THIN FILM METALLIZATION
FOR MICRO-BIMETALLIC ACTUATORS

By

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In this study, eleven different thin film metallization systems were evaluated for use in micro-bimetallic actuators for microelectromechanical structures. These films were evaporated or sputtered onto silicon wafers. The film stress and stress relaxation were determined by measuring changes in the wafer curvature. The phases and microstructure of these films were evaluated with, scanning electron microscopy, transmission electron microscopy, Auger electron spectroscopy, electron probe micro-analysis, X-ray diffraction and line shape analysis, and atomic force microscopy.

Bimetallic actuator may be operated to generate either force or displacement. The displacement mode is dominated by the coefficient of thermal expansion while the force mode is a function of both Young's modulus and coefficient of thermal expansion of the active layer material. In both modes the maximum displacement or force is determined by the material's yield strength. A figure of merit was developed to aid in material selection.

The 5052 aluminum alloy films showed that solid solution strengthening can double the yield strength of a thin film. The T201 aluminum alloy films showed that precipitates can increase yield strength by 2.5 times. The 2090 alloy film oxidized during
the first heating. Based on isothermal stress relaxation data and changes in the microstructure of the 5052 and T201 alloy thin films, two mechanisms involving logarithmic creep have been postulated to cause stress relaxation. One mechanism is movement of dislocations in slip systems that terminate at the surface while the other is dislocations moving in slip systems that terminate at grain boundaries.

Copper gold intermetallics films oxidized and plastically deformed before the order-disorder transformation occurred, but showed that ordered intermetallics have a lower stress relaxation rate than the solid solution phase. The Al₃Ti films showed no stress relaxation at 450°C, plastically deformed only above 500°C, and had limited oxidation up to 800°C.

Nickel, copper, titanium, and manganese films all oxidized on their first heating to 350°C. The copper film also oxidized at 50°C over 48 hours. Calculations also showed that the passivation oxide on aluminum alloys can significantly reduce performance a bimetallic actuator. Thus oxidation resistance is a significant requirement for materials for thermal actuation.
CHAPTER 1
INTRODUCTION

Motivation and Objective

The miniaturization of electronics has led to what is now called the information age. More and faster electronics packaged in ever smaller volumes allow massive information processing and exchange. Information processing systems are, however, limited by the devices that allow them to perceive and affect the physical world. Sensors and actuators have been connected to computers and control systems from the early days of computing, but these sensors and actuators have been, until recently, large electromechanical devices. Researchers have begun to miniaturize electromechanical devices using the technologies developed for microelectronics [Hog96]. These new micro sensors and actuators have created a new class of devices called MEMS, microelectromechanical systems [Mas95, Fra97, Ang83, Bea96, Mad97]. Integration of MEMS sensors and actuators is enabling the development of mechanical, chemical and biological “smart systems” that are able to interact with the physical world.

MEMS have already become a significant industry. Yearly sales are in the billions of dollars and the market continues to grow rapidly [Mas95]. This market is currently dominated by pressure sensors and accelerometers. The miniaturization of pressure sensors has reduced sensor cost to the point that in medical applications the sensors can be discarded after a single use. Accelerometers are predominately used to determine when to deploy automobile air bags. Micro actuators have yet made as many inroads into industry. Currently the biggest application of MEMS actuators is for ink jet print heads.
The market of MEMS actuators will continue to develop as actuators are needed to produce a truly “smart system” that can not only monitor processes but also control them. However, additional research and development are needed to improve the performance of micro actuators, and this is the general focus of this work.

Micro actuators have been designed based on a number of physical properties including electrostatic, electromagnetic, piezoelectric, magnetostriction and thermal activation (bimetallic, shape memory alloys, and thermopneumatic) [Mad97]. Table 1.1 shows a comparison of the different actuation techniques and their differences in performance. While all of these techniques have advantages for particular applications, this study focuses on the thermally activated bimetallic actuator. Bimetallic actuators are of interest because they can produce a relatively large force or displacement, the force is relatively constant throughout the travel of the actuator and bimetallic actuators are easily manufactured using semiconductor processing technology. Micro bimetallic actuators have already been employed in commercially available products [Mad97, Jer94]. Figure 1.1 shows a bimetallic actuated micro valve produced by EG&G IC Sensors produced by

Figure 1.1: SEM image of an EG&G IC Sensors bimetallic thermally actuated micro-valve.
Table 1.1: Comparison of actuation principles [Bel97].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bimetallic</th>
<th>Electrostatic</th>
<th>Piezoelectric</th>
<th>Electromagnetic</th>
<th>Thermo-hydraulic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Force per 1 mm², N</td>
<td>High (0.1..1)</td>
<td>Low (10⁻⁷..10⁻⁴)</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Deflection, mm</td>
<td>High (0.01..1)</td>
<td>Low (10⁻⁴..10⁻⁵)</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Work per cycle per 1 mm², J</td>
<td>High (10⁻⁷)</td>
<td>Low (10⁻³)</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Frequency range, Khz (limiting factor)</td>
<td>Low 0.1-100 (Heat Transfer)</td>
<td>(Mech. Resonant frequency)</td>
<td>High</td>
<td>(Mech. Resonant frequency)</td>
<td>Low (Heat Transfer)</td>
</tr>
<tr>
<td>Voltage, V</td>
<td>Low (3..12)</td>
<td>High (100..300)</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
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<tr>
<td>Current, mA</td>
<td>High (0.1..10)</td>
<td>Low (10⁻⁴..10⁻⁵)</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Power Consumption, W</td>
<td>High (10⁻⁴..0.1)</td>
<td>Low (10⁻³..10⁻⁴)</td>
<td>Low</td>
<td>High</td>
<td>High</td>
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<tr>
<td>Efficiency, %</td>
<td>0.01 .. 0.5</td>
<td>0.001..0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Size: Length, mm</td>
<td>Small (10⁻²..1)</td>
<td>Small</td>
<td>Large</td>
<td>Large</td>
<td>Large</td>
</tr>
<tr>
<td>Width, mm</td>
<td>Small (10⁻³..0.1)</td>
<td>Small</td>
<td></td>
<td></td>
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<tr>
<td>Additional requirements</td>
<td>High Voltage</td>
<td>High Voltage (Material Compatibility)</td>
<td>Magnetic field (magnets)</td>
<td>Media separation</td>
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<tr>
<td>Cost</td>
<td>Low</td>
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aluminum metallization on silicon. Even though silicon is not a true metal, this structure is still referred to as a bimetallic actuator.

The objective of this research is to improve the performance of micro-bimetallic actuators and broaden their range of operating parameters (stress, displacement, temperature range and stress relaxation) by identifying better or improve the materials of construction. In order to understand how to improve the performance of the bimetallic actuator, it is important to understand how the device works. A bimetallic actuator is made by bonding together two different materials that have a large difference in thermal expansion, such as aluminum and silicon, to create a bimetallic strip or spring that is heated or cooled. Upon heating, the material with the larger coefficient of thermal expa-
Figure 1.2: Diagram of a bimetallic strip, showing how the difference in thermal expansion between the active layer, aluminum, and passive layer, silicon, causes the bimetallic strip to bend.

Aluminum \hspace{1cm} \text{Active Layer}

Si\text{licon} \hspace{1cm} \text{Passive Layer}

Aluminum \hspace{1cm} \text{Silicon Expansion}

Silicon \hspace{1cm} \text{Aluminum Expansion}

20°C

100°C

sion, called the active layer, expands more than the material with the smaller coefficient, called the passive layer (see Figure 1.2). As these two materials are bonded together, a shear stress develops between the layers due to the different rates of expansion, producing a force that causes the structure to bend. Upon cooling the reverse processes occur and the bimetallic strip returns to its original position, or deflects in the opposite direction with continued cooling. The geometry may be a disk, cantilevered beam, or more complex geometry.

While the current generation of bimetallic actuators works well for a number of applications, their use could be significantly expanded by improving the position and force stability of these actuators and increasing the operable ambient temperature limit from 75°C to 500°C. Force and position stability have been found to be a problem in
some bimetallic actuators such as the one shown in figure 1.1. It is difficult to maintain a constant flow from these valves over extended periods of time. The opening of the valve decreases with time. Force and position instability in bimetallic actuators are caused by a relaxation in the shear stresses between the active and passive layers of the bimetallic strip which in turn reduces the force bending the structure. Figure 1.3 shows a cross sectional diagram of a bimetallic actuated micro-valve and the effects of stress relaxation on the valve operation. The inability to maintain a constant force or position for extend periods of time complicates the usefulness of the device. These limitations result primarily from creep in the active metal layer of the bimetallic actuators. Thus, improvements can be achieved through the identification and or development of better metal thin films.
While improvement of materials for bimetallic actuators may at first seem to be a narrow subject, it requires examining much broader materials questions. How can a thin metal film be strengthened? What are the atomic mechanisms responsible for the stress relaxation in thin films? What materials are sufficiently chemically stable at elevated temperatures to be useful? These questions are of general interest to the entire MEMS field because micro-machines use thin metal films as structural components, and structural failure and environmental stability are concerns in any mechanical device. Also, the continued reduction of interconnect widths in microelectronic integrated circuits lead to greater stresses in thin metal lines that may fail due to stress induced voiding (SIV) [Bow74]. Therefore, this research will examine questions of interest to many disciplines.

The temperature change of an actuator is normally accomplished by resistive heating. The passive layer of most micro-bimetallic actuators is silicon, and a resistive heater is easily made by doping the silicon. A thin silicon oxide layer grown on the silicon is all that is needed to keep the resistive heater from shorting to the active layer. Cooling is accomplished by conduction of heat to the valve body and the surrounding structure. The thermal masses of micro-bimetallic actuators are so small that they can be cycled rapidly. Other heating and cooling methods could be used, such as a Peltier element [Cad60]. In the present work, the mechanisms to change the temperature of the bimetallic actuator is not of direct interest. Instead the present research is concerned with the mechanical and thermal properties of the materials in the bimetal strip, and how they affect actuation. Optimization of the performance of bimetallic strips will be the focus, which directly translates into optimizing the performance of a bimetallic actuator.

Scope of Present Work

The three specific objectives of the present work are as follows. (i) The first objective is to determine the effectiveness of different strengthening techniques for thin
film metallization. There are a number of techniques used to increase the yield and ultimate tensile strength of bulk metal alloys, but their effectiveness in thin films has yet to be determined. Increased yield strengths of the metal thin films would increase the maximum force and displacement produced by an actuator, and could increase force and displacement stability. (ii) The second objective is to evaluate use of materials at elevated temperatures. The primary requirements for elevated temperature applications are high strength over the operation temperature range and resistance to creep and oxidation. (iii) The third objective is to identify the mechanism responsible for isothermal stress relaxation in thin films. It is this relaxation that causes the force and position instability seen over extended time periods.

To meet these objectives, eleven different materials were deposited and evaluated. The evaluation focused on determining the material’s strength, environmental stability and rate of stress relaxation. For those materials that showed promise and to understand the underlying mechanisms responsible for the stress relaxation, the morphology and microstructure of several samples were examined. The materials that were evaluated fall into three groups: (i) aluminum alloys, (ii) elemental metals, and (iii) intermetallics. The aluminum alloys were used to identify the mechanisms responsible for isothermal stress relaxation, and to determine the effectiveness of the different strengthening techniques. The elemental metals and intermetallics were evaluated at elevated temperatures. Some of the intermetallics also exhibited ordering and non-linear thermal properties. The evaluation of several materials systems allowed a wide variation in properties and therefore provided significant insight into the materials requirements for MEMS devices.

The organization of this dissertation is as follows. Chapter 2 is a review of the literature pertinent to this study. The experimental procedures used to deposit, test, and analyze the samples are presented in chapter 3. Chapter 4 contains the results of these tests and analyses. The results are discussed in chapter 5. The conclusions are summarized in chapter 6 and suggestions for future work are presented in chapter 7.
CHAPTER 2
LITERATURE REVIEW

Introduction

Thin film metallization for bimetallic actuators are the focus of this research, therefore a number of topics need to be reviewed. The first topic is the theory of the bimetallic strip. In examining literature, the concern is to determine how the different materials properties affect the performance of a bimetallic strip. With an understanding of the effects of materials properties, improved materials selection can be used to optimize performance. After their identification, the origin and interdependence of these properties can be discussed using the theories of atomic bonding and thermal expansion. In addition, there are a number of processes that may affect the metallization of a bimetallic strip, such as creep, plastic deformation, and oxidation. Lastly, these bimetallic actuators are manufactured with thin film technology and the effects of these processes are discussed. There is no perfect material for use in all bimetallic actuators, since different applications require different properties. With an understanding of the interdependence of the different materials properties, the tradeoffs that are needed for any given application can be better selected.

The Bimetallic Strip

The formulation of the bimetallic strip problem was first reported, in part, by G. Gerald Stoney [Sto09]. Stoney determined the relationship between curvature and stress in a bimetallic strip. S. Timoshenko [Tim25] then derived the equations for displacement
and force of a bimetallic strip versus change in temperature. Lastly, Townsend [Tow87] generalized the equations for a multi-layer structure.

The formulation and solution of the bimetallic strip problem are dependent on the geometry and boundary conditions used, therefore no single solution is generally applicable. *Roark's Formulas for Stress and Strain* [You89] provide solutions for many shapes and boundary conditions. This complexity of solutions and lack of solutions for unusual shapes has led to the widespread use of finite element analysis to design bimetallic actuators [Bar94] [Tsa92].

**The Simple Bimetallic Cantilever**

To determine the effects of materials properties on performance, the simple bimetallic cantilever, simply supported on only one end, is examined. The simplifying assumptions made in this case are that the length is much greater than the width or thickness, the materials are perfectly elastic, and the material returns to its original dimension once the load is removed [Mey84]. Figure 2.1 shows a diagram of this case where $E_1$ and $E_2$ are the Young’s moduli, $L$ is the length of the strip, $h$ is the thickness of the strip, $a$ and $b$ are the thickness of the first and second layer, $w$ is the width of the strip, $\alpha_1$ and $\alpha_2$ are the coefficients of thermal expansion, and the curvature of the bimetallic cantilever, $k$, for a given change in temperature, $\Delta T$, is [Tim25]

$$k = \frac{6(\alpha_2 - \alpha_1)(\Delta T)(1 + \frac{a}{b})^2}{h[3(1 + \frac{a}{b})^2 + (1 + \frac{aE_1}{bE_2})(\frac{a}{b})^2 + \frac{bE_2}{aE_1}]}.$$  \hspace{1cm} (1)$$

For the case of both layers of the strip being the same thickness $a = b$ and equal moduli the equation for curvature reduces to [Tim25]
The error induced by assuming the moduli are equal is only three percent for a factor of two change in either material's modulus. Therefore, the primary material's property affecting the displacement in this case is the difference in the coefficients of thermal expansion.

The equation for the restraining force, \( R \), that is needed to keep a bimetallic strip from moving for a given temperature change \( \Delta T \) is the maximum force a bimetallic strip can produce. This restraining force is given by equation 3:

\[
R = \frac{9}{4} \cdot \frac{\left( E_1 + E_2 \right)}{2} \cdot \frac{h^3}{12} \cdot (\alpha_1 - \alpha_2) \cdot \Delta T.
\]  

Thus the force produced by a bimetallic strip is a function of both the thermal expansion and the Young's moduli of the materials.

**The Bimetallic Disk**

To evaluate the effects of materials properties on performance for a more complex case, the bimetallic disk is examined. Due to the complexity of the equation describing
the bimetallic disk the evaluation was performed by calculating and plotting the equalpotential lines for maximum displacement (curvature) and force of a bimetallic disk as a function of Young’s moduli and the coefficient of thermal expansion, as shown in Figure 2.2 [Jer95]. This model is based on a bimetallic strip where the passive layer is silicon and both the active and passive layers are 5μm thick. In agreement with equations (2) and (3) this figure shows that displacement is predominately limited by the thermal expansion of the active layer material. There is some dependence on the Young’s modulus but this occurs only for a modulus lower than that found in most engineering materials. The equal potential line for force shows that thermal expansion is not as significant a factor as in displacement. Therefore, while the relationships shown in Figure 2.2 for a bimetallic disk are far more complex than the relationships determined by equations 2
and 3 for a single fixed cantilever, the trends and limiting materials properties are the same. Displacement in a bimetallic structure is primarily limited by the thermal expansion of the active layer material. In contrast, the force generated by a bimetallic strip is dependent on both the thermal expansion and Young's modulus of the active layer material. These trends and limitations are expected to hold for other configurations as well.

