STRAIN RATE AND TEMPERATURE DEPENDENT MECHANICAL BEHAVIOR OF NANOCRYSTALLINE GOLD

BY

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ABSTRACT

Nanocrystalline metal films are candidate materials for microelectronics and Microelectromechanical Systems (MEMS). The long term mechanical stability of metal films requires quantitative understanding of their thermo-mechanical behavior in the large range of operating strain rates and temperatures. This dissertation research studied (a) the role of thermally activated processes based on the strain rate and temperature dependent mechanical behavior of nanocrystalline Au thin films, and (b) deformation processes at nominally elastic loads that lead to creep strain over a moderate temperature range that is relevant to MEMS applications.

The rate dependent mechanical behavior of nanocrystalline Au thin films was first investigated at room temperature ~ 25 °C and at strain rates between 10⁻⁶ to 20 s⁻¹. The use of digital image correlation (DIC) facilitated repeatable and accurate measurements of full-field strain from free-standing nanocrystalline Au thin films. The experimental stress-strain curves were used to calculate activation volumes for two film thicknesses (0.85 μm, and 1.75 μm), which were 4.5b³ and 8.1b³, at strain rates smaller than 10⁻⁴ s⁻¹ and 12.5b³ and 14.6b³ at strain rates higher than 10⁻⁴ s⁻¹. The reduced activation volume and increased strain rate sensitivity at slow strain rates were attributed to grain boundary (GB) diffusional processes that result in creep strain.

The room temperature strain rate results were augmented with microscale strain rate experiments at temperatures up to 110°C. Two methods for heating free-standing microscale thin film specimens, namely uniform heating using a custom-built microheater and resistive (Joule) heating, were evaluated using a combination of full-field strain measurements by optical microscopy and full-field temperature measurements by infrared (IR) thermal imaging. It was shown for the first time that the Joule specimen heating method results in large underestimation of the inelastic material properties by about 50% due to the extended temperature gradient along the specimen gauge section that causes plastic strain localization. On the contrary, the microheater based uniform heating method results in uniform temperature and strain fields during tensile experiments and was more suited for experiments at elevated temperatures.
This uniform heating method was applied to annealed Au films with average grain size of 64 nm and for strain rates $10^{-5}$-10 s$^{-1}$, and temperatures 298-383 K. Activation volume calculations based on the combined temperature and strain rate experimental results pointed to two rate limiting mechanisms of inelastic deformation: Creep-driven and dislocation-mediated plasticity, with the transition occurring at increasing strain rates for increasing temperatures. The activation volume for the creep-dominated regime increased monotonically from $6.4b^3$ to $29.5b^3$ between 298 and 383 K, signifying GB diffusion processes and dislocation-mediated creep, respectively. The trends in the dislocation-mediated plasticity regime followed an abnormally decreasing trend in the activation volume values with temperature, which was explained by a model for thermally activated dislocation depinning. Furthermore, the experimental data allowed us to evaluate the hardening behavior for Au films and model it using a linear hardening law and exponential relationships for the state variable and the saturation stress.

The creep response of nanocrystalline Au films with 40 nm grain size was also obtained experimentally in an effort to assess its contribution to the overall mechanical response under uniaxial tension. Unusually high primary creep rates ($3.3 \times 10^{-5}$ to $2.7 \times 10^{-7}$ s$^{-1}$) and steady state creep rates ($5.5 \times 10^{-9}$ - $1.1 \times 10^{-8}$ s$^{-1}$) were measured with the primary creep regime lasting up to 5-6 hr for some stress amplitudes. A non-linear model based on the kinetics of thermal activation was applied to model the creep behavior of Au films, which captured very well the effect of applied stress on primary and steady-state creep. Additionally, multi-cycle creep experiments were conducted on annealed nanocrystalline Au films at four different temperatures. The creep exponents indicated a change in the dominant mechanism for inelastic deformation from diffusion and GB sliding at room temperature to dislocation climb at 110°C. It was also shown that about 50% of the accumulated strain during each forward creep cycle was recovered at zero load. The amount of strain recovery was weakly influenced by temperature which implies a dominant role of backstress in the recovery process.
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CHAPTER 1

Introduction

1.1 Motivation and Relevance

Inert metals have been regarded as excellent candidate materials for low power MEMS devices due to their excellent electrical and thermal conductivities as well as their lower stiffness compared to brittle materials. Such metallic films are either stand-alone MEMS components with thicknesses of the orders of hundreds of nanometers to a few microns, or serve as thin electrodes on piezoelectric and non-conducting films and have submicron thickness. Thin films of Au, Pt, and Ni have been used in radio-frequency (RF) MEMS, such as varactors, switches, tunable filters, and other microelectronic applications both as thin electrodes as well as structural and functional components. Although these metals have desirable electrical properties, their combined electrical and mechanical functionalities are subject to long term reliability issues. Although the same materials have been studied sufficiently for bulk applications, there are several differentiating factors between the bulk the thin film form that requires significant effort and research investment towards quantitative understanding of their mechanical behavior.

Specifically, (a) thin films for MEMS are fabricated by deposition methods that result in textured films with highly refined grain structure and grain size distributions spanning a few to tens of nanometers; such microstructures have been rarely encountered to date in bulk materials. (b) The small grain size and the extensive grain boundaries make these metallic films prone to temperature effects at temperatures that are quite benign for large grain metals. (c) MEMS devices are subject to very large numbers of operation cycles that open the possibility of high cycle fatigue and strain rate effects. Even though the
operating stresses can be low, creep and fatigue strain could accumulate to undermine the device reliability. Along these lines Hsu et al [1] showed that the capacitance of Ni and Au varactors for RF-MEMS suffers from quite short term drift as revealed by Figure 1.1. As shown in Figure 1.1(b), a drastic initial increase in capacitance lasting a few hundreds of hours was followed by a relatively constant rate of change. The capacitance drift is owed to a gradual reduction in the gap between the top plate shown in Figure 1.1(a) and the substrate, thus implying a mechanical cause. Furthermore, the trends in the curves in Figure 1.1(b) are reminiscent of the creep response of metals at high homologous temperatures. Therefore, it is inferred that such capacitance drift has its origins in the lack of long-term material stability.

Metal films are fabricated by various techniques including sputter deposition, electrodeposition and evaporation. The deposition process affects the details of the film microstructure and therefore the mechanical properties. Numerous early works have investigated the effect of the fabrication techniques on the strength of metallic films [2-5]. For instance, electrodeposition could result in high void content as indicated by low elastic modulus and strength values. On the other hand, sputtering has been shown to limit the void-content and result in high quality films. These fabrication techniques may also result in textured films and grain morphologies that vary from perfectly columnar to equiaxed. The effect of grain size, morphology and texture on the mechanical behavior has also been studied extensively in literature [4,6-11]. It has been established that the strength of metallic thin films increases with reduction in grain size, $d$, due to grain boundary strengthening until $d$ reaches a minimum value of 20-50 nm for different materials [9]. This behavior is commonly called the Hall-Petch effect. Further reduction in grain size leads to a decrease in strength due to the increased contribution of diffusional processes in high volume of grain boundary regions [6-12] and it is often referred to as the inverse Hall-Petch effect. The change in strength with grain size is shown in Figure 1.2 which has been adapted from [12].
Figure 1.1 (a) Confocal microscope image of an analog RF-MEMS varactor. The gap between the Ni plate and Au electrodes is 3 μm. (b) Measured (black) and fitted (red) capacitance results for the analog RF-MEMS varactor [1] © [2010] IEEE.

Although a number of works have concentrated on the effect of grain size and specimen size on the strength of metallic films [9,13], there is a paucity of literature investigating the role of temperature and strain rate on the quasi-static and time dependent
mechanical response of metal films. The effect of loading rate on the mechanical response is of particular interest for thin film applications, such as MEMS switches and varactors that are subject to a variety of loading rates. Similarly most MEMS and microelectronics employing metal films are designed to operate in conditions ranging from room temperature to moderately elevated temperatures (100-125 °C). Thus, a study of the combined effects of strain rate and temperature is highly relevant in order to obtain a complete and accurate description of their constitutive response. Furthermore, an investigation of the creep behavior of the same films would provide insights into long-term material stability and consequently device performance.

Figure 1.2 Compiled yield stress versus grain size data for Cu from various references ranging from coarse grain to nanoscale grain size. The trend reverses as the grain size falls below a critical size. Reprinted from [12], with permission from Elsevier.
1.2 Deformation Mechanisms in Nanocrystalline Metal Films

In order to increase the linear range of operation of thin film based devices, films with nanoscale grain size \( d < 100 \) nm have been employed which resulted in outstanding strength. Moreover the need for planar and near stress-free thin films resulted in layer by layer deposition processes that reduce the film grain size dramatically. The reduced grain size leads to increased yield strength due to grain boundary (GB) strengthening i.e. GBs act as obstacles to dislocation motion (Hall- Petch effect) but the increased volume fraction of GBs and triple points in the nanocrystalline face centered cubic (FCC) metals can lead to enhanced diffusion based creep [14,15] and relaxation processes that finally reduce the material yield strength for grain sizes smaller than \( \sim 20 \) nm [6,7,9-12]. The beneficial increased yield strength due to nanocrystallinity is eclipsed by increased strain rate sensitivity [2,5,16-18] and creep rates compared to films with larger grain sizes.

Nanocrystalline metals have large volume fractions occupied by GBs that control dislocation nucleation, pinning and annihilation [19,20] and GB mediated creep [21-23] while affecting the relative contribution of thermal and stress driven inelastic processes. These often competing mechanisms result in increased rate sensitivity which is not uniform across time scales: diffusion controlled processes are important at slow applied strain rates and may dominate in the case of very small grain sizes. The competition between GB and intra-granular deformation mechanisms is expected to control rate sensitivity and the activation volumes in nanocrystalline metals. The latter is a metric of the unit material volume in which a particular deformation mechanism occurs and it is expressed in terms of Burger’s vector units \( [b^3] \). For example, if atomic diffusion takes place involving individual atoms or vacancies, the corresponding activation volume is of the order of \( 1 \) \( b^3 \). At the other end of the spectrum of plasticity length scales, the activation volume for forest dislocation plasticity is of the order of \( 1,000 \) \( b^3 \) [5, 24, 25,26,27].

The dominant (rate controlling) deformation mechanisms in nanocrystalline metals are strongly dependent on the state of material, the temperature and the applied loading rate. It is also noteworthy that the rate controlling physical processes behind dislocation mediated plasticity in nanocrystalline metals subjected to high strain rates could be different from those for coarse-grained metals. Duhamel et al [28] suggested that the
dislocation cell size (average dislocation spacing) \( l_{\text{min}} \) calculated from the Taylor relation becomes comparable to the grain size of nanocrystalline metals. Thus, it is unlikely that forest hardening based dislocation plasticity seen in coarse grained FCC metals could occur in their nanocrystalline counterparts. On the other hand, a number of studies have also suggested that nucleation and annihilation of dislocations can take place at GB ledges, triple junction points and other GB imperfections which may also act as stress raisers. Thus, nucleation and annihilation of GB dislocations could become the rate controlling processes in nanocrystalline metals. Although dislocation emission from GB ledges was first suggested by Li [29] to explain the Hall-Petch effect, models based on energy considerations [30] as well as atomistic simulations on bicrystal interfaces [31] have recently shown that planar interfaces, i.e. without ledges or steps, could also emit dislocations. Molecular Dynamics (MD) simulations of 2D columnar and 3D nanocrystalline geometries have also lead to similar conclusions regarding the role of interfaces on dislocation emission [19,32,33]. It has also been suggested that GB dislocation emission is a thermally activated mechanism [28,32,34], although there are differences in the definition of the criterion for emission of trailing partial dislocations. Dislocations emitted at a GB could then be pinned at other GB locations and the ensuing thermally activated depinning of dislocations could become a rate controlling process [34,35].

Similarly, the deformation mechanisms responsible for creep in nanocrystalline FCC metals depend on the GB angle, crystallinity of GBs, temperature, applied stress and the porosity. Diffusional creep mechanisms such as coble creep, GB sliding, and grain rotation have been suggested as likely mechanisms for creep on the basis of a number of experimental works and numerical studies. It has long been suggested that GBs and triple junction points are preferred paths for self-diffusion, as opposed to the grain interior, with diffusivity values order of magnitude more than the latter. Thus, as the volume of GBs and triple junction points increases for nanocrystalline metals, the contribution of diffusional transport along these pathways leading to creep increases significantly. Kim et al [36] have documented this increased contribution of diffusional deformation mechanisms. However, the creep rates expected for a purely diffusional process (coble creep) are much lower than
those generally reported for nanocrystalline metals [37-39]. The higher creep rates observed in experimental studies have been attributed to other diffusion-based mechanisms, such as GB sliding and grain rotation [40]. A model for GB sliding has been developed by Langdon [41,42] in which sliding occurs by the movement of dislocations along, or adjacent to, the boundary by a combination of climb and glide leading to increased creep rates at smaller grain sizes. The first type of GB sliding refers to the relative displacement of adjacent grains where the grains essentially retain their original shape but they become visibly displaced with respect to each other. This type of GB sliding is designated as Rachinger sliding [43], see Figure 1.3(a). It occurs in a polycrystalline matrix under creep conditions where there is a net increase in the number of grains lying within the gauge length along the direction of the tensile stress as the diffusion along the GBs causes the grains in the transverse direction to migrate to axial direction under shear. The second type of GB sliding, known as Lifshitz sliding [44] and shown in Figure 1.3(b), occurs exclusively in Nabarro-Herring and Coble diffusion creep processes and it is related to boundary offsets that develop as a direct consequence of stress-directed diffusion of vacancies. The GB sliding that is expected in nanocrystalline metals is a combination of these two types of GB sliding; it should be understood that although it originates from the diffusional flow along GBs, the strain accumulated during this process needs to be accommodated via other deformation mechanisms. These strain accommodation mechanisms can be purely elastic at low loads while at high loads, sliding can be accommodated by dislocation mediated deformation mechanisms originating at GBs. Thus, GB sliding results in much higher creep rates than purely diffusional mechanisms such as Coble creep, which at room temperature, involves rates $10^{-10}$ to $10^{-7}$ s$^{-1}$ [17,37,39]. At high temperatures, the aforementioned creep mechanisms in nanocrystalline metals would cross-over to dislocation mediated creep including glide and climb of dislocations as immobile dislocation structures at GBs at room temperature can become mobile at elevated temperatures.
Figure 1.3 Illustrations of the types of GB sliding: (a) Rachinger sliding, (b) Lifshitz sliding. Redrawn following the original. Original copyright notice is given to [22] in which the material was originally published. With kind permission from © 2006 Springer Science and Business Media, Inc.

Although numerous studies have focused on the measurement of the mechanical behavior of thin films at room temperature and at fixed strain rates [2,16,17,45-49], the interplay of strain rate and temperature has not been explored for nanocrystalline films. The preceding discussion pointed out that both the tensile and the creep mechanical behavior of nanocrystalline metal films may be significantly different from that of their bulk scale counterparts as different fabrication methods for thin films (sputtering, electrodeposition, evaporation) lead to different microstructure. This dissertation comes to fill this void in our knowledge by investigating experimentally the dominant deformation mechanisms of nanocrystalline FCC metal films.

1.3 Research Objectives and Approach

This Ph.D. dissertation research aims at understanding the nature of inelastic and time dependent deformation processes, the role of strain rate and temperature and the effect of their interplay on the limiting mechanisms of inelastic deformation in nanocrystalline
FCC thin metal films. This objective involves (a) the development of accurate and reliable experiment tools and protocols for the study of the quasi-static and time-dependent behavior of Au film at different strains rates and temperatures, and (b) the development of semi-empirical descriptions of the mechanical behavior of nanocrystalline Au films which capture the deformation mechanisms identified in our experimental findings.

The dissertation research objective is pursued by accurate and reliable experimental measurements of strain and stress obtained from free-standing microscale specimens, spanning up to 8 decades of strain rate, provide the basis for the ensuing analysis. Strain is measured directly from the specimen surface using high magnification optical images recorded by an optical microscope mounted camera and calculations by Digital Image Correlation (DIC). The test material was nanocrystalline Au fabricated by surface micromachining which allowed for small scale samples and therefore larger strain rates.

