Mechanical Properties of Ultra Thin Metallic Films Revealed by Synchrotron Techniques

Von der Fakultät Chemie der Universität Stuttgart
zur Erlangung der Würde eines Doktors der
Naturwissenschaften (Dr. rer. nat.) genehmigte Abhandlung

Vorgelegt von

Dipl.-Ing. Patric Alfons Gruber

aus Salzburg, Österreich

Hauptberichter:	Prof. Dr. phil. Eduard Arzt
Mitberichter:	Prof. Dr. rer. nat. Ralph Spolenak
Tag der mündlichen Prüfung:	20.07.2007

Institut für Metallkunde der Universität Stuttgart
und
Max-Planck-Institut für Metallforschung Stuttgart

Stuttgart, Juli 2007

Patric Alfons Gruber

Mechanical Properties of Ultra Thin Metallic Films Revealed by Synchrotron Techniques

176 pages, 65 figures, 13 tables

Abstract

A prerequisite for the study of the scaling behavior of mechanical properties of ultra thin films is a suitable testing technique. Therefore synchrotron-based *in situ* testing techniques were developed and optimized in order to characterize the stress evolution in ultra thin metallic films on compliant polymer substrates during isothermal tensile tests. Experimental procedures for polycrystalline as well as single crystalline films were established. These techniques were used to systematically investigate the influence of microstructure, film thickness (20 to 1000 nm) and temperature (-150 to 200°C) on the mechanical properties. Passivated and unpassivated Au and Cu films as well as single crystalline Au films on polyimide substrates were tested. Special care was also dedicated to the microstructural characterization of the samples which was very important for the correct interpretation of the results of the mechanical tests.

Down to a film thickness of about 100 to 200 nm the yield strength increased for all film systems (passivated and unpassivated) and microstructures (polycrystalline and single-crystalline). The influence of different interfaces was smaller than expected. This could be explained by a dislocation source model based on the nucleation of perfect dislocations. For polycrystalline films the film thickness as well as the grain size distribution had to be considered.

For smaller film thicknesses the increase in flow stress was weaker and the deformation behavior changed because the nucleation of perfect dislocations became unfavorable. Instead, the film materials used alternative mechanisms to relieve the high stresses. For regular and homogeneous deformation the total strain was accommodated by the nucleation and motion of partial dislocations. If the deformation was localized due to initial cracks in a brittle interlayer or local delamination, dislocation plasticity was not effective enough to relieve the stress concentration and the films showed brittle fracture. In addition, thermally activated deformation mechanisms were enhanced leading to a strong temperature dependence of the mechanical properties. Based on the experimental results the thickness dependence of the deformation mechanisms, fracture toughness and activation energies could be determined.

Patric Alfons Gruber

Mechanische Eigenschaften von ultradünnen metallischen Schichten ermittelt mit Synchrotronmethoden

176 Seiten, 65 Abbildungen, 13 Tabellen

Kurzzusammenfassung

Eine Grundvoraussetzung, um das Skalierungsverhalten der mechanischen Eigenschaften von ultradünnen Schichten untersuchen zu können, ist eine geeignete Testmethode zur Verfügung zu haben. Deshalb wurden synchrotron-basierte *in situ* Testmethoden entwickelt und optimiert, um die Spannungsentwicklung während isothermer Zugversuche in ultradünnen Metallschichten auf verformbaren Polymersubstraten messen zu können. Dabei wurden sowohl polykristalline als auch einkristalline Schichten berücksichtigt. Diese Methoden wurden eingesetzt, um systematisch den Einfluss von Mikrostruktur, Schichtdicke (20 bis 1000 nm) und Temperatur (-150 bis 200°C) auf die mechanischen Eigenschaften zu untersuchen. Getestet wurden passivierte und unpassivierte Gold- und Kupferschichten sowie einkristalline Goldschichten. Besondere Aufmerksamkeit wurde der Charakterisierung der Mikrostruktur der Proben geschenkt, da diese für die korrekte Interpretation der Testergebnisse sehr wichtig war.

