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Tents and tunnels on martensitic films

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Abstract

In this paper we outline a strategy for producing certain deformable structures — tents and tunnels — on epitaxially grown martensitic single crystal films. These structures are intended to be the basic building blocks of micropumps and microactuators. We give specific predictions for the systems Ni_2MnGa, $PbTiO_3$ and Cu–Zn–Al.

Keywords: Thin-films; Micropumps; MEMS; Shape-memory alloys; Ferromagnetic shape-memory alloys; Ferroelectrics

1. Introduction

The explosive growth of microelectronic mechanical systems (MEMS) technology has created a great need for effective microactuators and micropumps. The delivery of reasonable work output is a significant challenge in view of the extremely small size of these devices. Phase-transforming materials with their high work per unit volume show great promise in this aspect. We outline in this paper a strategy for producing certain deformable structures — tents and tunnels — on epitaxially grown martensitic single crystal films. These structures are motivated by, and are designed to be the basic building blocks of micropumps. We consider material properties, orientation of the film, substrate material, lattice matching and thermally or electromagnetically induced deformations. We give specific predictions for the systems Ni_2MnGa, $PbTiO_3$ and Cu–Zn–Al.

2. Membrane theory of martensitic films

Consider a single crystal film of thickness h, which has been released on a certain region S but attached outside it. Starting from a three-dimensional theory of martensite (as in Refs. [1–3] augmented with a term for interfacial energy), Bhattacharya and James [4] study the behavior of energy minimizers as the thickness becomes small, and derive a limiting theory for a thin film.

In the limiting theory $\boldsymbol{x} = (x_1, x_2) \in S$ denotes a typical point on the film. The deformation of the film is characterized by two three-dimensional vector fields, $\boldsymbol{y}(\boldsymbol{x})$ and $\boldsymbol{b}(\boldsymbol{x})$ as shown in Fig. 1a. $\boldsymbol{y}$ describes the deformation of the mid-plane of the film while $\boldsymbol{b}$ describes the deformation of the film relative to the mid-plane. In order to prevent tearing the film $\boldsymbol{y}$ is assumed to be continuous, but $\boldsymbol{b}$ may jump at interfaces. The total energy of the film in the limiting theory is given by

$$E[\boldsymbol{y}, \boldsymbol{b}] = h \int_S W(\boldsymbol{y}_{,1} | \boldsymbol{y}_{,2} | \boldsymbol{b}) \mathrm{d}x_1 \mathrm{d}x_2 \tag{1}$$

where W is exactly the same stored energy per unit reference volume as in the 3d theory. The notation $\mathbf{A} = (\boldsymbol{a}_1 | \boldsymbol{a}_2 | \boldsymbol{b})$ means that the columns of the 3×3 matrix $\mathbf{A}$ are the vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ and $\boldsymbol{b}$; and $\boldsymbol{y}_{,i} = \partial \boldsymbol{y} / \partial x_i$. This energy includes effects of shearing and stretching the film, but does not contain bending energy. It can be shown [4] that bending energy comes in at higher orders of thickness (in fact at order h^3) and is therefore negligible for sufficiently thin films.

In martensitic materials, W has a multi-well structure. If we choose the high temperature *austenite* phase as our reference configuration, it is described by the

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identity matrix, **I**. The low temperature *martensite* phase has k symmetry-related variants[1] which are described by the matrices $\mathbf{U}_1$, $\mathbf{U}_2$, …, $\mathbf{U}_k$. These matrices are obtained from the *Bain* or *distortion* matrix $\mathbf{U}_1$ by symmetry: $\mathbf{U}_i = \mathbf{Q}\mathbf{U}_1\mathbf{Q}^T$, where $\mathbf{Q}$ is an orthogonal matrix in the point group of the austenite. Also, W is necessarily frame-indifferent, which implies that if $\mathbf{A}$ minimizes W then so does $\mathbf{RA}$ where $\mathbf{R}$ is any rotation matrix (i.e. $\mathbf{R}\mathbf{R}^T = \mathbf{I}$ and $\det \mathbf{R} = 1$). So, the minimizers of W consist of matrices of the form $\mathbf{R}$ above the transformation temperature, and $\mathbf{R}\mathbf{U}_1$, $\mathbf{R}\mathbf{U}_2$, …, $\mathbf{R}\mathbf{U}_k$ below the transformation temperature where $\mathbf{R}$ is any rotation matrix. In order to minimize the total energy, we look for $\boldsymbol{y}$, $\boldsymbol{b}$ such that $(\boldsymbol{y}_{,1}|\boldsymbol{y}_{,2}|\boldsymbol{b})$ takes values amongst the minimizers of W.