**The Effects of Plastic Deformation**

The assumption that a material performance is perfectly elastic is only valid for a range of applied stresses. Beyond this range of stress the material will not return to its original shape when the stress is removed and the material is said to have undergone plastic deformation [Mey84](see Figure 2.3). Plastic deformation in either layer of a bimetallic device invalidates the relationships in equations (1), (2) and (3), and would reduce the force or displacement produced from the strip. The effects of plastic deformation

![Typical stress strain curve](image-url)
tion can be modeled as a non-linear reduction of the thermal expansion or Young’s modulus of a material. While not considered in the above equations that predict the force or displacement of a bimetallic strip, the stress at which plastic deformation begins, called the yield strength [Ask89, Mey84] (see Figure 2.3) is also a critical materials parameter. A material’s yield strength determines the maximum force it can exert on another layer and in turn may determine the maximum force or displacement a bimetallic strip can achieve.

Therefore, the materials properties of interest depend upon whether the application requires force or displacement. In the displacement mode, the material’s thermal expansion and yield strength are the primary limiting properties. In the force mode, thermal expansion and Young’s modulus both contribute to the force generated by a bimetallic strip, and yield strength is a limiting materials property.

Atomic Bonding

The atomic bonds that hold a material together also determine its thermal expansion and Young’s modulus. There are a number of aspects of atomic bonding that affect these physical properties, and these aspects will be examined in this section. This review is not intended to cover all aspects of thermal expansion, but only those that affect the performance of a material in a bimetallic actuator.

The first aspect of atomic bonding that determines a material’s rate of thermal expansion and its Young’s moduli is the strength of the atomic bonds. Figure 2.4 shows the asymmetric potential energy well that an atom is drawn into when it bonds with another atom [Ask89]. The depth of this potential well determines the strength of the bond. The deeper the potential well, the stronger the bond. A deep potential well normally has a larger $dE/dx$ which is proportional to the Young’s modulus.

The rate of thermal expansion of a material is due to the asymmetry of the potential energy well. The addition of energy to a material causes an increase in vibration of
the atoms. This increase in atomic vibration causes the atoms to move up in the potential well. As the atoms move higher their time-averaged position increases (see Figure 2.4) and the material expands [Tou75]. The deeper the potential well, the smaller the change in the time-averaged position of the atoms for a given increase in temperature, and a lower thermal expansion is observed. The rate of thermal expansion is frequently expressed as the coefficient of thermal expansion, CTE. A material’s CTE is the derivative of its thermal expansion curve, $\Delta L/L$ versus temperature. To a first approximation, the thermal expansion is inversely proportional to the atomic bond strength. Thus, the Young’s modulus and thermal expansion of a material are inversely proportional. Appendix A shows the thermodynamic proof of this relationship.

The second aspect of atomic bonding that affects the rate of thermal expansion and the Young’s Modulus is the directionality of the bonding. The directionality of the bonding results from the type of bonds that form between atoms, the crystallography of
the material, the number of nearest neighbors, the coordination number, and the bond length. Graphite is a good example to illustrate the effects of directionality of bonding. Graphite has a layered structure where the bonds within a layer are strong covalent bonds, but the bonds between atoms in different layers are much weaker van der Waals bonds [Eva79]. This difference in bonding causes the c-plane coefficient of thermal expansion (CTE) to be 2.8x10^{-6}°C^{-1}, while between the planes the CTE is 4.4x10^{-6}°C^{-1}.

In many instances, the directionality of bonding does not change the bond type but still has a major affect on physical properties. Zinc illustrates this point well. The atoms in zinc are bonded into a hexagonal close packed crystal structure, with metallic bonds between all atoms. Along the c-axis the CTE for zinc is 5x10^{-6}°C^{-1}, but along the a-axis it is 65x10^{-6}°C^{-1} [Tou75]. Thus there is a 13-fold difference in CTE between different planes due to the crystallography that is determined by the bonding.

There are other materials with small anisotropy but unexpected physical properties due to unusual crystallographic structure. Manganese is one such metal [Dea52]. While α-manganese has a cubic structure, it does not have a simple face centered cubic (FCC) or body centered cubic (BCC) crystal structure [Ask89]. The unit cell is based on the BCC structure but contains 58 atoms in 29 pairs [Dea52]. The CTE for manganese is 22x10^{-6}°C^{-1}, almost double what would be expected for a material with a melting temperature of 1244°C. In comparison, beryllium melts at 1278°C and has a CTE of only 12x10^{-6}°C^{-1} [Wea76].

The directionality and crystallographic structure of a material are not always static. Pure iron undergoes two allotropic transformations between solidification at 1538°C and room temperature. Iron first solidifies into a BCC structure at 1538°C, converts to an FCC structure at 1394°C, and then converts back to a BCC structure at 912°C [Kra90]. At each allotropic transformation, there is a significant change in thermal expansion and other physical properties. Discontinuities in a material’s CTE could be useful in a bimetallic actuator. Unfortunately the transitions in iron are far above the
Figure 2.5: Linear thermal expansion for intermetallic compound CuAu and Cu₃Au. The discontinuity in thermal expansion is due to the order-disorder transion of these compounds [Tou75].

temperature currently being considered for practical devices. However, transformations are used in shape memory alloy actuators [Mad97].

Another change in bonding that can significantly affect properties is the order-disorder transformation exhibited by some intermetallic compounds [Tou75]. Intermetallic compounds are made up of two or more elements, A and B. In ordered alloys, the A-B bond may be stronger or weaker than the A-A or B-B bonds and thus there is a driving force to form one type of bond over the other [Cah83]. Ordered intermetallic compound may form directly upon solidification, as in Al₃Ti and NiAl. However, there are other intermetallic compounds that first solidify as a solid solution and then order at a lower temperature. CdMg₃, CuAu₃, CuAu, and Cu₃Au are all examples of materials that undergo a solid phase disorder/order transition [Hov64, Fed58, Cul78, War69]. The
material may undergo a substantial contraction upon ordering (see Figure 2.5). This contraction is due to the ability of the atoms to pack tighter in the ordered phases due to the stronger atomic bonding. This transition may also increase the material’s yield strength, reduce the creep rate, and increase electrical conductivity.

**Plastic Deformation In Metals**

As mentioned above, plastic deformation in either layer of a bimetallic actuator will limit the force and displacement of the actuator. Therefore, the yield strength determines the maximum force and displacement of an actuator. Atomic motion becomes rapid as the temperature of a metal exceeds half its melting point, therefore the homologous temperature, \( T_H \), is defined to be the ratio of the temperature to the melting point of the material in degrees Kelvin. At \( T_H < 0.5 \) dislocation motion is the dominant mechanism of plastic deformation. Inhibition of the motion of dislocations would strengthen the material. This is in contrast to the thermal expansion and Young’s modulus of a material that can not be changed by inhibiting dislocation motion. In addition, many of the methods used to inhibit plastic deformation do not significantly alter the CTE or Young’s modulus of the material. Therefore, improved yield strength can be used to produce a better actuator. In this section, the atomic processes responsible for plastic deformation will be examined, along with methods to inhibit these operations.

The two main processes that take place in a material during plastic deformation are: dislocation movement and multiplication. Movement of dislocations produces a change in shape of the material. However, the dislocation density in an annealed sample is not great enough to produce the observed plastic deformation. Thus the dislocation density is increased during plastic deformation by dislocation multiplication [Ree92, Cah83].

With respect to dislocation motion, they can move through a crystal by either dislocation glide or climb. Dislocation glide occurs when a dislocation moves on a slip
plane and in a slip direction of the crystal [Ree92]. The combination of a slip direction lying along a slip plane creates a slip system. There are a limited number of slip systems and they are determined by the crystallography of the material. Dislocation may not be able to glide in response to an applied force because a slip system is blocked. On the other hand, the stress resolved onto that slip plane in the slip direction may be below the critical value to cause motion of dislocation. This is known as Schmid’s law [Ask89].

The second way for a dislocation to move is by climb, in which it moves between parallel slip planes. Climb allows dislocations to move off blocked slip planes. It occurs by vacancy movement [Ree92], but both the vacancy concentration and movement are very dependent on the temperature of the material [Deh93]. Dislocation climb only becomes a dominant process at high homologous temperature $T_H$. For most metals dislocation climb becomes significant at $T_H>0.5$ and for most intermetallics at $T_H>0.7$. Above these temperatures dislocations may rapidly climb.

The process of dislocation multiplication can occur in many ways. One of the more significant is the Frank-Read source [Ree92] by which dislocation glide can increase the dislocation density. In a Frank-Read source, a dislocation line on a slip plane is pinned or blocked at two points. In response to an applied resolved shear stress the dislocation bows out between these two points and forms an incomplete dislocation loop. A critical stress exists, dependent on the dislocation line length, above which complete dislocation loops form. This mechanism is complicated by the fact that dislocations can pin one another, thus forming more Frank-Read sources. This is one of the reasons that metals harden when they are cold worked, which is known as “work hardening” [Bro82].

There generally exists an inverse relationship between temperature and yield stress independent of the mechanisms responsible for the deformation. For dislocation glide, random thermal excitation helps dislocation overcome the Peierls-Nabarro barrier [Mey84] and thus lowers the yield stress. The effects of temperature on dislocation
density and mobility have already been discussed and these effects also lead to reduced yield stress with increased temperature. While an inverse relationship exists between yield strength and temperature it is a non-linear function specific to each material.

The stress at which plastic deformation begins is also dependent on whether the force is applied in tension or compression. There is no general relationship between the compressive and tensile yield strength and most yield strength data for metals are for tensile yield strength. As the thin films in a bimetallic actuator can be in tension or compression the variation in the compressive versus tensile yield stresses could be significant.

Lastly, the crystallographic texture (which is the preference for one crystallographic orientation) of a material also affects its yield strength [Mey84, Bro82]. Baldwin [Bal46] showed up to 30% change in tensile yield strength based on the direction of the applied stress relative to the texture of rolled copper sheet.

**Creep in Metals**

In the preceding section the mechanisms responsible for the rapid plastic deformation of materials in response to an applied stress were examined. However, materials continue to plastically deform in response to applied stresses over extended periods of time (from minutes to years). Time dependent plastic deformation is known as creep. In this section the different types of creep and the mechanisms responsible for the time dependent plastic deformation will be discussed.

Figure 2.6 [Cah83] shows the four major types of creep that occur in materials as a function of the homologous temperature versus the resolved stress, $\sigma$, normalized by the shear modulus, $\mu$.

At stress levels below which dislocation can move ($\sigma_{\text{cross}}/\mu < 10^{-8}$) anelastic creep occurs. In anelastic creep, interstitial atoms move to interstitial sites that have been elongated by the applied stress [Cah83]. This movement of interstitial atoms creates a
small deformation of the material that is not permanent as the interstitial atoms will randomly redistribute once the applied force is removed. Since the materials examined in this study do not contain a significant percentage of interstitial atoms, this creep mechanism is of little concern.

Herring-Nabarro-Coble creep [Her50, Cob63] produces a deformation in the material by a net mass diffusion. In the Herring-Nabarro model, a net flux of vacancies move away from the axis of the applied stress produces a net flux of atoms to the axis of applied tensile stress, thus elongating the sample in the direction of the applied force. This mechanism of creep requires a high concentration of vacancies with high mobility, and only occurs at $T_H > 0.9$ [Cah83]. Coble expanded this idea of bulk diffusion to include the diffusion of atoms along grain boundaries. Grain boundary diffusion has a lower activation energy than bulk diffusion because a grain boundary is an array of
dislocations. This lower activation energy for diffusion slightly reduces the temperature at which the creep rate is significant. Coble creep still requires a $T_H > 0.85$ [Cah83] to become active and is therefore not of concern in this study.

The third type of creep is low temperature or logarithmic creep. In this mechanism, deformation occurs through dislocation multiplication, glide and climb. However, the sources for dislocation multiplication become exhausted. Therefore the creep rate starts at some initial higher value and logarithmically approaches zero as the number of mobile dislocations approaches zero [Cah83]. The rate of logarithmic creep is not a function of the applied stress, since the rate limiting steps are dislocation climb or multiplication which are driven by random thermal excitations. This type of creep is typically observed at low temperatures ($T_H < 0.5$).

The fourth creep mechanism shown in figure 2.6 is high temperature or Andrade creep [Cah83]. In this mechanism dislocation glide, climb and multiply in response to the applied force with the help of thermal excitation to overcome the higher activation energies. There are three stages to Andrade creep. In stage one, a stress applied to the sample at a given temperature causes an initial high strain rate that immediately begins to decline. The reason for the declining strain rate is that the sample begins to work harden. After a finite strain, equilibrium is established between the rate of work hardening and the rate of dynamic annealing. Annealing is a heat treatment that eliminates the effects of cold work, in dynamic annealing this processes is occurring at the deformation temperature as described below. Second stage creep is a steady state process that produces a constant strain rate. In the third stage of Andrade creep the sample begins to neck, grain boundary sliding occurs [Mey84] and voids form inside the sample. This reduces the area over which the force is carried thus increasing the stress which increases the strain rate, ultimately resulting in failure. This type of creep is typically observed for $T_H > 0.6$. 
Deformation Mechanism Maps (DMMs)

In the proceeding sections, several mechanisms have been discussed which lead to plastic deformation of metals. H.J. Frost [Fro82] has created deformation mechanism maps (DMM) relating stress, temperature and deformation mechanism. All DMMs are based on numerical models describing the different deformation mechanisms. This model is then used to generate a two dimensional contour plots (temperature and stress axis) that shows which deformation mechanisms are active. These plots are useful in selecting materials for a given application. If the stress and temperature levels for a given application are known, then the deformation mechanisms expected for a given application can be projected. The primary limitation to the use of DMMs is that detailed data required by the model are not available for all materials and conditions.

DMMs have been used to explain deformation and stress relaxation in thin film metallization [Kol86, Fro92, Tho93, She96]. These models have been able to accurately predict plastic deformation in thin films at high strain rates, but none of these DMMs were able to accurately predict the rate of isothermal stress relaxation. However, only bulk material properties are currently available to use in DMMs.

Annealing

In the preceding sections the mechanisms responsible for plastic deformation at high and low strain rates were discussed. However, since stress relaxation is of concern in this study, other mechanisms that transform metals must be considered, such as annealing.

Annealing is the process by which the stored energy in cold worked metal is released. When a metal is cold worked, that is plastically deformed below the temperature at which dislocation climb becomes significant, part of the deformation energy is stored in the metal as defects and lattice distortion [Ree92]. Hundreds of Joules per mole can be stored in a metal that has been heavily cold worked. The annealing process re-
leases this stored energy by reducing the defects, lattice distortion and residual stress. In the case of a thin metal film deposited on a substrate, the shear stresses between the film and the substrate may also distort the lattice and induce defects. The process of annealing should result therefore in stress relaxation.

There are four stages in annealing: recovery, recrystallization, grain growth, and secondary grain growth [Ree92]. For this study the first three stages are of most interest since they dominate the release of stored energy from cold work.

In recovery there is little change in the mechanical properties of metal, but the electrical resistance of the metal decreases. This reduced electrical resistance indicates that random dislocation tangles have begun to polygonize [Cah49] (see Figure 2.7). The polygonization of the dislocation tangle into subgrain boundaries reduces the free energy of the system. Ordering also reduces the number of electron scattering centers, resulting in a lower electrical resistivity. No dislocations are destroyed, therefore the yield stress does not change.

Figure 2.7: Distribution of dislocations in a bent crystal (a) before polygonization, (b) after polygonization and subgrain coalescence.
Polygonization and subgrain coalescence also lead to the second stage of annealing, recrystallization. In recrystallization new unstressed crystals nucleate and grow to replace the strained, disordered cold worked grains. One theory on the formation/nucleation of these new unstrained crystals is that subgrains coalesce to form high angle grain boundaries leaving an unstrained crystal in their wake [Cah83]. The difference in energies provides the driving force for the high angle grain boundary to move outward, consuming the strained crystals until they are all consumed. This is the growth stage of the annealing process and it is at this point that the energy of cold work has been removed and therefore stress has been relaxed.

Grain growth also affects the size and distribution of precipitates within a sample [Bro82]. Precipitates strain the matrix of the material in which they exist. There is therefore a driving force for precipitates to coalesce and reduce the strain in the matrix. In age hardened alloys this is called "over aging" as it reduces the yield strength of the material. This process would also produce a relaxation of stress.

**Strengthening of Bulk Metals**

In the preceding sections', mechanisms responsible for stress relaxation in thin metal films have been reviewed. We will now review the methods used to strengthen bulk metals to determine which could be used to strengthen thin metal films in bimetallic actuators. There is limited information on strengthening of thin films.

