Temperature effect on the mechanical properties of gold nano films with different thickness

C Birleanu¹, M Pustan¹, V Merie², R Müller³, R Voicu³, A Baracu³ and S Craciun¹

¹Mechanical Systems Engineering Department, Technical University from Cluj-Napoca, Cluj-Napoca, Romania
²Materials Science and Engineering Department, Technical University from Cluj-Napoca, Cluj-Napoca, Romania
³National Institute for Research and Development in Microtechnologies, IMT - Bucharest, Romania

E-mail: Corina.Barleanu@omt.utcluj.ro

Abstract. The microelectronic industry has been growing rapidly over the past 10–20 years, as has its reliance on thin-film deposition techniques for components manufacturing. As modern devices generate quite a bit of heat and peak temperatures can reach over 100°C, there is a need to provide adequate cooling for a device to stay operable. A series of chrome gold films with various thicknesses were prepared on silicon substrate. The structural and surface morphology, adhesion, friction, Young’s modulus and hardness of this thin film were studied for three different thicknesses under temperature variations between 20 to 100°C. The variation of the film thickness and temperature affects the structure, surface and mechanical properties of Cr/Au thin films. Obviously these thermal cycles are unavoidable and eventually lead to thermal fatigue damage and device failure. Consequently, the knowledge of mechanical properties of thin films at elevated temperatures is required for proper chip design and reliability assessments. Elastic modulus and hardness are two important mechanical properties of the thin-film structural materials used in microelectromechanical systems. The mechanical properties of electroplated chrome-gold thin film are found to be highly dependent on the manufacturing process and also of the thin film thickness. On the other hand it is important to find the effect of temperature on these properties. Investigated samples are made of thin layers of chromium and gold with differences in thickness. The three levels of nominal thicknesses of Au films are: 100, 300 and 500 nm. In order to obtain the relations between surface pattern/surface chemistry and nanotribological properties and adhesive behaviors of the films were evaluated with a noise- and vibration-isolated and environment–controlled XE 70–AFM from Park Systems, using the contact mode. The tests were performed at temperatures between 10°C - 100°C and at a relative humidity RH of 40%. Each measurement was repeated many times in order to improve the accuracy of the experimental results.

1. Introduction
Micro-electro-mechanical system (MEMS) is a special branch with a wide range of applications in sensing, switching and actuating devices. Designing the reliable MEMS requires understanding of the tribomechanical properties of the materials and structures sometimes to push the limits of materials behavior.
Thin films have attracted much attention in recent years as intelligent and functional materials because of their unique properties; along with some functional improvements, these thin coatings also significantly enhance the mechanical reliability of the components [1, 2].

Thin films with thickness of a few microns or a fraction of a micron are employed as components in MEMS and microelectronic devices. These films frequently serve as essential device functions. Sometimes the required mechanical conditions on thin films are different in several applications such as behavior under: friction and wear, creep, fatigue, etc. It is well known that methods to describe bulk material behavior fail to describe material response in this size regime [3].

The differences between the mechanical properties of small structures and bulk materials may be attributed to: differences in microstructure due to the fabrication [4]; possible effects on thin films and film size effects due to strain gradient plasticity phenomena [3]. There is, therefore, a need to study the mechanical properties of thin films at the appropriate scale.

Many researchers currently have experimental programs to study such characteristics [5, 6]. Frequently, each specific investigation involving micro devices tends to be particular to depend on the device and to introduce challenges and new fundamental questions. For instance, substrate material and etching techniques play a major role on film’s grain structure as well as the presence of initial defects.

In this work our special attention was focused to investigation on the effect of film thickness and temperature on the tribo-mechanical properties of the chromium-gold thin film. The extraordinary stability of gold has been the focus of study since ancient times. Gold’s resistance to oxidation and corrosion has led to its use in such diverse applications. Gold nanoparticles also have become the focus of increasing interest in part due to their potential optical, electronic and catalytic applications.