In this paper we focus on specific martensitic materials that support certain tent and tunnel structures on thin films, according to the theory based on Eq. (1). The Heusler alloy Ni_2MnGa undergoes a thermally induced cubic-to-tetragonal transformation ($k = 3$) with $\mathbf{U}_1 = \mathrm{Diag}[\beta, \alpha, \alpha]$, $\mathbf{U}_2 = \mathrm{Diag}[\alpha, \beta, \alpha]$, $\mathbf{U}_3 = \mathrm{Diag}[\alpha, \alpha, \beta]$. The measured values for Ni_2MnGa are $\beta = 0.9555$, $\alpha = 1.0163$. This alloy is interesting because it exhibits an unusually stable martensitic phase transformation and it is also ferromagnetic [5]. The easy axis of magnetization of the martensite is parallel to the c-axis.

An alloy of Cu–Zn–Al undergoes a cubic to monoclinic (DO_3 to 18R) transformation where the martensite phase is not twinned, but consists of a high density of stacking faults on the basal plane. A recent calculation has shown that microstructures in bulk specimens of this alloy can be rationalized by the choice of a new unit cell for the martensite phase [6]. With this choice of unit cell, $k = 12$ and one of the distortion matrices is

$$\mathbf{U}_1 = \begin{pmatrix} \alpha & \beta & 0 \\ \beta & \gamma & 0 \\ 0 & 0 & \delta \end{pmatrix}$$

The measured values for Cu-17at%Zn-15at%Al are $\alpha = 1.089$, $\beta = 0.0250$, $\gamma = 1.007$, and $\delta = 0.9093$. This alloy is of interest because it can form an austenite–martensite interface without twins.

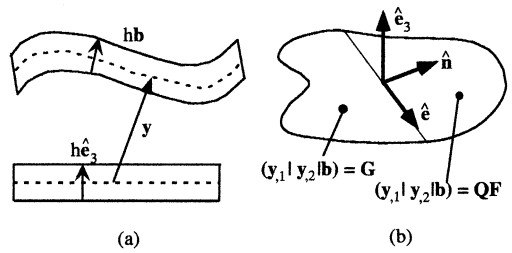

Fig. 1. (a) Deformation. (b) Interface.

[1] k depends on the change in symmetry during transformation.

2.1. Deformations with a single phase

The thin film theory allows a very rich class of energy minimizing deformations with a single variant: distort the film uniformly by the relevant matrix $\mathbf{I}$, $\mathbf{U_1}$, …, or $\mathbf{U}_k$ and then perform any deformation $\boldsymbol{y}(x_1, x_2)$ such that $(\boldsymbol{y}_{,1}|\boldsymbol{y}_{,2})$ equals the first two columns of a rotation matrix. The latter defines precisely the class of deformations that one can illustrate by deforming a flat sheet of paper (simple examples are deformations that take a flat sheet into a cone or cylinder). Hence, the thin film theory captures naturally the floppiness of thin films.

2.2. Deformations with two variants or two phases: interface conditions

More interesting are deformations that involve both phases, since they have the possibility of exhibiting a thermally-induced change of shape. Consider an interface that separates two variants or two phases in a film with normal $\hat{\boldsymbol{e}}_3$ shown schematically in Fig. 1b. Here, $\mathbf{F}$, $\mathbf{G}$ are matrices in the set $\{\mathbf{I}, \mathbf{U}_1, \ldots, \mathbf{U}_k\}$. A two phase deformation $\boldsymbol{y}$ of this type is continuous if and only if the invariant line condition holds:

$$(\mathbf{QF}\text{-}\mathbf{G})\hat{\boldsymbol{e}} = 0 \quad \text{for some } \hat{\boldsymbol{e}}\cdot\hat{\boldsymbol{e}}_3 = 0 \tag{2}$$

Here, $\hat{\boldsymbol{e}}$ contains the invariant line since $\mathbf{QF}\hat{e} = \mathbf{G}\hat{e}$. Our energetic argument implies that a thin film can overcome any incoherence in the thickness direction at the cost of a small elastic energy (of order h^2, in contrast to the membrane energy which is of order h).