The key to strengthening any non-brittle metal is to inhibit dislocation glide. This can be done in several ways. First, the matrix of the metal can be affected to increase the force needed to move a dislocation in a slip system. This can be done a number of ways, including straining the matrix with cold work or solid solutions. Second, hard particles or phases can be placed in the matrix of a material that will physically block the movement of dislocations. There are five commonly identified strengthening mechanisms that use
one or both of these general approaches. Also, many commercial alloys use two or more alloying elements and several of the five strengthening mechanisms to ensure that several means of inhibiting dislocation motion are used. The five strengthening methods used in bulk alloys and the means by which they inhibit dislocation motion are described below.

The first strengthening method is solid solution strengthening, in which soluble alloying elements are added to the host metal [Cah83]. Since most alloying elements have an atomic size different from the host element, the matrix of the metal is strained, and inhibits dislocation glide. The more the host matrix is strained, the harder it is for dislocations to move. However, alloying elements generally have limited solubility in host metals which limits the strengthening that can be achieved. For most of the commonly used engineering metals, the solubility and strengthening effects of many alloying elements have been determined experimentally. The Metals Handbooks Volumes 1 and 2 [Bak97] contain most of this information. For more unusual materials, the Hume-Rothery [Ree92] rules for substitutional solid solution strengthening are helpful.

Solid solution strengthening has a number of properties that make it unique compared with the other strengthening mechanisms. First, the solute atoms are in equilibrium with the host matrix atoms. Thus there are no driving forces to change the atom distribution in the metal and solid solution strengthened alloys are expected to be more stable at elevated temperatures than alloys using some of the other strengthening techniques. This is of particular importance for this study since materials will be used at elevated temperatures. Secondly, a solid solution strengthened material is expected to be homogenous. Thus there is limited possibility that electrolytic half cells would cause corrosion.

The second strengthening mechanism is to reduce grain size. Dislocations generally pileup at the grain boundaries as they cannot cross them. The strength of a material has been found to be proportional to the inverse of the square root of the average grain
size [Mey84, Ree92]. This relationship is called the Hall-Petch relationship. A potential limitation to using this strengthening technique is that grains coarsen at elevated temperatures ($T_h > 0.6$), and this generally reduces the strength of the material.

The third strengthening techniques is work hardening. When a metal is cold worked (i.e. worked below a temperature at which annealing occurs) the dislocation density increases greatly. With an increased density, dislocation will be pinned by other dislocations, which limits dislocation slip. Work hardening can produce seven fold increase in yield strength for pure aluminum. Fully annealed aluminum has a yield strength of 15-20 MPa that increases to 50-60 MPa for 40% cold work and 100-120 MPa for 90% cold work [Bak97]. A concern with work hardening is that the material will soften as dislocations climb at elevated temperatures during recrystallization.

The fourth way to strengthen some materials are by a martensitic transformation [Kra90]. This type of transformation occurs only in a few alloys and ceramics. It is widely known and used in ferrous alloys, but does occur in some copper, aluminum and titanium alloys. The martensitic transformation is a diffusionless non-equilibrium process that occurs by a coordinated shear displacement of atoms. This transformation stresses the matrix of the material which inhibits dislocation motion. The use of martensitic transformations to strengthen alloys is limited because there are few non-ferrous alloys which exhibit them [Pet70]. In addition, a martensitic transformation leads to a non-equilibrium state so there is always a driving force to transform to a lower strength phase.

The fifth way to strengthen a metal is by precipitation or multi-phase hardening. Alloying elements are added above their solubility limit in a host and precipitates form out of the solid solution to block dislocation motion [Bro82]. In certain cases, a fine ceramic powder is added to a molten metal in place of an alloying element to provide the particles in a modification called dispersion hardening. This leads to improved thermal stability of the alloy. For the greatest precipitation hardening, a large number of small
precipitates should be uniformly distributed throughout the host matrix. Thermal stability is a concern at elevated temperatures since precipitates may coarsen (over age) resulting in a weakened material.

The presence of a second phase can also strengthen a host matrix by straining it. A second phase with a coherent interface to the host matrix will increase the strain in the matrix. A coherent interface does not an array of dislocation between the precipitate and the matrix [Bro90]. Thus, in addition to blocking dislocation motion, a coherent precipitate strains the matrix, increasing the force needed to move a dislocation. Thermal stability is a concern, as precipitates may grow by thermally activated diffusion and the coherent interface may be lost. The loss of the coherent interface substantially reduces the strength of the alloy.

**Ordered Intermetallic Compounds**

Ordered intermetallic compounds [Cah85] are of interest in this study because they are noted for high strength at both room and elevated temperatures with good resistance to creep and oxidation [Wes95]. There are several reports on the use of intermetallics at high temperatures in jet engines [Lim97]. The basic structure of intermetallics was discussed above in the section on thermal expansion. The mechanical properties are discussed below.

Intermetallics are a class of materials with structures and properties between pure metals and ceramics [Pop87]. The general composition on an intermetallic is $A_xB_y$ where $A$ and $B$ are metallic elements and $x$ and $y$ are normally small integers. This more complex composition creates a more complex crystallographic structure which in turn make dislocation movement more difficult. There are several reasons for this. First, the number of atomic distances a dislocation has to move to reach an equivalent crystallographic site is much greater. In a simple AB intermetallic a dislocation has to move two atomic distances as compared with one atomic distance for a non-ordered metal. In many
instances a dislocation will break into pairs of partial dislocations which only move one atomic distance forming an anti-phase boundary [Bro82]. The creation of an anti-phase boundary requires energy and increases the critical resolved shear stress for dislocation glide. In a normal metal a dislocation must break A-A bonds and then reform them to move. In an intermetallic a dislocation must break the stronger A-B bond to move. Once the A-B bond is broken the weaker A-A and B-B bonds form (the anti-phase boundary), which then have to be broken to form the new A-B bond. This process requires more energy, and thus intermetallics have high yield strengths.

The more complex structure also inhibits creep. The self diffusion rate in intermetallics is unusually low [Pop87] due to the large distance between equivalent site, and a high activation energy for this process. As the creep rate for a material is proportional to the rate of self diffusion [Cah83], intermetallics have a low creep rate.

Some intermetallics are also resistant to oxidation. Oxidation resistant intermetallics form an adherent passivating oxide such as $\text{Al}_2\text{O}_3$ on compounds of aluminum, nickel and titanium.

A concern in using intermetallics in bimetallic actuators is their sensitivity to composition fluctuations. In AlNi, as little as 0.5% change in the composition of the intermetallic can cause dramatic changes in the strength of the metal [Lim96]. Therefore, the compositional stability of any intermetallic compound should be tested before selection.

**Thin Films**

Thin films have a number of unique properties versus their bulk counterparts. Since the materials examined in this study are use as thin films in bimetallic actuators, an understanding of their properties is needed. There are three primary reasons for the unique properties of thin films. First, thin films are deposited onto a substrate, resulting
in substrate-thin film interactions. Second, the surface area-to-volume ratio for a thin film is orders of magnitude higher than for a bulk material, so surface energies and kinetics play a much greater role. Last, the techniques used to produce thin films are very much different from the techniques used in the processing of bulk metals, which affects their microstructure.

There are at least three common categories of thin film deposition processes: chemical vapor deposition (CVD), physical vapor deposition (PVD), and electroplating [Ohr92]. In this study we have only used physical vapor deposition methods consisting of sputtering or thermal evaporation.

In all physical vapor deposition (PVD) processes, a vapor of the source material is created and condensed on solid surfaces, including the substrate of interest. All PVD is done in a high vacuum chamber so that the material vapor can travel from the source to the substrate without reacting with atmospheric gases. In thermal evaporation, the source material is simply heated until it vaporizes, a very simple and clean process useful to deposit single element films. The vapor pressure of different material varies so greatly that the composition of an alloy can not be maintained with thermal evaporation [Ohr92]. In the sputter deposition processes, an inert gas, normally argon, is ionized and ions are accelerated into the source material or target. When the inert gas ion strikes the target atoms, its momentum is transferred and by development of a momentum cascade, some of the target atoms are ejected from the surface. The sputter process is based on momentum transfer, therefore the vapor pressure of the target material does not control the rate at which atoms are ejected from the target surface. Sputtering can therefore be used to deposit metal alloys containing a number of elements [Ohr92]. However, differences in composition may be seen between the deposited film and source material [Zhe97].

After being sputtered or sublimed, the vaporized atoms condense and agglomerate to form a film [Sor95]. The morphology of the developing film is primarily determined by the mobility of the condensing atoms [Mac95]. For thermal evaporation, the condens-
ing atoms have little kinetic energy and the surface mobility is primarily controlled by the substrate temperature. Based on this, Movchen and Demishin [Kra90, Thor74] developed a model that predicts film morphology based on the homologous temperature of the substrate (Figure 2.8). In the Movchen and Demishin model, the film morphology is divided into three zones. In zone 1 ($T_H < 0.3$) the adatom mobility is so low that tapered crystals form with voids between the crystals. In zone 2 ($0.3 < T_H < 0.5$) the adatom mobility is great enough that most of the voids fill in and columnar grains form. In zone 3 ($T_H > 0.5$) the mobility is high enough that nearly equiaxed crystals form.

In the sputtering process, the kinetic energy of the condensing atoms can be controlled by the gas pressure and by biasing the substrate [Win92]. The effects of substrate temperature and gas pressure have been studied by J.A. Thornton [Tho74], who developed a model to predict the morphology of sputtered deposited films (see Figure 2.9). Thornton did not divide the sputtered morphology into zones as Movchen and Demishin did. There is some correlation between these two models as Krauss illustrated in figure 2.9 [Kra90]. It should also be noted that post deposition annealing of a thin film may cause the microstructure to develop similar to that which would have developed had the film been grown at that same temperature [Mac95, Kno91].
During the deposition process and post deposition annealing, thin films can develop a crystallographic texture [Mac95, Kno95]. There are two competing processes responsible for the development of the thin film texture. In the growth of a columnar microstructure, even from a melt, the crystallographic planes with the fastest growth cause the elongated axis of the column [Bro94]. In thin films there is also a large driving force to reduce surface energy. So the crystallographic planes that have the lowest surface energy have a thermodynamic advantage over faster growing planes with higher surface energies. The final texture that develops in a thin film is the balance of these two factors.

There are two types of stresses that develop in thin films: intrinsic and extrinsic. Intrinsic stresses are inherent to the deposition process and conditions, while extrinsic stresses are due to the difference in the thermal expansion of the film and substrate. Extrinsic stresses cause actuation of the bimetallic element.

Intrinsic stresses develop during the deposition process due to limited adatom mobility [Mac95]. This limited mobility causes the formation of voids and vacancies in the film. Voids tend to collapse and form grain boundaries. Vacancies migrate to grain
boundaries and are destroyed. This causes the film to attempt to contract, but instead it may develop a state of biaxial tensile stress because it is attached to a rigid substrate. In sputter deposition it is possible to increase the kinetic energy of the sputtered atoms, by reducing the sputter gas pressure or biasing the substrate. Under bias, ions may penetrate the first few layers of the deposited film. This “atomic peening” can reduce the intrinsic tensile stress and even produce a compressive stress [Mac95]. However, atomic peening injects a large number of trapped vacancies and implants gas [Mac95]. If the film is heated to a temperature where vacancies or gasses are mobile, they will migrate to the grain boundaries, be destroyed or evolved, and change the stress back to tension [Tow87].

In MEMS it is often desirable to have a residual stress near zero at room temperature. This allows for greater flexibility of design. While it is possible to achieve low stress by adjusting the sputter parameters, it is sometimes possible to reduce tensile stress by thermal cycling. If the thin film and substrate are thermally cycled to -196 °C (liquid nitrogen temperature) the metal film will normally contract more than the substrate. If the film is ductile, it will plastically deform and upon returning to room temperature, the film will experience a lower tensile stress or even a compressive stress [Bal94]. Unfortunately, elevated temperature cycling of the film will counteract this compressive shift in stress and re-introduce a tensile stress [Bal94].

A primary concern of this study is stress relaxation in the thin film, defined above to be a time dependent change in the state of intrinsic plus extrinsic stress. Stress relaxation changes the force or displacement of a bimetallic actuator, and may be caused by plastic deformation, creep, or diffusional processes including precipitation. The process of plastic deformation and dislocation movement in thin films is restrictive as compared with bulk metals. There are several reasons; first, a thin film is under a biaxial state of stress. Thus dislocations can only glide in slip systems that have a component in the z direction, normal to the film surface, since only these planes have a non-zero resolved shear stress [Nix89]. If the thin film is textured there will even fewer slip systems with a
resolved shear stress greater than the critical value. Second, a dislocation moving along a slip system must nucleate misfit dislocations at the film/substrate interface, which requires additional energy. If a passivating oxide forms on the surface of the film, as in the case of aluminum, misfit dislocations must be created at both interfaces [Nix89], further reducing dislocation glide.

The primary method used to test the mechanical properties of thin films is measurement of stress as a function of temperature. As the thin film expands at a different rate than the substrate, changing the temperature changes the stress in the film. This is an easy and non-destructive way to test a thin film, but it is limited because the stress and temperature cannot be varied independently. Instruments that measure stress in this way include the Tencor Flexus which was used in this study (see description in Chapter 3).
The result of this type of testing is a plot of stress as a function of temperature, shown in Figure 2.10, for sputtered pure Al and Al-1.5%Si-2%Cu. To evaluate stress relaxation the sample can be heated to a temperature and the stress plotted as a function of time.

For bimetallic actuators, a film that shows no hysteresis in stress versus temperature over the range used is desired. Hysteresis in this plot indicates that the film is plastically deforming. Figure 2.10 shows that the metals currently being used to manufacture bimetallic actuators [Jer96], both exhibit significant hysteresis over the temperature range from 20°C to 300-350°C. The pure aluminum shows little strength over 120°C, while the Al-Si-Cu alloy is only slightly stronger and plastically deforms above 170°C under a compressive stress of 50 MPa. The room temperature residual tensile stress for pure aluminum is 150 MPa, while the Al-Si-Cu is 200 MPa. Isothermal stress relaxation tests were also performed on pure aluminum and Al-Si-Cu alloy thin films [Jer96], with both films showing a 15% reduction in stress over 1000 minutes. At 50°C the pure aluminum film was initially under a tensile stress of 75 MPa, while the Al-Si-Cu alloy film was initially under a higher tensile stress of 150 MPa.

There have been only a few studies to examine isothermal, long term stress relaxation in thin films. The first was performed in 1985 by Hershkovitz, Blech and Komem. They identified three modes of stress relaxation in thin aluminum films. The first mode was identified as dislocation glide. The mechanism responsible for the other two modes were not determined. In 1991, Drapper and Hill studied stress relaxation in Al-Si-Cu thin films. They concluded that logarithmic creep was the dominant mechanism responsible for stress relaxation. However, Drapper and Hill assumed a single mechanism was responsible for the stress relaxation and fit their data with a single exponential function, ignoring the conclusions of Hershkovitz, Blech and Komem. The single figure of the data and curve fit in their article showed great inaccuracies between the data and the fit. In 1995 Witvrouw, Proost, Beweerdt, Roussel, and Imec also re-
ported isothermal stress relaxation data from highly tensile stressed Al-Si-Cu thin films. At low temperature (70°C) they attribute stress relaxation to dislocation glide. At higher temperatures (120°C to 140°C) they propose that the dislocations are cutting the Al₂Cu precipitates. From these limited studies, no complete model has been developed to explain isothermal stress relaxation in thin films.

A new mechanism proposed by J. Tersoff for the stress relaxation in epitaxial films is surface roughing [Ter94]. In this new mechanism the surface of the epitaxial layer becomes rough, allowing easy nucleation of dislocations. This mechanism has not yet been tested in polycrystalline thin films.

While strengthening of thin films to reduce stress relaxation and plastic deformation has not been extensively studied, work to reduce failures caused by thermal cycling has been reported. Much of this work was done to improve the reliability of Josephson superconducting devices (SQUID - Superconducting Quantum Interference Device) [Kir80], which were of interest for building ultrahigh-speed computers. These devices operate at temperatures below 10⁶K (-263°C), and need to be able to withstand temperature cycles form 20°C to -263°C. Basavaiah and Greiner found the addition of gold to the lead indium alloy reduced failures, but the mechanisms responsible for the reduction in failures was not determined [Bas77].

**Enviromental Stability of Materials**

Bimetallic actuators may operate in atmospheric gases at elevated temperatures, and the materials of construction must be stable. Environmental instabilities of these films would compromise their physical integrity and cause the device to fail. There are two environment reactions that need to be considered for this application: oxidation and corrosion.