We have concentrated on Cr/Au films since this alloy in bulk is known as a stable low resistance material. Due to their superior tribological properties, Cr/Au thin films have been proposed also to prevent stiction and to reduce friction. The quality and mechanical response of these films depends on many factors. On the one hand, the main issue is the existence of film thickness effects that arise because of geometrical constraints on dislocation motion and on the other hand, the effect on temperature on the tribo-mechanical behavior of gold thin films.

2. Experimental investigations

2.1. Samples investigated

The p-type Si wafers, <100> orientation, have been used in order to prepare the experimental samples. After a standard cleaning process in piranha solution, a silicon dioxide layer with a thickness of 1,7 μm has been grown by wet oxidation of the substrate. On this layer, we have deposited two thin metal films with different thicknesses. For the first sample denoted Au_100 we have deposited an adhesion chromium film with a thickness of 10 nm and the gold was 100 nm thick (Si/SiO2/Cr/Au - 1.7μm/10nm/100nm). For the second and third sample denoted Au_300 and Au_500, the films thicknesses were 30 nm for chromium and 300 nm for gold (1.7μm/30nm/300nm) and for the last one the thickness is: 1.7μm/50nm/500nm, respectively. In all cases the thickness of Si wafers can vary between 356-525 μm range depending on the provider and the metal films were deposited through Electron Beam Evaporation system.

To deposit thin film from gold and in order to ensure the substrate interface are necessary one or more metals to provide strong bonding. We focused on the two-component gold/chromium, respectively, because this package is the most resistant to atmospheric corrosion. The Cr film is used as an adhesive inner layer for the Au thin film. The processing technology for this system is well defined and easily accomplished.

2.2. Experimental procedure

At the beginning, the tests were performed at room temperature (22°C) and at a relative humidity RH of 40%. Each measurement was repeated many times in order to improve the accuracy of the
 experimental results. Then, the measurements were performed over a range of processing temperatures between 20°C and 100°C. A thermal controller stage was used to change and control the sample temperature to an accuracy of 0.1°C. However, the investigated sample was maintained at a given temperature for few minutes before measurements.

For tribological investigation with AFM contact mode the cantilever used was HQ-NSC 35/Hard/Al BS from Si₃N₄ with 30 nm aluminum on the backside coating, with a nominal value of the spring constant \( k = 5.4 \text{ N m}^{-1} \), the radius smaller than 20 nm, the cone angle of 40°, resonance frequency 150 kHz and geometrical parameters: length \( l = 130 \mu m \), width \( b = 35 \mu m \), thickness \( g = 2 \mu m \) and height \( s = 15 \mu m \). The set point was of 10 nN and the scan rate was 0.75 Hz.

The cantilever used for topography evaluation in AFM non contact mode was PPP-NCHR with 30 nm aluminum on the backside coating, with a nominal value of the spring constant \( k = 42 \text{ N m}^{-1} \), the radius smaller than 10 nm, resonance frequency 330 kHz and geometrical parameters: length \( l = 125 \mu m \), width \( b = 30 \mu m \), thickness \( g = 4 \mu m \).

In the same conditions using a nanoindenter modulus on XE 70–AF M were performed the nanoindentation tests. For these tests was used a Berkovich diamond pyramid (three–sided pyramidal) tip with a nominal value of the spring constant \( k = 144 \text{ N m}^{-1} \), the radius smaller than 25 nm, the side angle of 79°, resonance frequency 150 kHz and geometrical parameters of the tip: height \( s = 109 \mu m \), length \( l = 782 \mu m \) and thickness \( g = 24 \mu m \).

3. Results and Discussion

3.1. Topography evaluations

It has been known for a long time that the surface roughness is very important in the magnitude of the force required to separate two materials after they had been brought into contact. Atomic force microscopic analysis is ideal to quantitatively measure the nanometric dimensional surface roughness and for visualizing the surface texture of the deposited film.

For evaluating the surface topography of the sample was utilized the Non-Contact AFM mode (NC-AFM) based on the attractive inter-atomic force between the tip and a sample surface. In AFM, a sharp tip at the end of a cantilever is vibrated near the surface of a sample and was scanned over 5 μm × 5 μm surface area.