In [4] we show that given $\mathbf{F}$, $\mathbf{G}$ and the normal to the film $\hat{\boldsymbol{e}}_3$, we can find a rotation $\mathbf{Q}$ and a unit vector $\hat{\boldsymbol{e}}$ that satisfy Eq. (2) if and only if

$$\hat{\boldsymbol{e}}_3\cdot(\mathrm{cof}\,\mathbf{A})\hat{\boldsymbol{e}}_3 \le 0 \tag{3}$$

where $\mathbf{A} = \mathbf{F}^T\mathbf{F} - \mathbf{G}^T\mathbf{G}$ and $\mathrm{cof}\,\mathbf{A}$ denotes the matrix of cofactors of $\mathbf{A}$. If Eq. (3) holds, then one can find (i) two independent directions $\hat{\boldsymbol{e}}$ and (ii) a one-parameter family of $\mathbf{Q}$ for each $\hat{\boldsymbol{e}}$ that satisfy Eq. (2).

To understand Eq. (3) consider a unit square and stretch it by a quantity $\lambda_1 > 0$ along one side and a quantity $\lambda_2 > 0$ on another. As is well known by experts on martensite, it is possible to find an invariant line if and only if one of the two stretches is greater than one while the other is less than one, i.e. if and only if $(\lambda_1 - 1)(\lambda_2 - 1) \le 0$. Eq. (3) expresses exactly this condition in terms of the given distortion matrices $\mathbf{F}$ and $\mathbf{G}$ and the film normal $\hat{\boldsymbol{e}}$.

As an illustration of this interface condition, we note that, unlike in bulk material, it is typically possible to form an *exact* austenite–martensite interface in a thin film. This can be utilized to induce some unusually large changes of shape in a film that would be compromised by the fine twinning that almost always occurs during bulk transformation. For example, variant 1 of

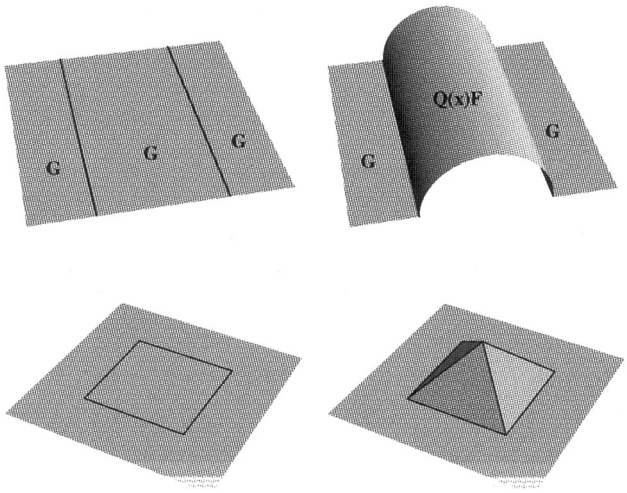

Fig. 2. Tunnel and tent.

martensite can form an exact interface with the austenite on a

- $(001)_c$ film of a material undergoing cubic to tetragonal transformation if $(\alpha^2-1)(\beta^2-1)\leq 0$; Ni_2MnGa satisfies this condition and the interface direction ($\hat{\boldsymbol{e}}$) is (0.5236, $\pm$0.852, 0).
- $(001)_c$ film of a Cu–Zn–Al alloy and the only interface direction ($\hat{\boldsymbol{e}}$) is ($-$0.2696, 0.9630, 0). In fact, this alloy satisfies Eq. (3) with an equality and can form an exact austenite–martensite interface on any film.

3. Tents and tunnels

We now examine if it is possible to form tunnels and tents as shown in Fig. 2. The idea is to deposit a film on a substrate, then release it in some region and look for the following behavior: the film is flat in one phase or variant (left), while it bulges up to a tunnel or a tent (right) as it transforms to another, perhaps under some back pressure. If this is possible, then it can be exploited to make micropumps, microvalves and other micromachine actuators.