Most metals oxidize, and some self-passivate while others require some protective coatings. This study has focused on metals which self passivate, such as aluminum,
copper, titanium, nickel. For a passivating oxide to be effective it should have the following four properties: high thermodynamic and kinetic stability, slow growth rate, adherence to the metal, and easily form or re-form [Wes95]. The growth rate is of greater importance in thin films as an oxide could consume the entire film. Most passivating oxides generally follow a parabolic growth rate equation given by

$$x^2 = k_p t$$

where $x$ is the thickness of the oxide, $k_p$ is the parabolic-growth-rate constant, and $t$ is time. Aluminum typically exhibits an inverse logarithmic dependence at low temperatures and parabolic at high temperatures. Thus for thin film applications, materials with a low parabolic-growth rate constant are needed, such as aluminum and silicon, for elevated temperature applications. In addition, the formation of an oxide and or a metal-oxygen solid solution will introduce some stress into the metal substrate. This change in stress could affect the force or displacement of a bimetallic strip. This change may be time dependent as can be seen from equation 4.

Corrosion is also a concern because these devices may be operated in moist air where the possibility of a galvanic cell exists. One area where a cell could exist is between the active and passive layers of the bimetallic strip. In this application, there is normally an oxide layer between these two layers of the bimetallic strip that electrically isolates them and so a galvanic cell cannot be formed. Disruption of this oxide would cause this to be a concern. Also, formation of micro-galvanic cells in a two phase alloy, should be tested [Ask89].
CHAPTER 3
EXPERIMENTAL PROCEDURE

Introduction

Eleven different materials were deposited as thin films and analyzed in this study (see Table 3.1). The deposition methods and procedures will be covered in this section. The films were first tested to determine their mechanical properties and the best materials were analyzed further to determine their microstructural and chemical compositions. A number of analysis techniques were used as discussed below.

Table 3.1: Materials examined in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Deposited Thickness μm</th>
<th>Composition or Purity, (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T201 Aluminum</td>
<td>1.3</td>
<td>Al - 4.6Cu - 0.57Ag - 0.36Mn - 0.2Mg - 0.27Ti</td>
</tr>
<tr>
<td>5052 Aluminum</td>
<td>1.3</td>
<td>Al - 2.5Mg - 0.25Cr</td>
</tr>
<tr>
<td>2090 Aluminum</td>
<td>1.3</td>
<td>Al - 2.57Cu - 2.1Li - 0.12Zr</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.8</td>
<td>99.98</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.55</td>
<td>99.99</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.4</td>
<td>99.9</td>
</tr>
<tr>
<td>Copper</td>
<td>0.9</td>
<td>99.9</td>
</tr>
<tr>
<td>Al,Ti</td>
<td>0.4</td>
<td>Al-99.99, Ti-99.99</td>
</tr>
<tr>
<td>Cu,Au</td>
<td>1.3</td>
<td>Cu-99.99 Au-99.99</td>
</tr>
<tr>
<td>CuAu</td>
<td>1.3</td>
<td>Cu-99.99 Au-99.99</td>
</tr>
<tr>
<td>CuAu,</td>
<td>1.3</td>
<td>Cu-99.99 Au-99.99</td>
</tr>
</tbody>
</table>
Thin Film Deposition

The thin films examined in this study were deposited by either sputtering or electron beam evaporation. All the films were deposited on 100mm diameter, [100] oriented, single crystal silicon wafers. The thickness of each film is shown in table 3.1. The wafers used for the aluminum alloy and copper gold intermetallics had a 100 nm thermal oxide grown on them before film deposition. All wafers were cleaned using the following procedure: 5 minute in an ultrasonic bath for each solvent with a de-ionized water rinse between solvent for, trichroloethane, acetone, and methanol, then five minutes in a solution of 75% sulfuric acid and 25% hydrogen peroxide-30% followed by a de-ionized water rinse and blown dry with dry nitrogen.

The aluminum alloy and copper gold intermetallic films were sputter deposited by Sputtered Thin Films, Inc., Santa Clara, CA, using an 8-inch DC magnetron sputter gun running at 5kW of power. The chamber was first pumped down to 2.8x10^-7 Torr, then back filled with argon to a pressure of 8 mTorr. The substrates were heated to 100°C. The aluminum alloy sputter targets were from bulk sheet stock. Copper gold intermetallics were produced by depositing four layers of pure copper and gold in the proper proportion to produce the required composition. Table 3.2 shows the thickness of the individual copper and gold films that were deposited for each of the average compositions.

Table 3.2: Layer thickness deposited for the copper/gold intermetallic films.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Copper Layer Thickness, μm</th>
<th>Gold Layer Thickness,μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₃Au</td>
<td>0.1132</td>
<td>0.4868</td>
</tr>
<tr>
<td>CuAu</td>
<td>0.2465</td>
<td>0.3533</td>
</tr>
<tr>
<td>CuAu₃</td>
<td>0.4059</td>
<td>0.1941</td>
</tr>
</tbody>
</table>
The copper, titanium, nickel, manganese and aluminum-titanium intermetallic films were deposited by electron beam evaporation. The evaporation system contained three Telemark Model 211 single pocket electron-guns in the vacuum chamber. These guns are powered and controlled by a Sloan PAK 12 series 12 kW power supply operated at 10 kV. The deposition rate and total deposited thickness were measured with quartz crystal monitors, either an Inficon XTC or Sycon model 100. The deposition rate was manually controlled and varied between 10 to 15 angstroms per second. The vacuum chamber was pumped down to 5x10⁻⁷ Torr before each deposition. Due to outgassing, the chamber pressure would rise to 5x10⁻⁶ Torr during deposition. The substrates were heated to 150°C +/- 10°C with resistive heaters, manually controlled with a variable transformer.

**Copper Gold Heat Treatment**

The copper gold compounds required a special heat treatment to homogenize the layers and to develop the long range ordered intermetallic structure [Fed58]. These heat treatments were performed in a vacuum of 5x10⁻⁶ Torr or better to inhibit oxidation of the copper. The heat treatments were 12 hours at 500°C to homogenize the film, and 12 hours at 275°C followed by 12 hours at 225°C to develop the long range order. All temperatures changes were ramped at 1°C per minute using an Omega CN3000 controller.

**Stress and Stress Relaxation Measurements**

Stress and stress relaxation in the samples were measured with a Tencor Flexus model 2320. The Flexus 2320 uses an optical lever to measure the curvature of the sample [Tur96]. Stoney’s equation [Sto09], Equation 4, was used to calculate the average biaxial stress, σ, in the film:

\[
\sigma = \frac{E \cdot h^2}{(1 - v) \cdot 6 \cdot R \cdot t}
\]
where $R$ is the curvature of the substrate, $t$ is the film thickness, $h$ is the substrate thickness, $E$ is the Young’s modulus for the substrate, and $v$ is Poisson’s ratio for the substrate.

The silicon substrate’s thickness and curvature were measured before the film was deposited. The curvature of the substrate was then measured after the film was deposited, and the change in curvature is used in Stoney’s equation to calculate the film stress. In addition to measuring stress at room temperature, the Flexus could heat a sample to 500°C or cool it down to -60°C under computer control and measure curvature. The Flexus could also temperature cycle a sample, taking measurements during the cycle to generate a stress versus temperature plot (see Figure 2.10).

The isothermal stress relaxation in aluminum alloy thin films was also measured with the Flexus. To obtain a similar starting condition for different tests, each sample was heated to 350°C at 1°C/minute, held at 350°C for 30 minutes, and cooled back down to room temperature at 1°C/minute. The sample was then taken to the test temperature, at 1°C/minute, and held at the test temperature for forty eight hours. Every 15 minutes the stress in the sample was measured, allowing stress to be plotted versus time (see Figure 3.1). Once the mechanical properties of a film had been measured with the Flexus, the samples was divided for chemical and microstructural evaluation.

**Powder X-Ray Diffraction (XRD)**

Powder x-ray diffraction was used to determine the long range ordering in the copper gold films [War69] and to evaluate crystallite size in the aluminum alloy films [Cul78]. The system used was a Philips APD 3720 x-ray diffraction systems controlled with an IBM-PC type computer running Microsoft windows 3.11 with Philips PW1877 Automated Powder Diffraction software, version 3.6g. X-rays from a copper anode operated at 40 kV and 2 milliamperes with a nickel filter were used.
Figure 3.1: Isothermal stress relaxation in 5052 aluminum alloy sample at 125°C.

X-ray diffraction is effective for detecting the change in structure that occurs in an order-disorder transformation. For the copper gold system, the disordered crystallographic structure is FCC, with atoms sitting randomly on lattice sites. In an ordered phase, one type of atom, either copper or gold, sits in the corner sites and the other atom will sit in the face sites. This creates two inter-linked simple cubic or simple tetragonal crystallographic structure. This change in the crystal structure causes the original diffraction peaks to change, and the different structure factor causes a number of new peaks to appear [Cul78]. With a true randomly oriented sample, it is possible to calculate the degree of ordering in the sample by comparing different peak heights [War69]. However, thin films have a crystallographic texture that complicates this procedure. As a result it was difficult to quantify the degree of order in the films.

For aluminum alloys the dislocation structure inside the aluminum crystals, the grain size and the strain were all evaluated using x-ray diffraction line shape analysis. In
this technique, the (111) and (220) diffraction peaks were selected for evaluation. The (111) peak was scanned from \(2\theta = 38^\circ\) to \(39.2^\circ\), and the (220) peak was scanned from \(2\theta = 64.24^\circ\) to \(66^\circ\) using \(0.02^\circ\) increments and 10 second dwell time. For line shape analysis, an unstressed quartz standard was scanned in the same diffractometer under the same conditions. The quartz standard was scanned from \(2\theta = 38.7^\circ\) to \(39.8^\circ\), and from \(2\theta = 63.5^\circ\) to \(64.7^\circ\).

Line shape analysis extracts the factors that cause the x-ray diffraction peaks to shift and/or broaden. There are three main causes of peak broadening in x-ray diffraction. The first is the diffractometer itself. Instrumental broadening is eliminated by comparison to the quartz standard. The other two causes of peak broadening are strain and crystallite size. Each of these produce a different shape. Strain effects produce a Gaussian distribution while the crystallite size produce a Cauchy distribution [War69]. The Phillips diffraction software can deconvolute these effects and determine the strain and crystallite size.

**Atomic Force Microscopy (AFM)**

A Digital Instruments Nanoscope III atomic force microscope (AFM) was used to determine the surface topology of the aluminum alloy samples [Hud92]. A silicon tip in the tapping mode was used to probe the surface of the samples. Digital Instruments software was used process the scanned images and calculate the RMS surface roughness.

**Scanning Electron Microscopy (SEM)**

A JEOL 6400 scanning electron microscope was also used to image the surface of samples. In addition to the secondary and back scattered electron detectors, this system has an energy dispersive spectrometer (EDS) that allowed qualitative elemental analysis of surface features [God92]. Samples were first viewed in the secondary electron mode to evaluate the surface topology. Very bright areas were viewed in the back scattered
electron mode. The true secondary electron yield from an area is more strongly dependent on the topology, whereas the back scattered electron intensity is dominated by the atomic mass of the excited atoms. Areas that appeared to have different atomic compositions were examined with EDS to determine the concentration of elements.

**Electron-Probe Microanalysis (EPMA)**

EPMA was used to quantitatively determine the compositions of the aluminum alloys and the copper gold intermetallic films [Gol92]. A JEOL 733 Superprobe with four wavelength dispersive spectrometers was used. For the aluminum alloy films the bulk aluminum alloy was used as the analysis standard to determine difference in composition between the bulk and thin film composition. For the copper gold intermetallic films, pure copper and gold standards were used with the ZAF (atomic number effects, X-ray absorption affects, and X-ray fluoresces effects) analysis technique to determine the composition of these films [Gol92].

**Transmision Electron Microscopy (TEM)**

A JEOL 200CX analytical transmission electron microscope was used to examine precipitates and the crystal size of the aluminum alloys. The samples were prepared by first cutting a 3mm disk from a silicon substrate with a deposited film. These samples were then thinned from the silicon side to between 150μm and 250μm. Using a dimpling grinder, the back sides of the samples were hollowed out so that the center of the samples were approximately 50μm thick. The thinned samples were encapsulated in paraffin and a small opening (1mm) was made in the paraffin over the dimple. The samples were etched in a solution of 50% HF and 50% HNO₃. The etching process was monitored by viewing the samples through a low power binocular microscope. Once the acid had etched through the silicon and reached the aluminum film, etching was stopped. These samples were ion milled until a small opening appeared in the aluminum, then viewed in the TEM.
In the TEM, the samples were first viewed in the bright field mode to evaluate the general structure of the sample [Lor94]. The dark field mode was used to better identify different phases. Electron diffraction images and patterns were also taken to identify the phases present by calculating the interplaner spacing. The inter plane spacing, \( d_{hkI} \) was calculated using:

\[
\lambda L = R d_{hkI}
\]  \( \text{(5)} \)

where \( L \) is the camera length (for the JEOL 200CX \( L = 82 \) cm), \( \lambda \) is the electron wavelength which is based on the accelerating voltage \( (\lambda = 0.0251 \text{nm based on an accelerating voltage of 200keV}) \) and \( R \) is the radius of the diffraction pattern.

**Etching**

Grain size is an important parameter when evaluating the strength of a metal. Etching is the primary means by which the grain size may be made visible in bulk metals, but this technique was found to be ineffective in this study. Etching thin films to define grains is problematic. Most etchants attach different crystallographic planes at different rates. In a material with a randomly oriented crystals, this type of etchant works well. However, thin films are strongly textured and tend to etch more uniformly, complicating the determination of crystal size. Some etchants that attack grain boundaries preferentially [Smi67, Gif70] and two were tested for aluminum alloys: 1% hydrofluoric acid and a 10% sodium hydroxide solution. Satisfactory definition of the grain boundaries was not achieved.

**Auger Electron Spectroscopy (AES)**

The Perkin-Elmer PHI 660 Scanning Auger Microprobe was used to evaluate the oxide thickness on the aluminum alloy films. Auger analysis is very surface sensitive,
containing information primarily from the top three or four atomic layers [Hol80]. The Auger system contained an argon sputter gun that enables depth profiles to be collected. To do so, an Auger spectrum was taken, the sample sputtered for 15 seconds, and another Auger spectrum taken. This process was repeated to the required depth. The aluminum alloy samples were sputtered until the oxygen signal had decreased to 10% of its original value. This technique gives a thickness in terms of sputter time. The conditions used result in an estimated sputter rate of 250 angstroms per minute. These data are primarily used to compare differences in oxide thickness from sample to sample.

**Curve Fitting**

To curve fit the stress relaxation data, curve fitting techniques were evaluated: polynomial, single exponential, and double exponential. The double exponential technique fit the data using the equation:

\[
\sigma(t) = A + Be^{m_1} + Ce^{m_2}
\]  

(5)

where \( \sigma \) is stress, \( t \) is time, and \( A, B, C, m_1 \) and \( m_2 \) are constants that are determined from the data. This technique fit most of the data with the least error.

The process for determining the constant was the linearization of the data. This was sometimes complex as the two exponential functions needed to be separated to be linearized. Separation is accomplished by first fitting the stress relaxation data for \( t > 380 \) minute. To linearize these data, the value of \( A \) in equation 5 was first manually selected and subtracted from the remaining data. The natural log for the remaining data was then taken and least squares linear fit to determine the slope, intercept and correlation factor. The \( A \) constant was iterated to obtain the best possible correlation factor. With this step completed, the first exponential was subtracted from the original data. The natural log of the difference was then taken and the resulting data again fitted with a linear least square
fit to determine the slope and intercept, $m_2$ and $C$. All calculations were done in MathCad Version 4.0.

**Numerical Modeling**

The effects of oxide thickness were found to be significant, therefore a numerical model was developed to quantify this effect. This model was based on the equation developed by Townsend [Tow87] and implemented in MathCad version 4.0. In this analysis a three layer structure was modeled. The first layer was a 5µm thick layer of silicon, and the second layer was 5µm of aluminum. The third layer of $\text{Al}_2\text{O}_3$ was varied from 0 to 1nm in thickness. This model was used to calculate the curvature of the structure, therefore the length was not required. The output was plotted as a percentage change in curvature for the structure with varying oxide thickness.
CHAPTER 4
RESULTS

Introduction

The results of the testing and analysis will be presented in this chapter which is organized by material to provide an understanding of their performance.

T201 Aluminum

Figure 4.1 shows the stress versus temperature plot for the T201 alloy film and may be compared to the literature data shown in figure 2.10. These data were collected after an initial temperature cycle to 350°C to stabilize the film’s microstructure after deposition. While the intrinsic stress in these films were a function of deposition parameters, the first cycle to 350°C annealed and consolidated the films and the extrinsic stresses were so high that they dominated the stresses reported as in Figure 4.1. As can be seen from these data, the room temperature residual tensile stress is almost 400 MPa and the film begins to plastically deform at approximately 200°C under a compressive stress of 50 MPa. This sample was also cooled to -196°C in an attempt to reduce its room temperature residual stress, but this procedure had no effect on the room temperature residual stress.