The expected rate sensitive mechanical response of the nanocrystalline Au films implies equally pronounced sensitivity to temperature. Thus, a technique was developed approach to conduct microscale experiments at temperatures 25-150 °C that are relevant to most microelectronics and MEMS applications, which otherwise would not be of any major effect on coarse grained metals. A reliable technique for specimen heating at the aforementioned temperatures is identified via an evaluation of Infra-Red (IR) based temperature fields and DIC-based strain fields obtained directly from the specimen surface. The experimental method of choice is implemented in the experimental apparatus from microscale strain rate experiments to carry out tests with thin Au films at strain rates $10^{-6} - 20 \, /s$ and at temperatures 25°C, 50°C, 80°C and 110°C.

It is expected that the mechanical behavior of nanocrystalline metals is influenced by diffusional creep at strain rates below $10^{-6} \, s^{-1}$, even at room temperature creep. Therefore microscale creep experiments are conducted at room and at high temperatures using the same apparatus after implementation of feedback control. The experiments focus to stresses below the elastic limit determined at the slowest quasistatic tensile tests conducted at room and at higher temperatures. In collaboration with a modeling group at the University of Illinois, a physical mechanism based model of the mechanical behavior of
nanocrystalline Au was for different strain rates and temperatures is pursued. The trends observed in temperature-strain rate experiments and the creep experiments at elevated temperatures serve as the means to identify possible deformation mechanisms and the corresponding semi-empirical mathematical modeling. Such a mathematical description of the material behavior for nanocrystalline Au films is used to obtain predictions for the long term mechanical response of these films.

1.4 Outline of this Dissertation

This thesis consists of six chapters describing the experimental techniques, measurements, and data analysis and model evaluation for the mechanical behavior of nanocrystalline Au films. The second Chapter describes an experimental method that facilitates reliable experiments with thin film materials over a wide range of strain rates as well as creep tests with thin films. The tensile test results for nanocrystalline Au thin films at rates between $10^{-6} - 20 /s$ at room temperature and a discussion of the inelastic properties are presented. The room temperature creep behavior of Au thin films is also briefly discussed and a non-linear phenomenological model based on the kinetics of thermal activation calibrated by the experimental data is presented.

Chapter 3 presents a technique for microscale experimentation at elevated temperatures. Two commonly employed methods for specimen heating, namely Joule heating and uniform specimen heating using an external heater are compared via full-field strain and temperature measurements directly obtained on the specimen surface. An evaluation of the efficacy of the two methods by using DIC and mid-IR microscopy is presented and the implications of using each of the two methods to obtain stress-strain curves and inelastic material properties are discussed.

The fourth Chapter presents the experimental results and discussion for the tensile experiments performed on nanocrystalline Au films over seven decades of strain rate and at temperatures ranging from room temperature to $110 \, ^{\circ}$C. Trends for inelastic properties are presented and the likely deformation mechanisms are discussed on the basis of
activation volume calculations using yield strength values. The trends for activation volume are modeled using a model for thermally activated depinning of dislocation loops at GBs, which has been suggested by Kato [35], and the activation energy for deformation mechanisms is determined.

The hardening behavior of nanocrystalline Au thin films is presented in the fifth chapter. The hardening curves are modeled using a linear hardening law with appropriate relationship for the state variable and the saturation stress. The time dependent mechanical behavior of nanocrystalline Au films, as obtained by creep experiments conducted at nominally elastic loads and at temperatures up to 110 °C, is also presented in the fifth Chapter. The stress dependence of creep strain at room temperature is modeled by a non-linear model based on the kinetics of thermal activation. The recovery of plastic strain at room temperature is also analyzed by using multi-cycle creep experiments and the history dependence of the creep deformation is briefly discussed. Finally, the Conclusions Chapter provides an assessment of the results of this dissertation research vis-à-vis the initially stated objectives.
CHAPTER 2

Rate Sensitivity and Creep of Au Thin Films at Room Temperature

Competing deformation mechanisms in nanocrystalline metals result in increased rate sensitivity which may not be uniform across all time scales: diffusion controlled processes are important at slow strain rates and may dominate for large fractions of GBs, while intragranular mechanisms are dominant at high strain rates. The competition between the two processes is expected to control the strain rate sensitivity and activation volumes in nanocrystalline metals.

Thus, probing the mechanical response of nanocrystalline metal films under different loading rates presents a means to capture the time scales at which different mechanisms play a rate controlling role. To date, such experiments have been limited to a small range of strain rates, typically $10^{-6}$ - $10^{-3}$ s$^{-1}$ [2,16,17]. The results have been indicative of rate sensitivity, but the range of time scales probed is rather too narrow to extract firm conclusions and separate the effects of creep [50] and anelastic stress relaxation [51] that are present at slow strain rates. In fact, the effect of material creep and relaxation has not been accounted for in the majority of studies on nanocrystalline metals. Its importance is often assessed in terms of the steady state creep rate, which for nanocrystalline FCC metals has been reported to be of the order of $10^{-10}$ - $10^{-7}$ s$^{-1}$ [37,52] at room temperature. However, these values are quite lower than the primary creep rate which is a function of the applied stress amplitude and affects the measured values for the elastic limit and the yield strength. Given that the elastic limit stress of nanocrystalline
metals can reach quite large values, it follows that the primary creep rates in nanocrystalline metals subjected to high elastic stresses could be an order of magnitude higher than those reported in literature for bulk metals. Therefore, unless experiments span regimes of strain rate significantly broader than $10^{-6} - 10^{-3}$ s$^{-1}$, it may not be possible to separate the effects of stress induced plasticity and creep strain or stress relaxation. Recent experiments with Pt films that covered a broad range of strain rates, namely $10^{-6} - 20$ s$^{-1}$, showed a consistent rate sensitivity factor at all strain rates [45]. On the contrary, the microscale tension experiments with Au films reported in [2] have shown a sharp reduction in yield and maximum tensile strength after $10^{-5}$ s$^{-1}$. Therefore, there is sufficient evidence that Au films will be more prone to the aforementioned competition between deformation mechanisms.

It should be noted that there are additional considerations in experimentation with thin films arising from the small film thickness, the grain size and their relative dimensions [2,13,17]. Espinosa et al [13] reported an inverse relationship between the film thickness and the yield strength of Au and Al films. More recently, Chauhan and Bastawros [53] investigated in detail the interplay between grain size and film thickness. The thin Au films employed in this dissertation had grain sizes that were 20-40 times the film thickness and, therefore, such finite size effects are not considered as a potential issue. The role of the grain size itself is an important one but given the large number of experimental parameters involved in the experiments presented in this dissertation research (strain rate, temperature) the grain size was held constant.

This experimental investigation focused on relationships between the strain rate and inelastic mechanical properties of Au films with nanoscale grain size and micrometer thicknesses. Using the same approach as in [45], the experiments conducted spanned the strain rate regime of $10^{-6} - 20$ s$^{-1}$ in order to quantify the effect of competing deformation mechanisms with different intrinsic time scales on the mechanical response of films. The experimental data are discussed in terms of activation volume calculations, and are corroborated by creep experiments to determine the primary and steady-state creep rates, and by fractographic studies to characterize damage evolution at slow and high strain rates.
2.1 Experimental Methods

2.1.1 Specimen Preparation and Materials Characterization

All specimens were fabricated by Dr. Hao-Han Hsu and Mr. Anurag Garg from Professor Peroulis’ research group at the Birck Nanotechnology Center-Discovery Park at Purdue University. Specimen fabrication started with a 500 nm layer of thermal oxide grown on a silicon (100) wafer followed by a 2 μm thick photoresist layer, as shown in step (A) in Figure 2.1(a). After patterning the photoresist layer in step (B), a trench was created in the oxide layer for depositing Au, as shown in step (C). The photoresist layer was then removed and a 20 nm thick Ti layer was deposited to assist the adhesion of Au to the oxide layer, which was deposited by RF sputtering. A second layer of 2 μm thick photoresist was then spin-coated and patterned to etch Ti/Au in a pattern that matched the final specimen dimensions, as shown in step (D). Finally, the second photoresist layer was removed and the silicon underneath the Au layer was etched with XeF₂. The free-standing Au films were prepared as shown in schematic (E) after 30 cycles of etching, each lasting for 15 s. This process produced Au specimens with thicknesses of 1.76 and 0.85 μm and gauge width and length of 100 and 1000 μm, respectively, as shown in Figure 2.1(b).

Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) studies were conducted to determine the thickness, average grain size and the texture of the Au films. Both in-plane and cross-sectional TEM samples were prepared to measure the grain size on the plane of the film and through the cross-section. For plan view TEM images, the 1.76 μm thick sample was mounted on a TEM grid to be ion milled for 30 min and obtain an electron transparent region. The bright field TEM micrograph in Figure 2.2(a) was used to obtain the grain size distribution shown in Figure 2.2(b). The average grain size, calculated from several TEM micrographs using the line averaging method, was 30 ± 6 nm. From the diffraction pattern analysis it was found that the texture was predominantly (111) in the grain growth direction, with some evidence of (110). The film texture was consistent with previous reports on sputtered Au thin films [17]. The wedge polishing technique was applied to obtain an electron transparent region for cross-sectional TEM sample preparation. In Figure 2.2(c), one can observe that the cross-section of the Au films was composed of several layers of deposition. Many grains
could be seen across the thickness of the film and the grain size was smaller in the cross-section compared to its in-plane dimensions. Finally, the cross-sectional SEM image in Figure 2.2(d) shows the cross-section of an Au film, prepared by milling and polishing the cross-section by a focused ion beam (FIB) milling process at low current. This cross-sectional SEM image also provides an indication of a finely layered structure.

Table 2.1 summarizes the details of the grain size, texture and lattice constant for each film thickness, as obtained by XRD. The correct value for the Au lattice constant ensures the accuracy of the XRD measurements. For all practical purposes the grain size of the two film thicknesses was considered to be the same ($d \sim 40$ nm) in evaluating the experimental results.

![Figure 2.1](image.png)

**Figure 2.1.** (a) Fabrication of microscale Au specimens: (A) deposition of thermal oxide and spin-coating of photoresist for patterning, (B) patterning of the photoresist by photolithography, (C) etching of the oxide layer, (D) removal of photoresist and sputter deposition of Au layer, and (E) dry etching of silicon under the specimens. (b) SEM micrograph of a free-standing test specimen.
Table 2.1. X-Ray diffraction results for the two Au film thicknesses.

<table>
<thead>
<tr>
<th>Film thickness (μm)</th>
<th>Grain size (nm)</th>
<th>Texture</th>
<th>Lattice constant (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.83</td>
<td>44</td>
<td>&lt;111&gt;</td>
<td>0.4091</td>
</tr>
<tr>
<td>1.76</td>
<td>38</td>
<td>&lt;111&gt;</td>
<td>0.4095</td>
</tr>
</tbody>
</table>

Figure 2.2. (a) Planar view TEM micrograph of an Au thin film, (b) distribution of grain sizes, (c) cross-sectional TEM image, (d) SEM image of the cross section showing the grain structure through the film thickness. Courtesy: The TEM imaging was performed by Dr. K. Jonnalagadda with the assistance of Dr. S.J. Suresha at Johns Hopkins University, MD.
2.1.2 Instrumentation and Methods for Microscale Mechanical Experiments

Experiments at time scales varying from microseconds to hours require a force sensor with fast time response, long-term stability and rate-independent compliance, as well as displacement actuators with fast response and minimal inertia. Similarly, strain must be measured directly from the specimen gauge section, preferably using a fine speckle pattern generated on the free-standing specimens with submicron scale particles. Such a fine speckle pattern was generated by using a custom-built apparatus to disperse silicon particles with 1 μm average size and a homogeneous distribution on the surface of free-standing Au films according to the method described in [45]. The particles adhered to the Au films by virtue of van der Waals forces, and followed the material point displacements. The application of DIC on digital images of the speckle patterned surfaces, which were obtained by high magnification light microscopy, provided high-fidelity axial and transverse displacement fields [45]. This measurement method can provide ~25 nm resolution in rigid body translations simply by using high magnification optical images [45], which is comparable to the resolution for experiments conducted inside SEMs and TEMs. The use of optical microscopy furnishes the additional capability of probing strain rates varying by almost eight orders of magnitude, which is not possible in experiments conducted inside electron microscopes.

In order to span the rate regime of \(10^{-6} - 10 \text{ s}^{-1}\), two loadcell types were employed: A strain gauge loadcell for loading rates of up to \(10^{-3} \text{ s}^{-1}\), and a piezoresistive loadcell for strain rates \(10^{-3} - 20 \text{ s}^{-1}\). A modular microscale tensile testing apparatus, which was developed by this group in the past, accommodated the two transducers [45]. A digital camera with a maximum frame rate of 15 fps and 1024×768 pixel resolution was used at low strain rates \((10^{-6} - 10^{-3} \text{ s}^{-1})\) and a high speed camera with up to 35,000 fps at pixel resolution 512×104 was used for experiments at strain rates \(10^{-3} - 20 \text{ s}^{-1}\). The strain in each experiment was computed from optical images, so the use of two apparatuses with components of different compliance did not affect the calculation of full-field displacements or strains by DIC as shown in [45]. In order to compare the measurements from the two apparatuses, Au specimens of 1.76 μm thickness were tested at the same strain rate \((6 \times 10^{-3} \text{ s}^{-1})\) by using the strain gauge loadcell (slow) and the piezoresistive
Figure 2.3 Engineering stress–strain curves at different strain rates for (a) 0.85 μm and (b) 1.76 μm thick Au films.
loadcell (fast). The two stress vs. strain curves overlapped almost until failure, which emphasizes the accuracy and repeatability of the present experiments [45]. Figures 2.3(a) and 2.3(b) show the engineering stress vs. strain curves for two film thicknesses at strain rates of $6 \times 10^{-6}$ - $20 \text{ s}^{-1}$. The precise strain rate was determined directly from the strain measured by the CCD camera. The engineering stress vs. strain plots were linearly elastic up to large stresses, followed by yielding and limited strain hardening before final failure.

2.2 Rate Dependent Mechanical Behavior of Nanocrystalline Au Films

The experiments on Au films with the apparatus described above have been described in detail in reference [45]. This dissertation research was focused on activation volume calculations based on the experimental results and auxiliary creep experiments at room temperature. As discussed in [45], the elastic modulus values at different strain rates were very consistent averaging $64.7 \pm 6.5$ and $66.6 \pm 2.5$ GPa for 0.85 and 1.76 lm thick specimens, respectively, and $66 \pm 4.5$ GPa for both thicknesses. The inelastic properties of the Au films, i.e. the elastic limit, the yield strength and the ultimate tensile strength, were significantly higher than the literature values at comparable strain rates [2,13,16,17] due to the Hall–Petch effect, which was pronounced due to the small grain size of ~40 nm. Furthermore, the trends in the elastic limit, the yield strength and the ultimate tensile strength in a range of almost eight decades of strain rate pointed to strain rate sensitivity, which was in agreement with previous results for Au [2,16,17] and other nanocrystalline FCC materials, such as Cu [50] and Ni [54]. The ultimate failure strain increased drastically for strain rates $\leq 10^{-5} \text{ s}^{-1}$ and for both thicknesses, thus indicating strong influence of creep at the lower strain rates. The small grain size promoted enhanced GB diffusion and concomitant inelastic deformation by increasing the net GB volume and contribution of GB based deformation processes. The significantly increased role of the latter changed the relative importance of the inelastic deformation mechanisms [18], thus resulting in increased strain rate sensitivity and reduced apparent activation volumes.