We can show [4] that such a tunnel is possible if and only if the two phases are compatible (in the thin film sense) across an interface and the relative deformation is a pure stretch normal to the interface; this in turn is equivalent to the conditions,

$$\hat{e}_3\cdot(\mathrm{cof}\,\mathbf{A})\hat{\boldsymbol{e}}_3=0 \quad \text{and} \quad \mathrm{trace}(\mathbf{A})-\hat{\boldsymbol{e}}_3\cdot(\mathbf{A})\hat{\boldsymbol{e}}_3>0. \qquad (4)$$

where $\mathbf{A}=\mathbf{F}^T\mathbf{F}-\mathbf{G}^T\mathbf{G}$ for $\mathbf{F}$, $\mathbf{G}$ relevantly chosen in the set $\{\mathbf{I}, \mathbf{U}_1, \ldots, \mathbf{U}_k\}$. Similarly, it is possible to form a n-sided pyramidal tent [4] with

1. faces consisting of martensite variants, surrounded by flat austenite, if the film is a plane of n-fold symmetry of the austenite and we satisfy Eq. (4) with $\mathbf{G}=\mathbf{I}$ and $\mathbf{F}=\mathbf{U}_1$ or,
2. faces consisting of martensite variants i, j, …, surrounded by flat martensite variant m, if the film is a plane of n-fold symmetry of the martensite variant m and we satisfy Eq. (4) with $\mathbf{G}=\mathbf{U}_m$ and $\mathbf{F}=\mathbf{U}_i$

Finally, we note that though this theoretical development is carried out for martensitic films and thermally-induced tunnel and tent formation, these ideas also hold for ferromagnetic shape-memory and for ferroelectric materials with slight modifications which are indicated below.

4. Epitaxial growth and lattice matching

The predictions outlined above call for single crystal martensitic films released from the substrate on certain regions. In this section we outline a strategy to grow single crystal films by molecular beam epitaxy (MBE) patterned by back etching the substrate. We focus on Ni_2MnGa.

In order to grow high quality single crystal films by MBE, the substrate should be single crystal, lattice matched, and atomically smooth and clean. The preparation of the substrate is critical to the quality of the epitaxially grown films (see for example the review [7]). The large range of lattice parameters, high crystalline quality and low cost of semiconductors, makes them ideal substrate materials. The lattice parameter of compound semiconductor crystals can be tailored by controlling the composition. For example, the lattice parameter of alloys of GaAs and InAs, $Ga_{1-x}In_xAs$, can be adjusted from that of GaAs (5.6533 Å) to that of InAs (6.0584 Å) by controlling the alloy composition. Unfortunately, although bulk crystals of GaAs and InAs are readily available, ones of $Ga_{1-x}In_xAs$ are not. However, $Ga_{1-x}In_xAs$ alloys can easily be grown by molecular beam epitaxy (MBE) on a number of semiconductor substrates including InP.

The austenitic phase Ni_2MnGa is a Heusler alloy with the cubic BiF_3 crystal structure with a lattice parameter of $a_0=5.825$ Å. The martensitic phase is tetragonal with $a=b=5.92$ Å and $c=5.566$ Å [8]. InP has a lattice parameter of 5.8686 Å, which falls in-between a and a_0. $Ga_{0.47}In_{0.53}As$ is lattice matched to InP. Hence, by growing a more Ga-rich $Ga_{1-x}In_xAs$ layer, the lattice parameter of the austenitic phase can be obtained and by growing a more In-rich $Ga_{1-x}In_xAs$ layer, the lattice parameter can be adjusted to match a and b of the tetragonal phase. In this manner, we intend to selectively grow either the austenitic or martensitic phases through lattice parameter tailoring of the substrate. An additional advantage of using $Ga_{1-x}In_xAs$ grown on InP as a substrate material is that selective etching of the InP and $Ga_{1-x}In_xAs$ is easily achieved, allowing free standing Ni_2MnGa films to be made in a relatively straight forward manner

using photolithography and selective etching from the substrate side.