The isothermal stress relaxation seen in these samples at different temperatures are shown in figures 4.2 through 4.6. These data were curve fit as describe above and the equation is shown in each plot. Below 125°C the stress relaxation data was fit well by a double exponential decaying function that suggesting that are two stress relaxation processes were occurring. At 125°C and 150°C the noise on the data are to large to allow fitting. Rather than heating at a rate of 1°C/minute samples were also heated rapidly
Figure 4.1: Stress versus temperature plot of T201 aluminum thin film.

Figure 4.2: Isothermal stress relaxation of T201 aluminum thin film at 50°C.

\[ \sigma(t) = 330.2 + 48.9e^{-5.465\times10^{-4}t} + 9.2e^{-5.096\times10^{-3}t} \]
Figure 4.3: Isothermal stress relaxation of T201 aluminum thin film at 75°C.

\[ \sigma(t) = 243 + 25.7e^{-5.163 \times 10^{-4} \cdot t} + 13.8e^{-4.359 \times 10^{-3} \cdot t} \]

Figure 4.4: Isothermal stress relaxation of T201 aluminum thin film at 100°C.

\[ \sigma(t) = 160.6 + 29e^{-7.121 \times 10^{-5} \cdot t} + 6.8e^{-4.445 \times 10^{-3} \cdot t} \]
Figure 4.5: Isothermal stress relaxation of T201 aluminum thin film at 125°C.

\[ \sigma(t) = 33 + 81 e^{-0.04 \times 10^{-4} t} \]

Figure 4.6: Isothermal stress relaxation of T201 aluminum thin film at 150°C.
(10°C/min) to the testing temperature to evaluate the effect of ramping rate on stress relaxation. The stress relaxation was little changed, showing that ramping rate had little affect on the stress relaxation seen in the samples. A compilation of the curve fitting parameters is shown in table 4.1.

In addition to the mechanical evaluation of the T201 thin films, microstructure and chemical composition was evaluated. Table 4.2 shows the results of the EPMA analysis of the thin films and the composition of the bulk alloy, as determined by an external lab. There are systematic differences in composition between the sputtered thin film and the bulk alloy presumably due to the sputter deposition process [Zhe97].

Figure 4.7 is a SEM micrograph of a T201 thin film sample that was heat treated for 60 hours at 100°C. Back scatter images of the same regions showed that the bright areas had a different atomic composition than the areas around them. Figure 4.8 is the EDS spectrum for the dark areas showing only aluminum. Figure 4.9 shows the EDS spectrum for the bright areas and both copper and aluminum are detected while silicon is not. Therefore, the bright areas on the SEM image are due to both topographic features and differences in chemical composition of the sample, presumably due to precipitates.

Table 4.1: Residual stress after infinite relaxation time, $\sigma_i$, change in stress at short ($\Delta \sigma_<$) and long ($\Delta \sigma_>$) times, and the time constants ($\tau$) for the two exponential equations for T201 aluminum.

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>$\sigma_i$ (MPa)</th>
<th>$\Delta \sigma_&lt;$ (MPa)</th>
<th>$\tau_&lt;$ (min)</th>
<th>$\Delta \sigma_&gt;$ (MPa)</th>
<th>$\tau_&gt;$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>330</td>
<td>9.2</td>
<td>196</td>
<td>49</td>
<td>1820</td>
</tr>
<tr>
<td>75</td>
<td>240</td>
<td>13.8</td>
<td>220</td>
<td>26</td>
<td>1940</td>
</tr>
<tr>
<td>100</td>
<td>160</td>
<td>608</td>
<td>220</td>
<td>29</td>
<td>1400</td>
</tr>
<tr>
<td>125</td>
<td>33</td>
<td>0</td>
<td>0</td>
<td>81</td>
<td>960</td>
</tr>
<tr>
<td>150</td>
<td>40</td>
<td>-3</td>
<td>200</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 4.2: Chemical composition of sputter deposited T201 aluminum alloy thin films determined by EPMA, and compared with the bulk alloy composition.

<table>
<thead>
<tr>
<th>Alloying Element</th>
<th>Bulk Alloy Weight Percent</th>
<th>Sputtered Thin Film Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>93.91</td>
<td>93.19 +/- 2</td>
</tr>
<tr>
<td>Ag</td>
<td>0.57</td>
<td>0.48 +/- 0.04</td>
</tr>
<tr>
<td>Cu</td>
<td>4.6</td>
<td>4.59 +/- 0.2</td>
</tr>
<tr>
<td>Ti</td>
<td>0.27</td>
<td>0.53 +/- 0.04</td>
</tr>
<tr>
<td>Mg</td>
<td>0.29</td>
<td>0.34 +/- 0.1</td>
</tr>
<tr>
<td>Mn</td>
<td>0.36</td>
<td>0.87 +/- 0.1</td>
</tr>
</tbody>
</table>

Figure 4.7: SEM micrograph of T201 aluminum sample after 60 hours at 100°C.
Figure 4.8: EDS spectra of dark area of SEM image shown in figure 4.7, showing a lack of copper and silicon.

Figure 4.9: EDS spectra for bright areas in SEM image, figure 4.7, consistent with a precipitate rich in copper.

Atomic force microscopy (AFM) was used to evaluate the surface morphology of the samples, with an image shown in Figure 4.10. Mounds or hillocks about 0.6μm high were present on the sample surface. The AFM was also used to evaluate the surface roughness of these films after different heat treatments. Due to the large mounds that form on the surface, the RMS roughness varied greatly from position to position on the same sample. An effort was made to scan areas unaffected by the mounds, but this required very subjective selection and exclusions of areas of the sample. Thus, the RMS roughness data were not reliable and are not reported.
The primary strengthening techniques used in the T201 alloy are solid solution strengthening (due to alloying elements of magnesium and manganese [Dav90, Bro82]) and precipitation hardening (due to alloying element copper). Silver is added to this alloy (0.57 % weight percent) to stabilize the copper precipitates [Dav90]. The effectiveness of precipitation hardening is controlled by the size and distribution of the precipitates in the host crystals [Cah83]. TEM was used to evaluate the formation of precipitates in the aluminum crystals. Figure 4.11a shows a plan view TEM image of a T201 sample. The small (10 nm to 30 nm) dark spots in this image are the CuAl₂ precipitates in the aluminum matrix. Figure 4.11b shows the indexed electron diffraction pattern from this sample with the aluminum diffraction rings and the CuAl₂ diffraction spots identified.

The bright field TEM images also give some indication as to the size of the aluminum crystals. Caution must be used in evaluating grain size from this image because the etching process used in the sample preparation would likely attack small crys-
Figure 4.11: TEM micrographs of T201 thin film sample. (a) bright field image showing aluminum crystals and \( \text{CuAl}_2 \) precipitates; (b) indexed electron diffraction pattern showing the diffraction rings for the Al (111) and (200) planes and for the AlCu\(_2\) (422) plane.
tals faster than large crystals. Also, a TEM image only examines a small area of the sample, and a large area must be viewed to determine the true grain size distribution. The apparent average crystal sizes was between 1 and 2 µm.

While direct measurement of the aluminum grain size by etching was unsuccessful, formation of the copper rich precipitates gives some indication of the aluminum grain size. Precipitates tend to nucleate and grow at triple points where three crystals come together [Ree92]. While the direct calculation of grain size from the precipitation density is questionable, the comparison of different samples and inferring changes in crystal size based on changes in precipitation density is reasonable. Figure 4.12 shows a SEM micrograph of a T201 sample that was heated to 350°C and then cooled to 25°C over 48 hours to test the stability of the microstructure. The number of copper rich particles in figure 4.12 are of the same order as that of figure 4.7, i.e.150 +/- 10 particles in the ~ 20 by 10 µm area of the micrograph. Therefore, the precipitate size and density of these samples is apparently stable over several temperature cycles to 350°C.

Figure 4.12: SEM image of T201 aluminum sample after temperature cycling from 350°C to 25°C over 48 hours.
Figure 4.13: Auger depth profile of T201 thin film. The film was sputtered with 3 keV argon in a 3x3 mm raster.

The effect of oxidation on a bimetallic actuator’s performance is a concern. AES analysis was used to measure the oxide thickness on a T201 thin film sample that had been cycled to 350°C 5 times. Figure 4.13 shows the Auger depth profile. The rastered ion gun used in this analysis sputtered $\text{Al}_2\text{O}_3$ at an approximate rate of 25 nm per minute. Thus the oxide thickness on this sample is approximately 25 to 30 nm.

Powder x-ray diffraction analysis was also performed on the T201 thin film samples. A broad 2θ scan was taken of a sample cycled to 350°C once to determine the phases present in the sample. Only elemental aluminum and silicon from the substrate were detected in these scans. XRD scans were then run on samples that were heat treated at 50°C or 125°C for up to 32 hours. The samples were scanned for their (111) and (220) peaks. Figures 4.14 and 4.15 show the diffraction peaks after different stress relaxation times at 125°C. Note that there is a substantial shift in the peak position between the initial scan and those that have undergone stress relaxation for the shortest time of two
Figure 4.14: Aluminum (111) x-ray diffraction peaks for T201 thin film samples after various stress relaxation times at 125°C.

Figure 4.15: Aluminum (220) x-ray diffraction peaks for T201 thin film samples after various stress relaxation times at 125°C.
hours. Line shape analysis was performed on the X-ray data to determine crystallite size as a function of stress relaxation, but the crystallite sizes varied randomly and no correlation was found.

**5052 Aluminum**

Figure 4.16 shows the stress versus temperature plot for the 5052 aluminum alloy thin film. These data were collected after an initial temperature cycle to 350°C to stabilize the film’s microstructure. As can be seen from these data, the room temperature residual tensile stress in the film is 300 MPa versus 400 MPa for T201, 200 MPa for Al-Si-Cu, and 150 MPa for pure AL. The film begins to plastically deform under a compressive stress of 25 MPa at 200°C. A 5052 sample was also cooled to -196°C in liquid nitrogen to reduce the room temperature residual stress. Upon warming to room tempera-
ture, the tensile stress was reduced from 300 MPa to 125 MPa, a 58% reduction. Starting at the reduced room temperature stress of 125 MPa the film begins to plastically deform at a lower temperature of 125°C under a compressive stress of 25 MPa. Upon cooling from 350°C to room temperature, the tensile stress returned to 400 MPa.

The isothermal stress relaxation seen in these films at different temperatures is shown in figures 4.17 through 4.21, along with the fitted curve and the equation. At 50°C the stress relaxation was best fit with a single exponential curve. For temperatures between 75°C and 125°C the stress relaxation data was fit well by a double exponential curve. At 150°C the noise in the stress relaxation data is so large that the fitted curve is unreliable. Samples were also heated at 10°C/minute to the testing temperature to evaluate the effect of ramping rate on stress relaxation. Again, this had little affect on stress relaxation. The curve fitting parameters are compiled in table 4.3.

\[ \sigma(t) = 240.5 + 29.7e^{-3.522 \times 10^{-4} \cdot t} \]

Figure 4.17: Isothermal stress relaxation in 5052 aluminum thin film at 50°C.
Figure 4.18: Isothermal stress relaxation in 5052 aluminum thin film at 75°C

\[ \sigma(t) = 146.9 + 32.8e^{-6.592\times10^{-3}t} + 11.5e^{-4.927\times10^{-3}t} \]

Figure 4.19: Isothermal stress relaxation in 5052 aluminum thin film at 100°C

\[ \sigma(t) = 112.9 + 29e^{-7.252\times10^{-3}t} + 18.5e^{-5.996\times10^{-3}t} \]
Figure 4.20: Isothermal stress relaxation in 5052 aluminum thin film at 125°C.

\[ \sigma(t) = 80 + 17.1e^{-4.494 \times 10^{-4}t} + 9.5e^{-6.378 \times 10^{-3}t} \]

Figure 4.21: Isothermal stress relaxation in 5052 aluminum thin film at 150°C.

\[ \sigma(t) = 57.7e^{-2.017 \times 10^{-3}t} \]
Table 4.3: Residual stress after infinite relaxation time, \( \sigma_i \), change in stress at short (\( \Delta \sigma_\varepsilon \)) and long (\( \Delta \sigma_\gamma \)) times, and the time constants (\( \tau \)) for the two exponential equations, for 5052 aluminum.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>( \sigma_i ) (MPa)</th>
<th>( \Delta \sigma_\varepsilon ) (MPa)</th>
<th>( \tau_\varepsilon ) (min)</th>
<th>( \Delta \sigma_\gamma ) (MPa)</th>
<th>( \tau_\gamma ) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>240</td>
<td>0</td>
<td>0</td>
<td>30</td>
<td>2800</td>
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<td>75</td>
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<td>12</td>
<td>200</td>
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<td>110</td>
<td>19</td>
<td>170</td>
<td>29</td>
<td>1380</td>
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<tr>
<td>125</td>
<td>80</td>
<td>10</td>
<td>160</td>
<td>17</td>
<td>220</td>
</tr>
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<td>150</td>
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<td>0</td>
<td>0</td>
<td>58</td>
<td>50000</td>
</tr>
</tbody>
</table>

Table 4.4: Chemical composition of sputter deposited 5052 aluminum alloy determined by EPMA, compared with the bulk alloy composition.

<table>
<thead>
<tr>
<th>Alloy Element</th>
<th>Bulk Alloy Weight Percent</th>
<th>Sputtered Film Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>97.25</td>
<td>98.9 +/- 0.5</td>
</tr>
<tr>
<td>Mg</td>
<td>2.5</td>
<td>1.73 +/- 0.03</td>
</tr>
<tr>
<td>Cr</td>
<td>0.25</td>
<td>0.16 +/- 0.06</td>
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</tbody>
</table>

The sample that was cooled to -196°C was tested for stress relaxation at 75°C. At this temperature the tensile stress in the film was 50 MPa and there was no stress relaxation observed over forty-eight hours of testing.

The EPMA chemical analysis of the 5052 samples is shown in Table 4.4. Again, there are differences in composition between the sputtered thin film and the bulk alloy, presumable due to sputter deposition effects [Zhe97].
Figure 4.22: SEM micrograph of 5052 aluminum alloy thin film sample that was temperature cycled to 350°C at 1°C/minute and held at 350°C for 30 minutes and then cooled to room temperature over 48 hours.

Figure 4.23: SEM micrograph of 5052 aluminum alloy thin film that was held at 100°C for 60 hours.
Figure 4.24: AFM height image of 5052 aluminum alloy thin film without heat treatment. Scan area is 5 µm by 5 µm, Z-range 32nm and RMS roughness is 3.77 nm.

Figure 4.25: AFM height image of 5052 aluminum alloy thin film heat treated at 125°C for 32 hours. Scan area is 5 µm by 5 µm, Z-range 60nm and RMS roughness is 7.09 nm.
Table 4.5: RMS roughness and Z-range for 5052 aluminum alloy thin films that have undergone different heat treatments.

<table>
<thead>
<tr>
<th>Time at Temperature (Hours)</th>
<th>50°C</th>
<th>125°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RMS Roughness (nm)</td>
<td>Z-Range (nm)</td>
</tr>
<tr>
<td>0</td>
<td>3.77</td>
<td>32.4</td>
</tr>
<tr>
<td>2</td>
<td>5.9</td>
<td>47.5</td>
</tr>
<tr>
<td>4</td>
<td>4.6</td>
<td>35.7</td>
</tr>
<tr>
<td>8</td>
<td>5.8</td>
<td>51.1</td>
</tr>
<tr>
<td>16</td>
<td>6.3</td>
<td>49.4</td>
</tr>
<tr>
<td>32</td>
<td>5.6</td>
<td>51.7</td>
</tr>
</tbody>
</table>

Figure 4.22 and 4.23 show SEM micrographs of 5052 alloy thin films that have undergone different heat treatments. EDS was used to examine the difference between the light and dark areas seen in figure 4.23. No difference in composition between these two areas was found.

The changes in AFM surface roughness with stress relaxation in samples that were heat treated at 50°C and 125°C for up to 32 hours is shown in Table 4.5 and figures 4.24 and 4.25. The RMS roughness and Z-range (the height difference between the highest and lowest point on the sample) are reported in Table 4.5. Figure 4.24 shows the AFM height image of a 5052 alloy sample with no heat treatment and figure 4.25 shows the AFM height image of a sample that had been held at 125°C for 32 hours. The size of features in these images are nearly the same, but the RMS roughness and the Z-range have doubled for the sample held a 125°C (Table 4.5). The data in Table 4.5 shows that the change in surface roughness occurred in the first two hours of the heat treatment, and that heat treatment temperature has little effect on the rate or the magnitude of the rough-
Figure 4.26: Auger depth profile of 5052 alloy thin film. Film sputtered with 3 keV argon in a 3 mm x 3 mm raster.