Figure 2.4(a) is the log-log plot of the elastic limit and yield strength vs. the applied strain rate, both following bilinear trends, i.e. power laws. The calculated rate sensitivity
factors are indicated next to each fitted line segment. For example, using the elastic limit, the strain rate sensitivities were 0.03 for strain rates $10^{-4} - 20$ s$^{-1}$ and for both film thicknesses, and 0.07 and 0.15 for the small and the large thickness films, respectively, at strain rates of $10^{-6} - 10^{-4}$ s$^{-1}$. Strain rate sensitivities of 0.01 - 0.03 have been reported before for nanocrystalline Ni based on tensile and nanoindentation experiments [55] at strain rate regimes corresponding to the fast strain rates applied in this study. The trends above are similar to those using the 0.2% yield strength, but, given that the elastic limit is the first indication of deviation from the elastic behavior, it is considered to be a better parameter to assess the contribution of GB processes to the overall inelastic deformation compared to the graphically calculated 0.2% yield strength, which inevitably includes hardening.

Figure 2.4(b) is a plot of the natural logarithm of the applied strain rate vs. the elastic limit for the two film thicknesses, from which the activation volume $v$ at a temperature $T$ can be calculated as [24]

$$v = \sqrt{3} k T \frac{\partial \ln(\dot{\varepsilon})}{\partial \sigma}$$

where $k$ is the Boltzmann’s constant. Similarly to the strain rate sensitivity factors, the activation volumes followed bilinear trends. At low strain rates ($\leq 10^{-5}$ s$^{-1}$), which are within the rates covered by most literature data for Au films [2,16,17], GB diffusion, GB sliding mediated by diffusion and dislocation activity are the primary reasons for increased rate sensitivity, which is also corroborated by the small activation volumes, i.e. 4.5 b$^3$ and 8.1 b$^3$. It should be noted that the value of 8.1 b$^3$ has been derived using a narrow range of strain rate data and, thus, the true value is expected to be smaller.

However, even at considerably faster strain rates ($10^{-4} - 20$ s$^{-1}$), the activation volumes were 12.5 b$^3$ and 14.6 b$^3$, which are low compared to large-grain Au, and are potentially due to the significant fraction of GB which control dislocation nucleation and pinning [34], and to the small grain size which limits the average dislocation line length. Activation volume of 14 b$^3$ has also been reported before from tensile experiments with nanocrystalline Ni with 20 nm grain size [18]. The larger activation volumes at rates of $10^{-4} - 20$ s$^{-1}$ are a strong indication of intra-granular dislocation based plasticity, as opposed to
the slower strain rates when GB processes dominate. Smaller activation volumes, between 2.7 b³ and 5.6 b³, have been reported from Al nanopost compression experiments at the nominal strain rate of 0.02 s⁻¹ [56].

The activation volumes from nanopost experiments have been related to dislocation nucleation. The smaller activation volumes in the current work at lower strain rates represent the combined effect of GB diffusion and GB sliding; Dislocation nucleation is required to mediate these two mechanisms. The low activation volumes reported from nanopost experiments at rates comparable to our fast strain rates are in agreement with experimental observations where the activation volumes calculated from nanoindentation experiments (7b³) were half of those calculated from tensile experiments (14 b³) for the same nanocrystalline Ni [18,55].

Similar arguments can be made about the strain rate sensitivity plots. There is a fivefold increase in the strain rate sensitivity factors at ≤ 10⁻⁴ s⁻¹ for 1.76 μm films, supporting the aforementioned argument for significant contribution of room temperature creep to the total inelastic deformation. At the high stresses of 450-700 MPa at which the Au films reached their elastic limit at loading rates 10⁻⁴ - 20 s⁻¹, it is expected that dislocation plasticity [4,36] dominates, while at the slower strain rates of 10⁻⁶ - 10⁻⁴ s⁻¹, GB diffusion and other diffusional creep mechanisms play a major role in inelastic deformation, as supported by the marked change in the rate sensitivity factor at 10⁻⁴ s⁻¹.
Figure 2.4 (a) Rate sensitivity plots for the elastic limit and yield stress for 1.76 μm thick Au specimens. (b) Logarithm of strain rate vs. elastic limit for nanocrystalline Au films with 0.85 and 1.76 μm thickness, with the apparent activation volume, $V$, also shown.
2.3 Room Temperature Creep at Intermediate Stresses

At nominally elastic stresses, the mechanical stability of nanocrystalline metal films is strongly influenced by creep strain [1,57]. However, the majority of relevant research to date has been focused on the quasi-static elastic-plastic response as a function of microstructure [6,7] and specimen size [9,13]. As shown in Section 2.2, the mechanical behavior in the slow rate regime ($\leq 10^{-4}$ s$^{-1}$) is strongly influenced by diffusional creep. Dislocation-based mechanisms are dominant at higher strain rates and are different from those for coarse grained metals as GB regions play an important role in dislocation activity.

![Figure 2.5 Creep strain vs. time for applied loads between 100 - 350 MPa.](image)

Prior stress relaxation and creep studies on metallic films mainly employed nanoindentation [58-60] and bulge experiments [51,61], while uniaxial tension experiments have been scarce [62]. In this dissertation, uniform tension creep experiments were conducted on free-standing nanocrystalline Au films of 1 mm gauge length, 50 μm width and 1.76 μm thickness. The average grain size was 40 nm and the films had preferred $<111>$ texture in the grain growth direction as described in Section 2.1.1. The experimental
apparatus described in Section 2.1.2 was used to perform the creep experiments with a feedback loop to maintain constant stress with an accuracy of 1 MPa or better. The creep strain was measured directly from the specimen surface by DIC [45] with strain resolution of the order of 0.001%. Results from creep experiments, conducted at stresses below the elastic limit, \( \sigma_{\text{elastic}} = 350 \) MPa determined by low strain rate microscale tension experiments \((6 \times 10^{-6} \text{ s}^{-1})\), are shown in Figure 2.5. During the three cycle creep experiments, the Au films were held at constant load for 8 - 21 hr and then were allowed to relax at zero load for 3 hr. The creep strain exhibited a strong primary (transient) component both in terms of duration (5-6 hr) and magnitude of the initial creep rate \((3.3 \times 10^{-8} - 2.7 \times 10^{-7} \text{ s}^{-1})\). The secondary, or steady-state creep, commonly used to identify the physical mechanism for creep, had significantly lower rates of \(5.5 \times 10^{-9} \) to \(1.1 \times 10^{-8} \text{ s}^{-1}\). Notably, the creep rates at stresses near the elastic limit (350 MPa) were considerably higher than those at nominally elastic stresses, due to the increased contribution of dislocation-based creep.

Creep in nanocrystalline metals has been described using the Coble creep model [21], the modified Ashby model [22], or a phase mixture model [36]. Although GB sliding has been suggested as a likely deformation mechanism for creep in nanocrystalline metals, it must be accommodated by accumulation of strain by other elastic and plastic deformation mechanisms [63,64]. At low stresses, GB sliding can be accommodated via elastic and diffusional mechanisms, while the contribution of dislocation-based mechanisms increases significantly at higher stresses [42]. Although direct observation of GB sliding in in-situ TEM experiments is quite difficult [40,65,66], GB sliding can manifest itself in the form of its accommodation mechanisms such as dislocation activity originating at GBs [67].

It has been shown that relaxation of thin Al and Au films [68] at stresses of the order of 100 MPa or less can be described well by linear viscoelasticity assuming Boltzmann superposition: the material response to an applied stress (or strain) change is independent of the stress history, so the overall material behavior after multiple stress (or strain) changes can be described by adding all previous strain (or stress) response functions. Although Boltzmann’s superposition may hold for low stresses where GB sliding could be accommodated by elastic and diffusional mechanisms, higher loads involved an increased contribution of dislocation-based strain accommodation mechanisms, thus leading to the
nonlinearities in the isochronous creep curves during the first cycle for each stress, which are shown in Figure 2.6.

![Figure 2.6 Isochronous creep curves for 1.76 μm thick nanocrystalline Au films at different times, t, after instantaneous loading to prescribed values of stresses.](image)

This non-linearity is owed to thermally activated creep mechanisms for the nanocrystalline grain size; the kinetics of thermal activation suggest that an exponential relationship could capture the effect of the applied stress, $\sigma$, and the energy barriers $a_p$ and $a_{ss}$ for thermally activated primary and steady-state creep [69], respectively, as:

$$\eta_1 = \exp(a_p - a_1 \sigma) \tag{2.2}$$

$$\eta_2 = \exp(a_{ss} - a_2 \sigma) \tag{2.3}$$

The creep strain $\varepsilon_c$ for the total creep response of the material can follow an equivalent nonlinear Burgers viscoelastic model as:
\[
\varepsilon_c = \frac{\sigma}{E_h} \left( \frac{E_h}{\eta_2} t + \left( 1 - \exp \left( \frac{-E_h}{\eta_1} t \right) \right) \right) = \frac{\sigma}{E_h} \left[ \frac{E_h}{\exp(a_{ss} - a_2 \sigma)} t + \left( 1 - \exp \left( \frac{-E_h}{\exp(a_p - a_\sigma)} t \right) \right) \right]
\]

(2.4)

where \( E_h \) corresponds to the delayed elasticity component quantifying the duration of primary creep and is a direct consequence of competition between strain hardening and recovery in the material. It should be noted that, if a linear hardening law is assumed, the delayed elasticity term can be described as \( E_h = a_3 - a_4 \sigma \). A similarly modified nonlinear viscoelastic model has been used before to describe the nonlinear viscoelastic behavior of epoxy adhesives [70]. The stress nonlinearity introduced in the exponential relationships is a direct consequence of the kinetics of thermal activation for creep deformation and provides an adequate representation of the overall creep behavior of nanocrystalline Au films.

In its current form the model is not calibrated for history dependence of creep i.e. evolution of creep with subsequent cycles, but is shown to capture well the stress dependence of creep strain. The model described by Equation (2.4) has been calibrated using the experimental data for the first creep cycle, as shown in Figure 2.7. As expected, the accuracy of the model for the high stress of 350 MPa was poor indicating that the creep mechanism may change to dislocation-mediated processes. However, the experimental data in the range of 100-250 MPa provide predictions for the long-term strain response of nanocrystalline Au films subjected to cyclic loads at low frequencies (period ~ 4-60 min) and for extended periods of time by numerically integrating the nonlinear differential equation associated with Equation (2.4) [71].
2.3.1 Predictions by Thermally Activated Model for Non-linear Creep

The non-linear dependence of the creep strain with applied stress not only affects the mechanical response at constant stress but also has profound impact on the mechanical response for cyclic stresses. This long term effect of creep under cyclic loading has been explored by calculations carried out in collaboration with Mr. Fernando Stump [72]. In this analysis the material response was calculated for instance for a square loading profile with mean stress, $\sigma_m = 175$ MPa and amplitude, $A = 75$ MPa, i.e. stress profile with a minimum value of $\sigma_{\text{min}} = 100$ MPa and a maximum value of $\sigma_{\text{max}} = 250$ MPa. The curves for the lower
bound of creep strain as a function of time for stress amplitudes 25, 50 and 75 MPa and a mean stress of 175 MPa are shown in Figure 2.8. The material response for constant mean stress of 175 MPa, i.e. zero oscillation amplitude, is also shown in Figure 2.8. As explained by McLean et al [68], if the creep response followed a linear viscoelastic law, the effective cyclic creep response represented by the lower bound, i.e. the difference between the total strain and the initial elastic strain at $\sigma_{\text{min}}$, should be identical to the creep strain produced by the mean stress. Due to the nonlinearity of Equation (2.4), the effective creep in Figure 2.8(a) depends not only on the average applied stress but also on the stress amplitude. This non-linearity also affects the relative contributions of the primary and secondary creep, which are assessed by the accumulated primary creep strain, i.e. the strain accumulated due to the effective primary creep for cyclic loads, and the secondary creep rate, i.e. the effective steady-state creep response, shown in Figure 2.7. These two quantities normalized by the corresponding values for the creep curve at mean stress of 175 MPa are shown in Figure 2.8(b): The accumulated primary creep strain increased by 25%, while the secondary creep rate decreased by 21% for high stresses. From a long-term material stability perspective, it is important to note that the accumulated total creep strain can be effectively controlled by changing the amplitude of the applied cyclic stress. The difference in the accumulated primary creep strain could arise from the strong influence of the non-linear dependence of the primary creep rate on stress, thus leading to high creep rates at the maximum value of applied stress, which cannot be completely recovered at smaller driving force, leading to accumulated primary creep strain. The opposite trend is observed during the secondary creep phase as the secondary creep rate is reduced with increasing amplitude. The primary creep response at $\sigma_{\text{min}}$ lasts much longer than the cycle period and hence the strain recovery due to the reduction in stress from $\sigma_{\text{max}}$ to $\sigma_{\text{min}}$ is larger for increasing stress amplitudes. Consequently, for increasing stress amplitudes the increase in strain recovery at $\sigma_{\text{min}}$ is larger than the increase in creep strain accumulated at $\sigma_{\text{max}}$. Thus, the reduction in the effective steady state creep rate is a direct consequence of the long duration of primary creep leading to higher strain recovery at low bounds of cyclic stress.
Figure 2.8 (a) Effective cyclic creep strain for a material point subjected to a square stress profile with mean stress of 175 MPa, a period of 3 min and different amplitudes. (b) Accumulated primary creep strain and steady-state creep strain rate normalized with the corresponding parameters from the creep curve at 175 MPa [72].
2.4 Conclusions

The strain rate sensitivity of free-standing nanocrystalline Au films with 40 nm average grain size was experimentally investigated over a wide range of strain rates, namely $6 \cdot 10^{-6} - 20 \text{ s}^{-1}$. The experimental apparatus and methods were verified for their accuracy at all applied strain rates by the consistent elastic moduli measured from free-standing Au films, averaging $66 \pm 4.5 \text{ GPa}$. Au films of thicknesses 0.85 μm and 1.76 μm were found to be strain rate sensitive and were characterized by small activation volumes ($4.5 \text{ b}^3$ and $8.1 \text{ b}^3$ vs. $12.5 \text{ b}^3$ and $14.6 \text{ b}^3$ at strain rates lower and higher than $10^{-4} \text{ s}^{-1}$, respectively) and by very high inelastic property values. All of the above results could be attributed to the nanoscale grain size that promotes strengthening.

The very high elastic stresses even at slow loading rates increased the contribution of primary creep at an initial rate $\geq 10^{-7} \text{ s}^{-1}$, which influenced the slow strain rate response and increased the material rate sensitivity at loading rates smaller than $10^{-4} \text{ s}^{-1}$. The two different regimes of strain rate sensitivity established with respect to rates $10^{-5} - 10^{-4} \text{ s}^{-1}$ pointed to the important realization that knowledge of the inelastic material parameters of nanocrystalline films at the commonly used strain rate of $10^{-4} \text{ s}^{-1}$ is not sufficient because this rate could be a pivotal point in their inelastic mechanical behavior.

Experiments showed that the primary creep of nanocrystalline Au films has significant duration, thus accumulating large strains, which presents long-term reliability concerns. Contrary to the creep response at low stresses, $\sigma < 100 \text{ MPa}$ for which diffusional transport along GBs can be described by a linear viscoelasticity model, the creep response at higher stresses (100-250 MPa) requires nonlinear viscoelasticity models, which are only valid for stresses smaller than the elastic limit, above which creep associated with dislocation glide and climb may be described by a power law relationship. Such a nonlinear viscoelasticity model describes the material behavior in the transition regime between purely diffusional transport along GBs at low stresses ($\sigma < 100 \text{ MPa}$) which is described by a linear model, to dislocation glide and climb which is described by a power law relationship at stresses above the elastic limit. This model for intermediate stresses applied in this research was based on thermal activation and related energy barriers associated with
deformation processes without assuming specific deformation mechanisms. An estimate of
the long-term mechanical response of nanocrystalline Au films subjected to cyclic loading
was obtained by virtue of this creep calibrated model. The effective primary creep due to
cyclic loading was found to increase, while the effective secondary creep rate decreased
for increasing stress amplitude.
CHAPTER 3

Microscale Experiments at Elevated Temperatures

The strain rate sensitivity and creep of nanocrystalline metal films at room temperatures documented in Chapter 2 are further accentuated at elevated temperatures which are common in thin film applications: RF-MEMS switches can experience operating temperatures in the range of -40° to 120 °C. Knowledge of the mechanical behavior of thin films in this range of temperatures is very limited, however, thus, impacting our ability to design metallic microdevices that operate in this regime. The main reason for the lack prior research in this area is that high temperature experiments with microscale specimens are not straightforward if the actuation and measurement instrumentation must be included inside a hot or cold chamber.