Typically, $Ga_{1-x}In_xAs$ is grown on GaAs or InP substrates. When a slightly mismatched layer grows on a substrate, it will initially be strained to be pseudomorphic on the substrate material (i.e. its in-plane lattice parameter will be the same as the substrate). Above a critical thickness, it is no longer energetically favorable for the film to be strained to the substrate and misfit dislocations form in the growing film, resulting in the film relaxing to its bulk lattice parameter. While the threading component of these misfit dislocations has detrimental effect for electronic device applications, we anticipate that for the overgrowth of martensitic materials, these will be of less importance, and may in fact play a useful role as in bulk shape memory alloys.

5. Field-induced tunnel formation

5.1. Ni_2MnGa

Because the easy axis of the martensite in Ni_2MnGa is parallel to the c-axis, this alloy exhibits negative magnetostriction: as the magnetization is forced to align with a magnetic field of increasing strength, the film contracts along the direction of the applied field by growth of the appropriate variant [5]. A variety of designs for field-induced tunnel formation can be conceived to exploit this behavior, depending on the choice of the spring-back mechanism and, in turn, on the selection of a stable configuration in the absence of applied fields.

One possible design, utilizing demagnetization effects, is the following. A substrate matching the martensitic variant with c-axis orthogonal to the film (i.e. a (001) film) is cut as a rectangle elongated along [100]. Using techniques described above, a single crystal film of variant 3 of martensite is grown epitaxially. After deposition, a channel parallel to [010] is back-etched through the substrate as shown in Fig. 3. Note that the interfacial Eq. (3) is satisfied with $\hat{\boldsymbol{e}} = [010]$, $\mathbf{Q} = \mathbf{I}$, $\mathbf{F} = \mathbf{U}_3$, and $\mathbf{G} = \mathbf{U}_1$.

In addition to the usual sources of energy associated with martensitic phases, there is also in this alloy a demagnetization energy arising solely from the state of magnetization. The demagnetization energy favors in-plane magnetizations parallel to the long axis [100]. This magnetic configuration induces a contraction in the portion of the film released from the substrate. This is the stable configuration in the absence of applied fields, which should then be fixed to a support. Application of a magnetic field orthogonal to the film will then induce an extension in the [100] direction, causing the film to bulge out as shown in Fig. 3.

Incidentally, Fig. 3 shows the case that (i) the film is so thin that exchange effects dominate; and (ii) anisotropy energy is larger than demagnetization energy. In this case the magnetization in the part of the film that adheres to the substrate is expected to be normal to the film, as shown. In thicker films but still with high anisotropy (as in Ni_2MnGa) the magnetization on this part of the film would be expected to exhibit 180° walls with magnetization up–down–up. However, this does not affect the deformation and hence the compatibility conditions.

5.2. $PbTiO_3$

A closely related idea is proposed for the tetragonal phase of the ferroelectric $PbTiO_3$, and the orientation is in fact as shown in Fig. 3 except the tunnel is inflated without the applied field and flat in its presence. Tetragonal $PbTiO_3$ is polarized along the c-axis, and this direction is elongated ($c/a = 1.065$ [9]). Tetragonal c-axis films (film normal $(001)_t$) can be grown on various substrates including $KTaO_3$ and MgO (e.g. [9]); the polarization is now perpendicular to the film. After deposition, a strip parallel to [010] is released; electrostatic energy favors the polarization to be parallel to [100] in the released part of the film. This causes the film to elongate in the [100] direction and bulge up like a tunnel. Application of an electric field perpendicular to the film (i.e. parallel to [001]) causes the polarization to rotate to [001] in the released part causing the film to collapse to the flat configuration.

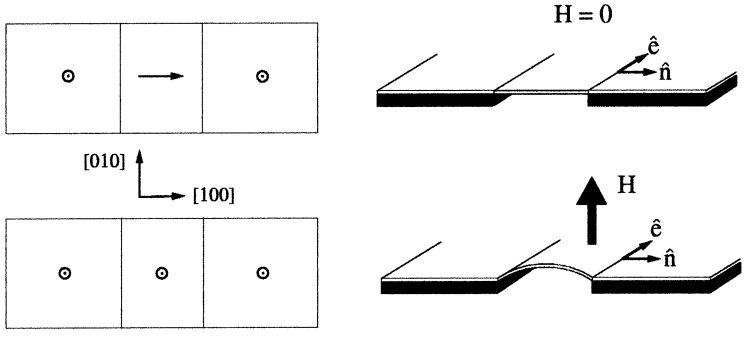

Fig. 3. Field-induced tunnel.