The AES depth profile data in Figure 4.26 shows that the surface oxide was between 20nm and 30nm thick.

Powder x-ray diffraction analysis of 5052 thin films heat treated at 50°C or 125°C for up to 32 hours showed that the (111) peak shifted low 0.1° for heat treated (2 to 32 hours) versus unheated samples. No additional peak shifts were detected for samples heat treated longer than two hour. The peak shift for the (220) showed the same trend with a shift of 0.1°. Samples were also scanned to detect changes in the Al$_3$Mg$_2$ peak heights or widths that would indicate a change in these precipitates. No measurable change was seen in these peaks indicating that the precipitates had not coarsened. Line shape analysis was also performed on the X-ray data to determine crystallite size as a function of stress relaxation, but no correlation was found with stress relaxation time or temperature.
Figure 4.27: Stress versus temperature plot of 2090 aluminum alloy thin film.

2090 Aluminum

Figure 4.27 shows the stress versus temperature plot for the 2090 aluminum alloy thin film for the first and second temperature cycle to 350°C. The as deposited tensile stress in this film is 250 MPa before the first cycle. During the first temperature cycle, after deposition the film stress decreases linearly with increasing temperature up to 140°C. Between 140°C and 200°C the stress in the film increases with increased temperature, presumable due vacancies migrating to and being destroyed at the grain boundaries [Tow87]. This behavior was typical for T201 and 5052 films also during the first thermal cycle. Once the excess vacancies were eliminated, the slope again becomes linear up to 275°C. At 275°C the slope increases and becomes unstable up to 350°C, where the film is under a compressive stress of 70 MPa. Upon cooling, the slope of the stress-temperature curve is much less than during heating and the film only reaches a tensile stress of 80
MPa at room temperature. On the second temperature cycle the film attains a slightly higher compressive stress of 80 MPa at 350°C and returns to a tensile stress of 80 MPa upon returning to room temperature. When the sample was removed from the Flexus it was noticed that the specular reflection of the film was greatly reduced due to surface oxide.

Based on the reduced specular reflection and the lower slope of the stress temperature curve it was assumed that the film had oxidized badly. This was confirmed by the Auger depth profile data from that sample, (see Figure 4.28). As can be seen, the oxygen concentration falls off very gradually. This indicates that the film had oxidized to a depth greater than the 5052 or T201 films (see figures 4.26 and 4.13).
Copper

The stress versus temperature plot for the copper thin film is shown in figure 4.29. While this plot is quite complex the data are consistent with the film being oxidized during heat treatment. As the stress-temperature plot indicates, the film was stable during the first thermal cycle to only 100°C. Another film was tested for stress relaxation at 50°C for 22 (see figure 4.30). The copper film oxidized in this test, as indicated by a greatly reduced the specular reflection, and the film stress increased after 14 hours due to oxidation.

To inhibit the oxidation of the copper thin film, a 75 nm thick protective aluminum layer was deposited on the copper. This sample was then heated to 500°C for 6 hours in a tube furnace to test the stability of this protective coating. The film retained its specular reflection during this test. From an Auger depth profile on this sample the oxide thickness is approximately 200nm (see figure 4.31).

Figure 4.29: Stress versus temperature plot for a copper thin film.
Figure 4.30: Isothermal stress test of a copper thin film conducted at 50°C.

Figure 4.31: Auger depth profile of a copper film coated with a protective layer of aluminum 750 nm thick. The film was sputtered with 3keV argon in a 3x3 mm raster.
Titanium, Manganese and Nickel

The stress versus temperature plots for titanium, manganese, and nickel are shown in figures 4.32 through 4.34. All of these films oxidized severely during their first temperature cycle up to 500°C, 250°C, and 500°C for titanium, manganese and nickel respectively. This was evident from a change in specular reflection, color change of the samples and by the stress-strain data. For titanium (figure 4.32) the rapid reduction in tensile stress at 350°C to a compressive stress of over 600 MPa at 500°C and the film maintaining a high tensile stress (375 MPa) upon cooling to room temperature indicates some changes in the film from oxidation. Oxidation of the manganese film (figure 4.33) results in an 800 MPa shift in the stress, becoming highly tensile at just over 200°C. The nickel film (figure 4.34) shows a change in slope of the stress strain curve at 275°C and the residual stress at room temperature dropped from 1000 MPa before to 600 MPa after the
Figure 4.33: Stress versus temperature plot for a manganese thin film.

Figure 4.34: Stress versus temperature plot for a nickel thin film.
thermal cycling due to oxidation. An aluminum protective coating was deposited onto a manganese sample, but did not inhibit oxidation of the sample.

**Copper-Gold Intermetallics**

After the copper-gold films had undergone the homogenization and ordering heat treatment, their chemical composition was analyzed by EPMA (see Table 4.6). The films were within 2 to 3 percent of the desired composition.

In powder x-ray diffraction all of the films showed a shifts in the diffraction peak positions form disordered to the ordered state, and additional peaks were observed from the long range order. As reported above, for textured thin films it was not possible to calculate the degree of ordering.

The films were thermally cycled in the Flexus up to 450°C in an argon atmosphere. Figures 4.35 through 4.37 show the results of these tests. The Cu₃Au films did not show a change in stress near the order-disorder temperature, 400°C (figure 4.35). The CuAu film showed a marked change in stress at the transition temperature (figure 4.36) as did to a lesser degree the CuAu₃ film (figure 4.37). However, the order-disorder transition occurs well above the temperature (300°C) at which the films begin to plastically deform.

**Table 4.4: Chemical composition of copper-gold thin films.**

<table>
<thead>
<tr>
<th></th>
<th>Atomic % Cu</th>
<th>Atomic % Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₃Au</td>
<td>77 +/- 0.2</td>
<td>23 +/- 0.2</td>
</tr>
<tr>
<td>CuAu</td>
<td>53 +/- 0.4</td>
<td>47 +/- 0.5</td>
</tr>
<tr>
<td>CuAu₃</td>
<td>22 +/- 0.4</td>
<td>78 +/- 0.4</td>
</tr>
</tbody>
</table>
Figure 4.35: Stress versus temperature plot for a Cu₃Au thin film.

Figure 4.36: Stress versus temperature plot for a CuAu thin film.
Figure 4.37: Stress versus temperature plot for a CuAu, thin film.

Figure 4.38: Isothermal stress relaxation of ordered and disordered CuAu₃ thin films at 150°C.
A series of isothermal stress relaxation tests were performed on these samples. These tests were conducted in argon since these films oxidize if heated to 150°C in air. The tests were run at 150°C to maximize mobility in the samples. Figure 4.38 shows the isothermal stress relaxation data for an ordered and a disordered CuAu₃ thin film. The ordered film has a 2 percent reduction in stress over two days while the disordered film has a 7 percent reduction in stress over the same period. The isothermal stress relaxation in the CuAu and Cu₃Au films showed no difference between the ordered and disordered states.

**Aluminum-Titanium Intermetallics**

The as-deposited tensile stress in the layered Al₃Ti film was 200 MPa. On the first temperature cycle to 500°C the slope of the stress-temperature curve changed at 350°C, indicating a change in the structure of the film. At 500°C the film was in a state of no stress. When the film cooled to room temperature it was under a tensile stress of 800 MPa as shown in figure 4.39. The film was cycled up to 500°C two additional times and showed no hysteresis in the stress-temperature plot. An isothermal stress relaxation test was performed on this sample at 350°C and the film showed no stress relaxation over a 48 hour period.

The sample was then tested at Tencor up to 800°C. The results of this test are shown in figure 4.39. The Al₃Ti film begins to plastically deform above 500°C under a compressive stress of 200 MPa. At 800°C the film still maintains a compressive stress of 300 MPa. Upon returning to room temperature the film was under a tensile stress of nearly 1000 MPa. An isothermal stress relaxation test was also performed at 450°C and again the film showed no stress relaxation over a 48 hour period.

The native passivating oxide held up well for all tests at all temperatures. The specular reflection of the sample was high after all the tests. There was no visible change in the oxide after cycling to 500°C. Figure 4.40 shows the Auger depth profile for an
Al₃Ti film that was heated to a maximum of 500°C. The oxygen concentration drops sharply after 5 minutes of sputtering. Figure 4.41 shows the Auger depth profile for a sample heated to 800°C. The oxygen concentration drops to near zero after 25 minutes of sputtering, indicating that the surface is passivated, but the oxide layer is about three times thicker for samples heated to 800°C than samples heated only to 500°C.

Modeling the Effects of Oxide Thickness on a Bimetallic Actuator’s Curvature

As has been seen with many of the materials examined in this study oxidation has a significant impact of the performance of the material. For the aluminum alloys, it was not possible to test for the effects of the oxide layer since one always forms when aluminum is exposed to air. To evaluate the effect of the oxide on the performance of a bimetallic strip, the change in curvature of a bimetallic strip as a function of the Al₂O₃ layer thickness was calculated. This calculation is based on a bimetallic strip that consists of
Figure 4.40: Auger depth profile of Al₃Ti sample that was heated to 500°C.

Figure 4.41: Auger depth profile of Al₃Ti sample that was heated to 800°C. 5 µm of aluminum on 5 µm of silicon with an oxide whose thickness varied from 0 to 1
Figure 4.42: Curvature of a bimetallic strip as a function of oxide thickness as a percentage of maximum curvature.

\[ \text{Al}_2\text{O}_3 \text{ Thickness (microns)} \]

\[ \% \text{ of Max. Curvature} \]

\[ 0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1 \]

\[ 0 \quad 20 \quad 40 \quad 60 \quad 80 \quad 100 \]

\[ \mu m \]

Figure 4.42 shows the results of this calculation. From this calculation it can be seen that the 30 nm oxide layer found on the aluminum alloy samples reduces the curvature of the bimetallic strip by 0.5 percent, but thicker oxides would have a more significant impact. Therefore, controlling the oxide thickness is critical to maximizing the performance of a bimetallic strip.
CHAPTER 5
DISCUSSION

Introduction

In this chapter the results and conclusions that have been drawn from this research will be presented and discussed with respect to the three objectives of this research. (i) effectiveness of strengthening techniques in thin films. (ii) identification of the mechanism responsible for isothermal stress relaxation in thin films. (iii) identification of materials for high temperature applications. In addition, to assist the development of bimetallic actuators, a figure of merit has been developed and a number critical parameters have been identified to assist in the selection of materials for this application.

Thin Film Strengthening

Of the five strengthening techniques used in bulk metals, this study examines the effectiveness of two of these, solid solution strengthening and multiphase hardening (precipitation/age hardening) in thin films. While not normally considered a strengthening technique, the effectiveness of ordered intermetallics to resist stress relaxation was also examined. Solid solution and precipitation/age hardening were selected because of their effectiveness in strengthening bulk metals and because these mechanisms are relatively insensitive to small variation in composition, which improves manufacturability. The order/disorder transition that occurs in some intermetallics was also of interest due to the large change in volume that frequently occurs at this transition. The order/disorder transition provided a means of evaluating the effectiveness of the ordered phase to resist stress relaxation.
With respect to measuring the strengthening effects of these techniques, there are a number of parameters that are of interest. With bulk materials, strengthening is usually evaluated by measuring the yield strength or ultimate tensile strength of the material at a temperature. In thin film bimetallic structures, this is not possible since stress and temperature are dependent on one another. Thus the temperature and stress at which plastic deformation begins are interrelated, and is the point on the stress versus temperature curve where the slope significantly departs from linear. This study is also concerned with the stress relaxation that occurs in thin films, which determines the stability of a bimetallic actuator. So the strengthening techniques must be evaluated with respect to their effectiveness at increasing both the temperature and therefore the stress at which plastic deformation occurs and at reducing isothermal stress relaxation in the film.

While it would be reasonable to assume that the bulk strengthening techniques would be effective in thin films, the AlSiCu alloy used in microelectronics would suggest that the strengthen mechanisms are less effective in thin films. In the AlSiCu alloy, silicon could provide some solid solution strengthening, but the solubility of silicon in aluminum at room temperature is very low. Copper could provide precipitation strengthening, but due to processing is generally in the overaged condition. As shown in Figure 2.9, the strength of the AlSiCu alloy is only 30% greater than pure aluminum. In contrast, age hardened bulk aluminum copper alloys can have yield strengths of five times those of pure aluminum. While this suggest that bulk strengthening mechanism may not be as effective in thin films, it must also be noted that the AlSiCu alloy was not developed for strength but to reduce aluminum spiking into silicon wafer (Si) and to reduce electromigration (Cu) [Bow74]. On the other hand, the alloys evaluated in this study were developed for strength.

**Solid Solution Strengthening**

The aluminum alloy 5052 was selected to test solid solution strengthening. This alloy is solid solution strengthened by the addition of magnesium. While the majority of
the magnesium stays in solution, some $\text{Al}_3\text{Mg}_2$ and $\text{Al}_2\text{Mg}$ precipitates form. However, these precipitates do not provide the primary strengthening. Comparing the stress temperature curve for 5052 aluminum (Figure 4.16) with the curves for pure aluminum and the AlSiCu alloy (Figure 2.10) clearly shows that solid solution strengthening is effective in thin films. The room temperature residual stress for the 5052 alloy is 300 MPa as compared to 150 MPa for pure aluminum and 200 MPa for the AlSiCu alloy. Also plastic deformation begins in the 5052 alloy sample at 225°C under a compressive stress of 40 MPa while the pure aluminum and AlSiCu alloy begin to deform under the same stress but at much lower temperatures of 125°C and 175°C, respectively. Therefore solid solution strengthening has significantly increased the performance of the film.

Testing also showed that the 5052 alloy film is more resistant to stress relaxation than a pure aluminum or AlSiCu films. At 50°C, pure aluminum and the AlCuSi alloy films experience a 17% reduction in stress over 48 hours while the 5052 alloy film only experience a 6.7% reduction in stress over the same time period. This is even more significant because the 5052 alloy film was under a tensile stress of 150 MPa while the pure aluminum was under only a 80 MPa compressive stress.

In addition to the 5052 aluminum alloy the copper / copper gold systems were examined. The copper gold system was examined primarily because it undergoes an order disorder transition. However, in the disordered phase it can be considered a solid solution of the two elements and it can be compared to pure copper. From (Figure 4.29) the room temperature residual tensile stress for pure copper is 50 MPa and the films began to plastically deform above 250°C under a compressive stress of 300 MPa. The stress temperature plot for $\text{Cu}_3\text{Au}$ (Figure 4.35) shows a residual room temperature tensile stress in the film of 575 MPa and the film begins to plastically deform at 300°C under a compressive stress of 50 MPa. As with aluminum, solid solutions of copper and gold nearly doubled the strength of the film. Stress relaxation tests were not done on the pure copper films due to oxidation.
Given the results of the 5052 aluminum and copper gold, it is clear that solid solutions are effective in strengthening thin films. It has also been shown that this strengthening mechanism is effective at reducing stress relaxation in aluminum alloys.

**Precipitation and Multiphase Hardening**

The T201 aluminum alloy was selected to determine the effectiveness of precipitation hardening to reduce stress relaxation. The T201 aluminum alloy is not strengthened only by precipitation hardening. Magnesium and manganese are added for solid solution strengthening and titanium is added to reduce grain size. Copper is the primary alloying element and it leads to strengthening by precipitates. Silver is added to stabilize the copper precipitates. Table 4.2 shows the complete composition of the T201 alloy. Since this alloy is precipitation and solid solution strengthened, comparisons must be made to pure aluminum, AlSiCu alloy, and the 5052 alloy to evaluate the effectiveness of the precipitation strengthening.

Figure 4.1 shows the stress-temperature plot for the T201 alloy. The room temperature residual stress is nearly 400 MPa, which is 100 MPa higher than the 5052 alloy. (Figure 4.16), 2.5 times greater than pure aluminum and 2 times greater than the AlSiCu alloy (Figure 2.10). The T201 alloy began to plastically deform at 225°C under a compressive stress of 75 MPa, again much higher than pure aluminum or the other aluminum alloys. At 50°C the T201 alloy thin film undergoes a 12% reduction in stress over 48 hours (Figure 4.2) as compared to 7% for the 5052 samples (Figure 4.17) and a reported value of 15% for the pure aluminum and AlSiCu alloy. However, at 50°C, the T201 film is under a tensile stress of 390 MPa as compared to 270 MPa for the 5052 alloy films, 75 MPa for the pure aluminum film and 150 MPa for the AlSiCu alloy film. At 125°C, the T201 sample undergoes a 2% stress relaxation over 48 hours under a 114 MPa tensile stress (Figure 4.5) while the 5052 alloy film undergoes an 18% stress relaxation under a
104 MPa tensile stress (Figure 4.20). Therefore, precipitation/age hardening is effective at reducing stress relaxation in thin films.