3.1 State-of-art in Microscale Experiments at Elevated Temperatures

Existing experimental methods have used either thin films attached to a thick compliant substrate, or free-standing structures with thicknesses varying from hundreds of nanometers to hundreds of microns. Unfortunately, most of these methods are not compatible with microscale surface micromachined MEMS either because of the use of a specimen carrier (substrate or testing frame) or the need to fabricate thick specimens or large films to accommodate specimen manipulation and gripping. Yet, in the past, thermal expansion coefficients have been measured from thin microbeams and thin film structures
by using both resistive (Joule) and uniform specimen heating [73-76]. Gruber et al [77] performed high temperature tension tests on metallic thin films deposited on thick polyimide substrate carriers using a custom heating assembly and temperatures −150 to 200 °C. They computed 2D strain fields from optical measurements by DIC while the stresses were computed from diffraction data. However, the presence of a thick elastic substrate with different stiffness and Poisson’s ratio controlled the strain in the thin film specimens and dictated the evolution of plastic deformation in the film. Similarly, films attached to substrates have been tested by instrumented nanoindentation using a custom heating assembly at temperatures 20-200 °C [78,79].

In terms of free-standing structures, Emery et al [80] investigated the strain rate dependence of Au thin films of 2.1 μm thickness at 200–400 °C by placing their test apparatus in a custom built furnace. Oh et al [81,82] developed a technique for testing free-standing polysilicon films with millimeter dimensions (4 mm×0.6 mm×3.5 μm) at 700 °C by resistively heating the films via a DC current. Measurements by an optical pyrometer along the gauge section showed significant temperature variations, but the temperature in a 250 μm center region was the highest and according to the authors within ±10 °C. Because of this temperature variation, resistive heating may be appropriate to obtain tensile strength data under brittle failure as opposed to determining the evolution of the entire elastic/plastic material behavior. This is especially true when crosshead displacements from such experiments are used to construct engineering stress-strain curves. Zupan et al [83,84] also employed the aforementioned approach to test 318-500 μm thick Ni superalloy samples and 500 μm thick γ-TiAl alloy samples. The thick specimens allowed for high specimen temperatures via resistive heating, which, according to the authors, varied by approximately 75 °C along the specimen gauge section, while the measurement of temperature along the sample was conducted with an optical pyrometer with spot size of 290 μm. These methods have been demonstrated on large or very thick samples and are not directly applicable to significantly thinner (1-3 μm) and smaller (100×1,000 μm²) surface micromachined specimens. In terms of thin specimens, Haque et al [85] performed uniaxial tension tests with ultra-thin free-standing aluminum films at temperatures up to 160 °C by attaching a bulk micromachined chip onto a hot plate. They measured the chip temperature
by a thermocouple because direct temperature measurements were not possible due to the small specimen size. They used the electrical resistance of a specimen placed inside an oven to calibrate the temperature on the hot plate. Kalkman et al [86] used bulge testing to apply monotonic loading and perform creep tests with thin film samples at temperatures up to 300 °C by heating the air in a pressure chamber and measuring the temperature by a thermocouple near the sample. Other groups also performed creep [62,87], stress relaxation [51] and fatigue experiments on thin films [88] at elevated temperatures using the aforementioned heating methods.

These methods, however, are appropriate for non-surface micromachined specimens and often result in non-uniform or not directly measurable temperature and strain profiles. This dissertation describes the first microscale tension experiments with free-standing thin films at uniform elevated temperature via a custom-built microscale heater where full-field strain measurements were obtained by means of DIC. The results are compared with experiments on thin film specimens heated to elevated temperatures by resistive (Joule) specimen heating. Comparisons are made on the grounds of strain and temperature distributions obtained by DIC analysis of optical images and infrared (IR) pictures, respectively. The spatial resolution of the IR camera is 15 μm which is appropriate for surface micromachined specimens that are tens of microns wide. Benchmark experiments were conducted at 110°C which represents an upper temperature limit for metallic films used in MEMS and microelectronics. The spatially resolved temperature profiles and the full-field strains along the specimen gauge section, which were used to construct the stress-strain curves, provided a quantitative comparison of the accuracy of resistive specimen heating of Au thin film specimens with 850 nm thickness.

3.2 Experimental Methodology

The Au specimens fabricated by the procedure described in Section 2.1.2 were annealed at 150 °C for 12 hr to eliminate residual stress relaxation and defect annihilation occurring during heating and testing at different temperatures. The duration and temperature of heat treatment were considerably longer than those experienced by the
samples during experimentation. XRD measurements on the annealed films revealed a slight increase in the average grain size to 64 nm from an original average grain size of 55 nm.

The microtensile experimental apparatus described in [45] was modified to integrate the two heating methods to conduct tension experiments under an optical and an IR imaging camera-lens system. A nominal (crosshead) strain rate of $9 \times 10^{-5}$ s$^{-1}$ was applied in all optical and IR imaging experiments although the setup could be used for strain rates $10^{-6}$–20 s$^{-1}$ and at different temperatures.

### 3.2.1 Calibration of IR Measurements

Calibration of the IR camera at the relevant temperature regime was performed by taking into account spatial variations in sensor sensitivity to position the specimen’s area of interest on the same physical IR sensors. All IR images were recorded by a liquid nitrogen cooled Stress Photonics’ IR camera (DT1410) coupled with a 4× microscopic IR objective at exposure time 192 ms, which gave the best combination of temporal and temperature resolution at all applied temperatures. During calibration, the sample die was mounted onto the microscale tension testing setup and attached to the loading grip, and a low tensile load (resulting in a small tensile stress of 20-30 MPa) was applied to straighten the sample in order to eliminate the initial specimen curvature. Alignment of the thin films with respect to the camera plane is critical in IR imaging of small scale specimens: a slight specimen tilt results in a gradient of IR intensities along the specimen gauge section. T-type thermocouples were attached to the die surface at the specimen anchor as well as the interior of the microheater itself where the strain gauges were attached (see detailed description below). For all specimens, uniform IR intensities along the specimen gauge section were recorded at all temperatures, while the specimen top surface was consistently at 2-5 °C lower temperature than the microscale heater interior. The IR intensity levels along the gauge section of the thin films varied at all temperatures by a constant noise level of 10-20 au (arbitrary units), which can be attributed to the noise floor of the IR sensors. As can be inferred from Figure 3.1, the constant noise floor has a more pronounced effect.
at low temperatures where the temperature sensitivity (slope of the curve) is lower. Another important factor in temperature calibration was the effect of the background materials on the intensity recorded along the specimen gauge section. It was noted that the free-standing part of the specimens generally had higher intensity than its ends that are attached to the Si die, leading to a temperature difference of 5-7 °C between the free-standing gauge section and the fixed regions of the specimen. Even though all the dies carrying tensile specimens were fabricated in the same batch, each die was calibrated individually because differences in the sample surface roughness resulted in differences of 100–300 au in the IR intensity levels. However, it should be noted that the temperature calibration curves remained very consistent within the same die.

Figure 3.1 Calibration curve of average IR intensity on the gauge section for a 0.83-μm thick Au specimen vs. the temperature recorded by a thermocouple on the specimen surface.
3.2.2 Microheater Based Uniform Specimen Heating

A home-built microscale heater, tested at temperatures up to 160 °C, was built as shown in Figure 3.2(a) to conduct the uniform temperature heating experiments. The heater was built on a MACOR ceramic sheet with the same dimensions as the die holding the test specimens, i.e. 1×1 cm² in surface area and 4 mm in thickness. The temperature of this open-loop heater was controlled by resistive heating elements embedded inside a 4 mm plate. The heating elements were two resistance strain gauges (350 Ω ± 0.015%) with thickness of 150 μm. The strain gauges were attached to the MACOR block with a high temperature cyanoacrylate adhesive. A 0.5 mm thick aluminum plate was attached on top of the strain gauges to serve the flat plate for uniform heating. A T-type thermocouple element was attached inside the microscale heater and a second onto the die surface to monitor the temperature as a function of the applied DC voltage. The 1×1 cm² die carrying the free-standing specimens was attached to the aluminum plate. Special care was taken to thermally isolate the loadcell from the microheater assembly. An insulating spacer separated the specimen holder (with the integrated microscale heater) from the loadcell limiting the temperature near the loadcell to less than 30 °C after hours of operation of the microheater at the maximum temperature. A calibration of the temperature compensated loadcell performed at 23-33°C showed that the loadcell calibration factor varies by only 0.4% in this temperature range.

The thin film specimens were aligned under an optical microscope and attached to the gripping assembly by a high temperature UV curable adhesive and were heated by applying a DC voltage up to 15 V to the heater while the experimental apparatus was placed under the IR camera to determine the temperature profile along the specimen gauge section. Because the IR camera and the optical microscope could not be used concurrently to image the specimen surface, the apparatus was moved from the IR to the optical microscope after the temperature profile measurement. Complete experiments were also conducted exclusively under the IR camera at the maximum camera frame rate of 1 fps to record the temperature evolution along the specimen during tension testing.
Figure 3.2 (a) Schematic of the custom-built microheater for uniform specimen heating. (b) Top view of resistive specimen heating method. The square die in both images, carrying 6 or 10 free-standing specimens, is 1×1 cm².
The majority of experiments were conducted under the optical microscope at magnification 200× and at strain rates $10^{-6}$ to $20 \text{ s}^{-1}$ with the use of a slow frame rate (15 fps) and a high frame rate (up to 100,000 fps) camera, depending on the applied strain rate. The results presented in this chapter were obtained at the nominal strain rate of $9 \times 10^{-5} \text{ s}^{-1}$ and at 110 °C. The quality of the optical image/DIC strain measurements strongly hinged upon the quality of the speckle pattern on the specimen surface for the application of DIC, and the ability to maintain the thin film plane at the focal plane of the microscope objective during an experiment. Two methods were used to generate this speckle pattern: In the first, a pattern was deposited on the specimen surface with the use of submicron sized particles according to the works by Jonnalagadda et al [45] and the pattern was visualized by bright field optical microscopy as shown in Figure 3.4. A finer pattern was naturally generated by the use of monochromatic light from a mercury source and dark field optical microscopy as shown later in Figures 3.7 and 3.8. The second approach was easier to implement but it was possible only at high optical magnifications. The effectiveness of the two patterns was found to be equivalent in terms of strain resolution, which, as computed from the axial displacement field using the approach in was $\sim 0.01\%$.

3.2.3 Resistive Specimen Heating

In resistive (Joule) heating microscale experiments, a practical challenge lies with the ability to ensure a conductive path between the apparatus grips and the specimen as shown in Figure 3.2(b). In most micro and nanoscale experiments, the specimens are attached with adhesives which have poor electrical conductivity. Because of the small loads involved in such experiments, excellent electrical conductivity could be achieved by high purity silver paint that allowed the application of 0.3–0.7 V to resistively heat the 850 nm thick specimens. Although several prior studies implemented resistive heating of mesoscale samples to achieve high temperatures, adaptation of this method for surface micromachined micro and nanoscale samples requires further qualification. A major uncertainty arises from the determination of the temperature profile along the specimen gauge section, which, although of uniform width, is not at uniform temperature because of
the immensely larger thermal mass of the grips acting as heat sinks, thus generating an uneven temperature distribution along the specimen. Prior works employed single point measurement pyrometers to determine the temperature distribution in microscale specimens, which have fast response but also a large spot size (∼300 μm) compared to MEMS dimensions. To circumvent this difficulty, a mid-wavelength IR camera (wavelength 3-5 μm) and a high magnification microscopic IR objective resulting in 15 μm pixel size were employed. The IR images showed highly non-uniform temperature profiles generated by resistive specimen heating. For consistency with the uniform heating experiments, the maximum temperature at the center of the resistively heated specimens was selected to be 110 °C, as determined from the IR images within the aforementioned pixel resolution. The resistive heating experiments were also conducted at the same nominal strain rate of $9 \times 10^{-5}$ s$^{-1}$ as the uniform heating experiments. It is clear, though, that the inelastic strain rate in the region of peak temperature in resistively heated specimens is considerably larger than that in uniformly heated specimens.

3.3 Results and Discussion

3.3.1 Experiments under Uniform Specimen Temperature

As stated earlier, relatively low temperature gradients (<5 °C) were observed along the uniformly heated thin film samples. Figure 3.3(a,b) shows that the temperature profiles along the specimen gauge section subjected to uniaxial tension remained nearly the same even at high engineering strains. The temperature line profiles along the centerline of the specimen gauge sections showed an apparent rise near the right side of the specimen gauge section, where the specimen grip was located, due to the different emissivity of the silver paint/adhesive applied to the grip. The contrast and color distribution in IR images are affected by the angle of the specimen surface with respect to the camera plane and, therefore, reliable IR images were not always possible at engineering strains >10% because of rippling of the films at the long edges of the gauge section. For the same reasons, at strains larger than ∼10%, crosshead displacements were used to construct the engineering stress-strain curves using the approach shown later in Figure 3.8.
Figure 3.3 IR intensity and temperature distribution along the specimen gauge centerline from an Au specimen subjected to uniaxial tension under uniform temperature at (a) 0% strain and (b) 10.3% strain. Note that the temperature calibration is valid only for the dog-bone specimen fabricated of Au. The surrounding material is not Au and consequently has different emissivity which was not calibrated in the particular IR images. The horizontal dashed lines show the average temperature in the gauge section. The dashed vertical lines in the IR images indicate the location for which temperature profiles shown below each IR image.
Figure 3.4 Full field strains obtained for uniform temperature tension experiments performed on Au thin film samples at 110 °C and for (a) 0.5%, (b) 1.0%, (c) 2.5% and (d) 4.0% average strain.

The uniform temperature fields in Figure 3.3 resulted in uniform strain distributions that were resolved from optical images by DIC. As shown in Figure 3.4(a-c), the axial
strain distribution along the gauge section was fairly homogeneous for a range of strains, and only in Figure 3.4(d) specimen end effects are seen at the right end of the specimen. This deviation could be due to a small gradient in temperature distribution along the gauge section, as shown in the temperature line profiles in Figure 3.3 because of the large external mass of the grip shown in Figure 3.2(b), which was used to grip the specimens in both heating methods. Despite this small deviation, the DIC-derived strain distributions indicated that this method for uniform specimen heating provides reliable high temperature experiments at the microscale.

3.3.2 Experiments with Resistive Specimen Heating

Unlike the uniform temperature experiments, the temperature profiles along the gauge section of resistively heated specimens were highly non-uniform even at low strains. The temperature non-uniformity increased during an experiment due to the change in the sample electrical resistance because of strain localization and local reduction in the mid-section specimen thickness where the temperature was the highest. The result was a cascade in temperature increase promoting local yielding and failure at the center of the specimen.

The specimen’s electrical resistance changed at a very slow rate during each experiment, as shown in Figure 3.5, with a rapid change at the end of each experiment when sample tearing took place. The films tested in this study had nanocrystalline grain size which supports extensive voiding at low strain rates even at room temperature [89,90]. Such voiding is further accentuated at higher temperatures because of increased creep and material ductility, which eventually lead to film tearing due to the out-of-plane bending of the film edges. Resistive heating further accentuates this out-of-plane deflection of the film edges. After initiation of tearing, crack progression takes place slowly due to the high ductility of gold. As shown in Figure 3.6(a–c), the temperature profiles were highly nonuniform at the beginning of each experiment with the temperature along the gauge section ranging between 50 and 110 °C. The temperature profiles seen in Figure 3.6 are not symmetric due to the different electrical resistance and the thermal mass of the silver paint.
used to grip the sample in the right hand side of the images. However, there was no appreciable change in the temperature distribution along the gauge section during the early stages of an experiment because of the small, but gradual, change in the electrical resistance of the film upon stretching, see Figure 3.5.

![Graph showing electrical resistance over time](image)

**Figure 3.5** Electrical resistance of a 0.85 µm thick free-standing specimen during a tension experiment as a function of time (strain). The rapid increase in resistance is owed to fracture initiation.

