

Diffusion effect of intermetallic layers on adhesion and mechanical properties of electrical contacts

Abstract

Multilayer thin films are used as metallic contacts or relays in microelectromechanical systems (MEMS). The sublayers of this sandwich are chosen based on the application of the MEMS. The Au, Ag and Cu are commonly used as a conduction layer and Cr, Ti, Pt and etc. are usually employed as an adhesion layer or diffusion barrier. Heat treatment, oxygen treatment, and methods of fabrication have an effect on the diffusion of the central layer into the conduction layer, thus effective the properties of the overall film. While heat treatment of multilayer films increases the diffusion, oxygen treatment in some cases forms a diffusion barrier. While diffusion of intermetallic layers increases the adhesion, it also results in increasing the contact resistance which is not satisfactory. This paper presents the research done on the diffusion effect of the intermetallic contact layers on electrical properties, such as contact resistance or resistivity and mechanical properties such as adhesion. It will introduce the importance of the analysis and identification of the optimum combination of the intermetallaic layers, and the motivation of the research in employing it to the MEMS application. Also the literature review, background, and the application of the research will be discussed.

1 Background and Introduction

The microelectromechanical systems (MEMS) are employed widely as intelligent integrated electrical systems, such as DC electrical contacts and relays, hybrid circuits (high frequency), optical detectors, mirrors, and radio frequency (RF) switches [1]. Although the micro size the system have many advantages, the small size results in large surface area to volume ratio which increases the effect of the surface forces on the performance of the systems[2]. Some of the surface forces negatively effect the application of the MEMS, such as surface welding, change of the contact resistance, wear and etc.

To ensure the continued integrity of the desired properties of these separable electrical contacts, multilayer thin films are prepared to fulfill some of the criteria of reliability with respect to current conduction, low friction, and wear resistance [3]. Since they involve movable parts, control and determination of mechanical properties are also an important factors for long term stability, performance, and reliability of the thin films [4]. The sandwich layers offer the properties needed based on the application of the MEMS, but the diffusion of the layers will effect the mechanical and electrical properties of both the individual layers and the overall multilayer thin films.

Ti or Cr is commonly used in assembly of different metals in multilayer thin films in electrical contact relays, as an adhesion/diffusion layer. Ti oxidizes readily in the presence of oxygen, and the oxidized layer does not have a high adherence.

In the assembly of the multilayer thin films studied for the electrical contact relays, 700 nm of gold electron beam deposited on the thermally oxide layer on Si wafers with 20 nm electron beam evaporated Ti or Cr as an adhesion layer has been under investigation for the purpose of determining of the best quality contact layers by providing the highest performance in electrical and mechanical behavior of these contact relays. The interest in this study is to determine the most appropriate layers for conduction and adhesion purposes, and provide the desired mechanical and electrical properties. The selection of the metals can be restrained by diffusion effect on some of the desired properties. This paper provides the research which has been done on the effect of diffusion of the intermetallic layers of Ti and Cr on the mechanical properties, such as adhesion of multilayer thin films, and electrical properties, such as resistance.

2 Literature Review

Cu, Ag and Au have been of interest for electrical contacts because of the low resistivity and good conduction and resistance to corrosion [5, 6]. But the adhesion between the noble metals such as Au or Ag and the oxide or oxidized layer on the substrate is weak. The oxide layer is commonly used in microcircuits, and in order to increase the adhesion of Au and the oxide layer, a few angstrom adhesion layers such as Ti, Cr or Pt are deposited to function as a glue between the film and substrate [6, 7]. On the other hand, some intermediate layers, such as Cr, Ti, Mo or Ta, have a high formation of oxidation after deposition, therefore the second film (i.e. Au) should be deposited immediately after the deposition of adhesion layer to prevent the formation of oxide on the adhesion layer. In some cases the formation of the oxidized layer with the intermediate layer improves the adhesion of film with the substrate [7]. Effect of diffusion of multilayer thin films has extensively been investigated in relation to electrical properties, but insufficient research has been done on how diffusion changes the mechanical properties of the thin films[8, 9].

Material science, chemistry, electrical and mechanical science, physics, and manufacturing process are all integrated into the process of fabrication and machining these films. The sublayers of the sandwich used in the multilayer thin films changes relative to the application of these films. Applications such as electrical contact relays requires a high conduction, reliability, and low resistance. In ohmic contacts, the low ohmic resistivity requirement provides a slightly different range of metals to choose from compared to the electrical or magnetic contacts. In electrical contacts, the surface requires to be somewhat smooth at the atomic level. The roughness of the surface results from the method of fabrication of multilayer thin films. While in the optical multilayer, the optimal surface would have rougher surface in the atomic level to enhance the giant magnetoresistance effect [10]. Therefore, fabrication of the thin films, as well as surface characterization and electrical properties characterization all influence the selection of the multilayer deposited on the films and, result in the diffusion effects on the properties of the sandwich multilayer. Pulsed laser deposition (PLD), chemical vapor deposition (CVD), electron beam evaporation, Langmuir-Blodgett films (LB), and Auger electron or ion deposition are a few of the deposition methods for the multilayer

thin films; each provides different mechanical, electrical, and magnetic properties to the multilayer.