The plane view TEM photomicrograph in Figure 4.11 verifies that precipitates were present in the aluminum thin film. In this image, precipitates are clearly seen within aluminum crystals and the diffraction pattern for CuAl₂ is seen. The size of these precipitates is on the order of 20nm to 30nm which is appropriate for age hardening [Bro82].

Based on the testing and microstructural examination of the sample it can be concluded that precipitation/age hardening is effective in thin films. It should also be noted that the addition of silver to this alloy stabilizes the CuAl₂ precipitates. Without this stabilization, the copper would precipitate at the grain boundaries, have a coarse dispersion rather than a fine dispersion, and be much less effective at strengthening the film. A coarse dispersion of "overaged" precipitates is the reason for lack of strength in the AlSiCu alloy [Bro82].

**Ordered Phases and the Order Disorder Transition**

While not normally considered a strengthen technique, ordered phases generally have a higher strength than their disordered counterparts. As mentioned above, order disorder transitions were also of interest due to a large change in volume that occurs during this transition. This volume change could generate large stress or deflection values in the design of thermally actuated MEMS. Figures 4.37, 4.38 and 4.39 show the stress temperature curves for the three copper gold compounds tested. While there is a substantial change in stress seen near the order disorder temperature, this occurs beyond the point at which the yield strength / temperature conditions lead to plastic deformation for these films and the order/disorder transition is not of use in this system.

Ordered phases were presumed to have a lower stress relaxation rate than disordered phases since the self diffusion rate, which determines the creep rate and stress relaxation rate for many materials, were expected to be lower in an ordered phases versus
a disordered phase [Cah83]. Figure 4.38 clearly shows that this presumption was true, for
Cu₃Au, the ordered phase showed a 1.6% reduction in stress over two days compared
with a 6.5% reduction in stress for the disordered phase. The disordered film's stress
relaxation rate is almost four time faster than the ordered phase, while the stress is only
8% higher on the disordered film. The Al₃Ti ordered intermetallic also showed no stress
relaxation at 450°C in two days.

**Stress Relaxation Mechanism in Thin Films**

While increasing the strength of the aluminum thin films reduced the stress
relaxation rates and magnitudes, it did not eliminate stress relaxation. Thus the mecha-
nisms responsible for stress relaxation in thin films needs to be discussed. In this study
three modes of stress relaxation have been observed. The first mode is plastic deforma-
tion of the thin film [Her85]. If the stress applied by the substrate is greater than the yield
strength of the material, the film will plastically deform and relax the stress. This is seen
as a change in slope of the stress-temperature curves upon heating (Figures 4.1, 4.16,
4.35, 4.36, 4.37, 4.39). The second mode of stress relaxation occurs over several tens of
minutes after a sample has reached temperature. This is seen in the stress relaxation
curves of the T201 and 5052 aluminum alloy films (Figures 4.2-4.4 and 4.18-4.20). The
third mode of stress relaxation occurs over a number of days and can again be seen in the
stress relaxation plots of the T201 and 5052 samples.

The challenge in determining the stress relaxation mechanisms in thin films on a
substrate is that film stress and temperature can not be independently varied. This elimi-
nates the use of an Arrhenius equation to calculate the activation energies of the processes
under investigation. It is possible to manipulate samples at different temperatures to the
same stress, however the microstructure and dislocation array of a material are not state
functions. Therefore, their structures will be quite different at different temperatures even
if the stress is the same. In addition, removing the film from the substrate would, in many
cases, substantially change the film in a number of ways. For self passivating materials, such as examined in this study, the back side of the film would oxidize upon exposure to air. It has been shown that dislocations interact differently with oxidized surfaces [Nix89]. It would also be difficult to create and apply a biaxial stress to a free standing thin film and to measure strain in the film. Therefore, direct determination of an activation energy and thus the mechanisms responsible for the different modes of stress relaxation is not possible. Other data are needed to determine the mechanisms responsible for stress relaxation in thin films.

It should be noted that the change in total strain and temperature to reduce the stress in these films is very small. A change in stress of 10 MPa is roughly equivalent to a temperature change of only five degrees. For aluminum on silicon, this is a strain of only 0.00012. Thus very small changes in the dimensions of a film can result in large changes in the stress in the film.

The inability to calculate activation energies for stress relaxation modes 2 and 3 makes it very difficult to identify their mechanisms. All plausible relaxation mechanism must be considered including: recovery, recrystallization, logarithmic creep, Andrade creep, bulk diffusion, gain boundary migration, grain boundary sliding, surface to grain boundary diffusion, polygonization/subgrain coalescence, and precipitate formation or coarsening. Several of these mechanism can be eliminated as possible causes of both modes 2 and 3 stress relaxation.

For the aluminum alloys at 150°C, the $T_H$ is less than 0.5, which is slightly lower than the temperature at which Andrade creep would be expected. In addition, none of the stages of Andrade creep would produce an exponential decay as is seen in the stress relaxation data. Samples heated at higher rates showed no transition from stage 1 creep to stage 2 creep. In the early stages of relaxation the stress relaxation rate decrease, but does not go to zero, and the stage 1 strain rate is not a simple exponential [Cah83] decay.
as seen in the data. Stage 2, steady state creep has a constant strain rate that would produce a constant stress relaxation rate that is not seen in the data. The strain rate in stage 2 creep has some dependence of the applied stress, but this relationship is not a simple exponential [Cah83]. In the third stage of Andrade creep the strain rate increases and so is not consistent that data that has been collected. Therefore, Andrade creep does not appear to be responsible for the stress relaxation.

Diffusional creep processes are generally significant at temperatures of, $T_H > 0.6$, which is well above the temperatures at which the current stress relaxation is seen ($T_H < 0.5$). Diffusional process increase exponentially with temperature [Cah83] while the present stress relaxation shows an inverse relationship to temperature. Diffusional processes should result in a zero stress at infinite time instead of the finite residual stress projected from the curve fits (Tables 4.1 and 4.3).

X-ray line shape analysis did not detected polygonization or subgrain coalescence, so these mechanism can be eliminated. In addition, subgrain coalescence [Cah83] is a preliminary step to recovery and recrystallization, and the microstructure of the samples did not change during stress relaxation (Figures 4.7 and 4.12). Thus recovery, recrystallization and grain boundary migration do not appear to be responsible for the stress relaxation. The formation or coalescence of precipitates does not appear to be a factor. X-ray diffraction showed no significant change in precipitate concentration over time. In addition, the same two modes of stress relaxation have been seen in pure aluminum [Her85]. Having eliminated these potential mechanism of stress relaxation it is necessary to separately consider the mechanism applicable to each mode.

Mode 2 Stress Relaxation

Mode 2 stress relaxation occurs relatively quickly. It is virtually complete in two hours. During this time there is a measurable increase in the surface roughness of the film (Table 4.3). There is also a $0.1^\circ$ shift in the (111) x-ray diffraction peak. The in-
crease in surface roughness equates to a 0.15% change in the thickness of the 1.2μm film which is of the same order as the change in the d spacing calculated from the x-ray peak shift of 0.1°. This indicates that the processes affecting the surface is occurring throughout the thickness of the film. Surface to grain boundary diffusion is not the likely cause of this stress relaxation since diffusional processes are temperature sensitive as discussed above [Ask89], while the roughness and peak shifts are temperature insensitive. Grain boundary sliding is also not consistent with the results obtained since it normally has a very high activation energy [Mey84]. A high activation energy is not consistent with a process that occurs rapidly at low temperature. The film also has a columnar grain structure [Kra90, Tho74] so the resolved shear stress on most of the grain boundaries will be very small. If some crystals have a tilted grain boundary, these grains should be visible with the AFM. Therefore, grain boundary sliding is eliminated as a potential explanation of stress relaxation.

The only mechanism not yet eliminated to explain stress relaxation is logarithmic creep which results from dislocation glide on slip systems. It is postulated that mode 2 stress relaxation is caused by the movement of dislocation on slip planes that terminate as the surface of the film. Dislocation moving in these slip systems should not encounter dislocation pile ups as would be encountered in slip system that terminate at grain boundaries. Thus these dislocations should move and be eliminated quickly. The degree of relaxation should only be limited by the number of sources of mobile dislocations. The increase in roughness could be caused by dislocation bands. Also because of the stress level and temperature of these films, the DMM’s predict that logarithmic creep would be the dominant process (Figure 2.5) [Cah83].

**Mode 3 Stress Relaxation**

The mechanisms not yet eliminated for mode 3 stress relaxation are grain boundary sliding, surface to grain boundary diffusion, and logarithmic creep. Surface to grain
boundary diffusion is a diffusional process that should be exponentially dependent upon temperature. It could increase surface roughness as atoms migrate from the surface to the grain boundary. However, the data do not show a large temperature dependence and the surface roughness does not increase over stage 3. The temperature at which the stress relaxation is occurring is also low for a diffusional process to be active ($T_H < 0.5$). Therefore, surface to grain boundary diffusion does not appear to be the mechanism responsible for this mode of stress relaxation. Grain boundary sliding also not likely to be the mechanism responsible for this stress relaxation, since grain boundary sliding should also increase surface roughness. In addition, the activation energy for grain boundary sliding is very high and it normally only occurs just before mechanical failure. Furthermore, in a columnar structure the resolved stress on most grain boundary should be very low. This only leaves logarithmic creep, which was concluded to be the mechanism for mode 2 stress relaxation. However, how can the same mechanism have a different rate constants? Different resolved stresses on different slip directions could explain this in part, but, the slip systems are all equivalent within each of the (100), (110) and (111) oriented crystals. For this to be the cause of change in relaxation rate, the different oriented crystals would have to relax at different rates, and this should be noticeable in the AFM images. Also, no increase in the roughness of the film was seen in mode 3. It is known that dislocations pile up at grain boundaries [Mey84]. Dislocation climb could move some of these dislocations into the grain boundary. This would result in a reduction of stress and no increase in surface roughness. Therefore this mechanism is consistent with the observation made in this study and is postulated to be the origin of the mode 3 stress relaxation.

**High Temperature Application**

Micro actuators are needed that can operate in severe environments, such as inside jet engines. In these severe environments oxidation was assumed to be a major concern.
High temperature application also require materials that maintain their strength at the operating temperatures. These topics will be examined in this section.

**Oxidation**

During this study it was found that oxidation is a pervasive problem affecting all temperatures ranges. As is shown above and in Appendix C, a 30nm thick oxide forming of the surface of a 5μm Al - 5μm Si bimetallic strip reduces the curvature of the strip by 0.5%. The 2090 aluminum lithium alloy was found to be unsuitable for bimetallic actuators because the lithium increased the oxidation rate (Figure 4.29). The other elements tested also behaved poorly. At elevated temperatures, copper, titanium, manganese, and nickel all oxidized (Figures 4.31, 4.32, 4.34, 4.35). In bulk metals application the thickness of the passivating oxides is of little concern as long it remains intact. In thin films the passivating oxide can consume a large fraction of the thickness. This is very damaging to a bimetallic actuator because most oxides have a very low CTE which will reduce the displacement of the device. Thus, a material’s oxidation rate is a critical parameter and those metals with the slowest oxidation rate are best suited for this application. Aluminum and silicon both have very low oxidation rates due to the formation of passivating oxides and both are well suited for elevated temperature applications [Wes95]. A thin aluminum layer was also found to be effective at protecting less resistant materials, such as pure copper.

**Strength at Elevated Temperatures**

As discussed above, intermetallics have a high resistance to creep due to their low self diffusion rates. This is of interest for elevated temperature application where a lower melting point intermetallic with a higher CTE could be used in place of a standard higher melting point alloy with a low CTE. The Al₃Ti intermetallic performed well, showing no
stress relaxation at 450°C and no oxidation. Unfortunately nickel and copper oxidized, so comparisons of stress relaxation could not be made.

**Figure of Merit**

To assist engineers who design bimetallic actuators in selecting the active layer material, a figure of merit has been developed. The figure of merit is designed to provide an initial evaluation of the type of material that should be used, i.e. aluminum or nickel. The figure of merit, FOM, is expressed in equation 5.1 as:

\[
FOM = \left( \frac{MHT}{MP} \right) \cdot \left( \frac{MOT}{MP} \right)^2 \cdot YS^5 \cdot \left( \frac{FD \cdot CTE \cdot 10^6 \text{°C}}{E \cdot 10^{10} \text{Pa}^3 \cdot (1 - FD)} \right) \]  \tag{5.1}

where MHT is the maximum homologous temperature (the homologous temperature above which the yield strength of the material rapidly declines, equal to 0.4 for most metals and 0.65 for most intermetallics), MOT is the maximum operating temperature of the actuator, YS is the yield strength of the material at room temperature, CTE is the coefficient of thermal expansion for the active layer material, E is Young’s modulus for the active layer material and FD, determines whether the priority of the device is force or displacement (0 to maximize force, and zero to maximize displacement). Table 5.1 shows a comparison of the different figures of merit for different materials at different operating temperatures and for force or displacement. Note that the values for tin are negative, indicating it is not suitable at the temperatures. In general the large CTE of aluminum alloys give the FOMs of \(~ 10^8\) for displacement while the higher Young’s modulus and moderate CTE’s of nickel and stainless steel give them FOMs of \(~10^{11}-10^{12}\) for force. Note the FOM at 500°C of 1015 for cobalt. This figure of merit is complex, but could be expanded to also include the environmental stability of the materials.
Table 5.1: Figure of merit ratings for different materials at different operating temperatures and optimized for displacement, D, or force, F.

<table>
<thead>
<tr>
<th>Max. Temp.</th>
<th>100 (°C)</th>
<th>250 (°C)</th>
<th>500 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Force/Displacement</td>
<td>D</td>
<td>F</td>
<td>D</td>
</tr>
<tr>
<td>Sn</td>
<td>-5.8×10⁶</td>
<td>-3.4×10⁷</td>
<td>-2.9×10⁶</td>
</tr>
<tr>
<td>5052 Al</td>
<td>1.4×10⁸</td>
<td>8.8×10⁹</td>
<td>-2.8×10⁷</td>
</tr>
<tr>
<td>T210 Al</td>
<td>1.1×10⁸</td>
<td>1.2×10¹⁰</td>
<td>-2.4×10⁷</td>
</tr>
<tr>
<td>Mg</td>
<td>8.1×10⁷</td>
<td>8.0×10⁸</td>
<td>-3.2×10⁷</td>
</tr>
<tr>
<td>Anneal Al</td>
<td>2.8×10⁷</td>
<td>1.3×10⁹</td>
<td>-1.3×10⁷</td>
</tr>
<tr>
<td>75% c.w. Al</td>
<td>5.0×10⁷</td>
<td>2.4×10⁹</td>
<td>-2.3×10⁷</td>
</tr>
<tr>
<td>Cu</td>
<td>7.5×10⁶</td>
<td>1.4×10¹⁰</td>
<td>2.1×10⁷</td>
</tr>
<tr>
<td>Ni</td>
<td>1.0×10⁶</td>
<td>6.1×10¹⁰</td>
<td>1.7×10⁶</td>
</tr>
<tr>
<td>Co</td>
<td>4.2×10⁶</td>
<td>5.4×10¹³</td>
<td>6.5×10⁶</td>
</tr>
<tr>
<td>410 S.S.</td>
<td>2.4×10⁵</td>
<td>2.3×10¹¹</td>
<td>3.6×10⁵</td>
</tr>
</tbody>
</table>

c.w. cold worked
S.S. stainless steel
CHAPTER 6
CONCLUSIONS

In this study, the two modes of operation for a bimetallic actuator, force and displacement, were studied and each mode has different materials requirements to maximize performance. The displacement mode is dominated by the difference in the CTE’s of the materials of bimetallic strip, while performance in the force mode is a function of both Young’s modulus and the CTE difference. In both modes the yield strength limits the maximum displacement or force produced by an actuator. Based on these results this research examined mechanisms to strengthen high CTE thin film metallization.

Two strengthen mechanisms were evaluated, solid solution strengthening and multi-phase/age hardening. The 5052 aluminum alloy thin film, which is a solid solution strengthened alloy, was twice as strong as pure aluminum, having a room temperature residual stress of 300 MPa as compared to 150 MPa for pure aluminum. The T201 aluminum alloy thin film, which is a solid solution and multi-phase/age hardened alloy, was 2.5 times stronger than the pure aluminum with a room temperature residual stress of 400 MPa. Therefore, solid solution and multi-phase/age hardening are effective at strengthening thin films. However, as with bulk alloys, multi-phase/age hardening is susceptible to over aging as was seen in the Al-Si-Cu alloy films, which only showed a room temperature residual stress of 200MPa.