The local temperature distribution changed at large strains with the accumulation of localized plastic strain but the out-of-plane deflection of the specimen did not permit accurate IR imaging at strains larger than 8–10%. In order to further elucidate the effect of localized heating on the measured mechanical response of the Au films, full-field strain measurements were conducted and were compared with the IR temperature distributions in Figure 3.6. As shown in Figure 3.7(a), a fairly uniform strain field was recorded along the gauge section before strain localization was initiated in the specimen mid-section in Figure 3.7(b). The rather uniform strain in Figure 3.7(a) is expected, as the elastic modulus is insensitive to temperature in the particular range of temperatures.
Figure 3.6 (cont. on next page)
Figure 3.6 IR intensities and temperature distributions along the specimen axis of symmetry for resistively heated Au thin film specimens subjected to uniaxial tension and different strain amplitudes. Note that the temperature calibration is valid only for the gauge section of the dog-bone specimen fabricated of Au. The surrounding material is not Au and consequently has different emissivity that is not calibrated in the IR images. The horizontal dashed lines show the average temperature in the gauge section. The dashed vertical lines in the IR images indicate the specimen area for which the temperature profiles are shown below each IR image.

However, at inelastic stresses, the non-uniformity of the strain field increased drastically as localization occurred in the middle of the specimen where the temperature was the highest. This non-uniformity in strain is reflected in Figure 3.7(b–d) where the center of the specimen, at the highest temperature as indicated by Figure 3.6, is under much higher strain compared to the ends of the specimen.

At the average strain of 2.5%, the center of the specimen in Figure 3.7(d) is at local strain $\varepsilon=3.5\%$ while the ends of the specimen are at $\varepsilon=1.6\%$. The sides of the specimen gauge section can undergo out-of-plane bending at high applied strains. This film edge deflection is further accentuated by the non-uniform strain fields developed by resistive heating, compared to uniform specimen heating, as the center of the specimen undergoes plastic deformation while the ends of the specimen may still be elastic. At higher average strains, the temperature in the mid-specimen gauge section increased from an initial value of 110 °C to approximately 150 °C, while the ends of the sample still remained at 50 °C as shown in Figure 3.6(d). As a result, the temperature gradient and the strain at the specimen center increased further, leading to slow specimen tearing that is evidenced in Figure 3.5.
Figure 3.7 Axial strain distribution in a resistively heated Au specimen. The strains indicated next to each plot are the engineering strains calculated by the cross-head method in Figure 3.8.

Since the strain distribution was not uniform along the resistively heated specimens, engineering stress-strain plots could be constructed only via crosshead measurements, which were can be conducted by using virtual tabs at the ends of the gauge section. As shown in Figure 3.8, two virtual strain gauges were selected at the two ends of the gauge section with the minimum width of a single correlation square. The pixel displacement between the two markers, as resolved by DIC, was used to compute the engineering strain which is plotted in Figure 3.9 for three specimens heated resistively, and one specimen
tested under uniform heating. Although technically speaking one cannot directly compare the material response from an experiment with a uniform strain field to one with highly non-uniform strain, this plot clearly shows the uncertainties associated with the latter and the large differences in the resulting engineering stress vs. strain curves.

**Figure 3.8** Cross-head method to calculate the engineering strain in resistively heated films by applying DIC in the reference areas marked by the two rectangles.

**Figure 3.9** Comparison of engineering stress-engineering strain response of Au thin films at high temperature using different heating methods.
Table 3.1 Comparison of properties of Au thin films tested at 110 °C derived from the stress-strain curves shown in Figure 3.9 for the two heating methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Elastic Limit (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>Failure strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform heating</td>
<td>140</td>
<td>165</td>
<td>224</td>
<td>27.4</td>
</tr>
<tr>
<td>Resistive heating</td>
<td>94 ± 8.3</td>
<td>111 ± 9.2</td>
<td>132 ± 2.5</td>
<td>16.8 ± 1.3</td>
</tr>
</tbody>
</table>

A direct comparison of the engineering stress-strain curves is complicated by the fact that resistive heating also results in non-uniform strain rate along the specimen length and at different strain amplitudes which is not as important in uniform heating experiments. The temperature gradient along the specimen in a resistive heating experiment caused early necking and inelastic strain localization, consistently resulting in early yielding and reduced load bearing capacity of the thin film specimens, as well as considerably smaller measured yield and ultimate tensile strengths compared to the uniformly heated specimens. The process leading to localization of strain is illustrated by the strain fields in Figure 3.7 (a–d) where a maximum strain at the center of the specimen is seen at strains larger than 0.7%. On the contrary, the specimen deformation in uniformly heated specimens was homogeneous in the entire gauge section, Figure 3.4 (a–c), and strain non-uniformities, associated with temperature variation at the right end of the gauge section, were observed only at large strains. As a result, the lack of early strain localization allowed for engineering strengths that were 70% larger than those for resistively heated specimens and at the same time 80% larger ductility due to the uniform inelastic deformation of the Au films. Table 3.1 summarizes the properties that are conventionally calculated from engineering stress-strain plots. It can be easily deduced that a resistive heating experiment would underestimate all property values including the yield and ultimate tensile strength values.
3.4 Conclusions

Two methods for microscale tension experiments with surface micromachined free-standing films at elevated temperatures, namely uniform specimen heating and resistive specimen heating, were evaluated by a combination of optical/DIC full-field strain measurements and IR-based full-field temperature measurements. Resistive specimen heating provided practical advantages, such as achieving high temperatures and minimal effect on the measurement instruments because of the small amount of heat generated. However, the temperature and strain profiles showed that this method results in highly non-uniform temperature distribution in the range 50-110 °C. The axial strain were relatively uniform during the initial elastic deformation, since the elastic modulus is insensitive to this temperature range, but, soon after yielding the axial strain field became non-uniform varying by a few percent along the gauge section. Uniform temperature heating, on the other hand, although more difficult to implement by using a custom-built microheater operated at up to 110 °C, provided homogeneous temperature fields as evidenced by IR imaging of microscale free-standing specimens. A slight, 1-2°C, temperature gradient along the specimen gauge section was due to the disproportionally larger thermal mass of the specimen grip. DIC-based strain calculations for uniformly heated specimens showed uniform strains along the gauge with a small non-uniformity at the specimen end attached to the grip. The engineering stress vs. strain plots for resistively heated specimens were highly repeatable. However, the extracted elastic limit, yield strength and ultimate tensile strength considerably lagged those obtained from uniformly heated specimens. The ~50% underestimate in engineering properties was due to localized inelastic deformation at the center of resistively heated specimens, which limited their force bearing capacity and the total strain imparted to the gauge section. Therefore, the properties calculated from resistive specimen heating experiments are not representative of the true material behavior and should be avoided.
Deformation of Nanocrystalline Au Thin Films at Elevated Temperatures

Plastic deformation of nanocrystalline FCC metals is heavily influenced by the applied strain rate due to competing mechanisms of dislocation plasticity at higher temperature-compensated strain rates and creep mechanisms at lower temperature-compensated strain rates. Several studies have investigated in the past the rate dependent mechanical behavior of nanocrystalline metal films in the range $10^{-3}$–$10^{-6}$ s$^{-1}$ [12,17,54,63]. In Chapter 2 of this dissertation, the strain sensitive behavior of free-standing Au thin films has been documented over almost eight decades of strain rate, i.e. from 20 to $10^{-6}$ s$^{-1}$. The Au thin films with $d \sim 40$ nm demonstrated a marked change in the dominant deformation mechanism from dislocation-mediated plasticity to GB-mediated creep at a strain rate of $10^{-4}$ s$^{-1}$. The important role of GB-mediated creep was verified by activation volume calculations and measurements of the initial primary creep rate, which was found to be $\geq 10^{-7}$ s$^{-1}$ at stresses well below the elastic limit.

The creep rates for nanocrystalline FCC metals are expected to increase with temperature, thus their strain rate sensitivity and the activation volume should greatly depend on temperature. At temperatures higher than room temperature, the GB-mediated diffusional creep rate is surpassed by dislocation glide and climb-driven creep rates. The combined effect of strain rate and temperature on inelastic deformation has been documented for bulk nanocrystalline Ni using stress relaxation and strain rate jump experiments at the low homologous temperatures of 77–373 K [91]. The dominant
thermally activated mechanism was suggested to originate in three processes, all involving interactions of mobile dislocations with GBs. On the other hand, creep mechanisms, such as Coble creep and other diffusional processes, were ruled out on activation volume grounds.

Table 4.1 X-ray diffraction results for as-deposited and annealed Au films. Both films had pronounced \{111\} texture. The grain size is estimated only along the film growth direction.

<table>
<thead>
<tr>
<th>Material</th>
<th>Grain size (nm)</th>
<th>Lattice constant (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited Au films</td>
<td>56</td>
<td>0.40746</td>
</tr>
<tr>
<td>Annealed Au films</td>
<td>64</td>
<td>0.40776</td>
</tr>
</tbody>
</table>

Although the mechanical behavior of bulk nanocrystalline FCC metals at elevated temperatures has been investigated in the past [28,58,91], reports on free-standing nanocrystalline FCC thin films are very limited because of inherent difficulties with mechanical experimentation at small scales and high temperatures [80]. In this dissertation, the experimental methods based on microheater based uniform specimen heating, described in section 3.2.2, was employed to investigate the contribution of different mechanisms of inelastic deformation in nanocrystalline Au thin films studied in the range of strain rates $10^{-5}–10 \text{ s}^{-1}$ and temperatures 298–383 K. Activation volumes were calculated for different temperature and strain rate ranges as the means to identify thermally activated mechanisms responsible for inelastic deformation in different temperature/strain rate regimes. The dog-bone-shaped microtensile specimens of radio frequency sputter-deposited Au films, fabricated according to the process described in section 2.1.1. While testing at elevated temperatures, the films undergo annealing that may lead to microstructural changes. In order to prevent such an undesirable effect, the Au films were first annealed at 150 °C for 12 hr, which was much longer than any of testing times used in this chapter. At this low annealing temperature, the residual stresses and the initial defect density were reduced without significant grain growth. As a result of annealing, the average
grain size of the Au films increased from 56 to 64 nm, as shown in Table 4.1, with the number of smaller grains being significantly reduced, leading to a narrow distribution of grain sizes. Thus, low-temperature annealing resulted in slight grain growth while maintaining the preferred texture in the grain growth direction.

4.1 Experimental Results

Microscale tension experiments were conducted at nominal strain rates between $10^{-6}$ s$^{-1}$ and 10 s$^{-1}$ and temperatures of 25°C, 50°C, 80°C and 110°C. The specimens were first loaded and unloaded within the elastic regime, then reloaded until failure. Full-field strain measurements were obtained via DIC from images recorded at frame rates of 15–40,000 fps. Different dies with specimens were used for each temperature and the experiments on each die were conducted in a decreasing order of strain rate to reduce the cumulative specimen exposure to an elevated temperature. From the load cell measurements (accuracy ±0.5 MPa) and the average strain calculations (accuracy ~ 0.01%) the engineering stress vs. strain curves were obtained as shown in Figure 4.1, which, in turn, were used to calculate the elastic modulus, yield strength, elastic limit, ultimate tensile strength and failure strain. Note that the uncertainty bars for the measured force or strain are smaller than the size of the symbol for each datum point and are not visible in Figure 4.1. Since all experiments were conducted at constant actuation rate (displacement rate), the true material strain rate was calculated from the strain vs. time plots, and was almost constant until yielding.
Figure 4.1 (cont. on next page)
Figure 4.1 Engineering stress vs. strain response for 850 nm thick Au thin films for various strain rates at temperatures (a) 25 °C, (b) 50 °C, (c) 80 °C and (d) 110 °C.
4.1.1 Elastic Material Response

The unloading elastic modulus, $E$, obtained for each strain rate and temperature was $64.6 \pm 4.5$ GPa, and was independent of strain rate and temperature, as shown in Figure 4.2. It is noteworthy that the value of the elastic modulus was the same as that for Au films tested before annealing reported in section 2.2. It also agreed well with that reported before for Au thin films tested by this and other groups [2,16,17], but was lower than the modulus of bulk Au ($E = 78$ GPa). In spite of the \{111\} texture, the elastic modulus is lower than the Reuss ($E_r = 81$ GPa) and Voigt bounds ($E_v = 97$ GPa) for \{111\} texture. Such a lower modulus is commonly reported for nanocrystalline films tested in tension; it has been discussed extensively before and in some reports was attributed to the additional compliance of the extended GB regions [92]. TEM imaging conducted on the present Au films did not provide evidence about film porosity which would explain low modulus values. The presence of mobile defects in the extensive GB network of nanocrystalline metals could also result in reduced elastic modulus. This argument has been made before to explain observations by Emery and Povirk [16]: similarly to their results obtained at a fixed strain rate, the loading modulus derived from the present experiments decreased with increasing temperature at strain rates slower than $10^{-4}$ s$^{-1}$. On the other hand, the elastic modulus increased with increasing strain rate at elevated temperatures until it reached the value of the unloading modulus, which, as mentioned, was insensitive to temperature and strain rate. Thus, a mechanism for reduced elastic stiffness due to mobile defects in the extensive GBs could explain our experimental measurements and observations. Additional effects have been reported in the literature on the anelastic response of thin films at room temperature and slightly higher [78,93,94]. Considering the strain rate- and temperature independent unloading elastic response, the Au films investigated in this work did not exhibit any discernible anelastic behavior.
4.1.2 Inelastic Material Response

The elastic limit, yield strength and ultimate tensile strength of the Au films demonstrated high average values compared to bulk Au, due to the nanoscale grain size of 64 nm. The tensile strength was slightly reduced compared to as-deposited Au films presented in section 2.2, potentially due to the small increase in grain size and the reduction in the number of smaller grains during annealing. Nevertheless, the present inelastic property values are high compared to most reports for nanocrystalline Au films [2,16,17], and further enforce the visual observation of the absence of porosity in the Au films. Similarly, the tensile strength increased with increasing applied strain rate and reduced temperature, as shown in Figures 4.3(a,b), except at strain rates higher than $10^{-1} \text{s}^{-1}$, at which both the yield and the tensile strength converged at all temperatures. Despite their high strength, nanocrystalline metals generally have limited ductility. However, at the slowest strain rate and at room temperature, the present Au films exhibited failure strains
as high as 22%. The ductility decreased with increasing strain rate and decreasing temperature. At room temperature, the ductility increased dramatically at \( \leq 10^{-4} \text{ s}^{-1} \), following very similar behavior to as-deposited Au films (Chapter 2).

At 50 °C, the pivotal strain rate at which the ductility had a marked increase reached \( 10^{-2} \text{ s}^{-1} \), indicating increased creep rate with temperature. At the highest temperature, the ductility was as high as 10%, even at strain rates of \( \sim 10^{-1} \text{ s}^{-1} \). Creep rates comparable to such high loading strain rates cannot be attributed purely to GB sliding or diffusion. Thus, dislocation-based creep was active at the higher temperatures employed in this study. Physically, the large ductilities seen here were the result of extensive microcracking and voiding that occurred not only near the fracture surface, but also throughout the samples, as shown in Figure 4.4.

![Figure 4.3](image-url)
Figure 4.3 (a) Yield strength, (b) tensile strength and (c) failure strain of 850 nm thick Au thin films as functions of strain rate and temperature.
4.1.3 Effect of Strain Rate and Temperature on Failure Mode

Temperature and strain rate have a concerted role at large deformations and at failure as evidenced by the SEM micrographs of fracture sections in Figure 4.5. Although there were no pre-existing voids in the Au films, failure at large strains (10-30%) was characterized by voiding at all temperatures and strain rates. Nucleation and growth of voids in nanocrystalline FCC metals has been reported to be a dominant damage mechanism in a number of earlier reports [89,90]. Our thin film samples experienced shear dominated failure at high strain rates, as shown in Figures 4.5(b,d,f,h), and tearing at slow rates prone to creep behavior, as shown in Figures 4.5(a,c,e,g), at the respective strain rates and temperatures. Specimens loaded at slow strain rates and high temperatures underwent out-of-plane bending of their edges at strains larger than 10% and were subjected to slow tearing with increasing strain. As shown in Figures 4.5(a,c,e,g), the film free edges experienced shear failure at approximately 45° angle with respect to the loading direction, which was followed by tearing. At higher strain rates, the films failed at considerably smaller strains with consistent shear failure across the entire film. Damage nucleated and
evolved in the form of distributed voids throughout the film cross-section: void formation at the lower strain rates took place as far as 100 μm away from the failure line, while at higher strain rates voiding was restricted to a region near the fracture surface. Thus, the void-based damage in Au thin films was more distributed at rates prone to creep while the damage at higher rates was more localized near the fracture surface and was due to shear driven void nucleation and growth. As expected, void growth and density increased with increasing temperature and reduced strain rate.