Holloway et. al. in 1976 studied the in situ formation of diffusion barrier using oxygen treatment in thin films metalization systems[6]. His studies on Au/Cr/Si showed the diffusion of Cr in gold as the Cr film was exposed to different oxygen treatment. The oxygen in Cr forms the Cr_2O_3 which decreased the diffusivity and forms a diffusion barrier, but no significant change in the resistivity was seen compared to the bulk gold. He stated the oxygen treatment should be applicable for the metalization of reactive metals for adhesion with noble metals for conduction. His studies advanced a new method on fabrication of multilayer film for electrical contacts. Holloway et. al. later in 1980 studied the problems of Au/Cr/Si in manufacturing process of hybrid circuits and how the manufacturing environment will change some of the characteristics of the multilayer thin films. The Holloway paper had an influential effect on the assembly of the layers [11].

3 Theoretical Background

The spontaneous intermingling of the particles of two or more substances as a result of random thermal motion is called diffusion. Diffusion changes the properties of the substance [12]. The diffusion effect of intermetallic layers (i.e. Cr) with Cu, which is commonly used in electrical contact, was investigated on the resistivity of the thin films by Ono et. al. The diffusivity of sublayers was studied using x-ray diffraction, and Rutherford backscattering spectra (RBS) with respect to heat treatment of the films [5]. In Figure 1 left image shows the RBS spectroscopy of Cu/Cr/Si before and after annealing at 600C for 1 hr. As deposited spectra shows the distinguished multilayer of Si, Cr and Cu, but after annealing one layer represents the intensive diffusion of sublayers. In the right image of figure 1, x-ray diffraction shows the different pattern peaks for as-deposited vs. annealed specimen. The peaks after annealing became weak and new peaks formed from the compound of Cu and Si.

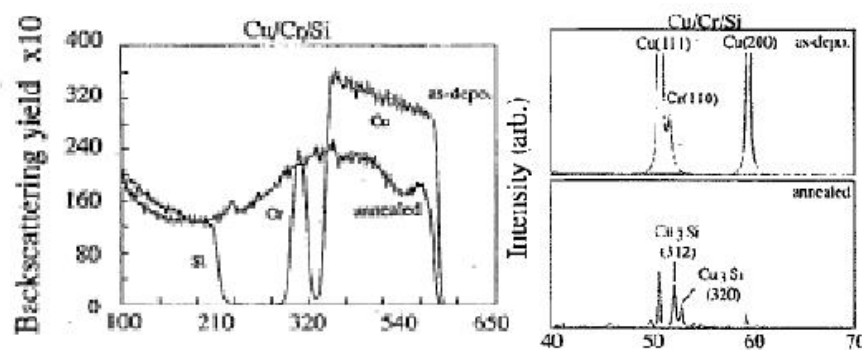


Figure 1: (Left) RBS result of Cu/Cr/ Si, (right) X-ray diffraction result of Cu/Cr/Si

Ono et. al. also studied the effect of diffusion for different intermetallic layers on resistivity using four point probe Table2 . All except W and Ta seem to increase the resistivity significantly. Concentration of diffused Cu in Si was measured using secondary ion mass spectroscopy (SIMS).

Metal	Resistivity change	Cu intensity change	Cu concentration (count)
	$\Delta R/R(\%)$	$\Delta I/I(\%)$	
Ti	24900	0.07	1.10×10^6
Cr	2300	0.28	1.06×10^6
Nb	2700	0.78	1.20×10^6
Mo	3900	18.8	8.52×10^5
W	10	65.5	2.19×10^4
Ta	-5	73.7	3.39×10^4

Figure 2: Change in properties of Cu/M/Si Multilayer (M=Cr, Ti, Nb, Mo, Ta, W) before and after annealing at 600 C

Ono et. al. also provided the change in resistivity as a function of annealing temperature (Figure3). The resistivity of the Cu/Ti/Si and Cu/Cr/Si increased abruptly at above 400C while Mo and Nb changed abruptly above 500C and W and Ta above 600C. The sudden change in resistivity was explained by rate in formation of one of more binary phases of Ti, Cr and etc with Cu [5].