Bis zu einer Schichtdicke von ungefähr 100 bis 200 nm nahm die Fließgrenze für alle Schichtsysteme (passiviert und unpassiviert) und Mikrostrukturen (polykristallin und einkristallin) zu. Der Einfluss der verschiedenen Grenzflächen war jedoch kleiner als erwartet. Dies konnte mit Hilfe eines Versetzungsquellenmodells erklärt werden, welches auf der Nukleierung von vollständigen Versetzungen basiert. Für polykristalline Schichten musste sowohl die Schichtdicke als auch die Korngrößenverteilung berücksichtigt werden.

Für kleinere Schichtdicken wurde der Anstieg der Fließgrenze schwächer und das Verformungsverhalten änderte sich, da die Nukleation von vollständigen Versetzungen zunehmend schwieriger wird. Stattdessen nutzten die Schichtmaterialien andere Verformungsmechanismen, um die hohen Spannungen abzubauen. Eine homogene Verformung wurde durch die Nukleierung und Bewegung von Partialversetzungen erreicht. Wenn die Verformung durch einen Riss in einer spröden Zwischenschicht oder durch eine lokale Ablösung lokalisiert wurde, reichte die Versetzungsplastizität nicht aus, um die Spannungskonzentration abzubauen und die Filme brachen spröde. Außerdem wurden thermisch aktivierte Verformungsmechanismen beschleunigt, was zu einer starken Temperaturabhängigkeit der mechanischen Eigenschaften führte. Basierend auf den experimentellen Ergebnissen konnte die Schichtdickenabhängigkeit der Verformungsmechanismen, der Bruchzähigkeit und der Aktivierungsenergien bestimmt werden.

Table of contents

1 Introduction

During the last decades technological progress has been driven predominantly by the modern information and communication technology. The steadily increasing data output and functionality of devices has required an ongoing miniaturization of their structural elements. In the design and manufacturing of actual microelectronic and microelectromechanical systems/MEMS thin metallic films play an important role. Beside the optical, magnetic or electronic properties, which determine the performance of a device, the knowledge of the mechanical properties of thin films is crucial in order to ensure the reliability and functionality of the device during its lifetime.

Like many other properties, the mechanical properties begin to deviate from that of bulk materials when characteristic dimensions become small. Such deviations may occur when either microstructural features or object dimensions approach length scales of defects, defect interactions or deformation mechanisms. Unlike other physical properties, which deviate from continuum models only close to atomistic dimensions, mechanical properties change at surprisingly large length scales, often in the micrometer regime. For thin films this is especially important since films with thicknesses down to several tens of nanometers are widely used. Such thin films sustain very high stresses which can be several times higher than the flow stress of the corresponding bulk material. This has been attributed to constraints on dislocation motion or diffusion imposed by the interfaces with the surrounding layers and to the smaller grain size that is often found in thin films.

The combination of the tremendous technological driving force and wealth of unfamiliar behavior has led to much interest and work in this area. However progress has been slow. This is mostly due to experimental difficulties in measuring the mechanical properties of thin films. Restricted volumes and geometries as well as very small displacements and forces that have to be controlled preclude classical experimental techniques. Many efforts have gone into developing new testing techniques that allow to measure small samples, films and patterned structures by a variety of means with good strain and stress resolution. Nevertheless, until now the ideal testing technique does not exist and many questions concerning the mechanical properties of ultra thin metallic films are still under debate.

A novel synchrotron-based X-ray diffraction technique has been developed by which it is possible to characterize the evolution of mechanical stress in a polycrystalline metallic film thinner than 40 nm during an isothermal tensile test [Böhm et al. 2004]. The metallic films are deposited on compliant polyimide substrates such that the tensile tests can be performed up to total strains of more than 10% and in a temperature range between 110K and 573K. The unique combination of an isothermal test, very small film thickness, short measuring times and high total strain reveals some new aspects and insight in the mechanical properties of thin films which will be discussed in detail in this thesis.