Figure 4.5 (cont. on next page)
Figure 4.5 SEM micrographs of fractured Au films at (a) $6 \times 10^{-6}$ s$^{-1}$ and 25°C, (b) $6 \times 10^{-5}$ s$^{-1}$ and 25°C, (c) $7 \times 10^{-6}$ s$^{-1}$ and 50°C, (d) $5 \times 10^{-2}$ s$^{-1}$ and 50°C, (e) $5 \times 10^{-4}$ s$^{-1}$ and 80°C, (f) $4 \times 10^{-2}$ s$^{-1}$ and 80°C, (g) $5 \times 10^{-4}$ s$^{-1}$ and 110°C, and (h) $4 \times 10^{-1}$ s$^{-1}$ and 110°C.

4.2 Discussion

Once temperature and strain rate data are available, a relationship between the flow stress and the strain rate or temperature can provide a relatively accurate prediction of the physical behavior of metals having a dominant thermally activated deformation mechanism, where the total stress is the sum of a thermally activated component $\sigma^*$ and an
athermal component, \( \sigma_a \): \( \sigma = \sigma^* + \sigma_a \). The strain rate under such deformation mechanism can be calculated by [69]:

\[
\dot{\varepsilon} = \dot{\varepsilon}_0 \exp \left( -\Delta G_0^* + \frac{\tau^* v^*}{kT} \right)
\]  

((4.1))

where \( \Delta G_0^* \) is the activation energy and \( v^* \) is the true activation volume. The true activation volume is the amount of matter involved in the thermally activated event and is an indicator of the dominant mechanism of plastic deformation. For uniaxial tension, the true activation volume can be obtained as [24]

\[
v^* = \sqrt{3}kT \frac{\partial (\ln \dot{\varepsilon})}{\partial \sigma^*}
\]  

((4.2))

In the absence of experimental values for the athermal component of stress, strain-rate jump experiments or monotonic loading experiments over a range of strain rates can provide values for the apparent activation volume, \( v \), which is calculated by replacing \( \sigma^* \) with the applied stress \( \sigma \) in Equation (4.2), and has a higher value than \( v^* \). Despite the obvious shortcoming, the apparent activation volume can point to the dominant deformation mechanism at a given state.

The activation volumes associated with dislocation glide in nanocrystalline metals are generally smaller than 50\( b^3 \) (\( b \): Burgers vector) [18,28,56,91], compared to dislocation based mechanisms in coarse-grained FCC metals with \( v = 100-1000 \) \( b^3 \) [26,27]. The small activation volumes or nanocrystalline metals are attributed to the small grain size that is comparable to the dislocation cell size for forest dislocations. Although TEM studies have reported the grain interior in nanocrystalline metals to be generally dislocation free [89], GBs can have sessile and immobile dislocations [95].

Equation (4.2) provides a value for the apparent activation volume which can also be computed from the plot of the logarithm of strain rate vs. yield stress normalized by the respective temperature, as shown in Figure 4.6. The slope of the best fit lines gives the apparent activation volume using the yield stress as the flow parameter. As shown in Figure 4.6, a bilinear trend exists at most temperatures; this is corroborated by the ultimate failure
strain trends in Figure 4.3(c). In both plots, the pivotal strain rate of slope change takes place at the same strain rate for each temperature. The slope of the best fit lines in Figure 4.6 was used to compute the apparent activation volume vs. temperature, the results of which are presented in Table 4.2. Based on the trends indicated in Figure 4.6, the activation volume values computed for each temperature could be divided into two distinct regimes: a regime of (i) creep-influenced inelastic behavior, which occurs at slow strain rates (regime I); and (ii) dislocation-mediated plastic behavior (regime II), which is relevant to high strain rates. Although the transition from regime I to regime II should occur smoothly, for simplicity it is approximated in Figure 4.6 as a bilinear response. The dashed/dotted line in Figure 4.6 indicates the approximate rate-temperature locus of the transition between the two deformation regimes, which occurs at progressively higher strain rates with increasing temperature due to increased primary creep rate. As shown before in Section 2.3, the primary creep rate is significant in value (>10^{-7} s^{-1}) and duration of hours even at room temperature, and such severity is characteristic for pure nanocrystalline FCC metal films. The designation of deformation regime is assigned based on our expectations for increased dislocation plasticity with increasing temperature. It is explained in the following section along with the aid of a model to rationalize the trends in regime II.

**Table 4.2** Activation volumes calculated for different temperatures using the yield strength values as the flow parameter. Regimes I and II are defined in Figure 4.6.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Regime I</th>
<th>Regime II</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>6.4 b^3</td>
<td>19.7 b^3</td>
</tr>
<tr>
<td>50</td>
<td>15.3 b^3</td>
<td>15.3 b^3</td>
</tr>
<tr>
<td>80</td>
<td>20.2 b^3</td>
<td>12.7 b^3</td>
</tr>
<tr>
<td>110</td>
<td>29.5 b^3</td>
<td>11.4 b^3</td>
</tr>
</tbody>
</table>
Figure 4.6 Strain rate-temperature superposition plot for the calculation of the apparent activation volume using the yield stress as flow parameter. The slope of the best fit lines is proportional to the apparent activation volume. The diagonal dashed line is provided for graphic reasons to indicate the separation of deformation regimes.

4.2.1 Regime I: Low Strain Rates

At the lower strain rates, $10^{-5} - 10^{-2}$ s$^{-1}$, deformation mechanisms such as GB diffusion, dislocation based creep and GB sliding play an important role in plastic deformation. Coble creep ($v \sim 1 b^3$) with strain rates $10^{-7} - 10^{-9}$ s$^{-1}$ has been suggested to operate in nanocrystalline metals [37,38]. Similarly, GB sliding may occur even at low homologous temperatures and low stresses in nanocrystalline metals [39] as GBs have been shown to undergo sliding due to diffusional processes [65]. Although GB sliding can initially be accommodated elastically, dislocation activity near GBs is eventually necessary [41]. Thus, GB sliding involves material volumes that are larger than purely diffusional
mechanisms, resulting in $v \sim 10b^3$. Finally, at elevated temperatures, dislocation based creep dominates with much higher activation volumes.

In the low strain rate regime (regime I) $v$ varies monotonically between $6.4b^3$ at room temperature and $29.5b^3$ at 110 °C, as indicated in Figure 4.6. The room temperature apparent activation volume compares well with earlier reports for nanocrystalline Au and Ni at room temperature [56,58] as well as activation volumes calculated in Chapter 2. Such a low activation volume at room temperature points to GB creep controlled by GB diffusion or sliding. These GB processes occur together with other deformation mechanisms that ensure geometrical compatibility [96]. In other words, a coupling of no less than two deformation mechanisms is necessary. Among possible processes are GB sliding, diffusion, dislocation glide, intragranular dislocation climb and intragranular elastic deformation. Since most of these processes are thermally activated, their contribution would vary with strain rate and, perhaps more importantly, temperature. Thus, the activation volume for GB diffusional processes would be higher than the expected true activation volume of $1b^3$ for a purely diffusional process. At low homologous temperatures, diffusional creep involves conventional lattice dislocation slip to accommodate GB sliding [97]. In this mechanism, lattice dislocations are supplied from GBs as the motion of GB dislocations along the GBs leads to generation of lattice dislocations in order to accommodate the incompatible sliding process [96]. Such dislocation based accommodation processes for GB sliding would also result in an increase in activation volume as compared to purely diffusional processes.

At the other extreme of temperatures, the value of $v = 29.5 b^3$ at 110 °C indicates a change in the dominant creep mechanism from GB processes to dislocation based creep. Atomistic simulations for Cu and Ni crystals [98] estimated that the true activation volume for cross-slip processes could be of the order of $20 b^3$ which is an order of magnitude lower than continuum predictions [99]. During the process of GB sliding, GB dislocations slide along the GBs and would pile up at the triple points. The resulting stress concentration generated at triple points can lead to dissociation of GB dislocations into crystal dislocations that result in slip in the grain interior, and GB dislocations that can glide and climb along the adjacent GBs resulting in grain rotation. Elevated temperatures would
result in an increased contribution of such a thermally activated dislocation climb based mechanism due to pileup of GB dislocations at the triple points and would result in increased activation volume. Such a climb based GB sliding mechanism has been described by Gifkins [100] with an equation that was found to be similar to that derived by Mukherjee [101] for diffusion based GB sliding. The only difference between the equations for the two models was the activation volume term: ‘$2b^3$’ in Mukherjee’s model and ‘$64b^3$’ in Gifkin’s model. Since dislocation glide in pure metals is a relatively rapid process in the absence of dislocation forests, dislocation climb would be the rate controlling process determining the activation volumes we derived at temperatures higher than room temperature and for the slower strain rates ($10^{-5}$ - $10^{-2}$ s$^{-1}$).

### 4.2.2 Regime II: High Strain Rates

In this regime and at strain rates between $10^{-3}$ - $10$ s$^{-1}$, the rate controlling deformation process can be mediated by dislocations at GBs, analogously to forest hardening in coarse-grained FCC metals, but the amount of material participating in the rate limiting process is restricted by GBs, thus, resulting in lower activation volumes. In regime II, GB defects, such as GB ledges and sessile dislocations, act as dislocation sources due to high local stresses [102]. Due to small grain size, the time for dislocation propagation may not be the rate limiting process any more, and dislocation nucleation due to GB defects assumes this role in nanocrystalline metals. The apparent activation volumes calculated in regime II in Figure 4.6 are close to those reported before for dislocation mediated plasticity [28,56,91,27]. In this work, $\nu$ was found to change from 19.7 $b^3$ to 11.4 $b^3$ with increasing temperature. Such a reduction in activation volume is not expected from Equation (4.2), in which the activation volume is proportional to temperature. There have been reports in the literature for the activation volume of bulk nanocrystalline Ni, which decreased from 40 $b^3$ to 17 $b^3$ between 100 K and 373 K [91]. Kato explained this unexpected trend in activation volume by incorporating a thermally activated depinning process into a model for dislocation bow-out from a GB [35]. A dislocation, or a partial, nucleated at a GB can move across a grain with its ends moving along the GB. During this
process, the dislocation ends can be pinned at an obstacle at the GB. The depinning of such a dislocation is a thermally activated event and can be the rate limiting process in plastic deformation. These dislocation mediated deformation mechanisms involve GBs and hence result in much smaller activation volumes compared to coarse grain measurements. In Kato’s model, an expression for the activation volume for dislocation depinning was obtained as follows:

\[ v^* = r^2 b \sin^{-1} \left( \frac{L + w^*}{2r} \right) \]

\[ - \left( \frac{L + w^*}{2r} \right) b \sqrt{r^2 - \left( \frac{L + w^*}{2r} \right)^2} - \]

\[ - \left[ r^2 b \sin^{-1} \left( \frac{L}{2r} \right) - \left( \frac{L}{2r} \right) b \sqrt{r^2 - \left( \frac{L}{2r} \right)^2} \right], \]

where \( L \) is the distance between the pinning points, \( w^* \) is the activation distance, \( b \) is the Burgers vector and \( r \) is radius of the dislocation loop. The radius of the dislocation loop can be defined in terms of the dislocation line tension \( T_L \), effective shear stress \( \tau^* \) and the Burgers vector \( b \). Substitution of empirical definitions for \( T_L \) and \( \tau^* \) leads to the final expression for the radius of dislocation loop as,

\[ r = \frac{T_L}{\tau^* b} = \frac{L}{2} \left[ 1 - \left( \frac{k T \ln \left( \frac{\dot{\gamma}_0}{\dot{\gamma}} \right)}{q} \right)^\frac{1}{p} \right], \]

where \( p, q \) are empirical constants in the mechanical threshold stress model, \( k \) is the Boltzmann constant, \( T \) is temperature, \( \dot{\gamma} \) is the applied strain rate, and \( \dot{\gamma}_0 \) is the reference material strain rate.
Figure 4.7 Temperature dependence of activation volume as predicted by a theoretical model for thermally activated depinning of dislocations [35] as applied for different values of activation energy and for \( p=1, q=1, \) and strain rate equal to \( 10^{-2} \text{ s}^{-1}. \) The triangles are the experimentally determined apparent activation volumes.

Figure 4.7 is a plot of the aforementioned model for thermally activated depinning of dislocations for different values of the activation energy \( G_0, \) material constants for Au, and fitting parameters \( p=1, q=1, \) which is plotted against our experimental data at the strain rate \( 10^{-2} \text{ s}^{-1}. \) Kato’s model fits the experimental data in regime II rather well for the reasonable value of activation energy of \( G_0 = 1.2 \text{ eV}. \) Such value for activation energy is high for a GB diffusion based process \( (G_0 \sim 0.8-0.9 \text{ eV}) \) [103,104] while it is lower than that for forest dislocation based deformation processes in bulk Au \( (G_0 \sim 1.5 \text{ eV}) \) [105]. Although data for activation energies in nanocrystalline Au are very scarce, a comparison with the activation energy for nanocrystalline Ni predicted by Kato reveals similar trends in connection with expectations for glide and diffusion based processes. Thus, the unexpected decrease in the activation volume with increasing temperature levels can be explained effectively by assuming thermally activated depinning of dislocations, and therefore, this mechanism could be dominant in regime II for nanocrystalline Au films.

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is important to note that this mechanism is consistent with MD simulations which have also suggested that thermally activated depinning of dislocations can be a rate controlling mechanism in nanocrystalline metals [102].

4.3 Conclusions

Nanocrystalline Au thin films with 850 nm thickness and average grain size of 64 nm were tested in tension in the strain rate range of $10^{-5} - 10$ s$^{-1}$ and at temperatures 25 - 110 °C. The nanoscale grain size resulted in high values for the elastic limit, yield strength, and ultimate tensile strength at room temperature, which increased with strain rate. The apparent activation volumes calculated from the yield strength values as a function of temperature and strain rate followed bilinear trends, which indicated that, in a given combination of temperature and strain rate, the rate limiting mechanism could fall in one of two regimes: regime I that is dominated by creep influenced plastic deformation, and regime II that is dominated by dislocation mediated plasticity. At room temperature, the activation volume was ~6.4 b$^3$ which was an indication of a limiting GB diffusive creep mechanism. This activation volume increased with temperature to ~29.5 b$^3$ at 110 °C, which indicates a shift in the dominant creep mechanism to dislocation climb creep, as an accommodation mechanism for GB sliding. On the contrary, the apparent activation volumes in regime II decreased with temperature. Thermally activated depinning of dislocations was identified as the possible rate controlling mechanism for this unexpected trend in activation volumes in regime II, which was supported by a literature model for dislocation depinning in nanocrystalline metals.
CHAPTER 5

Hardening and Creep of Nanocrystalline Au at Elevated Temperatures

Significant effort has been devoted to date to the study of the inelastic deformation of nanocrystalline metals and the effect of grain size, strain rate, temperature and specimen size on the onset of plastic deformation [4-7,10-12,18,37-39,45-50]. Yet, there is limited literature discussing the evolution of plastic deformation in terms of work hardening. In this dissertation, the stage III hardening behavior of nanocrystalline Au films was quantified and modeled using Voce’s linear hardening law assuming appropriate functional forms for the state variable. A series of creep experiments were carried out at different temperatures and a phenomenological creep model was used to rationalize the experimental creep strain data. The creep exponents obtained for different temperatures indicated a significant change in the origin of creep strain even at the slightly elevated temperature of 110 °C. The room temperature creep response of the annealed Au films presented in this Chapter has been described using the non-linear creep model presented in Section 2.3. Moreover, the effect of loading history on the creep response at different temperatures was measured and is discussed in this Chapter.