The roughness can be characterized by several parameters and functions such as height, wavelength, spacing and hybrid. The root mean square (RMS) roughness of the thin films was studied from 3D AFM images (see figure 1) and is by definition the standard deviation of the surface height profile from the average height [7]. \( R_{q} \) - what was formerly called root-mean-square or RMS is more sensitive to occasional highs and lows, making it a valuable complement to \( R_{q} \). \( R_{q} \) are the geometric average height of roughness-component irregularities from the mean line measured within the sampling length.

![Figure 1. 3D - Non-Contact AFM image for all three gold thin film samples.](image-url)
The morphology and surface roughness of different thin film samples was investigated at various temperatures. The results indicated that RMS roughness becomes slightly smaller as temperature increases from 20°C to 100°C. For improved accuracy of results have been made the scanning on the maps of surfaces, and for these measurements were done a statistical interpretation of the results being calculated the dispersion values. The results are presented in table 1. It is observed that RMS roughness values increase with an increase in the thickness of the thin film.

Surface roughness may have a significant influence on the adhesion between an elastic solid and a substrate. Initially, this topic was studied by Fuller and Tabor [8], it was found that relatively small surface roughness could reduce or even remove adhesion. This perspective was accepted for a long time until Briggs and Briscoe [9] reported their experimental results in which rubber could stick to a rigid slightly rough surface much better than to a relatively smooth one [10]. In order to find the mechanisms, many theoretical and numerical models have been developed in which the effect of surface roughness on adhesion is considered [11-14].

| Sample | Thickness of the film (nm) | Root mean square RMS (nm) | Dispersion values |
|--------|---------------------------|--------------------------|------------------|
| Au_100 | 100                       | 0.95                     | 0.02             |
| Au_300 | 300                       | 2.21                     | 0.04             |
| Au_500 | 500                       | 2.62                     | 0.02             |

3.2. Adhesion

The subject of thin film adhesion measurement has been of great interest since the development of microelectronic devices. As mentioned in [15] adhesion of an elastic solid on a rough substrate involves competition between the attractive adhesion energy, which mainly arises from the region where the two solids are in atomic contact at the interface and the repulsive elastic energy associated with the bending of the elastic solid so that it comes in direct atomic contact with the substrate.

For numerical simulations and lifetime predictions, most often the quantitative adhesion values are desired for understanding factors contributing to thin film adhesion. Adhesion is very important in determining the durability of thin film devices. The performance of thin films is dictated by adhesion forces.

In this work the force of adhesion between nanoscale rough surfaces was calculated from pull–off force measurements made with AFM, using the spectroscopy in point. The AFM tip was brought in contact with the thin film surface and the adhesion force was measured from the pull–off point on the force distance curve. No additional loading force was applied during the point of contact.

A minimum load called pull-off force or critical load can be determined from (1) and (2), based on Johnson, Kendall, and Roberts (JKR–theory) and Derjaguin, Müller, and Toporov (DMT - theory). The assumption of the theory is that the forces of attraction at the contact area are identical to those outside of the area and give access to the thermodynamic work of adhesion.

\[ F_{\text{C(JKR)}} = -\frac{3}{2} \cdot \pi \cdot \omega \cdot R, \]  
\[ F_{\text{C(DMT)}} = -2 \cdot \pi \cdot \omega \cdot R. \]
where $R$ is tip radius in nm (18 nm) and $\omega$ is the work of adhesion in J m$^{-2}$.

### 3.2.1. Effect of nanofilm thickness on adhesion

The investigated area was divided into $16^{th}$ equal parts in the form of a square grid which were analyzed and collecting the adhesion (pull–off) forces. More exactly, the first measurement is made, then tip retracts to its original position and then moves without contact in the second point measurement, and so on up to 16 points without scratching the sample. The XEI software in its current form is able to extract the adhesive force from the data it collects.