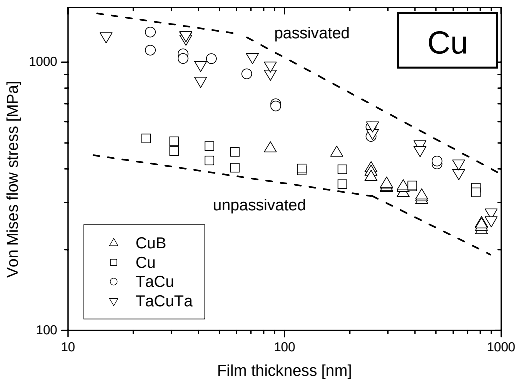
First, in chapter 2 the literature is critically reviewed concerning the technological relevance of thin films, the current understanding of thin film mechanics and the latest trends in mechanical testing of thin films and small structures. Chapter 2 also outlines the motivation for this study. In chapter 3 the principles of the novel synchrotron-based tensile testing technique will be presented. The results of RT tensile tests on Cu, Ta/Cu and Ta/Cu/Ta thin film systems are reported in chapter 4 and 5. Chapter 4 focuses on the size and interface effect on the yield strength of these film systems while chapter 5 deals with the deformation behavior of the different film systems up to high total strains of about 8%. Here, a size effect in crack formation is observed and discussed with respect to fracture mechanics of thin films on substrates. Up to this point the mechanical behavior has been investigated only at room temperature. In chapter 6 a first series of tensile tests at different temperatures on ultra thin Au films is presented and compared to bulk materials; a much stronger temperature dependence on the mechanical properties is found. The investigation of polycrystalline films suffer from the fact that in most cases film thickness and grain size cannot be varied independently and thus the interpretation of the scaling behavior of the mechanical properties is often difficult. In chapter 7 a novel experimental route for the preparation and testing of single crystalline Au films is presented. In combination with TEM investigations a detailed picture of the deformation mechanisms in single crystalline films is obtained. Finally, chapter 8 summarizes and discusses the variety of results and highlights new aspects in the mechanical properties of ultra thin metallic films.

8 Summary: Novel aspects in the mechanical properties of ultra thin metallic films

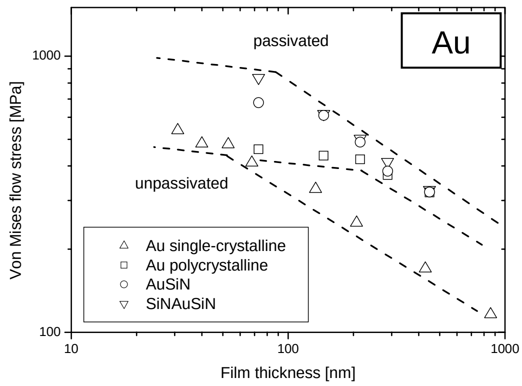
The goal of this thesis was to develop a basic understanding of the plasticity of ultra thin metallic films. An accurate measurement of the mechanical properties of the films was the first step toward that objective. Therefore synchrotron-based *in situ* tensile testing techniques were developed and optimized in order to characterize the biaxial stress evolution in ultra thin metallic films on compliant polymer substrates during isothermal tensile tests. Experimental procedures for polycrystalline as well as single crystalline films were established. Thereby, the variable wavelength of the synchrotron radiation was the key feature for the experiments. For polycrystalline films monochromatic X-rays of defined energy were necessary to adapt for the very strong <111> fiber texture in the films, whereas a polychromatic X-ray beam was used for single crystalline films. The stress determination during the tensile tests was realized in a transmission geometry. Thus, no sample rotation or tilting was necessary and the whole information could be recorded on a big CCD area detector during a single X-ray exposure (15 to 120 s, complete Debye-Scherrer rings for polycrystalline films and Laue patterns for single crystalline films). In this way, the complete stress tensor of polycrystalline as well as single crystalline films with film thicknesses down to 20 nm could be measured with a strain resolution of 10^{-4} and at strain rates up to 10^{-4} s^{-1}. By these techniques, a unique field of testing parameters for ultra thin metallic films, like microstructure (interfaces, polycrystalline, single crystalline), temperature and deformation behavior at high total strains was established.