5.1 Work Hardening in Nanocrystalline Au

There are 12 crystallographically identical slip systems of the type {111} <110> in FCC metals. Plastic deformation begins with easy glide and a corresponding low hardening
rate by activation of the primary slip system where the applied stress has the highest resolved shear stress compared to all other slip systems [106,107]. This stage I hardening of easy glide spans a small range of strain and is followed by a rapid increase in hardening, represented by a region of constant tangent modulus in stress-strain curves. The region of athermal hardening, known as stage II hardening, depends on the crystallographic orientation and is subsequently followed by stage III hardening where the tangent modulus decreases steadily with strain accumulation until it reaches a zero slope, namely a saturation stress. Temperature has strong influence on stage III hardening, while the stage II hardening regime is reduced with increasing temperature and decreasing rate of deformation. This Chapter focuses only stage III hardening of nanocrystalline Au films which is modeled using the Voce’s law and appropriate relations for the state variable, and is calibrated with experimental data from strain rate experiments at different temperatures.

5.1.1 Stage III Hardening Model

The flow stress of FCC metals is known to be a function of temperature, strain rate and state variables i.e. \( \sigma = f(T, \dot{\varepsilon}, S_1, S_2, \ldots, S_n) \). Assuming a single state variable, \( S \), the expression for flow stress is given by:

\[
\sigma = f(T, \dot{\varepsilon}, S)
\]  

(5.1)

In the form of partial differentials, Equation (5.1) becomes

\[
\delta \sigma = \left( \frac{\delta \sigma}{\delta \dot{\varepsilon}} \right)_{T,S} \delta \dot{\varepsilon} + \left( \frac{\delta \sigma}{\delta T} \right)_{\dot{\varepsilon},S} \delta T + \left( \frac{\delta \sigma}{\delta S} \right)_{\dot{\varepsilon},T} \delta S
\]  

(5.2)

For a tensile test at constant temperature and strain rate, the first two terms in Equation 5.2 become zero as \( \delta \dot{\varepsilon} = 0 \) and \( \delta T = 0 \). In this case the evolution of flow stress depends on the evolution of the state variable, \( S \), with increasing strain. The state variable, \( S \), is generally related to the dislocation density, \( \rho \), in coarse-grained metals and the evolution of such variable has been explained in terms of two terms, namely athermal hardening and dynamic recovery of dislocations. The athermal hardening term is related to
the rate of dislocation accumulation and, thus, the average dislocation spacing, while the
dynamic recovery term is temperature and strain rate dependent. The evolution of the state
variable with strain accumulation can, therefore, be described by a linear hardening law as

\[ \frac{\delta S}{\delta \varepsilon} = \theta_0 \left( 1 - \frac{\sigma}{\sigma_s} \right) \]  

(5.3)

where \( \theta_0 \) is a parameter related to the athermal hardening and \( \sigma_s \) is the saturation stress
which is also temperature and strain rate dependent and can follow an Arrhenius
relationship of the form

\[ \frac{\sigma_s}{\sigma_{s0}} = 1 - \frac{k_b T}{\Delta G_{ss}} \ln \left( \frac{\dot{\varepsilon}_0}{\dot{\varepsilon}} \right) \]  

(5.4)

where \( \sigma_{s0} \) is the saturation stress at 0 K, i.e. the athermal component of saturation stress,
\( \Delta G_{ss} \) is the activation energy associated with the saturation stress, and \( \dot{\varepsilon}_0 \) is a reference
strain rate (\( \dot{\varepsilon}_0 \sim 10^7 \text{ s}^{-1} \)) for FCC metals. A similar relationship can be assumed to describe
the temperature and rate dependent behavior using the energy term \( \Delta G_f \):

\[ \frac{\sigma}{\sigma_s} = 1 - \frac{k_b T}{\Delta G_f} \ln \left( \frac{\dot{\varepsilon}_0}{\dot{\varepsilon}} \right) \]  

(5.5)

By using Equations (5.3) and (5.5), an expression for the tangent modulus, \( \theta \), can be obtained as

\[ \theta = \frac{\delta \sigma}{\delta \varepsilon_p} = \theta_0 \left( 1 - \frac{k_b T}{\Delta G_f} \ln \left( \frac{\dot{\varepsilon}_0}{\dot{\varepsilon}} \right) \right) \left( 1 - \frac{\sigma}{\sigma_s} \right) \]

or

\[ \frac{\sigma}{\sigma_s} = \left( 1 - C_1 \frac{\delta \sigma}{\delta \varepsilon_p} \right) \]

(5.6)

Equation 5.6 can be used to fit the hardening data from tensile experiments by
plotting the tangent modulus against the stress normalized by the saturation stress under
different strain rates and temperatures. The linear fit obtained from such a plot can then be
used to obtain values for constants such as \( \Delta G_f \) and \( \theta_0 \).
Hardening Behavior of Nanocrystalline Au

Hardening curves for nanocrystalline Au films were obtained using the results in Figure 4.1 for tensile experiments at different temperatures. The tangent modulus \( \theta = \frac{\delta \sigma}{\delta \varepsilon_p} \) was calculated from these experiments by linear interpolation at small plastic strains \( (\varepsilon_p \sim 0.01\%) \) and considering the slope obtained from such a piecewise linear fit as the tangent modulus \( \theta \). The resulting hardening curves for the range of strain rates and for different temperatures are shown in Figures 5.1(a-d). The hardening curves begin at different stress levels for different strain rates and at each temperature because of the different elastic limit for each strain rate; the tangent modulus becomes unbounded near the elastic limit for each strain rate. The lower segment of each hardening curve in Figure 5.1 is almost linear for all strain rates and temperatures, thus implying that the tangent modulus, \( \theta \), is a linear function of stress once the plasticity has fully evolved. Thus, the linear hardening law described in Section 5.1.1 may be appropriate to describe the evolution of plastic deformation in nanocrystalline Au. Recently, Ames et al have also employed a linear hardening law based on Voce’s law to model the hardening behavior of a bulk nanocrystalline Pd-Au alloy undergoing shear deformation [108]. If the saturation stress can be described by Equation (5.5), the two constants \( \sigma_{s0} \) and \( \Delta G_{ss} \) can be obtained by plotting the saturation stress as a function of the temperature compensated strain rate, \( \varepsilon_T = T ln(\dot{\varepsilon}_0/\dot{\varepsilon}) \), for different strain rates and temperatures.

Assuming that \( \dot{\varepsilon}_0 = 10^7 \text{ s}^{-1} \), a linear fit for the saturation stress in Figure 5.2 gives \( \sigma_{s0} = 1,024 \text{ MPa} \) and \( \Delta G_{ss} = 1.12 \text{ eV} \) by using Equation (5.4). The fitting parameter \( C_1 \) in Equation (5.6) can be obtained if the tangent modulus \( \theta \) is plotted against the stress normalized by the saturation stress for each experiment. A plot for \( \theta \) as a function of normalized stress at room temperature is shown in Figure 5.3. Using a similar fitting procedure as in Figure 5.3, the values of \( C_1 \) were obtained for each temperature.
Figure 5.1 (cont. on next page)
Figure 5.1 Tangent modulus, $\theta$, vs. engineering stress for 850-nm thick Au films subjected to various strain rates and temperatures (a) 25°C, (b) 50°C, (c) 80°C and (d) 110°C.
Figure 5.2 Saturation stress $\sigma_s$ as function of temperature compensated strain rate, $\varepsilon_T$. A linear fit using Equation (5.4) is used to obtain the constants $\sigma_{s0}$ and $\Delta G_{ss}$.

Figure 5.3 Tangent modulus, $\theta$, plotted at room temperature as function of normalized stress for different strain rates. The black fit lines provide values for $C_I$ by using Equation (5.6).
From Equation (5.6), it follows that the parameter $C_i$ is itself a function of strain rate and temperature:

$$\frac{1}{C_i} = \theta_0 \left( 1 - \frac{k_B T}{\Delta G_f} \ln \left( \frac{\dot{\epsilon}_0}{\dot{\epsilon}} \right) \right)$$  \hspace{1cm} (5.7)

Thus, if $1/C_i$ is plotted as a function of $\epsilon_T = T \ln \left( \frac{\dot{\epsilon}_0}{\dot{\epsilon}} \right)$, as shown in Figure 5.4, the constants $\theta_0$ and $\Delta G_f$ can then be obtained and the hardening behavior of nanocrystalline Au can be described over the broad range of temperatures and strain rates. The values for these constants calculated using the linear fit from Figure 5.4 are $\theta_0 = 380$ GPa and $\Delta G_f = 0.96$ eV. The unrealistically high value for $\theta_0$ is indicative of the fact that the material would have no hardening at 0 K and would behave in an elastic-perfectly plastic manner. Note that $\Delta G_f$ and $\Delta G_{ss}$ are close to the values for the activation energy calculated using Kato’s model described in Section 4.2.2.

**Figure 5.4** Parameter $1/C_i$ plotted as function of temperature compensated strain rate. The best fit line provides the values for $\theta_0$ and $\Delta G_f$ using Equation (5.7).
5.2 Temperature Dependence of Creep Strain in Nanocrystalline Au

Recent MD simulations by Wang et al. [109] suggested that the mechanism responsible for creep in nanocrystalline metals can change from Coble creep (GB diffusion) to GB sliding, and finally to dislocation nucleation mediated plasticity depending on the temperature and applied stress. The creep exponents corresponding to these mechanisms can vary from $n=1$, for Coble creep, to $n=5$ for dislocation mediated creep [109]. Nanoindentation [110,111] and uniaxial tension experiments [37,38,93] with bulk nanocrystalline metals have indicated that the dominant mechanism leading to creep strain at room temperature may be mostly diffusional, such as GB diffusion, GB sliding and grain rotation. Nanoindentation studies on nanocrystalline metal films also suggested similar diffusional mechanisms, although in some reports, the high stresses under an indenter tip resulted dislocation nucleation based creep and very high creep rates [112].

On the contrary, studies of creep in nanocrystalline metals and alloys at elevated temperatures are limited even for bulk samples [58,113]. Simulations [109] and experiments [113,114] with bulk nanocrystalline metals have shown that the creep exponents increase with increasing temperature. Besides the limited literature on the study of creep of nanocrystalline metal films by means of nanoindentation [110,111], there are no experiments with thin films subjected to uniform and well-controlled stresses. The heterogeneous stress distribution under an indenter tip limits the interpretation of creep data obtained by this method. Given the available experimental tools for microscale tension experiments, microscale creep experiments with nanocrystalline Au films were performed at a variety of low homologous temperatures and at stresses below the nominal elastic limit at the slowest applied rate for each temperature.

5.2.1 Microscale Creep Experiments at Elevated Temperatures

As discussed in Section 4.2.1, the activation volume increase from 6.4 to 29.5 b$^3$ in the low strain rate regime in Figure 4.6 for temperatures changing from room temperature to 110 °C marks a clear change in the inelastic deformation mechanism. At higher temperatures, the shift from GB dominated to dislocation driven plasticity took place at
increasingly higher strain rates, thus indicating a strong influence of temperature on creep rate. Knowledge of the latter as a function of temperature and strain rate would allow us to determine the pivotal point of strain rate at which dislocation plasticity commences. In order to carry out such experiments, the microscale experimental apparatus described in Section 3.2.2 was outfitted with the microheater shown in Figure 3.2 to produce uniform specimen heating while a computer feedback loop programmed in LabView maintained constant stress within ±1 MPa. A natural speckle pattern was generated on the specimen surface by dark field optical imaging at 400×, while digital images of 2448×2050 pixel count were recorded by a SONY XCG 50005E GIGE camera. During experimentation, the temperature on the sample surface and near the loadcell was monitored using T-type thermocouples. Both specimen and loadcell temperatures were maintained constant within ±0.5 °C as shown in Figure 5.5.

![Figure 5.5](image)

**Figure 5.5** Temperature of specimen surface and the loadcell as function of time during the first creep cycle at 75 MPa for 50 °C, 80 °C and 110 °C. The dashed lines indicate the loadcell temperature while the solid lines for each color indicate the specimen surface temperature.
As mentioned in Section 3.2.2, a coaxial spacer between the loadcell and the specimen mount prevented heating of the loadcell and possible drift due to specimen heating. Multiple cycle (3-5 cycles) creep experiments were carried out with dog-bone shaped nanocrystalline Au specimens of 1.75 μm thickness, 100 μm width and 1,000 μm gauge length, at different elastic stresses, and at temperatures 25 °C, 50 °C, 80 °C and 110 °C. Prior to testing, the Au films were annealed at 150 °C for 12 hr, similarly to the films discussed in Chapter 4, thus resulting in the microstructural details. During each creep cycle, the specimens were held at constant stress for a given time followed by a stress free period of equal time. DIC was applied to a large number of images (>1,000 images) obtained at each condition to construct the creep vs. time curves.

5.2.2 Experimental Results and Discussion

5.2.2.a The Role of Temperature and Stress on Creep Strain

Multiple cycle creep experiments were performed with 1.75 μm thick Au films at nominally elastic stresses, namely below the elastic limit for each respective temperature, and at temperatures 25 °C, 50 °C, 80 °C and 110 °C. The creep curves for the first cycle for different loads and temperatures are shown in Figure 5.6. The primary creep component of annealed Au films did not last as long as that for the as-deposited Au films discussed in Section 2.3, which was 5-6 hrs. The creep parameters for each temperature and applied stress are tabulated in Table 5.1. At room temperature, the primary creep rates were between $7 \times 10^{-7}$ - $2 \times 10^{-5}$ s$^{-1}$ and resulted in up to 1% creep strain. The steady state creep rates were much lower with values ranging from $4 \times 10^{-7}$ to $1 \times 10^{-6}$ s$^{-1}$ obtained at stresses between 50 - 175 MPa. As shown in Figures 5.6(b-d), the duration of primary creep decreased with increasing temperature while the primary creep strain was steadily rising. The steady state creep rates were as high as $10^{-5}$ s$^{-1}$ at 100 MPa and 110 °C, while the primary creep component with an initial rate of $1.4 \times 10^{-4}$ s$^{-1}$ lasted for only for 200 s. These results are in direct agreement with trends in ductility at different temperatures which were discussed in Section 4.1: an enhancement in ductility took place at three orders of magnitude higher strain rate for slightly elevated temperatures.
Figure 5.6 (cont. on next page)
Figure 5.6 Creep strain of nanocrystalline Au films subjected to uniform tension at nominally elastic stresses and at (a) 25 °C, (b) 50 °C, (c) 80 °C and (d) 110 °C.
Table 5.1 Primary creep strain rate and strain, and steady-state creep rate at various temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Applied Stress (MPa)</th>
<th>Primary creep rate (s⁻¹)</th>
<th>Primary creep strain (%)</th>
<th>Steady-state creep rate (s⁻¹)</th>
</tr>
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<tr>
<td>25</td>
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<td>0.17</td>
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<td></td>
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</tr>
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<td></td>
<td>75</td>
<td>1.30 × 10⁻⁵</td>
<td>0.07</td>
<td>3.20 × 10⁻⁷</td>
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<td></td>
<td>100</td>
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<tr>
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<td>1.69 × 10⁻⁶</td>
</tr>
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<td>1.53 × 10⁻⁷</td>
</tr>
<tr>
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<td>4.22 × 10⁻⁷</td>
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<tr>
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<td>0.58</td>
<td>9.00 × 10⁻⁶</td>
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</table>

5.2.2.b The Role of Loading History on Creep Strain

The loading history plays an important role in the creep response of thin films at all temperatures, as shown before by Vinci and coworkers [51,68] and also evidenced by the three cycle creep strain curves in Figure 5.7. In our experimental results, the creep response was highly repeatable after the first cycle for most stress values. The primary creep strain was reduced after the first cycle as some mobile defects may have been annihilated due to mechanical cycling. In some occasions, repeatable creep curves were recorded after the second creep cycle. This behavior was consistent at all temperatures and applied stresses revealing a strong influence of the loading history on the creep response of annealed nanocrystalline Au films.
Figure 5.7 (cont. on next page)

(a) 150 MPa at 25 °C

(b) 75 MPa at 80 °C
These results are consistent with prior reports on submicron scale grain sized metals subjected to mechanical annealing that resulted in increased value of the measured “elastic modulus” [16]. It has been suggested that as-deposited nanocrystalline metals achieve mechanical stability via thermal or “mechanical” annealing. During our multiple cycle creep experiments, the specimens were held at zero stress for the same amount time as were being loaded, which resulted in 30-50% strain recovery during the recovery cycle at all stresses and temperatures including room temperature (Table 5.2). While Rajagopalan et al have reported plastic strain recovery of nanocrystalline Al by holding the specimen at zero stress at elevated temperatures [67], the present experimental results provide the first evidence of creep strain recovery in nanocrystalline thin films at room and at slightly elevated temperatures. Although the exact deformation mechanism for this recovery has not been determined, back-stresses developed during creep strain accumulation owed to
grain heterogeneity could drive a local stress-assisted recovery process. It is noteworthy that the percentage of strain recovery was not enhanced by temperature, which indicates that the responsible mechanism is mostly athermal in nature and the back-stresses developed during the forward creep cycle are the main driver for this process. In order to investigate whether strain could be completely recovered if the Au films were held at zero stress for extended amounts of time, a room temperature creep experiment was conducted at creep stress of 100 MPa where the specimen was held at zero stress for 90,000 s between 2 successive cycles of 10,000 s of a forward creep cycle. No significant change in the amount of recovered strain was observed despite the long hold time at zero load, thus providing a strong indication that the strain recovery process following creep is not temperature driven.