For instance, in figure 2 is presented the adhesion (pull–off) force between the AFM tip and sample Au_500. A statistical interpretation of the results was performed also for these data, calculating the dispersion values and the results are presented in figure 3. Based on two theories, DMT and JKR expressed by equations (1) and (2) and on the experimental values of the pull-off forces was determined the work of adhesion. The results for the work of adhesion as a function of thickness of the samples in ambient environment are presented in table 2.

#### Table 2. Work of adhesion based on the JKR and DMT theories.

| Sample   | $\omega_{\text{JKR}}$ (J m$^{-2}$) | $\omega_{\text{DMT}}$ (J m$^{-2}$) |
|----------|-----------------------------------|-----------------------------------|
| Au_100   | 2.499                             | 1.875                             |
| Au_300   | 1.515                             | 1.136                             |
| Au_500   | 1.076                             | 0.807                             |

*Figure 2.* Adhesion (pull–off) force between the AFM tip and the sample Au_500.

*Figure 3.* Variation of adhesive (pull–off) force as a function of thickness of the samples.

The increase in the thickness is responsible for the increases in the roughness of the film, and it also ensures a lower adhesion for gold nano films. One can see that the adhesion energy decreases, as a function of film thickness as shown in figure 3.

### 3.2.2. Effect of temperature on adhesion

The influence of temperature on adhesion was performed over a range of processing temperatures between 20°C and 100°C. A thermal controller stage was used to change and control the sample temperature to an accuracy of 0.1°C. The cantilever used for adhesion evaluation with temperature in AFM non contact mode was PPP-NCHR with 30 nm aluminum on the backside coating, with a nominal value of the spring constant $k = 42$ N m$^{-1}$, the radius smaller than 10 nm, resonance frequency 330 kHz and geometrical parameters: length $l = 125$ μm, width $b = 30$ μm, thickness $g = 4$ μm.

The results are presented in figure 4. It shows that once the temperature is higher than 50°C, increasing temperature causes a significant increases of adhesive force. At high temperatures,
desorption of water and reduce water surface tension of the film on the one hand and on the other due to local warming at nano scale the surface topology it's changing leading to increases in adhesive forces on the surface of the thin film of gold. However, when exposed to ambient air the gold thin film analyzed absorb oxygen and water vapor, this film has only a few water molecules which are adsorbed on the surface, the above mentioned mechanisms do not play a big role.

It is known that the reduction of stiction is particularly important in devices with smooth surfaces which involve relative movement under the application of smaller loads. Stiction may limit their lifetime and compromise the performance and reliability. In these devices such as MEMS devices which involve relative motion, in the presence of the water film, the meniscus force can be high and in some cases much higher than the external load. In close proximity a few nanometers of the surface van der Waals forces are also significant as value.

The adhesion forces for these three samples with different thickness as a function of temperature are plotted in figure 4. It is observed that in all cases a temperature over the room temperature increases the pull-off forces.

3.3. Effect of thickness and temperature on mechanical properties of gold nanofilm

Nanoindentation techniques have been used to measure the mechanical properties of gold nano thin films with different thickness under different temperatures. Mechanical properties of bulk Au commonly used in MEMS are: density $\rho = 19280$ kg m$^{-3}$; Young’s modulus $E = 78$ GPa; Poisson’s ratio $\nu = 0.44$. These values provide the designer a starting point from which to work. For design and fabrication, more specific information is required. Even if carefully recreating the process steps and conditions it is assumed that not identical results are obtained. A film deposited in one system may differ from a film deposited under identical conditions in a different system.

For bulk metals is appreciated a correlation between hardness $H$ and yield strength $\sigma_c$, typically $H \approx 3\sigma_c$, but this correlation has not been directly verified in films or hard coatings materials. Also it is well known that $\sigma_c$ decreases with temperature. Therefore, it can be anticipated that the hot hardness of coatings will be lower than that at ambient temperatures for which values are usually quoted. A functional relationship between $H$ and $T$ have been proposed by [16]:

$$ H = H_0 \cdot e^{-aT}. $$

Where $H$ is hardness in kg mm$^{-2}$, $T$ – temperature in °C and the constants $H_0$ in kg mm$^{-1}$ and $a$ in $10^{-4}$ °C$^{-1}$ are determined from experimental data.