Metal films were either deposited on compliant polyimide substrates or on NaCl substrates. The latter substrate was chosen to grow epitaxial Au films. These were subsequently coated with a polyimide layer. In a final step, the NaCl substrate could be dissolved in water and the single crystalline Au film remained on the polyimide layer. Polycrystalline Cu and Au films with and without passivation layers (Ta for Cu and SiN_x for Au) were prepared on polyimide substrates in order to investigate the role of different interfaces on the mechanical properties. In addition, freestanding Cu films were prepared and tested by Bulge testing. Special care was dedicated to the microstructural characterization of the samples which was very important for the correct interpretation of the results of the mechanical tests.

In figure 8.1 the room temperature flow stresses of the different Cu and Au film systems are plotted against the film thickness and compared. The behavior for polycrystalline Cu and Au films was very similar. The influence of different interfaces was much smaller than expected. The biggest effect was found for films with one stiff interlayer (TaCu or AuSiN). Films on polyimide behaved like freestanding films and showed lower flow stresses, whereas samples with an additional surface passivation (TaCuTa, SiNAuSiN) showed no further increase in flow stress. This indicated that the deformation behavior was not predominantly influenced by the interfaces, but that it was also determined by mechanisms within the grains and in the grain boundaries.



(a)



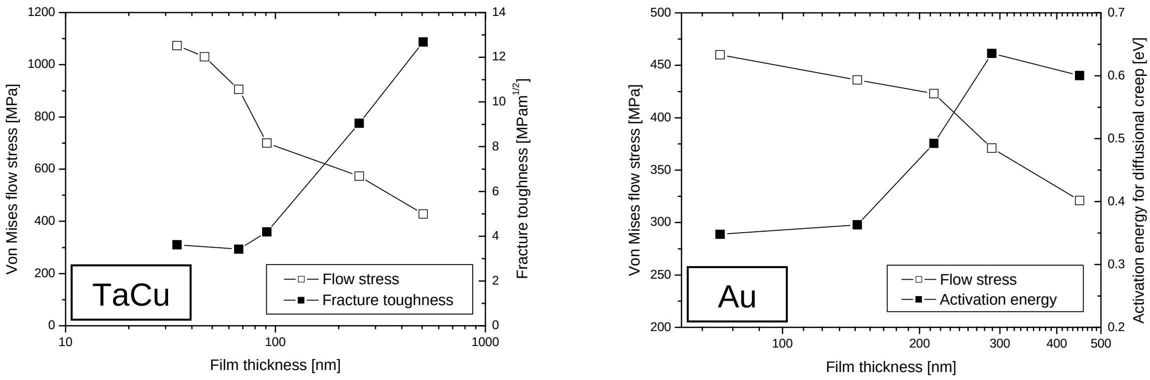
(b)

Figure 8.1: Room temperature flow stress for the (a) Cu and (b) Au film systems investigated in this study. The difference between passivated and unpassivated samples is similar for both materials. Below 100 nm film thickness, single crystalline Au films become as strong as polycrystalline Au films. In addition, a lower thickness dependence is found on this length scale for all film systems.

The scaling behavior of the flow stress could be described in the thickness regime between 100 and 600 nm by a modified dislocation source model which considers the activation of Frank-Read sources in the grains of the film. Anyway, it was not sufficient to implement only the film thickness, but the complete grain size statistics had to be considered to get good agreement to the experimental data. The yield stress of films thinner than 100 nm, however, could not predicted accurately by the model. A limit in nucleation stress had to be introduced, as the model predicted unreasonably high nucleation stresses for the smallest grains. This indicated that the nucleation of perfect dislocations became unfavorable for feature sizes below 100 nm and that a different deformation mechanism might be responsible for the stress plateau. The nucleation stress for partial dislocations was very close to the observed plateau stress. Therefore, it was argued that the smallest grains in the film deform predominantly by partial dislocations similar to first observations in nanocrystalline materials. This would also explain the strongly reduced strain hardening found for these films.