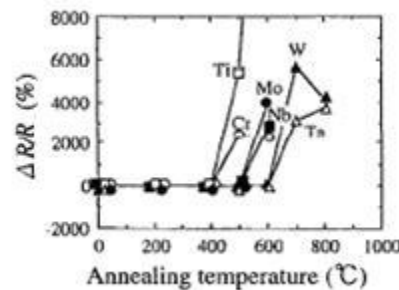


Figure 3: Effect of annealing temperature on resistivity of Cu/M/Si multilayer (M= Cr, Ti, Nb, Mo, Ta, W)

From studies of Ono et. al. Cr seems to be a more favorable intermediate layer of Cu compared to Ti, because of the less increase in resistivity. Miller in 2005 studied the Cr as an intermetallic layer with gold. In order to have a better understanding of mechanical properties and surface morphology of Au/Cr/Si multilayer thin films, he studied the effect of heat treatment and curvature (shape) on these films [1]. Miller indicated that annealing the Au/Cr/Si results in a grain growth and change in composition of the film which is a result of abnormal behavior of Cr. After annealing the grains become widely variable in size.

Madakson (1991) correlates the resistivity of thin films with diffusion effect of intermetallic layers. Madakson also studied the change of resistivity with respect to the annealing temperature. He also observed the rapid increase in resistivity in the Au/Cr/Si multilayer at about 300C, caused by the formation of bilayers of Au and Cr. The RBS result obtained in different annealing temperature of 350, 400, and 450 C represents the increase in interdiffusion of the sublayers by increasing the annealing temperature [13]. A similar study by Holloway et. al. (1976) showed the rapid diffusion of gold and Cr. Holloway et. al. stated that the Oxygen treatment of gold forms a diffusion barrier and an effect on the resistivity is inconsiderable.

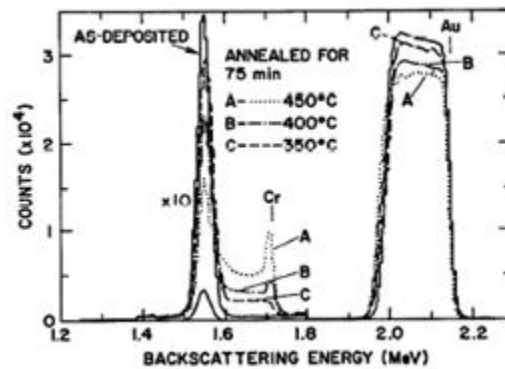


Figure 4: RBS results of Au/Cr/Si [13]

The electrical properties of electron beam evaporated Au(30 nm)/Ni(20 nm)/Pd(10 nm)/P-type GaN has been investigated and the microstructure at the interface of the layers were analyzed using x-ray photoelectron spectroscopy(XPS) and Auger electron spectroscopy(AES) as a function of annealing temperature[13]. The four point probe method was used to determine the contact resistance [14]. The Figure5(b) shows the diffusion of Pd and Ni in Au layer after annealing at 500 C while in Figure 5(a) no significant diffusion of Pd and Ni in Au is seen. Also Figure 5(b) shows the interdiffusion of Pd and Ni accompanied with penetration of the two layers to the GaN layers. Cho et. al. stated that annealing increases the binding energy and reduces the contact resistivity.

4 Current Research and Application

The determination of metallic layers depends on the application of the multilayer films. Au [9, 14, 3, 1], Ag [9], and Cu [15] are commonly used as a conduction layer and Ti, Cr, Mo, Ta, W, and Nb as an adhesion layer. Heat treatment increases the diffusion of the intermetallic layers. Increasing the adhesion of an intermediate layer to the surface layer can be made by immediate deposition of the active layer on the adhesion layer. The current state of the art method for determining diffusion in metallic films are: Auger electron spectroscopy (AES) [13, 6], x-ray photoelectron spectroscopy (XPS) [13], Rutherford backscattering spectroscopy

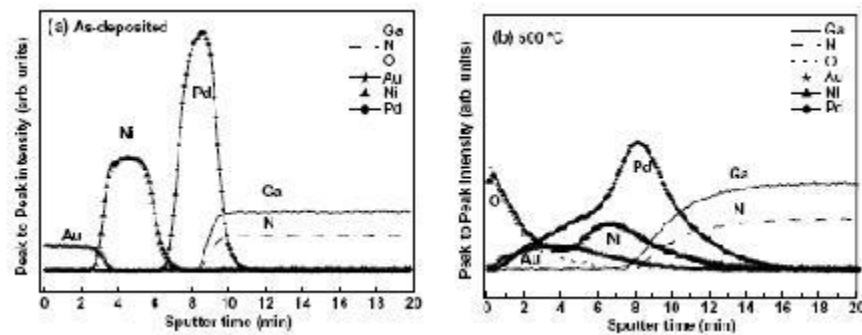


Figure 5: AES profile of (a) as deposited (b) annealed at 500C at 1 min of Au/Ni/Pd specimen

(RBS) [13], x-ray diffraction (XRD), and ion scattering [6]. Each method shows the diffusion of one metal into another using laser, electron, and photons.