For our samples in this paper, the hardness of the samples was determined from the load-displacement curve using the Oliver and Pharr method. Young’s modulus was evaluated from same
curve based on Hertzian contact theory. Considering the indentation size effect, the load of the indenter was chosen to limit the penetration depth less than one tenth of the film thickness in order to minimize the effect of substrate on mechanical properties of the thin film. A representation of a typical data set obtained with a Berkovich indenter is presented in figure 5. The indentation force was set at 50 µN and the test temperatures from 0°C to 100°C.

At test temperatures from 20 °C to 100 °C the elastic modulus drop with increased temperature is seen in figure 6 for the gold film with different thickness. Young’s modulus depends on the composition, crystal structure and orientation of the film material. With temperature a modulus drop is expected due to thermal expansion and an increased amplitude of atomic vibrations. For example at room temperature for Au_100 the modulus is around 56 GPa and drop to around 40 GPa when the temperature increases to 100°C. On the other hand for Au_300 in the same conditions the modulus of elasticity decreases from 64 GPa to 54 GPa. For Au_500 the modulus decreases from 89GPa at 20°C to 52 GPa to 100°C.

**Figure 5.** The load–displacement curve at 20°C and 80°C for Au_500.
Figure 6. Young’s modulus $E$ versus temperature for different thickness of the gold thin film.

Similar to the elastic modulus data presented in figure 6, behavior of gold thin film hardness with temperature seems to have the same downward trend (figure 7). This temperature effect is not as pronounced at indentation depths over 10-20% from film thickness where the substrate hardness comes into play.

During the tests it was observed that above a temperature of 60°C the effect of the thermal drift appeared to be substantial. Although we were tried to achieve thermal equilibrium between the indenter tip and the sample by keeping the tip at the sample surface for 1-2 minute before performing indentation experiments.

A general trend is observed that the nanomechanical properties of the Cr/Au increase with the film thickness. The general rules when testing mechanical properties of thin films is to indent only the first 10-20% of the film thickness to avoid the substrate effect on measurements.

Figure 7. Hardness $H$ versus temperature for different thickness of the gold thin film.

4. Conclusions
The motivation for the work described here has been the desire to understand the mechanical properties of the thin film materials used in microelectronic and magnetic devices. There is a need to
obtain information about the mechanical properties of individual features in the microstructures of structural materials. The thickness of a thin film is among the most important attributes on their nature. The reason is that thin film properties and mode of behavior depends on film thickness. Generally, the MEMS applications require the maintenance of precise and reproducible film thicknesses as well as lateral dimensions. Even more stringent thickness requirements must be adhered to in optical applications, particularly in multilayer coatings. The surface morphologies of the gold chromium thin films, prepared by electron beam deposition method, at different films thickness were measured by AFM. A statistical analysis of the surface parameters of thin films has been performed based showed that the relatively high kurtosis, positive skewness and minimum roughness of the films increased with the increase of the film thickness from 100 to 500 nm. It is important to note that adhesion is not a constant, but rather a very complicated variable property, a concept very important for understanding length scale effects in small volumes. As a result, a test that works with one film system may not necessarily work with another. The true work of adhesion is a constant for a given film/substrate pair. Reimanis, et al. [17], Lipkin and others [17] measured the thermodynamic work of adhesion of gold on sapphire to be 0.5 to 0.9 Jm⁻². The results obtained in this work for work of adhesion falls depending on film thickness between limits 2.5 Jm⁻² for Au_100 to 1 Jm⁻² for Au_500 after JKR model or on the other hand between 1.8 – 0.8 Jm⁻² after DMT theory. When the surface roughness is small, the nominal contact area is almost equal to the real contact area, which results in less elastic energy stored in the film. A similar explanation should also be true for the case of a surface with substantial roughness (if the wavelength is fixed, the larger the amplitude, the rougher the surface). For the case of a surface with intermediate roughness, more elastic energy stored in the bending film leads to a reduced effective interfacial one and, thus, a reduced adhesion force. For a determined roughness of a surface, the effective interfacial energy and the adhesion force would increase with decreasing thickness. Nanoindentation techniques were successfully applied for measuring a variety of thin films mechanical properties, from presently almost routine elastic modulus to more challenging. The dependence of film Young’s modulus with film thickness is a nonlinear relation which may be influenced by the film microstructure, confinement effects, and deposition method. Both the elastic modulus and hardness of Au films were shown to decrease with increasing temperature up to 100°C. A general trend is observed that the nanomechanical properties of the Cr/Au increase with the film thickness.