The proposed deformation by partial dislocations was also confirmed by the study of the single crystalline Au films. Here, the film thickness was the only microstructural parameter of relevance. For thicker films, the flow stress of the single crystalline films was lower than that for polycrystalline ones due to the missing constraint by the grain boundaries. However, the flow stress of the single crystalline films reached an almost identical stress plateau if the film thickness was below 100 nm (figure 8.1b). Transmission electron microscopy investigations on single crystalline films thinner than 160 nm showed an increasing density of twins. The twins resulted from the motion of partial dislocations on parallel glide planes. Pile-ups of partial dislocations within the twins were also found. No deformation twins were found in thicker single crystalline films which indicated a transition in deformation mechanism from perfect to partial dislocations if the film thickness or grain size is below 100 nm.

The tensile testing technique on polyimide substrates also allowed for investigating the deformation behavior of the metallic films at high total strains. Doing so, sudden stress decreases were found for film systems with weak adhesion or brittle surface or interlayers. This could be correlated to sequential cracking of the films. For TaCu samples with a Ta interlayer a detailed analysis of the cracking behavior was conducted. By combining the results of the *in situ* experiments at the synchrotron with those of *in situ* tests in a scanning electron microscope the strain energy per volume released by cracking as well as the crack area could be determined. Thus, it was possible to estimate the fracture toughness of the Cu films. It was found that the fracture toughness increases with film thickness. A comparison to existing models of thin film fracture mechanics showed the fracture mode of the thinnest films is brittle whereas it becomes more and more ductile if the film thickness increases. Figure 8.2a shows a comparison of flow stress and fracture toughness for TaCu films as a function of film thickness. The fracture toughness was minimal where the flow stress reached the plateau, which indicated that the constraint in plasticity was responsible for the decreasing fracture toughness of the thinnest films. However the dimensional constraint by the film thickness on the plastic zone should also have had an effect because Cu alloys of same strength show much higher fracture toughnesses than the Cu films in the TaCu film systems.



(a) (b)

Figure 8.2: (a) Fracture toughness and flow stress of Cu films in TaCu samples and (b) activation energy for diffusional creep and flow stress for Au samples vs. film thickness. For both the flow stress increases with film thickness whereas the fracture toughness or activation energy decreases.

In order to investigate the temperature dependence of the mechanical properties heating and cooling devices were implemented in the experimental setup. Experiments in a temperature range between -150°C and 200°C showed a strong temperature dependence of the flow stress for passivated and unpassivated Au films. For passivated films and unpassivated films at temperatures below 100°C the temperature dependence could be explained by thermally activated dislocation glide. Above 100°C the temperature dependence of the yield stress for unpassivated films became even more pronounced. The size effect in yield stress disappeared completely and flow stresses of the bulk material were reached. This could be attributed to diffusional creep, which was inhibited in passivated films. The activation energy for diffusional creep increased with film thickness and decreased with increasing flow stress (figure 8.2b). In any case, it was always lower than the corresponding activation energy for the bulk material indicating that diffusional flow is facilitated in thin films with free surfaces.

Overall one can say that by using the synchrotron-based tensile testing techniques the scaling behavior of the mechanical properties could systematically be investigated for films thinner than 100 nm. It was found that the flow stress did not increase irresistibly. Instead the thickness dependence became lower below 100 nm film thickness. On this length-scale the nucleation of perfect dislocations becomes unfavorable and partial dislocations are more likely nucleated. Tensile tests to higher total strains and at different temperatures did also show that the brittleness and the temperature dependence of the flow stress are strongly enhanced in ultra thin films. In this sense, one may conclude: Small is strong, but smaller is not always stronger…