Table 5.2 Creep strain, $\varepsilon_{\text{creep}}$, accumulated during each cycle and strain recovery, $\varepsilon_{\text{recovery}}$, after each cycle for three cycle creep experiments.

<table>
<thead>
<tr>
<th>Stress (MPa)</th>
<th>T (°C)</th>
<th>Loading time (s)</th>
<th>Recovery time (s)</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\varepsilon_{\text{creep}}$ (%)</td>
<td>$\varepsilon_{\text{recovery}}$ (%)</td>
<td>$\varepsilon_{\text{creep}}$ (%)</td>
</tr>
<tr>
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<td>25</td>
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<td>40000</td>
<td>0.27</td>
<td>0.13</td>
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<td>10000</td>
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<td>0.19</td>
<td>0.17</td>
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<td>0.3</td>
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<td>90000</td>
<td>0.36</td>
<td>0.16</td>
<td>0.21</td>
</tr>
<tr>
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<td>5000</td>
<td>0.47</td>
<td>0.06</td>
<td>0.3</td>
</tr>
<tr>
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<td>110</td>
<td>10000</td>
<td>10000</td>
<td>0.56</td>
<td>0.12</td>
<td>0.42</td>
</tr>
</tbody>
</table>

5.2.3 Discussion

An empirical power law creep model ($\dot{\varepsilon}_s \propto \sigma^n$) is generally considered to be good representation of the steady state creep response of metals. The value for the creep exponent $n$, depends on the specific mechanism: $n = 1$ for Coble creep, $n = 2$ for GB sliding,
\( n = 3-5 \) for dislocation glide based creep, and \( n = 5-8 \) for dislocation climb [24]. Therefore, the creep exponent can be a good indicator of the dominant creep mechanism. For the data at hand, the creep exponent can be computed from the logarithmic plot of the steady state creep rate vs. creep stress for the first creep cycle and at different temperatures, as shown in Figure 5.8: The dominant creep mechanism changes significantly as the temperature increases from ambient to 110 °C. The value of 2.6-2.7 for the creep exponent at room temperature and at 50 °C indicates that the active creep mechanisms may be a combination of GB sliding and dislocation glide. There is a gradual change in the creep exponent as the contribution of dislocation mediated creep becomes stronger with increasing temperature, reaching 3.8 at 80 °C and 4.9 at 110 °C. Dislocation mediated creep can explain the relatively high steady state creep rate of \( 10^{-5} \) s\(^{-1} \) at 110 °C and the creep exponents of 3.8 and 4.9 for 80 °C and 110 °C, respectively, which are calculated in Figure 5.8.

![Figure 5.8](image-url)

**Figure 5.8** Steady state creep rates plotted against creep stress. The slopes of the best fit lines are the creep exponents, \( n \), at different temperatures.
These mechanisms are in good agreement with the activation volume calculations in Chapter 4 for the low strain rate regime at which the measured stress-strain curves were influenced by creep and stress relaxation. For those strain rates the activation volume increased from 6.4 \( \text{b}^3 \) at room temperature to 29.5 \( \text{b}^3 \) for 110 °C. Thus, contrary to common wisdom for coarse grained metals, the contribution of dislocation mediated creep in nanocrystalline metals becomes dominant at only slightly elevated temperatures between 50 °C and 80 °C. Because of the change in the creep exponent with temperature, a single mechanism creep model cannot be used for all temperatures. The isochronous curves for room temperature creep experiments shown in Figure 5.9 indicate strong non-linearity of the creep response. Thus, following the discussion in Chapter 2, the non-linear creep model based on thermal activation may still be applicable at individual temperatures.

**Figure 5.9** Isochronous creep curves for 1.75 \( \mu \text{m} \) thick nanocrystalline Au films at different times, \( t \), after instantaneous loading to prescribed values of stresses at 25 °C.
An empirical form for the delayed elasticity term $E_h$ in Equation (2.4) could be assumed as $E_h = a_3 - a_4\sigma + a_5\sigma^2$ which is a better representation of the hardening response shown in Figure 5.1(a). At room temperature, the non-linear creep model was calibrated using the experimental creep data in Figure 5.6(a) and it is compared with the experimental data in Figure 5.10(a), demonstrating a very good agreement and therefore the suitability of the particular model. A similar procedure was applied to calibrate the creep model for elevated temperatures and obtain Figures 5.10(b-d) by assuming that the $a_p$ and $a_{ss}$ terms related to activation energy in expressions for $\eta_1$ and $\eta_2$ (equation 2.2 and equation 2.3) remain constant for all temperatures. The constants $a_1$ and $a_2$ associated with the activation volume for the primary and steady-state creep can be computed for each temperature by assuming that the total energy associated with thermal activation for primary and steady state creep is independent of temperature. According to the kinetics of thermal activation, $a_1$ and $a_2$ in Equations 2.2 and 2.3, respectively, are proportional to $1/T$ as shown in Figure 5.11. However, the subsequent cycles of multi-cycle creep experiments at different stresses cannot be treated using the aforementioned approach. A comparison between subsequent cycles of creep at different stresses is not accurate because the state of the material at the end of the first creep cycle will vary significantly between different loads. Thus, it is not possible to quantify the effect of loading history using the creep model described in Chapter 2 without a law governing the evolution of the state of the material as a function of stress and temperature.

The fitting of the parameter ‘$E_h$’ across all temperatures is more difficult as the exact form of its temperature dependence is not clear from the experimental data. Yet, the aforementioned non-linear viscoelastic model provides a very good description of the primary and steady state creep behavior of a nanocrystalline metal across all temperatures and for nominally elastic stresses.
Figure 5.10 (cont. on next page)
Figure 5.10 Prediction of creep strain at (a) 25 °C, (b) 50 °C, (c) 80 °C and (d) 110 °C by a non-linear four element Burgers model described by Equation (2.4) vs. measured creep strain, shown on a logarithmic scale.
5.3 Conclusions

The hardening behavior of nanocrystalline Au films was obtained experimentally. The results were found to satisfy well a modified Voce’s linear hardening relationship. A single state variable model was employed in the derivation with an exponential relationship to model the rate dependency of flow stress, while an exponential relationship was used to model the thermal activation of the saturation stress. Using a linear hardening law to fit the experimental data, the values of the activation energy terms associated with the exponential relationship, $\Delta G_{ss} = 1.12 \text{ eV}$ and $\Delta G_f = 0.96 \text{ eV}$, were in agreement with the activation energy $\Delta G = 1.2 \text{ eV}$ computed by the activation volume calculations for dislocation depinning at GBs in Section 4.2.2.

The strong influence of temperature on the creep response of nanocrystalline Au films was shown experimentally for the first time via a series of multiple cycle creep experiments with uniform applied stress at temperatures 25 °C, 50 °C, 80 °C and 110 °C, A temperature increase from room to 110 °C lead to an order of magnitude increase in the initial primary creep rate and an order of magnitude increase in the steady state creep rate.
The creep response of Au films followed the same curve after the first cycle and for all temperatures tested in this research. This result suggests a strong influence of the initial (defect) state of the material on creep response. The creep strain was partially recovered during the zero stress component of each creep cycle, including the experiments at room temperature. The percent of recovery was rather independent of temperature, which supports the argument that backstresses developed in the material during creep strain accumulation due to the grain heterogeneity drove strain recovery.

The calculated creep exponents suggest that the rate controlling mechanism at 110 °C was predominantly dislocation mediated creep, while diffusional creep processes controlled the creep response at room temperature. The contribution of dislocation mediated creep increased with temperature to dominate at 80 °C and higher, as suggested by the high steady state creep rates ($\dot{\varepsilon} > 10^{-6} \text{ s}^{-1}$). The convoluted effect of the different mechanisms at different temperatures prohibits the use of a single model, e.g. a non-linear Burgers creep model, with fixed activation energies to describe the creep response at all temperatures.
CHAPTER 6

CONCLUSIONS

The objective of this dissertation research was to obtain quantitative experimental information about the mechanical stability and the physical processes controlling the inelastic deformation of nanocrystalline FCC thin metal films. Nanocrystalline Au films were selected as the model material system that was tested under uniaxial tension over a wide range of strain rates and temperatures. This dissertation research developed or improved on experimental methods necessary for the aforementioned studies and the experimental results highlighted unique aspects of the mechanical behavior of nanocrystalline FCC metals not reported before in literature. In this Chapter, a brief assessment of the extent that the dissertation objectives were met is presented.

6.1 Experiments and Methods

A prerequisite to achieve the research objectives in this dissertation was a versatile experimental method for testing thin films at various strain rates and temperatures. This research added new capabilities to a previously developed apparatus by this group so that creep experiments under uniform tensile stress and at temperatures higher than room temperature could be carried out. These changes permitted probing deformation mechanisms that could not be uniquely identified solely based on strain rate experiments. Special attention was placed on evaluating the newly implemented capability for controlled specimen heating which overcame inherent flaws in prior state-of-the art methods. This experimental method ensured highly uniform temperature and strain fields as shown by
full-field IR-based temperature and DIC-based strain measurements obtained directly from the free-standing thin film specimen surface. The addition of close loop feedback control to maintain constant stress within ±1 MPa facilitated the first of their kind high temperature creep experiments with nanocrystalline thin films. These experiments gave us new insights into the prevailing mechanisms of inelastic deformation at low homologous temperatures.

6.2 Rate Dependent Inelastic Deformation at Elevated Temperatures

The experimental results and the ensuing analysis showed an increased strain rate sensitivity of nanocrystalline Au films at temperatures not exceeding 110 °C. The trends in the measured values of the elastic limit, yield strength and ultimate tensile strength increased monotonically with increasing strain rate. The opposite trends in properties were established for increasing temperature and fixed strain rate. More pronounced were the trends in ductility, which demonstrated a pivotal strain below which the ductility increased dramatically. This strain rate was $10^{-4}$ s$^{-1}$ at room temperature (ironically this is the strain rate at which the yield strength is reported in most publications and is used to construct Hall-Petch plots), and it shifted to $10^{-2}$ s$^{-1}$ and $10^{-1}$ s$^{-1}$ at 80°C and 110°C, respectively. The latter strain rates provided the first strong evidence for the competition between inelastic deformation mechanisms in nanocrystalline Au films; below this critical strain rate, creep strain rates become appreciable, especially at elevated temperatures. Thus, a strain rate vs. temperature map of the rate limiting mechanisms for inelastic deformation of nanocrystalline FCC films could be created that is comprised of two different regimes: Regime I that is relevant to high strain rates and the deformation is dominated by dislocation plasticity, and Regime II which is relevant to low strain rates and the overall deformation is influenced by creep strain and the associated mechanisms. Similar conclusions were derived from apparent activation volume calculations, which pointed out that the dominant creep mechanism shifts from GB diffusion based to dislocation based. The latter was better explained by the combination of strain rate and temperature measurements: The trend in apparent activation volume values at high strain rates was rather anomalous compared to coarse grained metals, which could only be explained if the
rate controlling step involves thermally activated depinning of dislocations at GBs. While the use of apparent activation volumes to discern the rate limiting deformation mechanisms is a common practice, the true activation is the actual indicator of the dominant deformation mechanisms. In [91], strain rate jump experiments were used to compute the athermal stress component and the true activation volume. Unfortunately, such a procedure is not possible for nanocrystalline metals as it requires strain jumps at flow stress values; as evidenced in this dissertation, the nanocrystalline Au films did not reach a flow stress at higher strain rates.

6.3 Time Dependent Behavior of Nanocrystalline Au Thin Films

The room temperature creep results indicated that primary creep played a significant role in the mechanical response of monotonically loaded as-deposited Au films, due to the magnitude of the initial creep rate and the duration of the primary creep regime. A non-linear viscoelastic creep model was assembled to describe the overall creep response of the Au films at room temperature. Such a non-linear model was justified on the basis of the isochronous curves computed from the experimental data and provided a very good description for the temporal evolution of creep strain for both the as-deposited and the annealed Au thin films. The creep strain rates for the primary and steady state regime increased significantly for the moderate temperature increase from room temperature to 110 °C. Creep experiments that involved multiple cycles of constant stress followed by zero stress relaxation regime showed that, upon annealing, the creep response was identical after the very first cycle. Therefore, it can be concluded that “mechanical annealing” can provide a stable and predictable mechanical response. Significant portion of the accumulated creep strain was recovered when the specimens were unloaded to zero stress at all temperatures including room temperature. The relative insensitivity of the fraction of creep strain recovered during the specimen rest period in each creep cycle indicated that backstresses built in the metal polycrystal during the forward creep play a dominant role.

The strain rate vs. temperature data allowed a close evaluation of the stage III hardening response which was assumed to obey a linear hardening law with an exponential
relationship for the state variable and the saturation stress. The creep exponent calculated using an empirical power law between the applied stress and the steady state creep rate showed a clear shift in the creep mechanism with temperature. The creep vs. temperature data on the other hand allowed for the calculation of the creep exponent for the temperature range under investigation. Clearly, dislocation mediated creep was dominant at 110 °C, while at room temperature and up to 50 °C a combination of GB sliding and GB dislocation processes were responsible for the enhanced primary and steady state creep rates. This swift change in the dominant creep mechanism within the small temperature range investigated in this dissertation is noteworthy. Unfortunately, this strong sensitivity in temperature does not allow for the development and application of a single model following a single deformation mechanism across all temperatures.

6.4 Future Prospects

The unique set of experiments described in this dissertation provided answers to some open questions on thermally activated mechanisms in nanocrystalline metal films, but also generated new and interesting questions. Similarly, the effect of loading history on the mechanical behavior of nanocrystalline metals was documented for the first time by this research, although the mechanisms responsible for the evolution of inelastic deformation and their mathematical description remain elusive.

The change in the dominant inelastic deformation mechanisms with strain rate and temperature has been established in this dissertation but the effect of grain size and length scale on the thermal activation in nanocrystalline FCC metals remains an open question. Experiments that shed light on the grain size dependence of the different creep and plasticity mechanisms would be useful towards identifying the exact deformation in a particular regime since several deformation mechanisms in nanocrystalline metals have similar stress and temperature dependence but have different size dependence.

The development of uniaxial tensile creep experiments where the applied load can be controlled directly using dead-loads could also help remove many uncertainties in the
current state-of-art using feedback loops which are sensitive to noise, drift and temperature variations. This would also permit creep experiments at very low loads ($\sigma < 50$ MPa) which are prone to loadcell related sensitivity limits. Finally, the development of a unified semi-empirical creep model based on the physical mechanisms that could describe the temperature and stress dependence of the overall creep response accurately would be critical towards the understanding of nanocrystalline metals.
REFERENCES


