2 Gaussian fit may account for the observed shifts in peak shape and position.

Figure 4. Lattice constant for a two Gaussian peak fit to (004) $\text{Ni}_{1+x}\text{TiSn}$ XRD peaks shown in fig. 3. A Linear fit is applied to each phase. Both phases appeared strained from their bulk values.

Figure 5. a) HAADF STEM image of a $\text{Ni}_{1.25}\text{TiSn}$ film along the $[110]_{\text{hH}}$ zone axis. Regions of fH and hH ordering can be observed throughout the film. b) HAADF STEM of a $\text{Ni}_{1.05}\text{TiSn}$ film showing a fH precipitate

Figure 6. Electronic properties from Hall and Seebeck measurements for $\text{Ni}_{1+x}\text{TiSn}(001)$ films performed at room temperature. a) Electrical resistivity b) 3D carrier concentration, and c) hall mobility. d) Seebeck coefficient and e) thermoelectric power factor. Thermoelectric performance shows an increase at low Ni excess.

Figure 7 Seebeck and power factor vs conductivity for $\text{Ni}_{1+x}\text{TiSn}(001)$ films. A log fit is applied to the Seebeck data. The blue dashed line represents the power factor calculated from the fit of the Seebeck data (highest conductivity point is excluded from the fit).

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