Two modes of isothermal stress relaxation were observed in the 5052 and T201 alloy thin films at temperatures between 50°C and 250°C. In the first mode, stress relaxation is caused by the movement of dislocation in slip systems that terminate at the thin film surface. The second mode is caused by the movement of dislocation in slip systems that terminate at grain boundaries.
The order-disorder transformation found in the copper gold system, while producing a large change in stress for a small temperature change, occurred at temperatures which generated stresses which were above their yield strengths. In addition, these films oxidized at the temperatures necessary for the order/disorder transition. Therefore, order/disorder transformations in the Cu/Au system is not useful for bimetallic actuation. These films provided a means of comparing the stress relaxation rates for ordered and disorder/solid solution phases. The ordered phase showed one quarter the stress relaxation as compared to the disordered phase. Therefore, ordered intermetallic thin films have a high resistance to stress relaxation. This was also seen in the Al$_3$Ti films that showed no stress relaxation over 48 hours at 450°C. The Al$_3$Ti films also showed high strength, only plastically deforming at 500°C or higher, and oxidation was only significant above 800°C. Al$_3$Ti is therefore a promising candidate for high temperature actuators.

Oxidation was found to have a pervasive effect on all materials evaluated in this study. The oxide formation on aluminum thin films has been shown to increase the strength of the film [Nix89], but calculation performed in this study showed that the oxide also reduces the displacement in a bimetallic actuator. Oxidation was found to have an even greater detrimental effect on some of the other materials tested. Copper, nickel, titanium, manganese, and the 2090 aluminum alloy thin films all oxidized severely upon their first heating to 350°C. The copper film even oxidized at 50°C over 48 hours. Therefore, materials for use in bimetallic actuators must have a very low oxidation rate.
CHAPTER 7
FUTURE WORK

In the area of strengthening mechanisms, additional work could be done to evaluate different solutes and precipitates that could be used. As for the stress relaxation mechanisms, additional theoretical and analytical work should be done to support or disprove the conclusions reached in this study. From the analytical perspective, the use of nickel as a base material has the advantages that TEM samples can be more easily produced with less concern that the sample preparation is affecting the data.

Oxidation presents an interesting problem for bimetallic actuators because it reduces displacement but also increases the strength of the thin film [Nix89]. Putting a protective polymer coating on an aluminum thin film to inhibit oxidation would significantly reduce the yield strength of the aluminum, but the oxide would not reduce displacement. How these two factors interact needs to be better understood. Also, as an oxides can strengthen a thin film what other surface treatments would be effective at strengthening thin films?

Protective coatings would require an additional patterning and deposition step in the manufacturing process and so are of limited interest. This put the focus of future work on self passivating or non-oxidizing materials.

Moving to topics not covered in this study, micro bimetallic actuators may be cycled millions of time. There is therefore concern about fatigue in the active layer material. This is an area that will become more critical as more actuators are more widely implemented.

Lastly, this study only examined thin films on wafers where the film had very little curvature or stress gradient through the thickness of the film. In real actuators, thin films
may be exposed to highly curved structures with large stress gradients across the film thickness. This could have dramatic effects on the stress relaxation within the films and should be examined.
APPENDIX A
DERIVATION OF RELATIONSHIP BETWEEN YOUNG’S MODULUS AND COEFFICIENT OF THERMAL EXPANSION

The following relationship between a material’s Young’s modulus and its coefficient of thermal expansion was derived by N. Kulkarni and R. DeHoff [Kul97]. Starting with the thermodynamic relationship given in equation A1 [Deh93],

\[ dV = V_\alpha dT - V_\beta dP \]  

where \( V \) is volume, \( P \) is pressure, \( T \) is temperature, \( \alpha \) is the coefficient of thermal expansion and \( \beta \) is the coefficient of compressibility. By algebraic manipulation and differentiation with respect to pressure while keeping the volume the same, equation A2 is derived.

\[ \frac{dV}{V_\alpha} = dT - \frac{V_\beta}{V_\alpha} dP \]

\[ \left( \frac{\partial T}{\partial P} \right)_V = \frac{V_\beta}{V_\alpha} \]

\[ \beta = \alpha \left( \frac{\partial T}{\partial P} \right)_V . \]  

The partial derivative of temperature with respect to pressure at constant volume is a positive valued function because the temperature of a system must increase in response to increased pressure for the system to maintain a constant volume.
Turning to the equations that define and relate the different materials properties [Die84], equation A3 define the bulk modulus, $K$, of a material:

$$\beta = \frac{1}{K}. \quad (A3)$$

The bulk modulus is then related to the shear modulus, $G$, and Young’s Modulus, $E$, by equation A4:

$$K = \frac{E}{9 - \frac{3E}{G}}. \quad (A4)$$

The shear modulus is related to the Young’s modulus by equation A5 where $\nu$ is Poisson ratio:

$$G = \frac{E}{2(1 + \nu)}. \quad (A5)$$

Combining equations A4 and A5, the relationship between the bulk compressibility and the Young’s modulus is obtained as equation A6:

$$K = \frac{E}{3 + 6\nu}. \quad (A6)$$

By combining equations A2 and A3 the relationship between the bulk compressibility and the coefficient of thermal expansion is obtained, equation A7:

$$K = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_{V} \alpha}. \quad (A7)$$
By combining equations A6 and A7, the relationship between the Young’s modulus and the coefficient of thermal expansions is derived in equation A8:

\[
E = \frac{3 + 6\nu}{\left(\frac{\partial T}{\partial P}\right)_V} \alpha. \tag{A8}
\]

Equation A8 clearly shows that there is an inverse relationship between the Young’s modulus and a material’s coefficient of thermal expansion.
APPENDIX B
CURVE FITTING OF STRESS RELAXATION DATA

The stress relaxation data were collected over a 48 hour period. Stress measurements were taken every 15 minutes producing 192 data points per stress relaxation test. These data were exported from the Tencor Flexus model 2320 into an ASCII formatted file. This ASCII file was then imported into Microsoft Excel where all but the 192 stress data points were eliminated. The data were exported as an ASCII data file containing only the 196 stress data points delimited by carriage returns and read into Mathcad version 4.0 where the following procedure was used to fit the data.

\[ \text{T201 Al @ 100}^\circ \text{C} \]

The data are being fit to an equation of the form

\[ \text{Stress}(t) = A + B \cdot \exp(m_1 \cdot t) + C \cdot \exp(m_2 \cdot t) \]

- \( i := 0..191 \) Used to index data points
- \( j := 0..166 \) Used to index data points when not using first 25 data points
- \( r := 0..3 \) Used to index columns of data

\[ D := \text{READPRN(a2100)} \quad \text{Reading in data} \]

\[ D_{i,0} := 0 \quad \text{Zeroing data array} \]

\( \sigma_{\text{not}} = 160.6 \) This is the A constant, and is manually selected

\[ D_{i,0} := D_{i,0} \quad D_{i,2} := \ln(D_{i,1} - \sigma_{\text{not}}) \] Setting up an array with the log of the data.

\[ D_{i,1} := D_{i,1} \quad D_{i,3} := 15 - D_{i,0} \] Converting data position to time, in minutes

\( x_i := D_{i,3} \quad y_i := D_{i,2} \) Converting data into single column arrays

\[ x_c := x_{j+25} \quad y_c := y_{j+25} \] Removing the first 25 data points for first fit.
Performing least squares linear fit to the natural logarithm of the data

\[ m := \text{slope}(x_c, y_c) \]
\[ m = -7.121 \times 10^{-5} \] Calculating the slope of the line. This is the \( r_1 \) constant

\[ b := \text{intercept}(x_c, y_c) \] Calculating the y intercept of the line
\[ b = 3.366 \] \[ B = \exp(b) \] \[ B = 28.963 \] Showing the B constant

\[ c := \text{corr}(x_c, y_c) \] Calculating the correlation factor for the fit
\[ c = -0.83362523 \]

\[ \text{cal}_i := m \cdot x_i + b \] Calculating the curve from data fit constants

Plot of fitting curve with log of data

---

![Plot of fitting curve with log of data](image-url)
Calculation of the fit to the data

Plot of first curve to data

Second data fit

\[ j = 0 \ldots 25 \quad x_j^2 = x_j \]

Setting up arrays

\[ \text{diff}_j = D_{j,1} - \text{ecal}_j \]

Removing the first curve fit component from the data

\[ \ln(\text{diff}) \]

Taking the natural logarithm of the data

Preforming least squares linear fit to the natural logarithm of the second set of data.

\[ m_2 = \text{slope}(x_2, \ln(\text{diff})) \]

Calculating the slope of the line. This is the \( r_2 \) constant

\[ b_2 = \text{intercep}(x_2, \ln(\text{diff})) \]

Calculating the y intercept of the line

\[ b_2 = 1.919 \]

\[ C = \exp(b_2) \]

Showing the C constant

\[ C = 6.815 \]

\[ c_2 = \text{corr}(x_2, \ln(\text{diff})) \]

Calculating the correlation factor for the fit

\[ c_2 = -0.917 \]
Calculating curve from data fit constants

\[ \text{cal}_j^2 = m^2 x_j^2 + b^2 \]

\[ \text{ecal}_j^2 = \exp(\text{cal}_j^2) \]

Plot of fitting curve with log of data
Calculating fitting Curve

Plot of fitted curve and data

\[ \text{calt}_2 = m2x + b2 \]
\[ \text{ecalt}_2 = \exp(\text{calt}_2) \]
\[ \text{ecal}_2 = \text{ecal}_1 + \text{ecalt}_2 \]

Plot of the two curve components

\[ \text{ecal}_1 = \text{ecal}_1 - \sigma_{\text{not}} \]
APPENDIX C
CALCULATION OF CHANGE IN CURVATURE OF A BIMETALLIC STRIP BASED ON OXIDE THICKNESS

The reduction in curvature of a bimetallic strip is calculated as a function of the oxide thickness that forms on the surface of the aluminum. In this model the base bimetallic strip is consisting of 5\(\mu\)m of aluminum on 5\(\mu\)m of silicon. The oxide thickness varies from 0 to 1\(\mu\)m in thickness with no change in the aluminum thickness. This model was based on the equations developed by P.H. Townsend [Tow87] and was implemented in Mathcad version 4.0.

\[
\text{layers} = 3 \quad \text{layer} = 1 \ldots \text{layers}
\]
\[
\text{delta} = 0 \ldots 10000
\]
\[
i = 1 \ldots 3
\]
\[
j = 1 \ldots 3
\]
\[
\text{DeltaT} = 200 \quad \text{Change in temperature}
\]
\[
d0 = 200 \cdot 10^{-6} \quad \text{Set step size increase in oxide thickness}
\]

Material properties

<table>
<thead>
<tr>
<th>Si</th>
<th>Al</th>
<th>Al(_2)O(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(t_{1,\text{delta}} = 5 \cdot 10^{-6}) m</td>
<td>(t_{2,\text{delta}} = 5 \cdot 10^{-6}) m</td>
<td>(t_{3,\text{delta}} = 1 \cdot 10^{-10}) m</td>
</tr>
<tr>
<td>CTE(_1) = 2.6 \cdot 10^{-6}</td>
<td>CTE(_2) = 25 \cdot 10^{-6}</td>
<td>CTE(_3) = 5.5 \cdot 10^{-7}</td>
</tr>
<tr>
<td>(E_1 = 1.9 \cdot 10^{11}) Pa</td>
<td>(E_2 = 7 \cdot 10^{10}) Pa</td>
<td>(E_3 = 3.8 \cdot 10^{11}) Pa</td>
</tr>
</tbody>
</table>

Calculation of curvature

\[
d_{\text{layer}} = \Delta \text{delta} T \cdot \text{CTE}_{\text{layer}} \cdot d0 - d0
\]
\[
t_{\text{TOT, delta}} = t_{1,1} + t_{2,1} + t_{3,\text{delta}}
\]
\[
B = \begin{bmatrix}
0 & 1 & 1 & 1 \\
-1 & 0 & 1 & 1 \\
-1 & -1 & 0 & 1 \\
-1 & -1 & -1 & 0
\end{bmatrix}
\]

106
\[
\gamma_{\text{layer}, \delta} = \sum_{i} B_{\text{layer}, i} t_{i, \delta} \delta
\]

\[
N_{\text{plain}, \delta} = \frac{t_{\text{TOT}, \delta}}{2} \frac{\sum_{i} E_{i} \frac{t_{i, \delta}}{2}}{\sum_{i} E_{i} t_{i, \delta}}
\]

\[
k_{\text{sub}, \delta} = \left[ \frac{N_{\text{plain}, \delta} \cdot t_{\text{TOT}, \delta}}{2} \left( \frac{t_{\text{TOT}, \delta}}{3} \right)^2 \right]
\]

\[
k_{\delta} = \sum_{i} E_{i} t_{i, \delta} \left( k_{\text{sub}, \delta} \right) + \left( t_{\text{TOT}, \delta} - N_{\text{plain}, \delta} \right) \frac{t_{i, \delta}}{2} \left[ \frac{\sum_{j} E_{j} t_{j, \delta} \ln(d_{j})}{\sum_{j} E_{j} t_{j, \delta}} \right]
\]

\[
D_{k, \delta} = \frac{k_{\delta}}{k_{0}} \times 100 \quad \text{Calculating curvature as a percentage of maximum curvature}
\]

\[
\mu_{\delta} = l_{3, \delta} \times 10^6
\]

% of Max. Curvature

Al₂O₃ Thickness
microns
APPENDIX D
MECHANICAL PROPERTIES OF EXAMINED METALS

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Melting Point (°C)</th>
<th>Young’s Modulus (GPa)</th>
<th>CTE (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>650</td>
<td>69</td>
<td>25</td>
</tr>
<tr>
<td>Al-Si-Cu</td>
<td>620</td>
<td>70</td>
<td>23</td>
</tr>
<tr>
<td>T210</td>
<td>620</td>
<td>70</td>
<td>22.7</td>
</tr>
<tr>
<td>5052</td>
<td>610</td>
<td>70</td>
<td>24.8</td>
</tr>
<tr>
<td>2090</td>
<td>610</td>
<td>70</td>
<td>23</td>
</tr>
<tr>
<td>Cu</td>
<td>1085</td>
<td>128</td>
<td>16.5</td>
</tr>
<tr>
<td>Ni</td>
<td>1453</td>
<td>207</td>
<td>13.3</td>
</tr>
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<td>Ti</td>
<td>1668</td>
<td>120</td>
<td>8.4</td>
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<tr>
<td>Mn</td>
<td>1244</td>
<td>120*</td>
<td>22</td>
</tr>
<tr>
<td>Al₃Ti</td>
<td>1340</td>
<td>100</td>
<td>14</td>
</tr>
<tr>
<td>Cu₂Au</td>
<td>950*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuAu</td>
<td>910*</td>
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<td>15</td>
</tr>
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<td>CuAu₃</td>
<td>925*</td>
<td></td>
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* - estimated
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<td>Hogan, H.</td>
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<td>Hol80</td>
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BIOGRAPHICAL SKETCH

Jonathan F. Gorrell was born on February 26, 1958, in Palo Alto, California to James and Billie Gorrell. He finished his secondary education at Monta Vista High School in Cupertino, California in 1976. He went to California Polytechnic State University at San Luis Obispo and in 1980 he received his Bachelor of Science degree in applied mathematics. Jonathan then started his professional career as a programmer writing assemblers for micro-processor. Over the next twelve years he worked in engineering, customer support, marketing and sales for a number of computer related companies. During this time he took a four year assignment in Europe. In 1991, Jonathan decided to change careers and move into materials engineering. He was accepted into the Materials Science and Engineering program at the University of Florida and started classes in the fall of 1992. Two years later, Jonathan joined Dr. Paul Holloway’s group and initially studied novel techniques for diamond growth. One year later he began examining thin film metallization for use in micro-machines. In May of 1998 Jonathan received his Ph.D. in Materials Science and Engineering. Upon graduation, Jonathan returned to industry accepting a position at Motorola Semiconductor in Phoenix, Arizona.
I certify that I have read this study and that in my opinion it is conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Paul H. Holloway, Chairman
Professor of Materials
Science and Engineering

I certify that I have read this study and that in my opinion it is conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Ashok Kumar
Assistant Professor of Mechanical Engineering

I certify that I have read this study and that in my opinion it is conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Robert T. DeHoff
Professor of Materials
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I certify that I have read this study and that in my opinion it is conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it is conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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