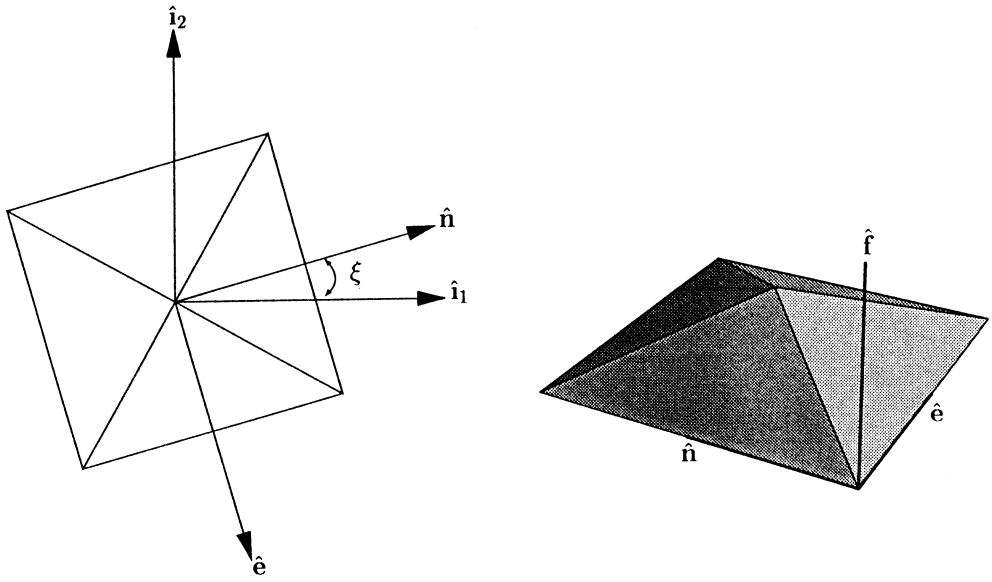

Fig. 4. The tent microstructure.

Further, in contrast to Ni_2MnGa, by patterning electrodes onto the part of the film that adheres, one could avoid the possible presence of the 180° walls mentioned above, which would likely improve reliability.

6. Tents

6.1. Cu–Zn–Al

This alloy is an ideal candidate for thin film shape memory applications for several reasons: first, an austenite–martensite interface is possible for every film orientation; and second, the tent microstructure is possible in films with [001] orientation. An example is shown in Fig. 4 for Cu-17at%Zn-15at%Al. The indenter needed in order to create the tent must have a specific orientation, angle $\xi = 15.6°$, with respect to the crystallographic axes $\hat{\mathbf{i}}_1 = [100]$ and $\hat{\mathbf{i}}_2 = [010]$ of the cubic unit cell. Some other properties of this tent are; the angle between the sides of the tent and the original plane of the film is 24.2°; and for an indenter 1 mm in width, the height of the apex of the tent is 450 μm and the volume under the tent is 0.6 $mm^3 = 0.6$ μl. Similar tent microstructures are possible in certain alloys from the systems Cu–Zn, Cu–Zn–Ga, and Cu–Al–Ni to name a few, which undergo either the B_2 to 9R transformation or the DO_3 to 18R transformation. In addition, tunnel microstructures are possible in films of these materials as well. Details can be found in reference [6].

6.2. $PbTiO_3$

A very similar tent microstructure can also be formed by tetragonal c-axis films of this ferroelectric material. We deposit the film as before and release it on a square whose sides are oriented in the [100] and [010] directions ($\xi = 0°$ in Fig. 4). The released portion is predicted to bulge up like a tent and application of an electric field as before will collapse it to the flat film.

Finally we note that martensitic Ni_2MnGa films are unable to form tents since we have contraction rather than elongation along the c-axis.

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