The majority of the current research centers on the investigation of the diffusive effects of the metals on the electrical property of the thin films. Newer research trends are recognizing that mechanical properties, such as hardness and elastic modulus may result in the modification of multilayer thin films to prevent wear or delamination of the surface, along with consideration of the electrical properties of the system.

The most exciting breakthrough is (i) the use of different deposition methods as a factor for a change of properties of the multilayer thin films. (ii) Also understanding the diffusion of the intermetallic layers can be used as a diffusion barrier or adhesion layer dependent on some of the variables, and (iii) understanding that geometry of the multilayer thin films has an effect on the properties is an issue to be considered.

The multilayer thin films are used in MEMS or nanoelectromechanical systems (NEMS) related technologies. MEMS are smart systems, integrated of mechanical elements, sensors, actuators, relays fabricated on a silicon substrate [16]. Multilayer of thin films that are fabricated using different methods to operate as micro size arms, brains, sensors, and eyes of a system; to control or sense the environment; and perform a movement, positioning, or pumping in return. A high-demand market for the micro size systems exists due to reduced cost, space, and reliable performance of these chips. Industry is promoting much of the research in this field and is committing resources for the improvement of the thin films by microfabrication and micromachining process.

The small size of the MEMS results in a large surface area to volume ratio which magnifies the effect of the surface forces. The effect of surface forces on the film causes surface welding, wear, delamination and other failures. Improved fabrication methods, which consider the mechanical and electrical properties of the surfaces, could resolve many of the current problems. More investigation and effort in this area is warranted. Further research in the area of mechanical properties, such as hardness and elastic modulus of the film, could resolve many issues on surface wear and delamination.

5 Future Directions

The outcome of the research on diffusion effect of the metals could result in a better adhesion of the intermetallic layers. Also better mechanical and electrical properties could lead to eliminating the wear, delamination, and surface fatigue problems, as well as increasing the reliability and stability of the MEMS. The diffusion layer in metals functions either as a diffusion barrier or an adhesion layer. The proper application and metals for intermetallic layers should be determined with low resistance, high conductivity, corrosion resistance, and wear resistance properties. If the proper sublayers are determined, as well as the thickness of layers, the properties provides the reliability and stability of the MEMS. The excessive number of factors which influence the properties of the thin films make the fabrication process very difficult. Factors such as heat treatment (the annealing time, and temperature)[6], the thickness of each individual layer[9], the method of fabrication, oxygen treatment[6], the selection of individual layers [5] and etc., significantly change the properties. The significant challenge that need to be overcome for further advancement is determining the proper fabrication of MEMS contacts and relays based on the desired properties.

6 Individual statement

The most important thing I learned from this course was learning that many types of equipment provide the desired information, but the resolution and the accuracy of each instrument is different. The verification of the result from other instruments and other methods ensure the result and give more credibility and validity to the obtained result. All different methods used in characterization and microscopy of the nanoparticles, provide different aspect and helped to understand few available instrument for research studies which will be very useful to know.

The only thing that would improve the class could be adding more labs to the class. The labs were very useful, helping to understand the concept of the material studied in the lectures. I think I understand the materials used in the lab more than other subjects in the class. The labs were interesting and very meaningful, as they followed the same principal concept of the class which was synthesizing, characterizing and self assembly analyzing of the polymer and organic nanoparticles.

Nanotechnology is a technology which emphasizes the nanosize (atomic size) of the science. As chemistry, physics and biology of the atoms and molecules have been an interest and known subject for a while, so did nanotechnology. But the new aspect of nanotechnology which is a "hot" topic of the research and industry emphasizes more on the synthesis, fabrication, assembly and manufacturing of the nanosize systems. Understanding the behavior of materials at the atomic level will improve the performance and development of new techniques and technologies, reducing the cost, space and increase the reliability and stability of the mechanical and electrical systems. Nanotechnology can help to develop and build materials from bottom to top, and the assembly of elements to our desired shape and format.

Earning little chemistry background from my disciplinary major, this class helped me understand (i) how the chemistry of materials is important to the properties of materials, (ii) that small changes in procedure could make a big difference in result, and (iii) how small factors could be vital to the result, such as drying the beaker before use and etc. It changes the mechanical and electrical property of the substance.

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