5. References
[1] Bhushan B 1998 Handbook of micro/nano tribology (CRC press)
[2] Birleanu C, Pustan M, Muller R, Dudescu C, Merie V, Voicu R and Baracu A 2015 Experimental investigation by atomic force microscopy on mechanical and tribological properties of thin films International Journal of Materials Research
[3] Espinosa H and Prorok B 2003 Size effects on the mechanical behavior of gold thin films Journal of Materials Science 38(20) pp 4125-4128
[4] Maboudian R, Ashurst W R and Carraro C 2002 Tribological challenges in micromechanical systems Tribology letters 12(2) pp 95-100
[5] Evans A and Hutchinson J 1995 The thermomechanical integrity of thin films and multilayers Acta Metallurgica et Materialia 43(7) pp 2507-2530
[6] Knauss W G, Chasiotis I and Huang Y 2003 Mechanical measurements at the micron and nanometer scales Mechanics of Materials 35(3) pp 217-231
[7] Jiang T, Hall N, Ho A and Morin S 2005 Quantitative analysis of electrodeposited tin film morphologies by atomic force microscopy Thin Solid Films 471(1) pp 76-85
[8] Fuller K and Tabor D 1975 The effect of surface roughness on the adhesion of elastic solids in Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences (The Royal Society)
[9] Briggs G and Briscoe B 1977 The effect of surface topography on the adhesion of elastic solids Journal of Physics D: Applied Physics 10(18) pp 2453
[10] Peng Z and Chen S 2011 Effects of surface roughness and film thickness on the adhesion of a bioinspired nanofilm Physical Review E 83(5) pp 051915
[11] Rabinovich Y I, Adler J J, Ata A, Singh R K and Moudgil B M 2000 Adhesion between nanoscale rough surfaces: I. Role of asperity geometry Journal of Colloid and Interface Science 232(1) pp 10-16
[12] Persson B 2002 Adhesion between elastic bodies with randomly rough surfaces Physical review letters 89(24) pp 245502
[13] Peng Z, Chen S and Soh A 2010 Peeling behavior of a bio-inspired nano-film on a substrate International Journal of Solids and Structures 47(14) pp 1952-1960
[14] Greenwood J and Williamson J 1966 Contact of nominally flat surfaces Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences (The Royal Society)
[15] Persson B and Gorb S 2003 The effect of surface roughness on the adhesion of elastic plates with application to biological systems The Journal of chemical physics 119(21) pp 11437-11444
[16] Ohring M 2001 Materials science of thin films (Academic press)
[17] Reimanis I E, Dalgleish B J, Brahy M, Rühle M and Evans A G 1990 Effects of plasticity on the crack propagation resistance of a metal/ceramic interface Acta metallurgica et materialia 38(12) pp 2645-2652
[18] Lipkin D, Clarke D and Evans A 1998 Effect of interfacial carbon on adhesion and toughness of gold–sapphire interfaces Acta materialia 46(13) pp 4835-4850

Acknowledgments
This work was supported by the Romanian Space Agency – STAR Project no. 97 - 2013 grant from the Research Program for Space Technology Development and Innovation and Advanced Research (STAR).